Even Moments and Moment-Based Distribution Functions of the Porod–Kratky Chain

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ABSTRACT: A method is developed for calculating the even moments $\langle r^{2k} \rangle$ of the end-to-end distance r of the Porod–Kratky wormlike chain, by adapting Hermans and Ullman's recurrence-formula method to computer calculations. Actual calculations are extended to $\langle r^{40} \rangle$. The whole range of the argument $t=L/(2a)$, (L and a being the contour and persistent lengths, respectively), is covered with an accuracy of 10^{-5} for up to $\langle r^{12} \rangle$. For higher moments there remains a range of t which is not effectively covered because of a loss of accuracy due to a serious cancellation in computational results. A good agreement is achieved by a proper adjustment of parameters between even moments (through $\langle r^{12} \rangle$) of the Porod–Kratky chain and of a realistic model for polyethylene. Exact distribution functions and some averages are calculated for $t > 10$ with recourse to a previously developed method of the moment-based distribution function. Daniels' distribution is found to be a satisfactory approximation. A further improved, closed distribution function is derived.

KEY WORDS Porod–Kratky Wormlike Chain / End-to-End Distance / Even Moments / Moment-Based Distribution Function / Daniels' Distribution /

For semiflexible polymer chains such as polypeptides and polynucleotides in helicoidal conformations in solution, the Porod–Kratky wormlike chain (the PK chain) has long been considered to be a good model for describing their average spatial dimensions, specifically the mean-square end-to-end distance $\langle r^2 \rangle$ and the mean-square radius of gyration. Much work has therefore been published on the theoretical study on these and other more complex quantities of the chain and on the application thereof to the analysis of experimental data. Recently it was demonstrated by Maeda, Saito, and Stockmayer² that the PK chain is a good model for typical flexible polymer chains of short length as well, if a proper adjustment of parameters is made (see also seq.).

The PK chain is not a tractable one. Its second moment was calculated by Porod and Kratky themselves,¹ and the fourth and sixth moments by Hermans and Ullman³ and Heine, Kratky, Porod, and Schmitz.⁴ Higher even moments have not yet been calculated, in contrast with realistic

chain models for which even moments up to $\langle r^{12} \rangle$ were computed.⁵ No closed, exact expression for the distribution function has been reported, and there is little chance of finding one. An approximate expression only was reported by Daniels.⁶

In an elaboration of the PK chain the author attempted to calculate even moments as high as possible, and has actually reached as far as $\langle r^{40} \rangle$. The underlying method is to solve with a computer a recurrence formula for Laplace transforms of even and other related moments, which was previously derived and solved manually by Hermans and Ullman.³ Even moments thus obtained are compared with those for realistic chain models, thereby gauging the usefulness of the PK chain. Moment-based distribution functions and some averages are calculated from these even moments by a method previously developed,^{5,7,8} and are compared with those of Daniels.⁶ An improved distribution function is derived by using the newly calculated eighth moment.

THEORY

Even Moments; Computer Adaptation of Hermans and Ullman's Method

Hermans and Ullman³ derived a differential equation for the distribution function for the displacement $\mathbf{r}$ of one end and the tangent $\boldsymbol{\omega} = (\alpha, \beta, \gamma)$ at that end with respect to the other end, for the PK chain of contour length t . This differential equation was,³ and has yet been, unsolvable analytically, but they derived therefrom the following recurrence formula:

$$a_m u_m^{(k)} = 2(k-m)u_{m+1}^{(k)} + m u_{m-1}^{(k-1)} + m(m-1)u_{m-2}^{(k-1)} \quad (1)$$

or

$$u_m^{(k)} = a_m^{-1} [2(k-m)u_{m+1}^{(k)} + m u_{m-1}^{(k-1)} + m(m-1)u_{m-2}^{(k-1)}] \quad (2)$$

where

$$a_m = p + m(m+1) \quad (3)$$

and $u_m^{(k)}$ is the dimensionless Laplace transform with respect to t of the average $\langle (\boldsymbol{\omega} \cdot \mathbf{r})^m r^{2(k-m)} \rangle$, (here $r \equiv |\mathbf{r}|$):

$$\begin{aligned} u_m^{(k)} &= L_{\text{dl}}[\langle (\boldsymbol{\omega} \cdot \mathbf{r})^m r^{2(k-m)} \rangle] \\ &= p \int_0^\infty \langle (\boldsymbol{\omega} \cdot \mathbf{r})^m r^{2(k-m)} \rangle e^{-pt} dt \end{aligned} \quad (4)$$

The dimensionless Laplace transform is related to the ordinary Laplace transform by

$$F(p) = L_{\text{dl}}[f(t)] = p L_{\text{od}}[f(t)] \quad (5)$$

as is apparent from eq 4, and hence

$$f(t) = L_{\text{od}}^{-1}[p^{-1}F(p)] \quad (6)$$

Therefore one can calculate $\langle r^{2k} \rangle$ through

$$\langle r^{2k} \rangle = L_{\text{od}}^{-1}[p^{-1}u_0^{(k)}] \quad (7)$$

It must be noted that in the derivation of eq 1 Hermans and Ullman³ used the reduced variables, i.e., $\mathbf{r}$ and t both measured in units of $2a$ where a is the persistent length.

Hermans and Ullman³ solved eq 1 for $u_0^{(1)}$, $u_0^{(2)}$, and $u_0^{(3)}$, and inverted the first two to obtain $\langle r^2 \rangle$ and $\langle r^4 \rangle$. Heine, *et al.*,⁴ inverted $u_0^{(3)}$ to obtain $\langle r^6 \rangle$. These calculations were all made manually. This approach becomes prohibitively difficult for higher moments because of the tremendous increase in the number of calculations involved. The author therefore attempted to solve eq 1 with a computer. This method also

meets with a difficulty because eq 1 involves the Laplace-transform parameter p while a computer treats only numerical values. The difficulty can be surpassed by the following device. Even moments are expressed in two forms which are alternative in a theoretical sense but supplementary practically.

(i) *Exponential Series Expression.* This expression is a familiar one, being a finite series whose general term is expressed $t^{j-1} \exp[-l(l+1)t]$. This expression is effective for large t .

For the adaptation of eq 1 to the computer calculation the explicit display of first several of $u_m^{(k)}$ is instructive:

$$u_0^{(0)} = 1 \quad (8)$$

$$u_1^{(1)} = a_1^{-1} \quad \text{and} \quad u_0^{(1)} = a_0^{-1} - a_1^{-1} \quad (9)$$

$$p^{-1}u_0^{(1)} = a_0^{-2} - \frac{1}{2}a_0^{-1} + \frac{1}{2}a_1^{-1} \quad (10)$$

$$\left. \begin{aligned} u_2^{(2)} &= \frac{1}{3}a_0^{-1} - \frac{1}{3}a_2^{-1} \\ u_1^{(2)} &= \frac{5}{6}a_0^{-1} - a_1^{-2} - a_1^{-1} + \frac{1}{6}a_2^{-1} \\ u_0^{(2)} &= \frac{10}{3}a_0^{-2} - \frac{26}{9}a_0^{-1} + 2a_1^{-2} + 3a_1^{-1} - \frac{1}{9}a_2^{-1} \end{aligned} \right\} \quad (11)$$

$$\begin{aligned} p^{-1}u_0^{(2)} &= \frac{10}{3}a_0^{-3} - \frac{26}{9}a_0^{-2} + \frac{107}{54}a_0^{-1} \\ &\quad - a_1^{-2} - 2a_1^{-1} + \frac{1}{54}a_2^{-1} \end{aligned} \quad (12)$$

$$\begin{aligned} p^{-1}u_0^{(3)} &= \frac{70}{3}a_0^{-4} - \frac{259}{9}a_0^{-3} + \frac{226}{9}a_0^{-2} - \frac{6143}{324}a_0^{-1} \\ &\quad + \frac{21}{5}a_1^{-3} + \frac{639}{50}a_1^{-2} + \frac{4743}{250}a_1^{-1} \\ &\quad - \frac{1}{54}a_2^{-2} - \frac{1}{81}a_2^{-1} + \frac{1}{4500}a_3^{-1} \end{aligned} \quad (13)$$

Equations 8–13 suggest that $u_m^{(k)}$ and $p^{-1}u_0^{(k)}$ are expressed

$$u_m^{(k)} = \sum_{l=0}^k \sum_{j=k-l+1}^1 c'_{kmlj} a_l^{-j} \quad (14)$$

$$p^{-1}u_0^{(k)} = \sum_{l=0}^k \sum_{j=k-l+1}^1 c'_{klj} a_l^{-j} \quad (15)$$

where c'_{kmlj} and c'_{klj} are numerical constants dependent on their arguments. $u_m^{(k)}$ is expressed in a computer as an array of $\frac{1}{2}(k+1)(k+2)$ computer words for c'_{kmlj} arranged in the order as

implied in eq 14, and similarly with $p^{-1}u_0^{(k)}$. Assuming one has already constructed such arrays for $u_{m+1}^{(k)}$, $u_{m-1}^{(k-1)}$, and $u_{m-2}^{(k-1)}$, two arrays each of $\frac{1}{2}(k+1)(k+2)$ words are reserved in the computer; one is for $u_m^{(k)}$ and the other is a working array. First one constructs $a_m u_m^{(k)}$ on this working array according to eq 1. The calculation involved is simply to add the three c'' 's corresponding to the same a_l^{-j} term, with appropriate factors (as given in eq 1) multiplied. Namely, if one writes

$$a_m u_m^{(k)} = \sum_{l=0}^k \sum_{j=k-l+1}^1 c_{kmlj}^{(3)} a_l^{-j} \quad (16)$$

then we have

$$c_{kmlj}^{(3)} = 2(k-m)c_{k,m+1,lj}'' + mc_{k-1,m-1,lj}'' + m(m-1)c_{k-1,m-2,lj}'' \quad (17)$$

The next step is to construct $u_m^{(k)}$ from this $a_m u_m^{(k)}$ according to eq 2. After division of eq 16 by a_m , the terms in its rhs, having the general form $c_{kmlj}^{(3)} a_m^{-1} a_l^{-j}$, are categorized into two groups: one for $m=l$ and the other for $m \neq l$. Consider initially the first group of terms. Since the latter group of terms do not yield terms of the form a_l^{-j} ($j > 1$) upon decomposition into partial fractions (see below), one finds

$$c_{kmmj}'' = c_{kmm,j-1}^{(3)}, \quad j = k-m+1, \dots, 3, 2 \quad (18)$$

Consider now the second group terms. Using the identity

$$a_m^{-1} a_l^{-j} = -[(a_l - a_m)^{-1} a_l^{-j} + (a_l - a_m)^{-2} a_l^{-(j-1)} + \dots + (a_l - a_m)^{-j} a_l^{-1}] + (a_l - a_m)^{-j} a_m^{-1} \quad (19)$$

One rearranges

$$\sum_{j=k-l+1}^1 c_{kmlj}^{(3)} a_m^{-1} a_l^{-j} = \sum_{j=k-l+1}^1 c_{kmlj}'' a_l^{-j} - c_{kml1}'' a_m^{-1} \quad (20)$$

where

$$c_{kmlj}'' = -[(a_l - a_m)^{-1} c_{kmlj}^{(3)} + (a_l - a_m)^{-2} c_{kml,j+1}^{(3)} + \dots + (a_l - a_m)^{-(k-l-j+2)} c_{kml,k-l+1}^{(3)}]$$

or

$$c_{kmlj}'' = (a_l - a_m)^{-1} (c_{kml,j+1}'' - c_{kmlj}^{(3)}), \quad j = k-l+1, \dots, 2, 1 \quad (21)$$

with $c_{kml,k-l+2}'' \equiv 0$. According to eq 20, c_{kml}'' , which is not comprehended in eq 18, is given by

$$c_{kmm1}'' = - \sum_{l \neq m} c_{kml1}'' \quad (22)$$

Thus the rule to construct $u_m^{(k)}$ from $a_m u_m^{(k)}$ is established; eq 18, 21, and 22. The passage from $u_0^{(k)}$ to $p^{-1}u_0^{(k)}$ is similar to the special case of the above described one, i.e., from $u_1^{(k)}$ to $u_0^{(k)}$.

The set of $u_m^{(k)}$'s for $m=0, 1, \dots, k$ requires too much information to be stored in the core memory simultaneously. Two magnetic tapes are used. Let the arrays for $u_{k-1}^{(k-1)}$, $u_{k-2}^{(k-1)}$, $\dots$, $u_0^{(k-1)}$ have already been computed and stored in this order in one of two tapes. Then, $u_{k-1}^{(k-1)}$ and $u_{k-2}^{(k-1)}$ are read into the computer, and $u_k^{(k)}$ is calculated from them and written out in the other tape. $u_{k-3}^{(k-1)}$ is read in, the now unnecessary $u_{k-1}^{(k-1)}$ being erased, and $u_{k-1}^{(k)}$ is calculated and written out. This procedure is repeated until $u_0^{(k)}$ is calculated and written out. At this point $p^{-1}u_0^{(k)}$ is calculated and stored in either tape. $u_m^{(k+1)}$'s are then calculated by using $u_m^{(k)}$'s just constructed. In this procedure the roles of two tapes are exchanged and $u_m^{(k+1)}$'s are stored in the first tape the unnecessary $u_m^{(k-1)}$'s therefore being erased. Ultimately one has in one of tapes the arrays for $p^{-1}u_0^{(0)}$, $p^{-1}u_0^{(1)}$, $\dots$, $p^{-1}u_0^{(k)}$, from which one can readily calculate even moments through $\langle r^{2k} \rangle$. The starting u is $u_1^{(1)}$, the array for it being expressed according to eq 9

$$u_1^{(1)} : (0 \ 0 \ 1) \quad (23)$$

$c_{kmlj}^{(3)}$, c_{kmlj}'' , c_{klj}' (and c_{klj} below) are found to vary between very small and large values for large k (see Table I for c_{klj}). An appropriate factor multiplied to all these c 's is necessary to prevent overflow and underflow. The factor 10^{-k+2l} is found to be appropriate, the $10^{-k+2l}c$ remaining within $10^{\pm 50}$ up to $k=20$.

Even moments are calculated through

$$\langle r^{2k} \rangle = L_{od}^{-1} [p^{-1}u_0^{(k)}] = \sum_{l=0}^k \sum_{j=k-l+1}^1 c_{klj} t^{j-1} e^{-l(l+1)t} \quad (24)$$

with

$$c_{klj} = c_{klj}' / (j-1)! \quad (25)$$

where the following theorem is used:

$$L_{od}^{-1} [(p+b)^{-j}] = \frac{1}{(j-1)!} t^{j-1} e^{-bt} \quad (26)$$

From eq 10, 12, and 13 one immediately obtains

Table I. c_{klj} in eq 24 for $\langle r^8 \rangle$, $\langle r^{10} \rangle$, and $\langle r^{12} \rangle^a$

$l \setminus j$	7	6	5	4	3	2	1
c_{4lj}							
0		2 1166666666	-2 7466666666	3 2369333333	-3 4165674074	3 3290746666	
1			-1 5039999999	-2 6177599999	-3 2416671999	-3 3290554844	
2				$\bar{1}$ 1587301587	$\bar{2}$ 8314436884	$\bar{1}$ 1911240687	
3					$\bar{3}$ 1777777777	$\bar{4}$ 7111111111	
4						$\bar{5}$ 1295756397	
c_{5lj}							
0	2 4277777777	-3 4206481481	4 2090135802	-4 6285698765	5 1109826353	-4 8999555774	
1		2 1386000000	3 2843279999	4 2087929485	4 6901139925	4 8999453333	
2			$\bar{1}$ 1385739480	$\bar{2}$ 593888349	0 1177750011	0 102441966	
3				$\bar{3}$ 1086419753	$\bar{4}$ 66941015	$\bar{6}$ 75598	
4					$\bar{6}$ 925540283	$\bar{6}$ 2644401	
5						$\bar{8}$ 4443609	
c_{6lj}							
0	3 1853703703	-4 2595185185	5 1850790740	-5 8331792016	6 2437762355	-6 4315409898	6 3559443112
1		-2 4324319999	-4 1334361599	-5 1574336845	-5 9258383197	-6 2803474356	-6 3559442505
2			$\bar{1}$ 1286758089	$\bar{1}$ 2818612957	-0 319190808	-0 43991907	$\bar{1}$ 6063456
3				$\bar{4}$ 6277091906	$\bar{4}$ 4070599	$\bar{4}$ 138378	$\bar{4}$ 38993
4					$\bar{6}$ 468780143	$\bar{6}$ 2273185	$\bar{7}$ 1443
5						$\bar{8}$ 2962406	$\bar{9}$ 6583
6							$\bar{10}$ 100156

^a Values are expressed in floating form: $a\ bcde \equiv 0.bcde \times 10^a$; $-\bar{a}\ bcde \equiv -0.bcde \times 10^{-a}$.

the well-known^{1,3,4} results

$$\langle r^2 \rangle = t - \frac{1}{2} + \frac{1}{2} e^{-2t} \quad (27)$$

$$\langle r^4 \rangle = \frac{5}{3} t^2 - \frac{26}{9} t + \frac{107}{54} - t e^{-2t} - 2e^{-2t} + \frac{1}{54} e^{-6t} \quad (28)$$

$$\begin{aligned} \langle r^6 \rangle = & \frac{35}{9} t^3 - \frac{259}{18} t^2 + \frac{226}{9} t - \frac{6143}{324} \\ & + \frac{21}{10} t^2 e^{-2t} + \frac{639}{50} t e^{-2t} + \frac{4743}{250} e^{-2t} \\ & - \frac{1}{54} t e^{-6t} - \frac{1}{81} e^{-6t} + \frac{1}{4500} e^{-12t} \end{aligned} \quad (29)$$

These relations are used to check the validity of the programing.

(ii) **Power Series Expression.** $u_m^{(k)}$ and $p^{-1}u_0^{(k)}$ are expressed in power series in p^{-1} and hence $\langle r^{2k} \rangle$ is in a power series in t . This expression is effective and limited for small t .

To find an appropriate way of adaptation to a computer it is advisable to write explicitly first severals of $u_m^{(k)}$. Expanding eq 9–10 one has

$$\left. \begin{aligned} u_1^{(1)} &= p^{-1} \sum_{n=0}^{\infty} (-1)^n 2^n p^{-n} \\ u_0^{(1)} &= 2p^{-2} \sum_{n=0}^{\infty} (-1)^n 2^n p^{-n} \end{aligned} \right\} \quad (30)$$

$$\left. \begin{aligned} u_2^{(2)} &= 2p^{-2} \sum_{n=0}^{\infty} (-1)^n 6^n p^{-n} \\ u_1^{(2)} &= 3! p^{-3} \sum_{n=0}^{\infty} (-1)^n 6^n [1 + n3^{-(n+1)}] p^{-n} \\ u_0^{(2)} &= 4! p^{-4} \sum_{n=0}^{\infty} (-1)^n 6^n [1 + n3^{-(n+1)}] p^{-n} \end{aligned} \right\} \quad (31)$$

These expressions suggest that $u_m^{(k)}$ is of the form

$$u_m^{(k)} = (2k-m)! p^{-(2k-m)} \sum_{n=0}^{\infty} (-1)^n [k(k+1)]^n f_{kmn} p^{-n} \quad (32)$$

Substitution of eq 32 into eq 1 yields the following recurrence relation for f_{kmn} :

$$\begin{aligned} f_{kmn} = & m(m+1)[k(k+1)]^{-1} f_{k,m,n-1} \\ & + 2(k-m)(2k-m)^{-1} f_{k,m+1,n} \\ & + m(2k-m)^{-1} [(k-1)/(k+1)]^n f_{k-1,m-1,n} \\ & - m(m-1)[(k-1)/(k+1)]^n \\ & \times [k(k-1)]^{-1} f_{k-1,m-2,n-1} \end{aligned} \quad (33)$$

The factor $(2k-m)!$ in eq 32 makes $f_{km0}=1$. This is readily seen as follows. From eq 33

$$\left. \begin{aligned} f_{km0} &= 2(k-m)(2k-m)^{-1} f_{k,m+1,0} \\ &\quad + m(2k-m)^{-1} f_{k-1,m-1,0}, \\ &\quad \text{for } m \neq k \end{aligned} \right\} \quad (34)$$

$$f_{kk0} = f_{k-1,k-1,0}$$

From eq 34 one finds that if $f_{k-1,m0}=1$ then $f_{km0}=1$. $f_{100}=f_{110}=1$ according to eq 30. This completes the mathematical-induction proof for $f_{km0}=1$ for all k and m . Calculation with a computer indicates that f_{kmn} , starting with unity at $n=0$, either remains unchanged, decreases, or first increases and then decreases, with increasing n ; ultimately it approaches an asymptotic positive value smaller than unity. All f_{kmn} are positive and do not exceed 1.5 for up to $k=30$.

The method of computer calculations is similar to case (i) above, with the only difference that the array for $u_m^{(k)}$ includes f_{kmn} ($n=0, 1, \dots, n_M$). It is impossible to store an infinite number of f_{kmn} , so one is obliged to truncate the series at some n, n_M . In the present calculation $n_M=499$ was used for all k and m , this choice being made in consideration of the size of core memories of the computer used. This truncation of the series does not introduce errors in f_{kmn} because the subscripts to f in the rhs of eq 33 do not include $n+1, n+2, \dots$. The rule to construct f_{kmn} , i.e., through eq 33, is much simpler than that for c_{kmij}' in case (i). The starting u is $u_0^{(0)}$, the array for it being, according to eq 8 and 32,

$$u_0^{(0)} : (1 \ 0 \ 0 \ \dots \ 0) \quad (35)$$

Even moments are expressed

$$\langle r^{2k} \rangle = (2k)! t^{2k} \sum_{n=0}^{\infty} (-1)^n [(2k+n)!]^{-1} [k(k+1)]^n f_{k0n} t^n \quad (36)$$

$\langle r^4 \rangle$ and $\langle r^6 \rangle$ in this form were obtained by Heine, *et al.*,⁴ by expanding eq 28 and 29. (In eq 5 and 6 of ref 4 the summation should start with $n=0$ in place of $n=4$ and 6.)

Expressions in terms of more familiar non-reduced parameters, persistent length a and contour length L , are obtained by replacing $\langle r^{2k} \rangle$ with $\langle r^{2k} \rangle / (2a)^{2k}$ and t with $L/(2a)$.

Moments-Based Distribution Functions and Some Averages

The distribution function $W_{t*}(\mathbf{r})$ can be ex-

pressed exactly in terms of even moments.^{5,7}

$$\begin{aligned} W_{t*}(\mathbf{r}) &= \left(\frac{2}{3} \pi \langle r^2 \rangle_* \right)^{-3/2} \exp \left(-\frac{3}{2} r^2 / \langle r^2 \rangle_* \right) \\ &\quad \times \left\{ 1 + 9 \langle r^2 \rangle_*^{-2} (r^2 - \langle r^2 \rangle_*) g_2' \right. \\ &\quad + 9^2 \langle r^2 \rangle_*^{-4} \left(r^4 - \frac{10}{3} r^2 \langle r^2 \rangle_* + \frac{5}{3} \langle r^2 \rangle_*^2 \right) g_4' \\ &\quad + \dots + 9^k \langle r^2 \rangle_*^{-2k} \sum_{m=0}^k (-1)^m (2k+1)! \\ &\quad \times [(2k-2m+1)! m! 6^m]^{-1} r^{2(k-m)} \\ &\quad \times \langle r^2 \rangle_*^m g_{2k}' + \dots \left. \right\} \quad (37) \end{aligned}$$

where $\langle r^2 \rangle_*$ is such part of $\langle r^2 \rangle$ as proportional to the chain length, being for the PK chain

$$\langle r^2 \rangle_* = t \lim_{t \rightarrow \infty} t^{-1} \langle r^2 \rangle = t \quad (38)$$

and

$$\left. \begin{aligned} g_2' &= (1/3!) (\langle r^2 \rangle - \langle r^2 \rangle_*) \\ g_4' &= (1/5!) (\langle r^4 \rangle - \frac{10}{3} \langle r^2 \rangle \langle r^2 \rangle_* + \frac{5}{3} \langle r^2 \rangle_*^2), \dots, \\ g_{2k}' &= \sum_{m=0}^k (-1)^m [(2k-2m+1)! m! 6^m]^{-1} \\ &\quad \times \langle r^{2(k-m)} \rangle \langle r^2 \rangle_*^m, \dots \end{aligned} \right\} \quad (39)$$

The value of $W_{t*}(\mathbf{r})$ at $\mathbf{r}=0$, $W_{t*}(0)$, and the average of r^{-1} , $\langle r^{-1} \rangle_*$, are of particular physical interest. There is no direct analytical method to calculate them in contrast with even moments, but they can be expressed in terms of even moments:

$$\begin{aligned} W_{t*}(0) &= \left(\frac{2}{3} \pi \langle r^2 \rangle_* \right)^{-3/2} [1 - 9 \langle r^2 \rangle_*^{-1} g_2' \\ &\quad + 135 \langle r^2 \rangle_*^{-2} g_4' - \dots + (-1)^k (2k+1)! \\ &\quad \times (k!)^{-1} (3/2)^k \langle r^2 \rangle_*^{-k} g_{2k}' + \dots] \quad (40) \end{aligned}$$

$$\begin{aligned} \langle r^{-1} \rangle_* &= \left(\frac{1}{6} \pi \langle r^2 \rangle_* \right)^{-1/2} [1 - 3 \langle r^2 \rangle_*^{-1} g_2' \\ &\quad + 27 \langle r^2 \rangle_*^{-2} g_4' - \dots + (-1)^k (2k)! \\ &\quad \times (k!)^{-1} (3/2)^k \langle r^2 \rangle_*^{-k} g_{2k}' + \dots] \quad (41) \end{aligned}$$

For graphical comparisons one uses, in place of $W_{t*}(\mathbf{r})$, the reduced distribution function

$$P_{t*}(\xi) = 4\pi \langle r^2 \rangle_*^{3/2} \xi^2 W_{t*}(\langle r^2 \rangle_*^{1/2} \xi) \quad (42)$$

where $\xi = \langle r^2 \rangle_*^{-1/2} \mathbf{r}$ and $\xi = |\xi|$. Hence

$$\begin{aligned}
P_{t*}(\xi) = & 4\pi \left(\frac{2}{3}\pi\right)^{-3/2} \xi^2 \exp\left(-\frac{3}{2}\xi^2\right) \\
& \times \left\{ 1 + 9\langle r^2 \rangle_*^{-1} g_2'(\xi^2 - 1) + 9^2 \langle r^2 \rangle_*^{-2} g_4' \right. \\
& \times \left(\xi^4 - \frac{10}{3}\xi^2 + \frac{5}{3} \right) + \dots + 9^k \langle r^2 \rangle_*^{-k} g_{2k}' \\
& \times \sum_{m=0}^k (-1)^m (2k+1)! [(2k-2m+1)! \\
& \times m! 6^m]^{-1} \xi^{2(k-m)} + \dots \left. \right\} \quad (43)
\end{aligned}$$

In actual calculations one is obliged to truncate the series insofar as it is not possible to calculate all even moments. $W_{t*}(\mathbf{r})$, $W_{t*}(0)$, $\langle r^{-1} \rangle_*$, and $P_{t*}(\xi)$, truncated at the k -th term, *i.e.*, involving g_{2k}' , are written as $W_{t*}^{(k)}(\mathbf{r})$, $W_{t*}^{(k)}(0)$, $\langle r^{-1} \rangle_*^{(k)}$, and $P_{t*}^{(k)}(\xi)$, respectively.

Jernigan and Flory^{9,10} proposed a modified distribution function and suggested that it was preferable for reasons of rapid convergence and others. It is

$$W_t(\mathbf{r}) = W_{t*}(\mathbf{r}) \text{ in eq 37, with } \langle r^2 \rangle \text{ in place of } \langle r^2 \rangle_* \quad (44)$$

Correspondingly one has

$$W_t(0) = W_{t*}(0) \text{ in eq 40, with } \langle r^2 \rangle \text{ in place of } \langle r^2 \rangle_* \quad (45)$$

$$\langle r^{-1} \rangle = \langle r^{-1} \rangle_* \text{ in eq 41, with } \langle r^2 \rangle \text{ in place of } \langle r^2 \rangle_* \quad (46)$$

$$P_t(\xi) = P_{t*}(\xi) \text{ in eq 43, with } \langle r^2 \rangle \text{ in place of } \langle r^2 \rangle_* \quad (47)$$

Also $W_t^{(k)}(\mathbf{r})$, $W_t^{(k)}(0)$, $\langle r^{-1} \rangle^{(k)}$ and $P_t^{(k)}(\xi)$ are similarly defined. It should be noted that in the above modification the explicit as well as implicit (*i.e.*, through g_{2k}') $\langle r^2 \rangle_*$ must be replaced with $\langle r^2 \rangle$.

Upon integration over angle coordinates, Daniels' distribution function⁶ becomes in the reduced variables

$$\begin{aligned}
W_{t*}^{(D)}(\mathbf{r}) = & \left(\frac{3}{2}\pi t\right)^{-3/2} \exp\left(-\frac{3}{2}r^2/t\right) \\
& \times \left(1 - \frac{5}{8t} + \frac{2r^2}{t^2} - \frac{33r^4}{40t^3}\right) \quad (48)
\end{aligned}$$

where the superscript D to W refers, unlike k , to Daniels. Originally Daniels' function also was

expressed in a series, but terms higher in t^{-1} than those in eq 48 were not given. His series expression corresponds to, and is better compared with, the author's $W_{t*}(\mathbf{r})$, because $\langle r^2 \rangle_* = t$ for the PK chain. Hence

$$\begin{aligned}
P_{t*}^{(D)}(\xi) = & 4\pi \left(\frac{2}{3}\pi\right)^{-3/2} \xi^2 \exp\left(-\frac{3}{2}\xi^2\right) \\
& \times \left(1 - \frac{5}{8t} + \frac{2\xi^2}{t} - \frac{33\xi^4}{40t^2}\right) \quad (49)
\end{aligned}$$

$$W_{t*}^{(D)}(0) = \left(\frac{2}{3}\pi t\right)^{-3/2} \left(1 - \frac{5}{8t}\right) \quad (50)$$

$$\langle r^{-1} \rangle_{t*}^{(D)} = \left(\frac{1}{6}\pi t\right)^{-1/2} \left(1 - \frac{1}{40t}\right) \quad (51)$$

In eq 49 $\xi = t^{-1/2}r$. Daniels' distribution is obtained from $W_{t*}^{(D)}(\mathbf{r})$ by discarding t^{-2} and exponential terms.

RESULTS AND DISCUSSION

Even Moments

Calculations were made with a single precision of the computer, *i.e.*, of 40 binary bits, and extended to $k=30$ for both cases (i) and (ii). However, the range of k and t for which the calculated even moments are actually useful is rather limited on account of limited accuracy. In the exponential series expression there occurs a serious cancellation for small t , as is apparent from eq 27 and 28. In the power series expression the series is of slow convergence as well as subject to a cancellation because it is an alternating series, these being more serious for larger values of k . Obviously the two expressions supplement each other. There is a range of t within which the accuracy of calculated moments is significantly diminished, or even completely lost, by either method. Such a range increases with increasing k . In the present calculations the author was able to cover the entire range of t with an accuracy of 10^{-5} or better, but only for values up to $k=6$, *i.e.*, $\langle r^{12} \rangle$.

c_{klj} for $\langle r^8 \rangle$, $\langle r^{10} \rangle$, and $\langle r^{12} \rangle$ are given in Table I. To obtain these, three runs of computations were carried out which are different in initial values of c_{111} of $u_1^{(1)}$ by one or two at the least-significant bit. Only those digits which are not affected by these changes are displayed. One sees that the accuracy is considerably diminished for

some c_{klj} . Fortunately, less accurate c_{klj} make less contributions to the total $\langle r^{2k} \rangle$. (Exact c_{klj} could be obtained by expressing $c_{klj}'' = \sum_{\mu, \nu} d_{klj\mu\nu} \times \mu^{-\nu}$ and storing $d_{klj\mu\nu}$ instead of c_{klj}'' , where μ is a positive integer, ν is zero or a positive integer, and $d_{klj\mu\nu}$ is zero or an integer. This procedure requires much more memory, however.)

Comparison with results obtained by the power series method indicates that c_{klj} in Table I give values of $\langle r^{2k} \rangle$ of the accuracy of 10^{-5} or better down to $t=0.4$, 0.6, and 0.8 for $k=4$, 5, and 6, respectively. For larger k , t must be larger to achieve the same accuracy, e.g., $t>2$, 12, and 30 for $k=10$, 20, and 30, respectively, according

Table IIa. $f_{4.0.n}$ in eq 36

n	n	n	n	n	n
1 1.199999999	10 0.8353347394	19 0.8229161995	28 0.8227055017	37 0.8227025140	46 0.8227024752
2 1.139999999	11 308493751	20 8364856	29 43491	38 4989	47 50
3 1.049714285	12 279325296	21 7863469	30 36343	39 4896	48 49
4 0.9776485714	13 260461579	22 7548775	31 31914	40 4838	49,50 48
5 0.9266399999	14 248322522	23 7351640	32 29173	41 4803	> 50 47
6 0.8917836571	15 240545437	24 7228369	33 27478	42 4781	
7 0.8682937371	16 235582590	25 7151412	34 26431	43 4768	
8 0.8525991951	17 232426782	26 7103441	35 25785	44 4760	
9 0.8421901850	18 230426391	27 7073580	36 25386	45 4755	

Table IIb. $f_{5.0.n}$ in eq 36

n	n	n	n	n	n
1 1.222222222	12 0.7395341234	23 0.7233958505	34 0.7230834973	45 0.7230784235	56 0.7230783480
2 1.157037037	13 347058250	24 2977716	35 818701	46 3990	57 76
3 1.051188712	14 312709411	25 2298008	36 807555	47 3823	58 74
4 0.9622781892	15 288354125	26 1827636	37 799925	48 3710	59 72
5 0.8957866666	16 271139113	27 1502563	38 794705	49 3633	60 71
6 0.8474092117	17 259006895	28 1278188	39 791137	50 3580	61-63 70
7 0.8124156432	18 250480150	29 1123497	40 788699	51 3544	64-102 69
8 0.7871332471	19 244502541	30 1016964	41 787034	52 3520	> 102 68
9 0.7688864093	20 240321740	31 0943673	42 785898	53 3504	
10 0.7557419746	21 237403912	32 0893298	43 785124	54 3492	
11 0.7462980897	22 235371544	33 0858706	44 784595	55 3485	

Table IIc. $f_{6.0.n}$ in eq 36

n	n	n	n	n	n
1 1.238095238	14 0.6491781827	27 0.6303915245	40 0.6299969588	53 0.6299899790	66 0.6299898658
2 1.169312169	15 443760349	28 2856324	41 50435	54 9476	67 53
3 1.051866249	16 407559630	29 2074624	42 36435	55 9247	68 49
4 0.9501288043	17 380324928	30 1498171	43 26207	56 9081	69 47
5 0.8716011853	18 359876979	31 1073491	44 18738	57 8960	70 45
6 0.8124275277	19 344554937	32 0760913	45 13287	58 8872	71 43
7 0.7679151708	20 333095745	33 0531045	46 09310	59 8808	72,73 42
8 0.7343308276	21 324541141	34 0362141	47 06410	60 8762	74,75 41
9 0.7089157585	22 318165904	35 0238129	48 04296	61 8728	76-112 40
10 0.6896467790	23 313422544	36 0147144	49 02756	62 8704	> 112 39
11 0.6750274062	24 309898738	37 0080437	50 01634	63 8686	
12 0.6639386341	25 307284682	38 0031563	51 00817	64 8674	
13 0.6555360227	26 305348110	39 0.6299995776	52 00223	65 8664	

to a comparison of differences in results of the three runs noted above. With the present precision of calculations $\langle r^{2k} \rangle$ for $k > 20$ are actually useless; they lack accuracies for small t where they are necessary, while they are unnecessary (because of the achieved convergence) for large t where they are sufficiently accurate. For very large k , terms for $l=0$ and 1 become dominant over others. For example, for $k=20$, $c_{20,lj}$ for $l \neq 0$ or 1 are smaller than those for $l=0$ or 1 by a factor of 10^{-13} or less. f_{k0n} for $k=4, 5$, and 6 are given in Tables IIa, b, and c. These f_{k0n} give $\langle r^{2k} \rangle$ of the accuracy of 10^{-5} or better up to $t=1.5, 1.2$, and 1.0 for $k=4, 5$, and 6, respectively.

$\langle r^{2k} \rangle / \langle r^{2k} \rangle_*$ calculated by the exponential series method are plotted against t with solid curves in Figures 1a and b. Here $\langle r^{2k} \rangle_*$ is the asymptotic value of $\langle r^{2k} \rangle$ at $t=\infty$, i.e.,

$$\langle r^{2k} \rangle_* = \frac{(2k+1)!}{k!6^k} \langle r^2 \rangle_*^k = \frac{(2k+1)!t^k}{k!6^k} \quad (52)$$

In Figure 1a are included for comparison the previously⁵ calculated results (broken curves) for the realistic, *trans*-*gauche* rotational-isomeric-state model for polyethylene (subchain of ref 5). n in the upper abscissa is the number of C—C bonds. It was assumed between n and t^*

$$n = 12.002t \quad (53)$$

* The adjustment of the realistic chain with the PK chain is made as follows. $\langle r^2 \rangle$ for very long (say, $n > 100$) realistic chains^{5,7} and the very long PK chain behave almost exactly as

$$\langle r^2 \rangle = An - B \quad (\text{realistic chains}) \quad (54)$$

$$\langle r^2 \rangle = 2aL - 2a^2 \quad (\text{PK chain}) \quad (55)$$

The first relation of the adjustment is, as usually made, to equate the leading terms in eq 54 and 55, i.e., $An = 2aL$. The second relation proposed here is to equate the second terms, i.e., $B = 2a^2$. Then one finds

$$a = (B/2)^{1/2} \quad \text{and} \quad L = A(2B)^{-1/2}n \quad (56)$$

$$t = L/(2a) = A(2B)^{-1}n \quad (57)$$

Numerical results for A and B (taken from eq 66a of ref 5) yielded eq 53. It is found that the adjustment proposed above analytically reproduces an empirical "best shift factor" of Maeda, *et al.*² Detailed discussions on the adjustment will soon be given elsewhere.¹¹

Figure 1. $\langle r^{2k} \rangle / \langle r^{2k} \rangle_*$ vs. t for the Porod-Kratky chain (solid curves), and $\langle r^{2k} \rangle / \langle r^{2k} \rangle_*$ vs. n for the polyethylene chain⁵ (broken curves). t is the contour length, n is the number of C—C bonds, and $\langle r^{2k} \rangle_*$ is the asymptotic value of $\langle r^{2k} \rangle$ at t or $n=\infty$. For the adjustment of parameters see text.

Broken curves for $k=1$ and 2 are very close to the corresponding solid curves, and hence are not included to avoid confusion. Though small systematic deviations occur for higher moments, the agreement is very satisfactory and encouraging.

$\langle r^{2k} \rangle / t^{2k}$ values calculated with a sufficient accuracy by the power series method are plotted against t in Figure 2. Obviously t^{2k} is r^{2k} for the stiff rod. The range of t effectively covered is rather limited, in particular for large k , as seen with curves $k=6$ and 10. The loss of accuracy

Figure 2. $\langle r^{2k} \rangle / t^{2k}$ vs. t . t^{2k} is r^{2k} for the stiff rod.

by a cancellation (from summation of terms of alternating sign) was found to be a more serious cause of it than the slow convergence of the series.

$$W_{t*}(0), W_t(0), \langle r^{-1} \rangle_*, \text{ and } \langle r^{-1} \rangle$$

In Figure 3 and 4, $W_{t*}^{(k)}(0)/W_{t*}^{(0)}(0)$ and $W_t^{(k)}(0)/W_t^{(0)}(0)$ are plotted against t . Here the denominators are the respective Gaussian analogs, i.e.,

$$W_{t*}^{(0)}(0) = \left(\frac{2}{3} \pi \langle r^2 \rangle_* \right)^{-3/2}$$

$$\text{and } W_t^{(0)}(0) = \left(\frac{2}{3} \pi \langle r^2 \rangle \right)^{-3/2} \quad (58)$$

In order to see the speed of convergence, these

Figure 3. $W_{t*}^{(k)}(0)/W_{t*}^{(0)}(0)$ vs. t for various k indicated. D refers to the consequence of Daniels' distribution, eq 50.

Figure 4. $W_t^{(k)}(0)/W_t^{(0)}(0)$ vs. t for various k indicated.

ratios are plotted against k for selected t in Figure 5. One observes that the convergence, though very protracted, is almost achieved at $k=16-18$ for $t=10$, and at smaller k for larger t . Thus one can regard $W_{t*}^{(18)}(0)$ and $W_t^{(18)}(0)$ as $W_{t*}(0)$ and $W_t(0)$ for $t > 10$ in Figures 3 and 4.

It is noteworthy that curve D for Daniels' distribution is very close to curve 18 in Figure 3, and curve 2 is very close to curve 18 in Figure 4, suggesting that $W_{t*}^{(D)}(r)$ and $W_t^{(2)}(r)$ may be good approximations for $W_{t*}(r)$ and $W_t(r)$, respectively. A closer, numerical comparison is made in Table III.

In Figure 6 and 7, $\langle r^{-1} \rangle_*^{(k)}/\langle r^{-1} \rangle_*^{(0)}$ and $\langle r^{-1} \rangle^{(k)}/\langle r^{-1} \rangle^{(0)}$ are plotted against t , where

$$\langle r^{-1} \rangle_*^{(0)} = \left(\frac{1}{6} \pi \langle r^2 \rangle_* \right)^{-1/2}$$

$$\text{and } \langle r^{-1} \rangle^{(0)} = \left(\frac{1}{6} \pi \langle r^2 \rangle \right)^{-1/2} \quad (59)$$

The general features are almost the same as in the case of $W_{t*}(0)$ and $W_t(0)$. The difference between curves D and 18 in Figure 6 is larger on graphs than that in Figure 4. This is due in most part to the difference in ordinate scales. Numerical results are given in Table IV.

$$P_{t*}(\xi) \text{ and } P_t(\xi)$$

$P_{t*}^{(18)}(\xi)$ and $P_t^{(18)}(\xi)$ are plotted against ξ for $t=10, 20$, and ∞ in Figure 8 and 9. Different types of plot for $P_{t*}^{(18)}(\xi)$ are shown in Figure 10, i.e., $\log_{10}[P_{t*}^{(18)}(\xi)/(4\pi\xi^2)]$, $\{\log_{10}[t^{3/2}W_{t*}^{(18)}(r)]\}$, vs.

Figure 5. Speeds of convergence of $W_{t*}^{(k)}(0)$ and $W_t^{(k)}(0)$ with increasing k .

Table III. $W_{t*}(0)$ and $W_t(0)$ in various approximations

t	$\frac{W_{t*}^{(18)}(0)}{W_{t*}^{(0)}(0)}$	$\frac{W_{t*}^{(D)}(0)}{W_{t*}^{(0)}(0)}$	$\frac{W_{t*}^{(N)}(0)}{W_{t*}^{(0)}(0)}$, eq 61	$\frac{W_t^{(18)}(0)}{W_t^{(0)}(0)}$	$\frac{W_t^{(2)}(0)}{W_t^{(0)}(0)}$	$\frac{W_t^{(N)}(0)}{W_t^{(0)}(0)}$, eq 63
10	0.9355	0.93750	0.93626	0.8660	0.86715	0.86689
11	416	4318	4216	8781	87877	87862
12	467	4791	4705	8882	88854	88846
13	510	5192	5119	8967	89686	89682
14	546	5535	5472	9039	90403	90402
15	577	5833	5778	9102	91027	91028
16	604	6093	6045	9157	91575	91577
17	627	6323	6280	9206	92060	92063
18	6488	6527	6489	92496	92493	92496
19	6675	6710	6676	92884	92881	92884
20	6843	6875	6844	93234	93230	93234
21	6994	7023	6995	93551	93547	93551
22	7132	7159	7133	93840	93836	93840
23	7258	7282	7259	94104	94100	94104
24	7373	7395	7374	94346	94343	94347
25	7479	7500	7480	94569	94566	94570
26	7577	7596	7577	94776	94772	94776
27	7667	7685	7668	94967	94964	94967
28	7751	7767	7752	95144	95141	95145
29	7829	7844	7830	95310	95307	95310
30	7902	7916	7902	95464	95462	95465

ξ^2 , which exaggerate distribution tails. Curve D is for Daniels' distribution. To examine the degree of convergence $P_{10*}^{(k)}(\xi)$ and $P_{10}^{(k)}(\xi)$ are plotted against k for selected ξ in Figure 11. one sees that both functions are almost convergent at $k=16-18$. Accuracies are sufficient for

$\xi < 2.4$, but are diminished and eventually lost with increasing ξ . The functions are more rapidly convergent and accurate up to larger ξ for larger t . Therefore, $P_{t*}^{(18)}(\xi)$ and $P_t^{(18)}(\xi)$ in the ordinates of Figures 8 and 9 can be regarded as $P_{t*}(\xi)$ and $P_t(\xi)$. Similarly, curves $t=10$ and

Figure 6. $\langle r^{-1} \rangle_*^{(k)} / \langle r^{-1} \rangle_*^{(0)}$ vs. t for various k indicated. D refers to the consequence of Daniels' distribution, eq 51.

Figure 7. $\langle r^{-1} \rangle^{(k)} / \langle r^{-1} \rangle^{(0)}$ vs. t for various k indicated.

Table IV. $\langle r^{-1} \rangle_*$ and $\langle r^{-1} \rangle$ in various approximations

t	$\frac{\langle r^{-1} \rangle_*^{(18)}}{\langle r^{-1} \rangle_*^{(0)}}$	$\frac{\langle r^{-1} \rangle_*^{(D)}}{\langle r^{-1} \rangle_*^{(0)}}$	$\frac{\langle r^{-1} \rangle_*^{(N)}}{\langle r^{-1} \rangle_*^{(0)}}, \text{ eq 62}$	$\frac{\langle r^{-1} \rangle^{(18)}}{\langle r^{-1} \rangle^{(0)}}$	$\frac{\langle r^{-1} \rangle^{(2)}}{\langle r^{-1} \rangle^{(0)}}$	$\frac{\langle r^{-1} \rangle^{(N)}}{\langle r^{-1} \rangle^{(0)}}, \text{ eq 64}$
10	0.99730	0.997500	0.997337	0.97204	0.973430	0.972087
11	756	7727	7592	7463	75755	74658
12	778	7916	7803	7677	77709	76796
13	796	8076	7980	7858	79373	78601
14	812	8214	8131	8013	80807	80146
15	825	8333	8254	8147	82055	81483
16	836	8437	8373	8264	83151	82651
17	846	8529	8473	83676	84121	83680
18	8557	8611	8560	84591	84986	84594
19	8636	8684	8639	85408	85762	85411
20	8706	8750	8709	86144	86461	86146
21	8770	8809	8772	86808	87095	86811
22	8828	8863	8829	87412	87673	87414
23	8880	8913	8882	87963	88201	87965
24	8928	8958	8930	88468	88686	88469
25	8972	9000	8973	88932	89133	88933
26	9013	9038	9014	89360	89545	89361
27	9050	9074	9051	89757	89928	89758
28	9085	9107	9086	90124	90283	90125
29	9117	9137	9118	90467	90615	90468
30	9147	9166	9148	90786	90924	90787

20 in Figure 10 can be regarded as for $P_{t*}(\xi)$. Open circles in Figure 11 are for Daniels' distribution. They are close to the asymptotic, exact values for $\xi < 1.0$, but discernibly deviate for larger ξ (see also Figure 10). However, deviations of $P_{t*}^{(18)}(\xi)$ from $P_{t*}^{(D)}(\xi)$ are much

smaller than those of $P_{t*}^{(18)}(\xi)$ from $P_{t*}^{(0)}(\xi)$. This can be seen clearly with the following numerical values: ξ , $P_{t*}^{(0)}(\xi)$, $P_{t*}^{(18)}(\xi)$, $P_{t*}^{(D)}(\xi)$; 0.4, 0.52180, 0.50345, 0.50479; 0.8, 1.01596, 1.04964, 1.04818, 1.2, 0.68850, 0.73334, 0.72598; 1.6, 0.22812, 0.19972, 0.20732; 2.4, 0.0042241, 0.000022,

Figure 8. $P_{t*}^{(18)}(\xi)$ vs. ξ for t indicated.

Figure 9. $P_t^{(18)}(\xi)$ vs. ξ for t indicated.

-0.0027357 . Thus $P_{t*}^{(D)}(\xi)$ is a good approximation for $P_{t*}(\xi)$ for $\xi < 2.4$ and $t=10$, and better up to larger ξ for larger t . The situation is similar for $P_t^{(2)}(\xi)$ as an approximation for $P_t(\xi)$. Degrees of approximation of $P_{t*}^{(D)}(\xi)$ and $P_t^{(2)}(\xi)$ are not much different if the whole range of $\xi < 2.4$ is considered. $P_{t*}^{(D)}(\xi)$ is preferred on account of its simplicity.

The author attempted to improve Daniels' distribution by including higher-order terms. In

Figure 10. $\log_{10}[P_{t*}^{(18)}(\xi)/(4\pi\xi^2)]$ vs. ξ^2 for t indicated. Curve D, $t=10$ is for Daniels' distribution. Curve N, $t=10$ for eq 60, not given, falls between curve $t=10$ and curve D, $t=10$, being closer to the former for $\xi^2 < 4.5$ and the latter for $\xi^2 > 4.5$.

this connection the following point should be noted $W_{t*}^{(2)}(\mathbf{r})$ yields exact, second and fourth moments while $W_{t*}^{(D)}(\mathbf{r})$ gives approximate ones. [$W_{t*}^{(D)}(\mathbf{r})$ gives even moments made up of two terms, these being exactly the same as the leading two terms in exact even moments: for example, $\langle r^4 \rangle = (5/3)t^2 - (26/9)t$ instead of eq 28.¹²] Nevertheless, $W_{t*}^{(D)}(\mathbf{r})$ is better than $W_{t*}^{(2)}(\mathbf{r})$. Exponential terms in even moments are negligible for $t > 5$. The difference between $W_{t*}^{(D)}(\mathbf{r})$ and $W_{t*}^{(2)}(\mathbf{r})$ is that the former contains *all* of the t^{-1} terms and *no* higher terms in $W_{t*}(\mathbf{r})$, whereas the latter has *all* of the t^{-1} terms and *part* of the t^{-2} terms in $W_{t*}(\mathbf{r})$. This fact suggests that an improvement could be made by retaining *all* of t^{-1} and t^{-2} terms and by discarding *all* higher-order terms in $W_{t*}(\mathbf{r})$. To this end one must take into account up to the $k=4$ term in eq 37.^{7,12} Hence

$$\begin{aligned}
 W_{t*}^{(N)}(\mathbf{r}) = & \left(\frac{3}{2} \pi t \right)^{-3/2} \exp \left(-\frac{3}{2} r^2/t \right) \\
 & \times \left[1 - \frac{1}{8t} \left(5 + \frac{7.9}{8t} \right) + \left(2 - \frac{32.9}{24t} \right) \frac{r^2}{t^2} \right. \\
 & + \left(-\frac{3.3}{4} + \frac{67.99}{16t} \right) \frac{r^4}{t^3} - \frac{34.41}{14} \frac{r^6}{t^5} \\
 & \left. + \frac{10.89}{32} \frac{r^8}{t^6} \right] \quad (60)
 \end{aligned}$$

Figure 11. Convergence of $P_{10*}^{(k)}(\xi)$ and $P_{10}^{(k)}(\xi)$ with increasing k for selected ξ . Open circles denote predictions of Daniels' distribution, eq 49, and filled ones those of eq 60 [of course converted to $P_{10}^{(N)}(\xi)$].

$$W_{t*}^{(N)}(0) = \left(\frac{3}{2}\pi t\right)^{-3/2} \left[1 - \frac{1}{8t} \left(5 + \frac{7.9}{8t}\right)\right] \quad (61)$$

$$\langle r^{-1} \rangle_*^{(N)} = \left(\frac{1}{6}\pi t\right)^{-1/2} \left(1 - \frac{1}{40t} - \frac{7.3}{448t^2}\right) \quad (62)$$

where the superscript N refers to Nagai, not do numerals. Numerical coefficients in eq 60–62 are exact. $W_{t*}^{(N)}(\mathbf{r})$ gives even moments composed of three terms, these being exactly the same as the leading three terms in exact even moments. $P_{t*}^{(N)}(\xi)$ is defined from $W_{t*}^{(N)}(\mathbf{r})$ by patterning after $P_{t*}^{(k)}(\xi)$ and $P_{t*}^{(D)}(\xi)$. Values of $P_{10*}^{(N)}(\xi)$ are shown by filled circles in Figure 11 (see also the caption for Figure 10). $P_{t*}^{(N)}(\xi)$ is definitely an improvement over Daniels' distribution $P_{t*}^{(D)}(\xi)$. $P_{t*}^{(N)}(\xi)$ is better than $P_{t*}^{(4)}(\xi)$ despite the fact that the former gives approximate even moments whereas the latter gives exact even moments up to $\langle r^8 \rangle$. Unasterisked counterparts of eq 61 and 62 can be obtained by writing t neighboring π in these expressions as

$$\begin{aligned} t &= \left(t - \frac{1}{2}\right) \left[1 + \frac{1}{2t} \left(1 - \frac{1}{2t}\right)^{-1}\right] \\ &= \left(t - \frac{1}{2}\right) \left(1 + \frac{1}{2t} + \frac{1}{4t^2} + \dots\right) \end{aligned}$$

i.e.,

$$W_t^{(N)}(0) = \left[\frac{3}{2}\pi \left(t - \frac{1}{2}\right)\right]^{-3/2} \left[1 - \frac{1}{8t} \left(11 - \frac{28.1}{8t}\right)\right] \quad (63)$$

$$\langle r^{-1} \rangle_*^{(N)} = \left[\frac{1}{6}\pi \left(t - \frac{1}{2}\right)\right]^{-1/2} \left(1 - \frac{11}{40t} - \frac{18.5}{448t^2}\right) \quad (64)$$

where higher than t^{-2} terms are discarded. Numerical results based on eq 61–64 are included in Tables III and IV.*

It was argued^{9,10} that eq 44 is preferred over eq 37 on account of the rapid convergence. Present calculations (Figure 11) indicate that speeds of convergence of both series are almost identical for the PK chain.

* It is found that numerical data are a little better fitted by the following equations than by eq 61–64:

$$W_{t*}^{(N)}(0) = \left(\frac{3}{2}\pi t\right)^{-3/2} \left[1 - \frac{1}{8t} \left(5 + \frac{1}{t}\right)\right] \quad (65)$$

$$\langle r^{-1} \rangle_*^{(N)} = \left(\frac{1}{6}\pi t\right)^{-1/2} \left[1 - \frac{1}{120t} \left(3 + \frac{2}{t}\right)\right] \quad (66)$$

$$W_t^{(N)}(0) = \left[\frac{3}{2}\pi \left(t - \frac{1}{2}\right)\right]^{-3/2} \left[1 - \frac{1}{16t} \left(22 - \frac{7}{t}\right)\right] \quad (67)$$

$$\langle r^{-1} \rangle_*^{(N)} = \left[\frac{1}{6}\pi \left(t - \frac{1}{2}\right)\right]^{-1/2} \left[1 - \frac{1}{120t} \left(33 + \frac{5}{t}\right)\right] \quad (68)$$

The author cannot be sure whether this result is real, i.e., eq 65–68 are really better, or just a consequence of some systematic errors in the computed results. Analytical eq 61–64 are preferred over empirical eq 65–68.

CONCLUSIONS

A general method for calculating even moments of the PK chain has been developed by adapting Hermans and Ullman's method to computer calculations, and these have actually been calculated up to $\langle r^{40} \rangle$. A good agreement is found between these even moments and those for a realistic model for polyethylene, if a proper adjustment of parameters is made.

These even moments have been used to calculate distribution functions and related quantities. The series are almost convergent at $k=16-18$ for $t=10$ and at lower k for larger t . This work is the first in which the series, eq 37 and 44, are calculated until a sufficient convergence is reached. Equations 37 and 44 are not tractable, but are unique, exact expressions available for models of physical interest,^{7,10,12} except for the simplest, *i.e.*, the random flight chain.¹³ If even moments are calculable for a model chain, they serve as a basis for judging the validity and usefulness of any approximate distribution functions, as done by us with Daniels' distribution for the PK chain.

Daniels' distribution is found to be satisfactory approximation despite its simplicity. $W_t^{(2)}(\mathbf{r})$ is equally good. $W_{t*}^{(N)}(\mathbf{r})$, derived in this paper, is better than both.

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