KUHN-GRÜN TYPE APPROXIMATIONS FOR POLYMER CHAIN DISTRIBUTIONS

H. E. DANIELS
UNIVERSITY OF BIRMINGHAM

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.

2. Physical background

As an example of the kind of physical problem motivating the paper we give a short account of the theory underlying the mechanical properties of rubber like substances. The kinetic theory of rubber elasticity, as originated and developed by W. Kuhn, Guth and Mark, and others (see, for example, Volkenstein [17]), assumes in its simplest form that the mechanical properties of rubber and similar polymers, like those of an ideal gas, depend only on the entropy of the system, which is a function of the distribution of configurations of the constituent chain molecules. Each molecule is made up of a long sequence of repeating units with a fair amount of freedom of independent movement between them. In the simplest version of the theory, the units are considered to be completely free to rotate in any direction relative to each other. Real chain molecules have considerable restrictions on the relative rotation imposed by fixed valence angles and steric hindrance, but they may often be conveniently regarded as "equivalent" to a smaller number of freely jointed links.

In the rubber like state, the chain molecules are connected by a relatively sparse system of cross links into a loose three dimensional network. The dimensional characteristics of such a network are determined to a large extent by the distances between the cross links, and hence by the end to end distances of the chains connecting them. The entropy of each chain is proportional to the logarithm of the total number of possible configurations for which the end separation has a specified value.

If a single random polymer chain has one end at the origin and is free to rotate about it, the distribution of the position $\mathbf{r}$ of the free end is spherically symmetrical. The probability density function of $\mathbf{r}$ is $p(r)$, where $r = |\mathbf{r}|$ and that of r is $P(r) = 4\pi r^2 p(r)$. The first of these is proportional to the required number of configurations, and the entropy S of a single chain is

$$S = \text{constant} + K \log p(r), \tag{2.1}$$

where K is Boltzmann's constant. The average tension in a single chain held at length r is then given by

$$F = -T\frac{dS}{dr}, \tag{2.2}$$

where T is the absolute temperature.

Stress-strain relationships for the whole network have been developed, with extra assumptions, by James and Guth, and many others (see Volkenstein [17]), though a completely satisfactory theory is not yet available, particularly for the treatment of large strains.

3. Freely jointed chain: the Kuhn-Grün approximation

The simplest model for a chain molecule is one of n freely jointed bonds each of length a. This is the classical problem of "random flights"; the usual

Gaussian approximation for the distribution of $\mathbf{r}$ leads to

$$S = \text{constant} - \frac{3Kr^2}{(2na^2)}, \tag{3.1}$$

and the average tension F of a single chain of length r is, from (2.2),

$$F = \frac{3KT}{na^2} r, \tag{3.2}$$

which is proportional to r. However, since the calculation of tension is based on $\log p(r)$ and not on $p(r)$, the approximation will break down as r approaches its maximum value na because the *relative* error of the Gaussian approximation to $p(r)$ cannot be uniformly bounded over the whole range of r.

Kuhn and Grün [14] were the first to provide an approximation to $\log p(r)$ which maintains its accuracy reasonably well over the whole range of r. They used a method familiar in statistical mechanics which we now outline. The following version corrects an error in the original demonstration pointed out by Jernigan and Flory [9]. No attempt is made to formulate the argument precisely.

The projection in the x direction of a completely free bond of length a is uniformly distributed over the interval $(-a, a)$. Consider a chain of n bonds where n is large. Let $-a = \xi_1 < \xi_2 < \cdots < \xi_k < \xi_{k+1} = a$ be a set of points subdividing $(-a, a)$ such that $\delta\xi_j = \xi_{j+1} - \xi_j$ are small. Let n_j of the n bonds have projections in (ξ_j, ξ_{j+1}), where $\Sigma\, n_j = n$ and n is assumed large enough for each n_j to be large. If the chain is unconstrained, the probability of the n_j is

$$P(n_1, n_2, \cdots, n_k) = \frac{n!}{n_1!n_2!\cdots n_k!} \prod_j \left(\frac{\delta\xi_j}{2a}\right)^{n_j}. \tag{3.3}$$

Suppose now that the total projection of the chain is constrained to have a value x. This adds the further condition $\Sigma\, n_j\xi_j = x$, and if (3.3) is summed over all values of n_j consistent with the two constraints, the result will be proportional to the probability density $f(x)$ of the projection x of the unconstrained chain. In the usual way, the summation over P is avoided by taking $P = \hat{P}$ at the most probable values $\hat{n}_j$ of n_j subject to the two constraints. Using a crude form of Stirling's approximation, one maximizes

(3.4)

$$\log P + \gamma \sum n_j + \kappa \sum n_j\xi_j$$
$$\sim \text{constant} + \sum n_j \log\left(\frac{\delta\xi_j}{2a}\right) - \sum n_j \log n_j + \sum n_j + \gamma \sum n_j + \kappa \sum n_j\xi_j,$$

and obtains

$$\hat{n}_j = \frac{1}{2a} \exp\{\gamma + \kappa\xi_j\}\, \delta\xi_j. \tag{3.5}$$

From the two constraints, we then have

$$n \sim e^{\gamma} \int_{-a}^{a} \frac{1}{2a} \exp\{\kappa\xi\}\, d\xi = \frac{1}{\kappa a} e^{\gamma} \sinh \kappa a \tag{3.6}$$

and

$$x \sim e^{\gamma} \int_{-a}^{a} \frac{1}{2a} \exp\{\kappa\xi\}\xi\, d\xi = e^{\gamma} \frac{d}{d\kappa}\left\{\frac{\sinh \kappa a}{\kappa a}\right\}. \tag{3.7}$$

The probability density $f(x)$ is approximately proportional to $\hat{P}$. Using these results, one eventually obtains

$$f(x) \sim \frac{C}{a}\left(\frac{\sinh \kappa a}{\kappa a}\right)^{n} \exp\{-\kappa x\}, \tag{3.8}$$

where κ is the unique real root of

$$\mathscr{L}(\kappa a) = \coth \kappa a - \frac{1}{\kappa a} = \frac{x}{na} = \frac{\bar{x}}{a}, \tag{3.9}$$

$\mathscr{L}(\cdot)$ is the so called Langevin function, (3.8) is usually called the Langevin approximation, C is a dimensionless normalizing constant, and $\bar{x}$ is the mean projection of a bond.

Kuhn and Grün assumed (3.8) to approximate to the probability density function (p.d.f.) $p(r)$ of r. Jernigan and Flory [9] used the relation

$$2\pi r p(r) = \left\{\frac{-df(x)}{dx}\middle| x = r\right\}, \tag{3.10}$$

in the manner of Treloar [16] to obtain the more correct approximation,

$$\hat{p}(r) = \frac{A\kappa}{ra}\left(\frac{\sinh \kappa a}{\kappa a}\right)^{n} \exp\{-\kappa r\}, \tag{3.11}$$

where A is a normalizing constant and

$$\mathscr{L}(\kappa a) = \frac{r}{na} = \frac{\bar{r}}{a}. \tag{3.12}$$

The effect of using either (3.8) or (3.11) is to replace the tension-extension relation (3.2) by a formula with the reasonable property that $F \to \infty$ as $r \to na$.

4. The saddle point approximation

The form of (3.8) or (3.11) immediately suggests its connection with the saddle point approximation $\tilde{p}(r)$ to the transform of the moment generating function (or partition function) for the radial distribution. It is surprising that this fact has not been fully exploited. Dobrushin [5] mentioned that (3.8) could be derived by the essentially equivalent Cramér extension of the central

limit theorem, and Kubo [11] used the saddle point method in an important study of more general chains which we refer to later. But the accuracy of the saddle point approximation is not fully appreciated. In the present case, (4.7) is more accurate than (3.11) and is applicable to quite short chains. Under conditions which are satisfied in the present application it has been shown (Daniels [4]) that the error in $\log \tilde{p}(r)$ is uniformly $O(n^{-1})$ over the whole range of r. In fact, when normalized, it is even more accurate than would be expected from this result.

For any general spherically symmetrical distribution with radial p.d.f. $P(r)$, we have

$$\Phi(\rho) = \int_0^\infty \frac{\sin r\rho}{r\rho} P(r)\, dr, \tag{4.1}$$

$$P(r) = \frac{2}{\pi} \int_0^\infty r\rho \sin r\rho \Phi(\rho)\, d\rho. \tag{4.2}$$

These are easily deduced from the polar form of the three dimensional characteristic function for $\mathbf{r}$. Since $\Phi(-\rho) = \Phi(\rho)$, (4.2) can be written as

$$P(r) = \frac{i}{\pi} \int_{-\infty}^\infty r\rho \exp\{-ir\rho\} \Phi(\rho)\, d\rho. \tag{4.3}$$

On putting $\kappa = i\rho$ and $\Phi(\rho) = M(\kappa)$, (4.1) and (4.2) become

$$M(\kappa) = \int_0^\infty \frac{\sinh r\kappa}{r\kappa} P(r)\, dr, \tag{4.4}$$

and

$$P(r) = \frac{1}{\pi i} \int_{c-i\infty}^{c+i\infty} M(\kappa) \exp\{-r\kappa\}\, r\kappa\, d\kappa, \tag{4.5}$$

where c is real and $M(\kappa)$ is the spherical moment generating function in an obvious sense.

For a freely jointed chain of n units, $M(\kappa)$ has the form $\exp\{n\mu(\kappa)\}$ with $\mu(\kappa) = \log(\sinh \kappa a/\kappa a)$ and the method of steepest descents can be applied to (4.5). Choosing c to be the real root κ of

$$\mu'(\kappa) = a\mathscr{L}(\kappa a) = \bar{r} = \frac{r}{n}, \tag{4.6}$$

which is a saddle point of the integrand, we obtain as an approximation to $p(r) = P(r)/4\pi r^2$,

$$\tilde{p}(r) = \frac{\kappa \exp\{n(\mu(\kappa) - \kappa\bar{r})\}}{r(2\pi n)^{3/2}\{\mu''(\kappa)\}^{1/2}}, \tag{4.7}$$

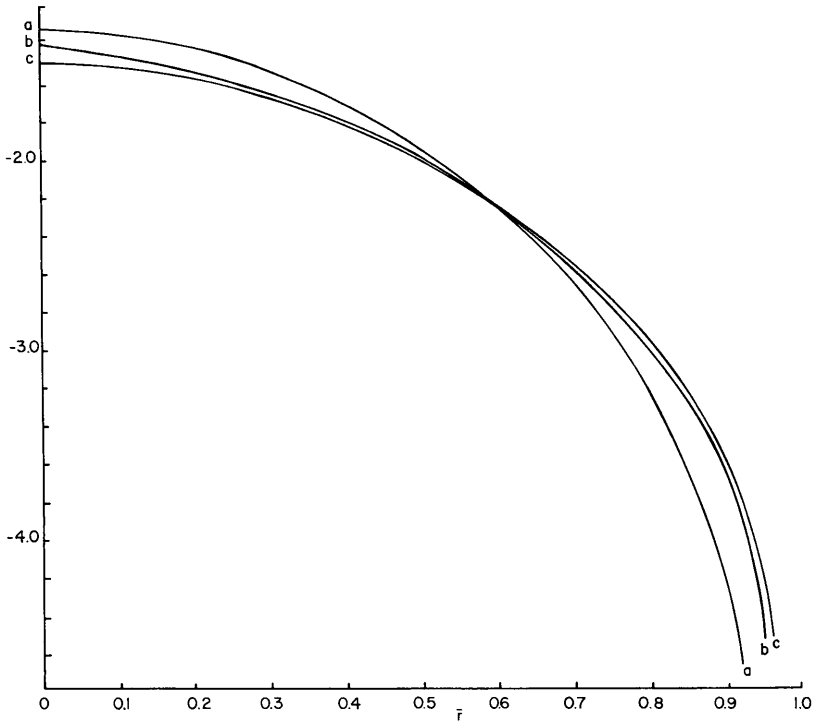

FIGURE 1
Distribution of vector length of freely jointed chain.
Comparison of approximations.
$n = 4$
a: $\log_{10} \hat{p}(r)$ (Kuhn-Grün); b: $\log_{10} p(r)$ (exact); c: $\log_{10} C\tilde{p}(r)$ (saddle point).

This differs from $\hat{p}(r)$ of (3.11) in having the extra factor $\{\mu''(\kappa)\}^{-1/2}$, where

$$\mu''(\kappa) = \operatorname{csech}^2 \kappa + \frac{1}{\kappa^2} = 1 - \bar{r}^2 - \frac{2\bar{r}}{\kappa}. \tag{4.8}$$

Its accuracy can be further improved by normalizing it to $C\tilde{p}(r)$ so that $C \int_0^\infty 4\pi r^2 \tilde{p}(r)\, dr = 1$.

Some idea of the accuracy of (4.7) can be got by comparing it with the exact values of $p(r)$,

$$p(r) = \frac{1}{2^{n+1} \pi r n (n-2)!} \sum_{s=0}^{n} (-)^s \binom{n}{s} \{(n - r - 2s)^+\}^{n-2}, \tag{4.9}$$

where $(x)^+ = \max\{x, 0\}$ (Treloar [16]). In Figure 1, $\log_{10} p(r)$ is compared with $\log_{10} \hat{p}(r)$ and $\log_{10} C\tilde{p}(r)$ for a chain of $n = 4$ units. Apart from the value at $\bar{r} = 0$, the normalized saddle point approximation is surprisingly good

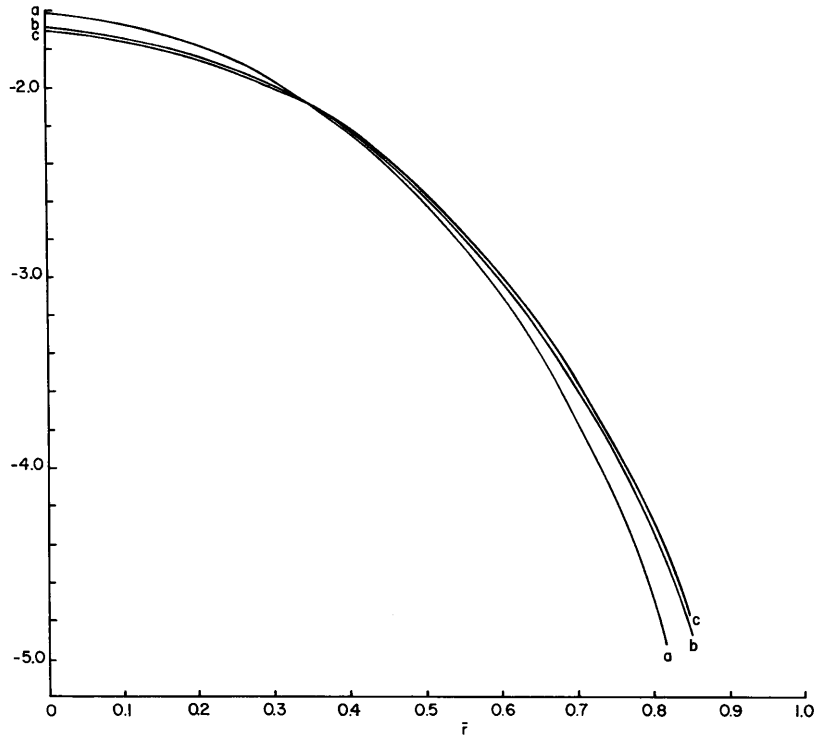

FIGURE 2
Distribution of vector length of freely jointed chain.
Comparison of approximations.
$n = 6$
a: $\log_{10} \hat{p}(r)$ (Kuhn-Grün); b: $\log_{10} p(r)$ (exact); c: $\log_{10} C\tilde{p}(r)$ (saddle point).

and has the advantage of maintaining its accuracy as $\bar{r}$ approaches its maximum, whereas $\log_{10} \hat{p}(r)$ becomes progressively worse. In the case of $n = 6$ shown in Figure 2, $\log_{10} C\tilde{p}(r)$ is practically indistinguishable from $\log_{10} p(r)$, but $\log_{10} \hat{p}(r)$ differs substantially from it, particularly as $\bar{r}$ increases.

For chains of more than about 20 units the extra factors in $\hat{p}(r)$ and $\tilde{p}(r)$ have little effect. The original Langevin approximation (3.8) (with r for x) is then quite adequate and has the merit of simplicity. The entropy takes the form

$$S = \text{constant} + nK\left\{\log\left(\frac{\sinh \kappa a}{\kappa a}\right) - \kappa\bar{r}\right\} \tag{4.10}$$

and the average force on a chain of length r is

$$F = KT\kappa = KT\mathcal{L}^{-1}\left(\frac{\bar{r}}{a}\right). \tag{4.11}$$

At large extensions, $1 - r/a$ is small and

$$\mu'(\kappa) = a\mathscr{L}(\kappa a) \sim a - \frac{1}{\kappa}. \tag{4.12}$$

Then $F \sim KT(1 - \bar{r}/a)^{-1}$ as $\bar{r}$ approaches its maximum value. We refer to this result later when discussing more general chains.

5. More realistic chain models

The simple model of a freely jointed chain of equal units is not adequate to describe the behavior of real chains except in the most general terms. The next most simple model is one where each unit is of fixed length, but free to rotate in a cone of fixed angle whose axis is the previous unit. This might be thought a suitable model for a simple molecule such as polymethylene. However, in reality the rotation is not completely free, but is restricted by the interactions between the groups of atoms making up each unit of the molecular chain. There is a nonuniform probability distribution of angular position, related by the Boltzmann formula to the nonuniform potential energy of angular position. The model assuming complete rotational freedom on the cone might be approached at high temperature.

A method of simplifying the general situation which has been extensively and fruitfully developed by Volkenstein, Flory, and their coworkers is to use the "rotational isomeric" approximation. In this approach, which originated in the work of Montroll [15] and was independently introduced by Kubo [12], the continuous distribution of angular position is replaced by a discrete set of angular states at the minima of the potential energy function, with suitable probabilities attached to them. The direction of the nth unit has a distribution governed by a Markov chain with these transition probabilities, each unit being referred to axes relative to the direction of the previous unit. (One is essentially considering a random walk on a sphere.) For a long chain, the dominant role of the principal eigenvalue is exploited.

The moments of the vector length distribution can be calculated by the methods of Flory [7], and used to approximate to the distribution by an Edgeworth expansion. But for approximations of Kuhn-Grün type the evaluation of the moment generating function itself, as described by Montroll [15], is necessary. Although essentially equivalent to Montroll's analysis, it is simpler to approach the problem directly in terms of the chain vector itself. Three similar attacks on the problem from this point of view were made independently by Kubo [11], Hermans and Ullman [8], and myself [3]. The first two specify the chain vector in terms of fixed axes, in which case in order to preserve the Markov property the vector of the final unit has also to be included in the specification of the system. My own treatment of the problem, like Montroll's, avoids this complication by the use of moving axes, and a brief account of the method now follows.

Suppose we have a chain of n bonds of fixed length a. It is convenient to choose the origin of the axes at the *end point* of the chain, and to let $\mathbf{r}$ be the vector of the *initial point*, relative to this origin, of the chain. The z axis is taken to lie along the nth bond, and the (z, x) plane contains the $(n-1)$th unit also. If $\mathbf{r}'$ is the corresponding vector for a chain of $n-1$ bonds, then the coordinates of $\mathbf{r}$ and $\mathbf{r}'$ are related by

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ a \end{bmatrix} + \begin{bmatrix} \cos\alpha\cos\beta & \cos\alpha\sin\beta & -\sin\alpha \\ -\sin\beta & \cos\beta & 0 \\ \sin\alpha\cos\beta & \sin\alpha\sin\beta & \cos\alpha \end{bmatrix} \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}, \tag{5.1}$$

where α is the bond angle and β the rotational angle. It will be assumed that α has a fixed value and β has p.d.f. $g(\beta)$ (though both a and α could also be random variables). We have a Markov chain with successive probability distribution functions $f_n(x, y, z)$ connected by

$$f_{n+1}(x, y, z) = \int_{-\pi}^{\pi} g(\beta)\, d\beta f_n(x', y', z'). \tag{5.2}$$

The characteristic function

$$\Phi_n(\xi, \eta, \zeta) = E \exp\{i(x\xi + y\eta + z\zeta)\} \tag{5.3}$$

satisfies

$$\Phi_{n+1}(\xi, \eta, \zeta) = \exp\{ia\xi\}\, \Phi_n(\xi', \eta', \zeta'), \tag{5.4}$$

where

$$[\xi, \eta, \zeta] = [\xi', \eta', \zeta'] \begin{bmatrix} \cos\alpha\cos\beta & \cos\alpha\sin\beta & -\sin\alpha \\ -\sin\beta & \cos\beta & 0 \\ \sin\alpha\cos\beta & \sin\alpha\sin\beta & \cos\alpha \end{bmatrix}. \tag{5.5}$$

The polar form of these relations is required. With $\xi = \rho\sin\psi\cos\omega$, $\eta = \rho\sin\psi\sin\omega$, $\zeta = \rho\cos\psi$, and $\phi_n(\xi, \eta, \zeta) = \Phi_n(\rho, \psi, \omega)$, (5.4) is

$$\Phi_{n+1}(\rho, \psi, \omega) = \exp\{ia\rho\cos\psi\} \int_{-\pi}^{\pi} g(\beta)\, d\beta\Phi(\rho, \psi', \omega'), \tag{5.6}$$

where

$$\cos\psi' = \cos\psi\cos\alpha + \sin\psi\sin\alpha\cos(\omega - \beta), \tag{5.7}$$

$$\sin\psi'\sin\omega' = \sin\psi\sin(\omega - \beta). \tag{5.8}$$

It is preferable in the present application to work in terms of the moment generating function. Writing $\kappa = i\rho$, $M_n(\kappa, \psi, \omega) = \Phi_n(\rho, \psi, \omega)$, (5.6) becomes

$$M_{n+1}(\kappa, \psi, \omega) = \exp\{\kappa a\cos\psi\} \int_{-\pi}^{\pi} g(\beta)\, d\beta M_n(\kappa, \psi', \omega'). \tag{5.9}$$

6. Free angular rotation

In the simplest, case β is assumed to be uniformly distributed on $(-\pi, \pi)$. This represents one extreme, corresponding to very high temperatures; the other extreme is the rotational isomeric model, where β can take only discrete values with certain probabilities, an assumption which should be nearly true at low temperatures. Both may be regarded as approximations to the true situation. The first case, which is usually described (rather confusingly) as "freely rotating" has the simplifying feature that the formulae become axially symmetric, (5.9) reducing to

$$M_{n+1}(\kappa, \psi) = \exp\{\kappa a \cos\psi\} \int_{-\pi}^{\pi} \frac{1}{2\pi} M_n(\kappa, \psi')\, d\omega, \tag{6.1}$$

$$\cos\psi' = \cos\psi \cos\alpha + \sin\psi \sin\alpha \cos\omega, \tag{6.2}$$

where $\omega - \beta$ has been replaced by ω.

There is a limiting form of this model which produces the "worm like chain" of Kratky and Porod [13]. It is got by allowing the angle α and the bond length a to tend to zero in such a way that α^2/a remains finite, say $4c$, when (6.1) becomes the differential equation

$$\frac{\partial M}{\partial t} = \kappa u M + c \frac{\partial}{\partial u}\left\{(1 - u^2)\frac{\partial M}{\partial u}\right\} \tag{6.3}$$

with $t = na$ and $u = \cos\psi$. A detailed discussion of the model is given in [3] and [8] and we omit it for brevity.

The function $M(\kappa)$ to be used in (4.5) for deriving the saddle point approximation to the radial distribution is, in the present context,

$$M_n(\kappa) = \tfrac{1}{2}\int_0^{\pi} M_n(\kappa, \psi) \sin\psi\, d\psi. \tag{6.4}$$

Since (6.1) has a positive kernel, $M_n(\kappa, \psi)$, and hence $M_n(\kappa)$ will ultimately become proportional to λ_0^n where λ_0 is the unique real positive maximal eigenvalue of (6.1).

There are two ways of calculating $M_n(\kappa)$. One is to compute it directly by numerical integration from (6.1) and (6.4), starting with $M_0(\kappa, \psi) = 1$. This is quite practicable and is discussed in Section 8. The other, which was used in [3] to develop Edgeworth type expansions based on the Gaussian approximation, is to expand $M_n(\kappa, \psi)$ as a series of Legendre polynomials,

$$M_n(\kappa, \psi) = \sum_{s=0}^{\infty} M_{n,s} P_s(\cos\psi), \tag{6.5}$$

where $M_{n,0} = M_n(\kappa)$. The addition theorem for biaxial harmonics enables $P_n(\cos\psi')$ to be replaced by $P_s(\cos\psi)P_s(\cos\alpha)$ the other terms vanishing on

integration, and we get

$$M_{n+1,s} = (s + \tfrac{1}{2}) \sum_{t=0}^{\infty} P_s(\cos \alpha) c_{s,t} M_{n,t}, \qquad s = 0, 1, 2, \cdots, \tag{6.6}$$

where

$$c_{s,t} = \int_{-1}^{1} \exp \{\kappa a u\} P_s(u) P_t(u)\, du. \tag{6.7}$$

The $c_{s,t}$ can be calculated from recurrence formulae. No generality is lost by assuming $a = 1$ which we do when convenient.

From this formulation, λ_0 is seen to be also the maximal eigenvalue of the infinite matrix $\mathbf{A}$ with elements

$$a_{s,t} = (s + \tfrac{1}{2}) P_s(\cos \alpha) c_{s,t}. \tag{6.8}$$

The simplest way of computing it was found to be the following one. If $D(\lambda) = |\mathbf{A} - \lambda \mathbf{I}|$ and $B(\lambda)$ is the principal minor of $D(\lambda)$, and if $C(\lambda) = D(\lambda)/B(\lambda)$, then A_0 is the largest real positive zero of $C(\lambda)$, and for large n,

$$M_n(\kappa) \equiv M_{0,\kappa} \sim \frac{\lambda_0^n}{C'(\lambda_0)}. \tag{6.9}$$

The saddle point approximation to $p(r)$ is given by a formula similar to (4.7), with $\mu(\kappa) = \log \lambda_0$, $\mu'(\kappa) = \bar{r}$, except that there is the additional factor $1/C'(\lambda_0)$.

The zeros of successively larger truncations of $C(\lambda)$ are computed until they settle down to a steady value λ_0, which happens quite rapidly unless κ is large. In the examples computed by this method, the next highest root was sufficiently far below λ_0 for (6.9) to be a good approximation for quite small values of n. However, when κ is large (corresponding to high extensions), convergence becomes slow and direct computation as in Section 8 is preferable.

A useful device, due to Kuhn, for comparing distributions for different chain models and different parameter values is to adjust the number n of units in each chain and the unit length a so that the chains have the same maximum length and the same mean square length. In particular, comparison with the freely jointed chain gives a reasonable definition of the number and length of "equivalent" freely jointed units. It is a well-known result that for large n the mean square length of a freely rotating chain of bond angle α is approximately

$$E(r^2) = \frac{na^2(1 + \cos \alpha)}{1 - \cos \alpha} \tag{6.10}$$

and its maximum extended length is, for even n, $r(\max) = na \cos \frac{1}{2}\alpha$, in which case the bonds have a planar zigzag configuration. For a freely jointed chain of N bonds of length b, we have $E(r^2) = Nb^2$, $r(\max) = Nb$. On equating these one finds that

$$N = n \sin^2 \tfrac{1}{2}\alpha, \qquad b = a(\sec \tfrac{1}{2}\alpha - \cos \tfrac{1}{2}\alpha). \tag{6.11}$$

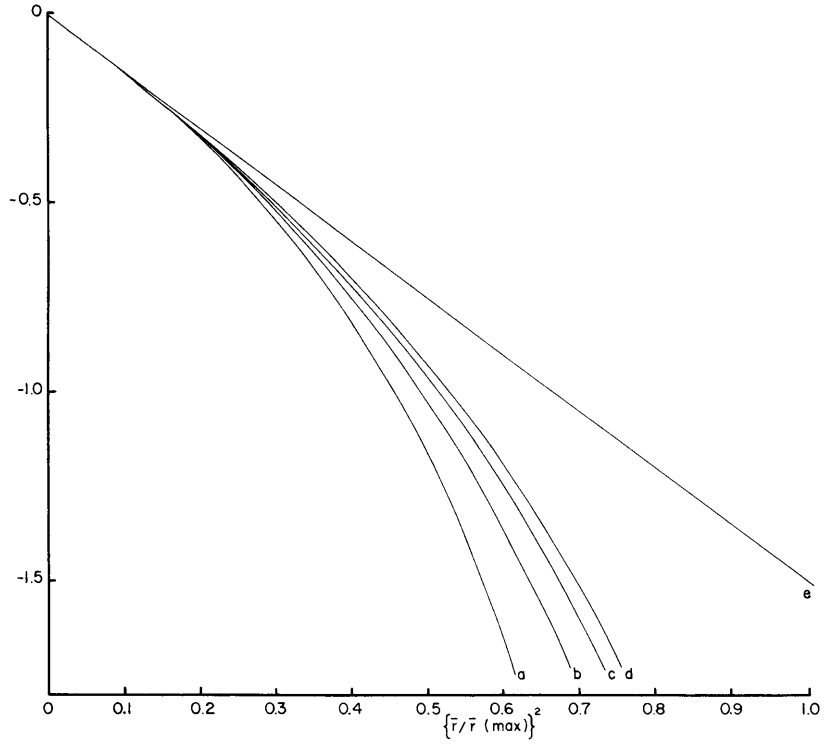

FIGURE 3
Kuhn-Grün type approximations for freely rotating chains.
$\{\mu(\kappa) - \kappa\bar{r}\} \sin^2 \frac{1}{2}\alpha$
a: $\cos \alpha = 0.9$; b: $\cos \alpha = \frac{1}{3}$; c: $\cos \alpha = 0$; d: freely jointed $\mu(\kappa) - \kappa\bar{r}$;
e: Gaussian approximation.

(In the limiting worm like chain model of (6.3), $\frac{1}{2}b$ tends to the so called "persistence length" $1/2c$ of the chain.) When n is large enough for the Kuhn-Grün approximation to be adequate the distribution is determined by $\mu(\kappa) - \kappa\bar{r}$, assuming $a = 1$, and for varying values of α the quantities to be compared are $\{\mu(\kappa) - \kappa\bar{r}\} \sin^2 \frac{1}{2}\alpha$ at the same value of $\bar{r}/\bar{r}(\max) = \bar{r} \sec \frac{1}{2}\alpha$.

The results of some calculations by my colleague R. L. Holder are shown in Figure 3. The function $\{\mu(\kappa) - \kappa\bar{r}\} \sin^2 \frac{1}{2}\alpha$ is plotted against $\{\bar{r}/\bar{r}(\max)\}^2$ for the three cases $\cos \alpha = 0.9$, $\frac{1}{3}$ and 0, together with the freely jointed (Langevin) case for comparison, and the straight line corresponding to the Gaussian approximation with which they all agree for small $\bar{r}/\bar{r}(\max)$. The values for higher $\bar{r}/\bar{r}(\max)$ were computed by the method of Section 8. It will be seen that for $\bar{r}/\bar{r}(\max)$ up to about 0.6 the distributions are not very different and the idea of "equivalent" freely jointed units is a useful one. Beyond this point the distributions begin to diverge and the idea is no longer meaningful for highly extended chains.

7. Asymptotic behavior of the distribution near maximum extension

It is of great interest to know the behavior of $\log p(r)$ in the region where r approaches its maximum value. Since it depends on the behavior of λ_0 when κ is large and convergence is slow by the methods discussed, we need to find an alternative asymptotic approach. This is a problem of some difficulty and the treatment given here is in the nature of a preliminary reconnaissance.

For freely jointed chains, we saw that when κ is large and $1 - \bar{r}/a$ is small, $\bar{r}/a \sim 1 - 1/\kappa a$. Kubo [11] stated without proof that for quite general chains a similar formula holds when κ is large, namely,

$$\frac{\bar{r}}{\bar{r}(\max)} \sim 1 - \frac{1}{\kappa a^*}, \tag{7.1}$$

where a^* is of the same order of magnitude as the unit length a and is characteristic of the chain model. I have not been able to construct a proof of this result, which can be stated in the alternative form

$$\bar{r} = a\mu'(\kappa) \sim \bar{r}(\max) - \frac{\nu}{k}, \tag{7.2}$$

where ν is a dimensionless constant, for the freely jointed chain $\nu = 1$. We now examine the limiting behavior of the integral equation (6.1) when κ is large, using heuristic arguments which strongly suggest that *for the freely rotating model* (7.2) *holds with* $\nu = \frac{3}{8}$, *whatever the bond angle* α.

When the chain is highly extended there is a considerable restriction on the possible configurations it can adopt, and indeed at its full extension it can only take the form of a planar zigzag with angles $\pm\alpha$ between successive bonds. Because of our particular choice of axes, a chain at full extension but otherwise free can rotate rigidly about one end bond lying along the z axis. With an even number $n = 2m$ of bonds, the vector $\mathbf{r}$ is uniformly distributed with fixed length $r = na \cos \frac{1}{2}\alpha$ on a cone of semiangle $\frac{1}{2}\alpha$; with an odd number $n = 2m + 1$, r is greater than $na \cos \frac{1}{2}\alpha$ and the semiangle of the cone is less than $\frac{1}{2}\alpha$, but the differences approach zero as n becomes large.

Consider a rod of length ℓ uniformly distributed on a cone of semiangle γ with axis along the z axis. It is easy to show that for this distribution,

$$M(\kappa, \psi) = \exp\{\kappa\ell \cos\psi \cos\gamma\} I_0(\kappa\ell \sin\psi \sin\gamma) \tag{7.3}$$

$$\sim \frac{\exp\{\kappa\ell \cos(\psi - \gamma)}{\sin\gamma (2\pi\kappa\ell)^{1/2}},$$

when κ is large. In fact, $M(\kappa, \psi)$ is appreciable only when $\psi - \gamma$ is $O(\kappa^{-1/2})$ and $\cos(\psi - \gamma)$ can be replaced by $1 - \frac{1}{2}(\psi - \gamma)^2$ in the exponent. This leads us to expect that for large values of κ corresponding to highly extended chains, $M_n(\kappa, \psi)$ will be concentrated near $\psi = \frac{1}{2}\alpha$ and negligible elsewhere.

Because chains with odd and even n behave differently, it is best to work with an equation relating chains with even n only. Assume $a = 1$ and consider

$$M_{2m+2}(\kappa, \psi) = \exp\{\kappa \cos\psi\} \int_{-\pi}^{\pi} \frac{1}{2\pi} \exp\{\kappa \cos\psi'\}\, d\omega \int_{-\pi}^{\pi} \frac{1}{2\pi} M_{2m}(\kappa, \psi'')\, d\omega', \tag{7.4}$$

where ψ, ψ', ω, and ψ', ψ'', ω' are related by (6.2). Note that

$$\cos\psi + \cos\psi' = 2\cos\tfrac{1}{2}\alpha\cos(\psi - \tfrac{1}{2}\alpha) - \sin\alpha\sin\psi(1 - \cos\omega). \tag{7.5}$$

Analogy with (7.3) suggests that $\Phi = \psi - \frac{1}{2}\alpha$ should be $O(\kappa^{-1/2})$, so from (6.2),

$$\Phi' = -\Phi + \tfrac{1}{2}\omega^2 \sin\alpha + O(\kappa^{-1}), \tag{7.6}$$

where ω^2 must also be $O(\kappa^{-1/2})$, and hence

$$\Phi'' = \Phi + \tfrac{1}{2}(\omega'^2 - \omega^2)\sin\alpha + O(\kappa^{-1}). \tag{7.7}$$

Writing $M_n(\Phi) \equiv M_n(\kappa, \psi)$ for brevity and using (7.5), we get as an approximation to (7.4),

$$M_{2m+2}(\Phi) = \exp\{2\kappa\cos\tfrac{1}{2}\alpha - \kappa\Phi^2\cos\tfrac{1}{2}\alpha\} \int_{-\infty}^{\infty} \frac{1}{2\pi} \exp\{-\tfrac{1}{2}\kappa\omega^2 \sin\alpha \sin\tfrac{1}{2}\alpha\}\, d\omega \cdot \int_{-\infty}^{\infty} \frac{1}{2\pi} M_{2m}(\Phi + \tfrac{1}{2}(\omega'^2 - \omega^2)\sin\alpha)\, d\omega', \tag{7.8}$$

when κ is large, the neglected terms being $O(\kappa^{-1/2})$. If we put $\sigma = \kappa\cos\frac{1}{2}\alpha$, $\Phi = \xi\sigma^{-1/2}$, $\frac{1}{2}\omega^2 \sin\alpha = \eta\sigma^{-1/2}$, $\frac{1}{2}\omega'^2 \sin\alpha = \zeta\sigma^{-1/2}$, and $M_{2m}(\Phi) \equiv Q_{2m}(\xi)$, (7.8) reduces to

$$Q_{2m+2}(\xi) = \frac{\exp\{2\sigma - \xi^2\}}{2\pi^2 \sin\alpha}\, \sigma^{-1/2} \int_0^{\infty} \exp\{-\eta\sigma^{1/2}\tan\tfrac{1}{2}\alpha\}\, \eta^{-1/2}\, d\eta \cdot \int_0^{\infty} Q_{2m}(\xi + \zeta - \eta)\zeta^{-1/2}\, d\zeta. \tag{7.9}$$

Now ω^2 was required to be $O(\kappa^{-1/2}) = O(\sigma^{-1/2})$, and hence η had to be $O(1)$. However, it will be seen from the exponential term in the integral that provided Q_{2m} is reasonably well behaved the effective range of η is in fact only $O(\sigma^{-1/2})$. We may therefore approximate again by ignoring η in $Q_{2m}(\xi + \zeta - \eta)$ and integrating out η to obtain

$$Q_{2m+2}(\xi) = \frac{\exp\{2\sigma\}\cos\frac{1}{2}\alpha}{(\pi\sin\alpha)^{3/2}}\, \sigma^{-3/4} \exp\{-\xi^2\} \int_0^{\infty} Q_{2m}(\xi + \zeta)\zeta^{-1/2}\, d\zeta. \tag{7.10}$$

Hence if κ is large, we can write

$$Q_{2m}(\xi) \sim \exp\{2m\kappa\cos\tfrac{1}{2}\alpha\}\, \kappa^{-3m/4}\, \frac{(\cos\frac{1}{2}\alpha)^{m/2}}{(\pi\sin\alpha)^{3m/2}}\, W_m(\xi), \tag{7.11}$$

where $W_m(\xi)$ is independent of κ and satisfies

$$W_{m+1}(\xi) = \exp\{-\xi^2\} \int_0^\infty W_m(\xi + \zeta)\zeta^{-1/2}\, d\zeta. \tag{7.12}$$

The conclusion from this discussion is that when κ is large enough it will occur in $M_n(\kappa, \psi)$ only within the factor $\kappa^{-3n/8} \exp\{n\kappa \cos \frac{1}{2}\alpha\}$, and hence that Kubo's result (7.2) holds with $\nu = \frac{3}{8}$ whatever the value of $\alpha > 0$. The force on a freely rotating chain at nearly maximum extension is, from (4.11),

$$F \sim \tfrac{3}{8}KT(a \cos \tfrac{1}{2}\alpha - \bar{r})^{-1}, \tag{7.13}$$

and it follows from (4.7) that in the extreme tail of the distribution $\tilde{p}(r)$ becomes proportional to $\{1 - \bar{r}/(a \cos \frac{1}{2}\alpha)\}^{3n/8-2}$.

However, apart from its heuristic nature, the discussion is not complete. A more detailed examination of the step from (7.9) to (7.10) (see Appendix) indicates that, relative to the dominant term, the term neglected at this stage is of order $\kappa^{-1/4}$. If the further approximation is to be acceptable $\kappa^{-1/4}$ must therefore be small, and this requires κ to be very large. If κ is not large enough, it appears that $\kappa(a \cos \frac{1}{2}\alpha - \bar{r})$ should lie somewhere between $\frac{3}{8}$ and $\frac{1}{2}$, depending on the value of κ. It may be that Kubo's limiting form is appropriate only for extensions so near the maximum that the assumption of a fixed bond angle is unrealistic.

There is also the fact that if both m and κ are to be large, a double limiting process is involved. One would like $W_m(\xi)$ in (7.12) to settle down for large m to the form $c^m W(\xi)$, where $c > 0$ is an eigenvalue of the equation

$$W(\xi) = c \exp\{-\xi^2\} \int_0^\infty W(\xi + \zeta)\zeta^{-1/2}\, d\zeta. \tag{7.14}$$

Unfortunately, it is known that an equation of this type has no bounded non-zero solution for any c. One can show that when $\xi > 0$,

$$W_m(\xi) = O\big((m!)^{-1/4} \exp\{-m\xi^2\}\big), \tag{7.15}$$

and when $\xi_1 > \xi_2 > 0$,

$$\frac{W_m(\xi_1)}{W_m(\xi_2)} = O\big(\exp\{m(\xi_1^2 - \xi_2^2)\}\big). \tag{7.16}$$

So on the positive axis $W_m(\xi)$ is "consumed" progressively from right to left as m increases, $W_m(0)$ dying away most slowly. Numerical iteration confirms this, and also suggests that for $\xi < 0$, $W_m(\xi)$ dies away even less rapidly (though I cannot prove it) and for large enough m, $W_m(\xi)$ will lie almost entirely on $\xi < 0$.

Nevertheless, whatever the limiting behavior of $W_m(\xi)$, our conclusions should hold for any fixed $n = 2m$ provided κ is large enough.

8. Direct computation from the integral equation

The computation of $M_n(\kappa, \psi)$ from (6.1) is a simple numerical operation most expeditiously conducted in terms of $u = \cos \psi$, so for convenience let us write $M_n(u)$ for $M_n(\kappa, \psi)$. Given that $M_n(u)$ is known for equally spaced values of u on $(-1, 1)$, $u' = \cos \psi'$ is computed from (6.2) for equally spaced values of ω and $M_n(u')$ is interpolated. Numerical integration then gives $M_{n+1}(u)$, and

$$M_n = \frac{1}{2} \int_{-1}^{1} M_n(u)\, du \tag{8.1}$$

is evaluated at each stage. The process is started with $M_1(u) = \exp\{\kappa u\}$ (assuming $a = 1$). However, $M_n(u)$ soon becomes unmanageably large as n increases, and if κ is large, $M_n(u)$ can take very large values for all values of n. It is better to modify the procedure by calculating

$$L_{n+1}(u) = \exp\{\kappa(u - \cos \tfrac{1}{2}\alpha)\} \int_{-1}^{1} \frac{1}{2\pi} \frac{L_n(u')}{L_n}\, d\omega, \tag{8.2}$$

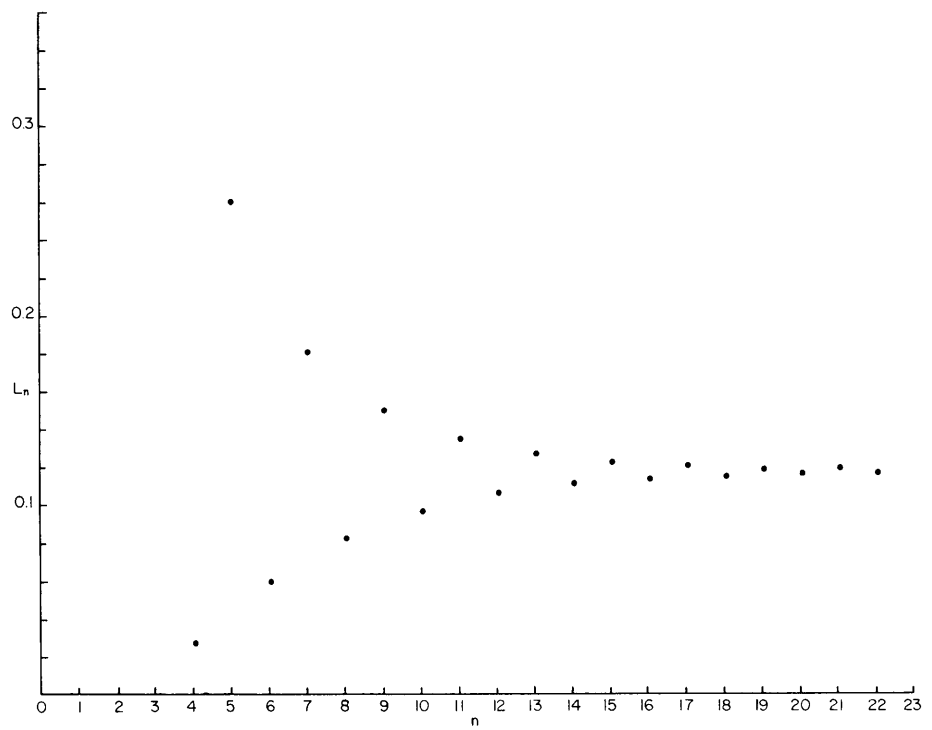

FIGURE 4
Convergence of L_n to limiting value as n increases.
$\cos \alpha_0 = \frac{1}{3}$; $\kappa = 30$; L_n against n.

where

$$L_n = \frac{1}{2}\int_{-1}^{1} L_n(u)\, du. \tag{8.3}$$

It is easily verified that

$$L_n = \frac{M_n}{M_{n-1}} \exp\{-\kappa \cos \tfrac{1}{2}\alpha\}, \tag{8.4}$$

and L_n settles down to $\exp\{\mu(\kappa) - \kappa \cos \frac{1}{2}\alpha\}$ as n increases. If n is large, this may be all that is required. The method of Section 6 produces the factor $1/C'(\lambda_0)$ in the approximation (6.6) to M_n. This factor can be recovered by the present method if $n^{-1}\,\Sigma_{j=1}^{n} \log L_j - \log L_n$ is computed at each stage, since it tends to $-\log C'(\lambda_0)$ for large n.

When κ is large, $L_n(u)$ becomes concentrated around $u = \cos \frac{1}{2}\alpha$ and a fine grid of values of u is needed if the numerical integration is to be accurate. Provided $C'(\lambda_0)$ is not required, it is preferable for such values of κ to start the process with an arbitrary distribution covering the expected range of values of u, to avoid using an unnecessary amount of computing time in the early stages.

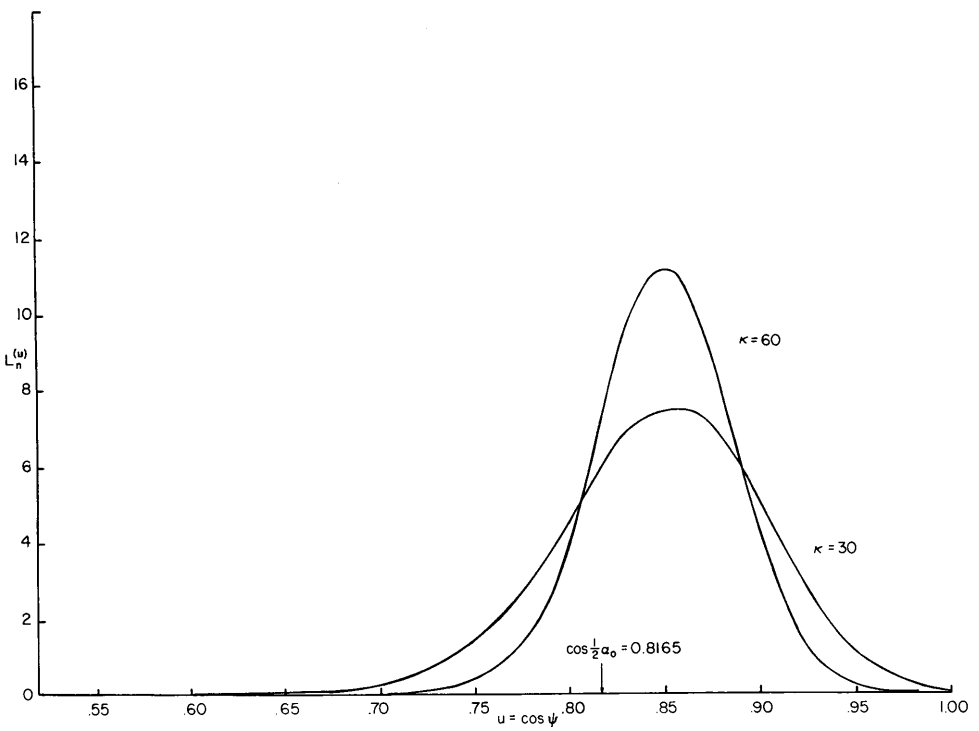

FIGURE 5
$L_n(u)$ for $\kappa = 30$ and $\kappa = 60$, $\cos \alpha_0 = \frac{1}{3}$.
L_n against $u = \cos \psi$ (n large).

The typical manner in which L_n converges to $\exp\{\mu(\kappa) - \kappa \cos \frac{1}{2}\alpha\}$ is shown in Figure 4 for $\cos \alpha = \frac{1}{3}$, $\kappa = 30$. It exhibits the oscillations to be expected for large κ because a highly extended chain behaves differently for odd and even n. The limiting forms of $L_n(u)$ for $\cos \alpha = \frac{1}{3}$ and $\kappa = 30, 60$ are also shown in Figure 5. These are interesting in view of the indication of Section 7 that when κ is very large $W_m(\xi)$ ultimately tends to lie entirely on $\xi < 0$, which implies that $L_n(u)$ should tend to lie entirely on $u > \cos \frac{1}{2}\alpha$. Clearly, $\kappa = 60$ is not large enough for this to happen, but the proportion of $L_n(u)$ for which $u > \cos \frac{1}{2}\alpha$ increases from 0.79 when $\kappa = 30$ to 0.89 when $\kappa = 60$.

9. Restricted rotation

The assumption of complete freedom of rotation is of course not true for real chains. The integral equation (5.9), or some generalization of it, can be used in a similar way when there is restricted rotation, though the abandonment of axial symmetry complicates the formulae considerably. (At the other extreme, we have the rotational isomeric model for which matrix methods are available.) For example, the approach of Section 6 can be used, but in place of (6.5), $M(\kappa, \psi, \omega)$ is expanded in a series of spherical harmonics,

$$M_n(\kappa, \psi, \omega) = \sum_{s=0}^{\infty} \sum_{\ell=-s}^{s} M_{n,s,\ell} P_s^{\ell}(\cos \psi) \exp\{i\ell\omega\}, \tag{9.1}$$

where $P_s^{\ell}(u)$ is the associated Legendre function which has an addition theorem involving Jacobi polynomials (see, for example, Edmonds [6]). The relation between the coefficients for n and $n + 1$ is

$$M_{n+1,s,\ell} = (s + \tfrac{1}{2}) \sum_{t=0}^{\infty} \sum_{m=-t}^{t} M_{n,t,m} (\sin \tfrac{1}{2}\alpha)^{\ell-m} (\cos \tfrac{1}{2}\alpha)^{\ell+m} P_{t-m}^{(\ell-m,\ell+m)}(\cos \alpha) c_{s,t}^{\ell} g_{\ell}, \tag{9.2}$$

where

$$c_{s,t}^{\ell} = \frac{(s-\ell)!}{(s+\ell)!} \int_{-1}^{1} \exp\{\kappa u\} P_s^{\ell}(u) P_t^{\ell}(u)\, du, \tag{9.3}$$

$$g_{\ell} = \int_{-\pi}^{\pi} \exp\{-im\beta\} g(\beta)\, d\beta, \tag{9.4}$$

$$P_h^{(j,k)}(x) = 2^{-h} \sum_{r=0}^{h} \binom{h+j}{r} \binom{h+k}{h-r} (x-1)^{h-r} (x+1)^r, \tag{9.5}$$

the last being the Jacobi polynomial. K. Kajiwara [10] has arrived at this formula independently in his studies of light scattering which use the characteristic function rather than the moment generating function (Burchard and Kajiwara [2]).

The required coefficient $M_{n,0,0}$ can be computed by finding λ_0 and using a formula like (6.6), but the convergence of the process is slower since the determinants are larger when truncated at a given value of s. The most practical approach seems to be to compute λ_0 directly from the integral equation (5.9) as in Section 8, though, as double integration is involved, the amount of computing time needed will be quite large. A study of the computational problems involved in both these methods is currently being carried out at Birmingham.

A theoretical investigation of the asymptotic behavior at high extensions, as in Section 7, is likely to involve new difficulties. One can imagine chain structures such that the rotational isomeric model has a different fully extended length from the real chain to which it approximates, because it rigorously excludes certain configurations. Then in cases where the rotational isomeric model is a good approximation one would expect a distinct change in the behavior of the distribution in the region beyond the maximum rotational isomeric extension.

APPENDIX

The substitutions $u = \zeta + \eta$, $v = \zeta - \eta$, $u = \mp |v| \cosh t$ reduce (7.9) to the form

$$Q_{2m+2}(\xi) = \frac{\exp\{2\sigma - \xi^2\}}{2\pi^2 \sin\sigma}\,\sigma^{-1/2} \cdot \int_{-\infty}^{\infty} \exp\{\tfrac{1}{2}v\sigma^{1/2}\tan\tfrac{1}{2}\alpha\}\, K_0(\tfrac{1}{2}|v|\sigma^{1/2}\tan\tfrac{1}{2}\alpha) Q_{2m}(\xi + v)\, dv, \tag{A.1}$$

where

$$K_0(x) = \int_0^{\infty} \exp\{-x\cosh t\}\, dt, \qquad x \geqq 0, \tag{A.2}$$

is a modified Bessel function of the second kind. When $x > 0$ is large, $K_o(x) \sim (\pi/2x)^{1/2}\exp\{-x\}$, and in fact $x^{1/2}\exp x K_0(x)$ increases monotonically from 0 to $(\frac{1}{2}\pi)^{1/2}$ as x increases from 0 to ∞.

Going from (7.9) to (7.10) is equivalent to ignoring the range $\sigma < 0$ in (A.1) and replacing K_0 by its asymptotic form in the range $\sigma \geqq 0$. Let us examine the effect of this operation. Consider first

$$I_1 = \int_0^{\infty} \exp\{Nv\}\, K_0(Nv) Q_{2m}(\xi + v)\, dv, \tag{A.3}$$

where $N = \frac{1}{2}\sigma^{1/2}\tan\frac{1}{2}\alpha$ is large. Since

$$0 < \left(\frac{\pi}{2}\right)^{1/2} - x^{1/2}\exp x\, K_0(x) < \varepsilon \tag{A.4}$$

for all $x > X(\varepsilon)$, we have

$$\text{(A.5)} \qquad \left| I_1 - \left(\tfrac{1}{2}\pi\right)^{1/2} \int_0^\infty Q_{2m}(\xi + v)(Nv)^{-1/2}\, dv \right|$$

$$= \int_0^\infty \left\{\left(\tfrac{1}{2}\pi\right)^{1/2} - x^{1/2} \exp x\, K_0(x)\right\} Q_{2m}(\xi + v)(Nv)^{-1/2}\, dv$$

$$< \left(\tfrac{1}{2}\pi\right)^{1/2} \int_0^{X(\varepsilon)/N} Q_{2m}(\xi + v)(Nv)^{-1/2}\, dv$$

$$+ \varepsilon \int_{X(\varepsilon)/N}^\infty Q_{2m}(\xi + v)(Nv)^{-1/2}\, dv$$

$$< (2\pi)^{1/2}\{X(\varepsilon)\}^{1/2} A N^{-1} + \varepsilon \int_0^\infty Q_{2m}(\xi + v)(Nv)^{-1/2}\, dv,$$

where $Q_{2m}(\xi + v) < A$. Next consider

$$\text{(A.6)} \qquad I_2 = \int_{-\infty}^0 \exp\{Nv\}\, K_0(N|v|) Q_{2m}(\xi + v)\, dv$$

$$< \left(\tfrac{1}{2}\pi\right)^{1/2} \int_0^\infty \exp\{-2Ny\}\, (Ny)^{-1/2} Q_{2m}(\xi - y)\, dy$$

$$< \left(\tfrac{1}{2}\pi\right)^{3/2} A N^{-1}.$$

The dominant part of the integral in (A.1) is therefore of order $N^{-1/2}$ and the neglected part is of order N^{-1}. In terms of κ, this means that the dominant part approximates to the integral to within a factor $1 + O(\kappa^{-1/4})$.

My principal debt is to Mr. R. L. Holder who collaborated with me extensively on the computational aspects of the work. A detailed account of our joint work will appear elsewhere. I am also grateful to Dr. D. M. G. Wishart and Professor G. E. H. Reuter for useful discussion, and to Professor M. Gordon for reviving my interest in the subject.

REFERENCES

[1] T. M. Birshtein and O. B. Ptitsyn, *Conformations of Macromolecules*, New York, Interscience, 1963.

[2] W. Burchard and K. Kajiwara, "The statistics of stiff chain molecules. I. The particle scattering factor," *Proc. Roy. Soc. Ser. A*, Vol. 316 (1970), pp. 185–199.

[3] H. E. Daniels, "The statistical theory of stiff chains," *Proc. Roy. Soc. Edinburgh, Sect. A*, Vol. 63 (1952), pp. 290–311.

[4] ———, "Saddle point approximations in statistics," *Ann. Math. Statist.*, Vol. 25 (1954), pp. 631–650.

[5] R. A. DOBRUSHIN, Review No. 2800 in *Refer. Ž. Matematika.*, Vol. 6 (1955), p. 89, review of "Statistical physics of linear polymers," by M. V. Volkenstein and O. B. Ptitsyn, *Usephi Phys. Nauk*, Vol. 49 (1953), pp. 501–568. (In Russian.)

[6] A. R. EDMONDS, *Angular Momentum in Quantum Mechanics*, Princeton, Princeton University Press, 1959.

[7] P. FLORY, *Statistical Mechanics of Chain Molecules*, New York, Wiley, 1968.

[8] J. J. HERMANS and R. ULLMAN, "The statistics of stiff chains with applications to light scattering," *Physica*, Vol. 18 (1952), pp. 951–971.

[9] R. L. JERNIGAN and P. J. FLORY, "Distribution functions for chain molecules," *J. Chem. Phys.*, Vol. 50 (1960), pp. 4185–4200.

[10] K. KAJIWARA, Private communication, 1970.

[11] R. KUBO, "Statistical theory of linear polymers. I. Intramolecular statistics," *J. Phys. Soc. Japan*, Vol. 2 (1947), pp. 47–50.

[12] ———, "Statistical theory of linear polymers, V. Paraffin-like chains," *J. Phys. Soc. Japan*, Vol. 4 (1949), pp. 319–322.

[13] O. KRATKY and G. POROD, "Röntgenuntersuchung gelöster Fadenmoleküle," *Rec. Trav. Chim.*, Vol. 68 (1949), pp. 1106–1122.

[14] W. KUHN and F. GRÜN, "Beziehungen zwischen elastischen Konstanten und Dehnungs-doppelbrechung hochelastischer Stoffe," *Kolloidzschr.*, Vol. 101 (1942), pp. 248–271.

[15] E. W. MONTROLL, "On the theory of Markoff chains," *Ann. Math. Statist.*, Vol. 18 (1947), pp. 18–36.

[16] L. R. G. TRELOAR, "The statistical length of long-chain molecules," *Trans. Faraday Soc.*, Vol. 42 (1946), pp. 77–82.

[17] M. V. VOLKENSTEIN, *Configurational Statistics of Polymeric Chains*, New York, Interscience, 1966.