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Treloar's distribution and its numerical implementation

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Abstract. A simple derivation of Treloar's distribution $W_Z(h)$ for the length h of a freely-connected chain made up from $Z-1$ bonds of the length b is given on the basis of Chandrasekhar's integral form. The recurrence equations derived from an integral form and also from that of Treloar allow successive computations of the distributions W_Z. These equations were used for numerical calculations of W_Z for all $Z \leqslant 800$ and proved to be very efficient. The course of several distributions is presented.

1. Introduction

The complete configurational description of the polymer molecule is given by a series of distribution functions for distances of the chain nodes from the chosen reference node. These functions are usually approximated by a statistical distribution for the length h of the chain; this length is understood to be the end-to-end distance.

The properties of actual polymers are studied on simplified models. Further, only the model of a freely-connected chain is dealt with; volume effects are neglected and the chain is assumed to consist of $Z-1$ bonds of the same length b, the space orientation of each bond being independent of the orientation of the other bonds (figure 1). For this

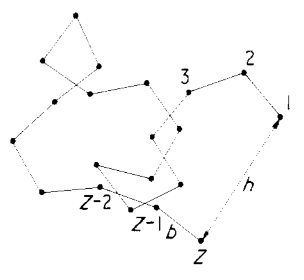

Figure 1. Freely-jointed chain.

model the density distribution function (DDF) W_Z was derived in several forms, the mutual relations of which are not clear from the derivation. The exact forms of this distribution are:

(i) Rayleigh's or Chandrasekhar's form (Rayleigh 1919, Chandrasekhar 1943)

$$W_Z(h) = \frac{1}{2\pi^2 b^2 h} \int_0^\infty \lambda \sin\left(\lambda \frac{h}{b}\right) \left(\frac{\sin \lambda}{\lambda}\right)^Z d\lambda \tag{1}$$

derived with the use of Markov's formula for DDF of the sum of independent random variables

(ii) Treloar's form (Treloar 1946)

$$W_Z(h) = \frac{1}{8\pi b^2 h}\frac{Z^{Z-2}}{(Z-2)!}\sum_{\nu=0}^{k}(-1)^{\nu}\binom{Z}{\nu}\left(m-\frac{\nu}{Z}\right)^{Z-2} \tag{2}$$

where $m = \frac{1}{2}\{1-(h/bZ)\}$, $k = [mZ]$ and $[\xi]$ denotes the entire part of ξ. The form (2) was derived with the use of the direct statistical methods of random sampling theory (distribution of the mean value for the sample of the given size from the population with the uniform distribution on [0, 1]).

Apart from the fact that the basic terms for the model of the freely-connected chain were developed a long time ago, methods of their use for numerical evaluation are still the subject of intensive investigations (Jernigan and Flory 1969, Flory 1969). In this paper the simplified derivation of Treloar's distribution is given directly from the integral form (1). Further, stable recurrence equations are derived allowing the successive computations of $W_Z(h)$ with accuracy, which cannot be obtained for greater values of Z by direct evaluation of $W_Z(h)$ according to (2). The equivalence of (1) and Treloar's distribution has been demonstrated using a different procedure by Flory (1969).

2. Derivation of Treloar's distribution

In order to obtain Treloar's distribution from the integral form (1) let us denote $x = h/b$ and integrate by parts in (1) $(Z-2)$ times. This leads to

$$W_Z(h) = \frac{1}{2\pi^2 b^2 h}\frac{1}{(Z-2)!}\int_0^{\infty}\frac{\mathrm{D}^{Z-2}(\sin\lambda x\sin^Z\lambda)}{\lambda}\,\mathrm{d}\lambda \tag{3}$$

where $\mathrm{D} = \mathrm{d}/\mathrm{d}\lambda$. Further, we have

$$\begin{aligned}\sin\lambda x\sin^Z\lambda &= \frac{1}{(2\mathrm{i})^{Z+1}}(\mathrm{e}^{\mathrm{i}\lambda x}-\mathrm{e}^{-\mathrm{i}\lambda x})(\mathrm{e}^{\mathrm{i}\lambda}-\mathrm{e}^{-\mathrm{i}\lambda})^Z\\ &= \frac{1}{(2\mathrm{i})^{Z+1}}\left(\sum_{\nu=0}^{Z}(-1)^{\nu}\binom{Z}{\nu}\exp\{\mathrm{i}\lambda(Z-2\nu+x)\}\right.\\ &\qquad\left.-\sum_{\nu=0}^{Z}(-1)^{\nu}\binom{Z}{\nu}\exp\{\mathrm{i}\lambda(Z-2\nu-x)\}\right).\end{aligned}$$

Let us put $\nu = Z-\nu'$ in the first sum and change ν' back into ν. After taking the derivative we have

$$\mathrm{D}^{Z-2}(\sin\lambda x\sin^Z\lambda) = \frac{1}{2^Z}\sum_{\nu=0}^{Z}(-1)^{\nu}\binom{Z}{\nu}(Z-2\nu-x)^{Z-2}\sin\{\lambda(Z-2\nu-x)\}$$

so that after integration of (3), with the use of

$$\int_0^{\infty}\frac{\sin\alpha\lambda}{\lambda}\,\mathrm{d}\lambda = \frac{\pi}{2}\operatorname{sgn}\alpha$$

we obtain

$$W_Z(h) = \frac{1}{16\pi b^2 h}\frac{1}{2^{Z-2}(Z-2)!}\sum_{\nu=0}^{Z}(-1)^{\nu}\binom{Z}{\nu}(Z-2\nu-x)^{Z-2}\operatorname{sgn}(Z-2\nu-x).$$

Let

$$\phi_1 = \sum_{\nu=0}^{k} (-1)^{\nu} \binom{Z}{\nu} (Z-2\nu-x)^{Z-2}$$

$$\phi_2 = \sum_{\nu=k+1}^{Z} (-1)^{\nu} \binom{Z}{\nu} (Z-2\nu-x)^{Z-2}$$

where the meaning of k is the same as in (2). Then

$$W_Z(h) = \frac{1}{16\pi b^2 h} \frac{1}{2^{Z-2}(Z-2)!} (\phi_1 - \phi_2).$$

But

$$\begin{aligned}\phi_1 + \phi_2 &= \sum_{\nu=0}^{Z} (-1)^{\nu} \binom{Z}{\nu} (Z-2\nu-x)^{Z-2} \\ &= \sum_{\nu=0}^{Z} (-1)^{\nu} \binom{Z}{\nu} \sum_{\mu=0}^{Z-2} (-1)^{\mu} \binom{Z-2}{\mu} (Z-x)^{Z-2-\mu} (2\nu)^{\mu} \\ &= \sum_{\mu=0}^{Z-2} (-1)^{\mu} \binom{Z-2}{\mu} 2^{\mu} (Z-x)^{Z-2-\mu} \sum_{\nu=0}^{Z} (-1)^{\nu} \binom{Z}{\nu} \nu^{\mu} = 0\end{aligned}$$

since the inner sums all equal zero (it follows by taking μ-fold derivative of the term

$$(1-e^{\xi})^Z = \sum_{\nu=0}^{Z} (-1)^{\nu} \binom{Z}{\nu} e^{\nu\xi}$$

for $\xi = 0$ and for $0 \leqslant \mu < Z$). Hence $\phi_2 = -\phi_1$ and we arrive at the following expression for $W_Z(h)$

$$W_Z(h) = \frac{1}{8\pi b^2 h} \frac{1}{2^{Z-2}(Z-2)!} \sum_{\nu=0}^{k} (-1)^{\nu} \binom{Z}{\nu} (Z-2\nu-x)^{Z-2}$$

this already being Treloar's form.

In this way the exact Treloar's form for DDF of the length h for the model of a freely-connected chain is derived directly from the integral expression (1). For the purpose of the numerical evaluation of $W_Z(h)$ Treloar's form is suitable for small Z values only. For larger Z the computations performed according to this form suffer from a considerable loss of accuracy. The reason for this is that W_Z is given as the sum of terms of alternating signs and these terms exceed many times the final value of the sum.

For this reason it is necessary to find another method for large Z, because Treloar's form does not solve the numerical determination of W_Z generally, apart from the fact that it gives W_Z in the form of a finite sum. In the following paragraph, the recurrence formulae for successive computations of $W_Z(h)$ are derived. Another possible way is numerical integration of (1). The tested methods (Longman and Filon integration) have failed for large values of Z. These methods are not able to obtain results with the required accuracy owing to the fast oscillations of the integrated function for such values of Z. Moreover, numerical integration becomes very time-consuming as Z increases. For these reasons numerical integration seems also to be unsatisfactory for large values of Z.

Values with close agreement to the exact ones can be obtained with the use of asymptotic forms of $W_Z(h)$. This analysis will be published later.

3. Recurrence formulae for W_Z

In the following, we shall use the length x of the chain, measured in units of b ($x = h/b$). If we denote as V_Z the distribution for the length x, then from the condition

$$V_Z(x)\,\mathrm{d}x = W_Z(h)\,\mathrm{d}h$$

we obtain for the integral form

$$V_Z(x) = \frac{1}{2\pi^2 b^2 x}\int_0^\infty \lambda \sin \lambda x\left(\frac{\sin \lambda}{\lambda}\right)^Z \mathrm{d}\lambda$$

and for Treloar's form

$$V_Z(x) = \frac{1}{8\pi b^2}\,\frac{1}{2^{Z-2}(Z-2)!}\,\frac{1}{x}\sum_{\nu=0}^{[(Z-x)/2]}(-1)^\nu\binom{Z}{\nu}(Z-2\nu-x)^{Z-2}$$

or equivalently

$$V_Z(x) = \frac{1}{16\pi b^2}\,\frac{1}{2^{Z-2}(Z-2)!}\,\frac{1}{x} \times \sum_{\nu=0}^{Z}(-1)^\nu\binom{Z}{\nu}(Z-2\nu-x)^{Z-2}\,\mathrm{sgn}(Z-2\nu-x). \tag{4}$$

Putting $Z \geqslant 3$ the distribution V_Z satisfies the recurrence formulae

$$V_Z(x) = \begin{cases} V_{Z-1}(1) & \text{for } x = 0 \\ \dfrac{1}{2}\dfrac{Z+x}{Z-2}\dfrac{x+1}{x}V_{Z-1}(x+1) + \dfrac{1}{2}\dfrac{Z-x}{Z-2}\dfrac{x-1}{x}V_{Z-1}(|x-1|) & \text{for } x > 0. \end{cases} \tag{5}$$

We shall carry out the proof of (5) by two methods.

(i) Starting from Treloar's distribution, let us denote

$$S_Z(x) = \sum_{\nu=0}^{Z}(-1)^\nu\binom{Z}{\nu}(Z-2\nu-x)^{Z-2}\,\mathrm{sgn}(Z-2\nu-x).$$

Then we have

$$\begin{aligned} S &= (Z+x)S_{Z-1}(x+1) + (Z-x)S_{Z-1}(x-1) \\ &= (Z+x)\sum_{\nu=0}^{Z-1}(-1)^\nu\binom{Z-1}{\nu}(Z-2-2\nu-x)^{Z-3}\,\mathrm{sgn}(Z-2-2\nu-x) \\ &\quad + (Z-x)\sum_{\nu=0}^{Z-1}(-1)^\nu\binom{Z-1}{\nu}(Z-2\nu-x)^{Z-3}\,\mathrm{sgn}(Z-2\nu-x) \\ &= -\sum_{\nu=0}^{Z}(-1)^\nu\binom{Z-1}{\nu-1}(Z-2\nu-x)^{Z-3}(Z+x)\,\mathrm{sgn}(Z-2\nu-x) \\ &\quad + \sum_{\nu=0}^{Z}(-1)^\nu\binom{Z-1}{\nu}(Z-2\nu-x)^{Z-3}(Z-x)\,\mathrm{sgn}(Z-2\nu-x) \end{aligned}$$

where zero terms have been appended. Hence

$$S = \sum_{\nu=0}^{Z} (-1)^{\nu}(Z-2\nu-x)^{Z-3}\left\{\binom{Z-1}{\nu}(Z-x)-\binom{Z-1}{\nu-1}(Z+x)\right\}$$
$$\times \operatorname{sgn}(Z-2\nu-x)$$
$$= \sum_{\nu=0}^{Z} (-1)^{\nu}\binom{Z}{\nu}(Z-2\nu-x)^{Z-2}\operatorname{sgn}(Z-2\nu-x) = S_Z(x).$$

Therefore $S_Z(x)$ fulfils the recurrence relation

$$S_Z(x) = (Z+x)S_{Z-1}(x+1)+(Z-x)S_{Z-1}(x-1)$$

and because it holds for even function V_Z

$$V_Z(x) = \frac{1}{16\pi b^2}\,\frac{1}{2^{Z-2}(Z-2)!}\,\frac{S_Z(x)}{x}$$

we arrive at the second part of the assertion. Because for $Z \geqslant 3$ we have on the one hand

$$V_Z(0) = \frac{1}{2\pi^2 b^2}\lim_{x\to 0+}\frac{1}{x}\int_0^\infty \lambda \sin\lambda x\left(\frac{\sin\lambda}{\lambda}\right)^Z \mathrm{d}\lambda = \frac{1}{2\pi^2 b^2}\int_0^\infty \lambda^2\left(\frac{\sin\lambda}{\lambda}\right)^Z \mathrm{d}\lambda$$

and on the other

$$V_{Z-1}(1) = \frac{1}{2\pi^2 b^2}\int_0^\infty \lambda \sin\lambda\left(\frac{\sin\lambda}{\lambda}\right)^{Z-1} \mathrm{d}\lambda = \frac{1}{2\pi^2 b^2}\int_0^\infty \lambda^2\left(\frac{\sin\lambda}{\lambda}\right)^Z \mathrm{d}\lambda$$

we arrive at the first part of the assertion as well.

(ii) Starting from the integral form, let us denote

$$T_Z(x) = \int_0^\infty \lambda \sin\lambda x\left(\frac{\sin\lambda}{\lambda}\right)^Z \mathrm{d}\lambda.$$

Then for $Z \geqslant 3$ we have

$$T'_Z(x) = \int_0^\infty \lambda^2 \cos\lambda x\left(\frac{\sin\lambda}{\lambda}\right)^Z \mathrm{d}\lambda = \int_0^\infty \lambda \cos\lambda x \sin\lambda\left(\frac{\sin\lambda}{\lambda}\right)^{Z-1} \mathrm{d}\lambda.$$

With the use of the term

$$\cos\lambda x \sin\lambda = \tfrac{1}{2}[\sin\{\lambda(x+1)\}-\sin\{\lambda(x-1)\}]$$

we get

$$T'_Z(x) = \tfrac{1}{2}T_{Z-1}(x+1)-\tfrac{1}{2}T_{Z-1}(x-1). \tag{6}$$

On the other hand, integrating by parts, we find

$$T'_Z(x) = \int_0^\infty \lambda \sin\lambda\left(\frac{\sin\lambda}{\lambda}\right)^{Z-1}\frac{\mathrm{d}}{\mathrm{d}\lambda}\left(\frac{\sin\lambda x}{x}\right)\mathrm{d}\lambda$$
$$= -\int_0^\infty \frac{\sin\lambda x}{x}\,\frac{\mathrm{d}}{\mathrm{d}\lambda}\left\{\lambda^2\left(\frac{\sin\lambda}{\lambda}\right)^Z\right\}\mathrm{d}\lambda$$

that is

$$T'_Z(x) = \frac{Z-2}{x}\int_0^\infty \lambda \sin\lambda x\left(\frac{\sin\lambda}{\lambda}\right)^Z \mathrm{d}\lambda-\frac{Z}{x}\int_0^\infty \lambda \sin\lambda x \cos\lambda\left(\frac{\sin\lambda}{\lambda}\right)^{Z-1}\mathrm{d}\lambda.$$

From this term, with the use of

$$\sin \lambda x \cos \lambda = \tfrac{1}{2}[\sin\{\lambda(x+1)\} + \sin\{\lambda(x-1)\}]$$

we get

$$T'_Z(x) = \frac{Z-2}{x} T_Z(x) - \frac{Z}{2x}(T_{Z-1}(x+1) + T_{Z-1}(x-1)). \quad (7)$$

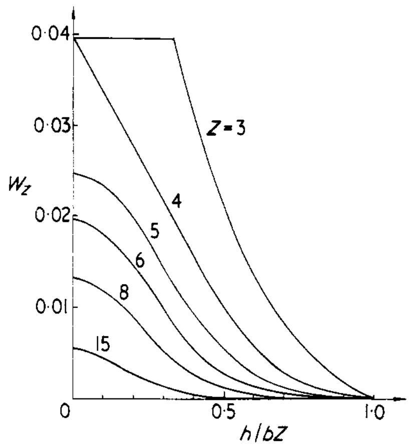

Figure 2. The course of $W_Z(h)$.

Table 1. Values of the exact DDF $W_Z(h)$ (The values not written out are of order 10^{-76} or less)

h/b	$Z = 200$	$Z = 400$	$Z = 800$
0	1·16208–4	4·11630–5	1·45670–5
1	1·15344–4	4·10094–5	1·45397–5
2	1·12790–4	4·05517–5	1·44583–5
3	1·08659–4	3·98003–5	1·43235–5
4	1·03127–4	3·87716–5	1·41370–5
5	9·64269–5	3·74880–5	1·39007–5
10	5·50681–5	2·83154–5	1·20791–5
20	5·82057–6	9·20887–6	6·88644–6
30	1·34439–7	1·41239–6	2·69839–6
40	6·55024–10	1·01724–7	7·26337–7
50	6·39186–13	3·41977–9	1·34206–7
60	1·16326–16	5·32416–11	1·70057–8
80	1·65957–26	1·22986–15	8·76308–11
100	5·85477–40	1·12961–21	9·81925–14
120	6·25803–58	3·57431–29	2·35505–17
140		3·21900–38	1·18542–21
160		6·41939–49	1·22276–26
180		2·03818–61	2·51257–32
200			9·94937–39
220			7·30573–46
240			9·51582–54
260			2·08931–62
280			7·29395–72
300			

By elimination of the derivative T'_Z from (6) and (7) we find

$$T_Z(x) = \frac{1}{2}\frac{Z+x}{Z-2}T_{Z-1}(x+1)+\frac{1}{2}\frac{Z-x}{Z-2}T_{Z-1}(x-1).$$

From this equation we arrive again at the second part of the assertion because of the term

$$V_Z(x) = \frac{1}{2\pi^2 b^2}\frac{T_Z(x)}{x}.$$

Equations (5) derived here were used for the evaluation of W_Z for $Z \leqslant 800$ where the developed method proved to be highly effective. The calculations were performed with the aid of a program written in FORTRAN-IV language on a GE-427 computer. The course of several distributions is given in figure 2 and for $Z = 200$, 400 and 800 by table 1.

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