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Asymptotic behaviour of the chain molecule distribution function

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Abstract. An asymptotic expansion for the distribution density W_Z of the length h of a freely jointed polymer chain neglecting volume effects is derived up to order Z^{-2}; $Z-1$ is the number of chain bonds. The derivation is performed on the basis of the exact Chandrasekhar form of this distribution. The relationship between the asymptotic expansion and the original and amended Langevin distribution has been found as well as the values of these distributions for $h = 0$. These values lead in turn to a better agreement of the approximations with the exact distribution than do the values determined from normalizing conditions. Further, the relationship of asymptotics to the gaussian distribution is shown and the range of its applicability is determined. In this way the topic of the exact distribution and its approximations is completed.

The asymptotics were further compared with the exact distribution and its approximations numerically. As a result the zero order asymptotics were shown to be a very close and uniform approximation for all h including very small values of Z. The agreement of the first order asymptotics with the exact distribution is almost complete (to several decimal places even for small Z). Hence the asymptotics can replace various approximations mainly in the range of considerable chain lengths.

1. Introduction

The exact form of distribution density W_Z (ED) for the length of a polymer chain has been derived by Chandrasekhar (1943) for the model of a freely jointed chain. This derivation neglects volume effects and uses the Markov formula for distribution density for the sum of independent random variables. Treloar (1946) has derived another form of the exact distribution with the direct use of some results of random sampling theory (the mean value for the sample of a given size from population with uniform distribution over [0, 1]). The application of these results (eg for thermodynamic function determinations) is complicated. The first procedure leads to the expression of W_Z given by the improper integral

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

whereas the second one gives W_Z in the form of a finite sum

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

where $m = \frac{1}{2}(1-h/bZ)$ and $[x]$ designates the entire part of x. Here and in what follows $Z-1$ is the number of chain bonds, b is the length of each bond and h is the length of the chain, that is its end-to-end distance. The relations (1) and (2) are equivalent.

The form (2) is not suitable for applications either; in fact, by (2) W_Z is defined piecewise, that is, by different analytical expressions in different intervals of h values. Therefore, it is significant to find approximations of the exact distribution W_Z by functions of a simpler form. Considerable attention has been paid to this question and intensive investigations are still in progress.

The first such approximation derived is the gaussian distribution (GD). Here W_Z is approximated by function $\mathscr{G}_Z$, where

$$\mathscr{G}_Z(h) = \left(\frac{3}{2\pi Z b^2}\right)^{3/2} \exp\left(-\frac{3h^2}{2Zb^2}\right). \tag{3}$$

(3) was derived from (1) for $h \ll bZ$.

Using the methods of physical statistics, another approximation of W_Z was derived by Kuhn and Grün (1942). In their work W_Z is approximated by the so called Langevin distribution (LD) $\mathscr{L}_Z$, where

$$\mathscr{L}_Z(h) = \frac{A}{b^3} \exp\left(-\beta\frac{h}{b}\right)\left(\frac{\sinh\beta}{\beta}\right)^Z \tag{4}$$

where the parameter β is defined by $h/bZ = L(\beta)$; L is called the Langevin function, $L(x) = \coth x - 1/x$. The value of A, which does not result from the original derivation, is determined (Volkenštejn 1959, Jernigan and Flory 1969) from the normalizing condition for W_Z, namely

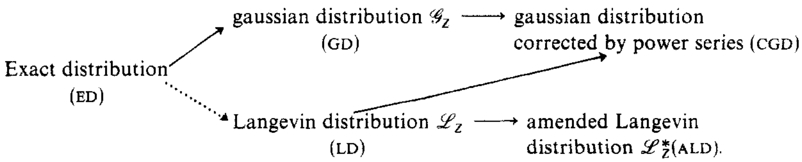
$$4\pi \int_0^{bZ} W_Z(h)h^2\, dh = 1 \tag{5}$$

where W_Z is replaced by its approximation $\mathscr{L}_Z$.

For the GD as well as the LD various amendments correcting the original approximations were derived; for instance using Treloar's relation between space and linear distributions the following amended form was derived by Jernigan and Flory (1969)

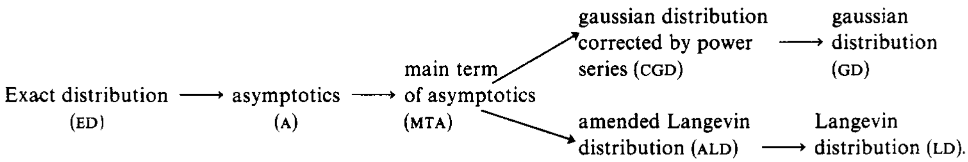
$$\mathscr{L}_Z^*(h) = \frac{A^*}{2\pi}\frac{\beta}{hb^2} \exp\left(-\beta\frac{h}{b}\right)\left(\frac{\sinh\beta}{\beta}\right)^Z \tag{6}$$

again A^* is determined by the normalizing condition (5) for $\mathscr{L}_Z^*$. The relations of the exact distribution and its cited approximations may thus be represented by the following diagram:



The connection between ED and LD does not follow from the derivation of the latter; hence it is marked by a dotted line.

Here the approximation of W_Z is approached from another point of view. Starting from the exact integral form (1) we will determine the asymptotics of W_Z for large Z and show their relation to GD, LD and also ALD. This procedure which is an extension of procedure described by Dvořák (1963) also makes it possible to determine the values of A and A^* which lead to a better approximation of ED than do the values determined from normalizing conditions. Further, the validity range of each approximation is determined; especially, the validity range of GD is determined precisely. The relationship diagram is changed in this approach and looks as follows:



2. Asymptotics of $W_Z(h)$

As described in the introduction, the basis of the following considerations is the asymptotics of W_Z for $Z \to \infty$. To derive this, let Z be a large number and $h < bZ$ arbitrary, but fixed. From (1) substituting $-\mathrm{i}\lambda$ for λ we find

$$W_Z(h) = \frac{\mathrm{i}}{2\pi^2 b^2 h} \int_0^{\mathrm{i}\infty} \lambda \sinh \lambda x \left(\frac{\sinh \lambda}{\lambda}\right)^Z \mathrm{d}\lambda$$

where $x = h/b$. From this we obtain further

$$W_Z(h) = -\frac{\mathrm{i}}{4\pi^2 b^2 h} \int_{-\mathrm{i}\infty}^{\mathrm{i}\infty} \lambda\, \mathrm{e}^{-\lambda x} \left(\frac{\sinh \lambda}{\lambda}\right)^Z \mathrm{d}\lambda.$$

The integral in the latter relation is of the same value as the integral of the same function taken along the line $\lambda = \beta + \mathrm{i}\tau$, $-\infty < \tau < \infty$. For the present β is an arbitrary positive number. Indeed, by integration along the rectangle C with vertices $-\mathrm{i}R, \mathrm{i}R, \beta+\mathrm{i}R, \beta-\mathrm{i}R$ (figure 1) we have according to Cauchy's theorem

$$\oint_{\mathrm{C}} = \int_{\mathrm{C}_1} + \int_{\beta-\mathrm{i}R}^{\beta+\mathrm{i}R} + \int_{\mathrm{C}_2} + \int_{\mathrm{i}R}^{-\mathrm{i}R} = 0. \tag{7}$$

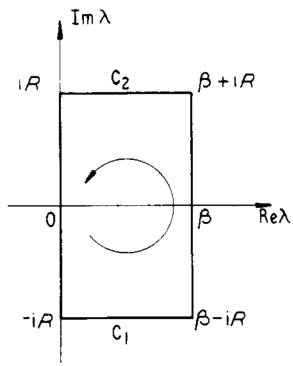


Figure 1. Integration path C.

However, it is easy to find the following estimation:

$$\left| \int_{\mathrm{C}_1} \right| \leqslant \frac{1}{R^{Z-1}} \int_0^{\beta} \exp\{\tau(Z-x)\}\, \mathrm{d}\tau.$$

Therefore for arbitrary fixed β and fixed $Z > 1$ and $R \to \infty$ this integral vanishes.

The same holds for $\int_{C_2}$. The integrated function is everywhere

$$F(\lambda, x) = \lambda \exp(-\lambda x)(\sinh \lambda/\lambda)^Z.$$

Therefore we can write

$$W_Z(h) = -\frac{i}{4\pi^2 b^2 h}\int_{\beta-i\infty}^{\beta+i\infty} \lambda \exp(-\lambda x)\left(\frac{\sinh \lambda}{\lambda}\right)^Z d\lambda = -\frac{i}{4\pi^2 b^2 h} \times \int_{\beta-i\infty}^{\beta+i\infty} \lambda \exp f(\lambda, Z)\, d\lambda$$

where $f(\lambda, Z) = -\lambda x + Z \lg(\sinh \lambda/\lambda)$. Defining now β by term

$$\frac{h}{bZ} = L(\beta) = \coth \beta - \frac{1}{\beta}$$

conditions $\partial f(\lambda, Z)/\partial\lambda|_{\lambda=\beta} = 0$ and $\operatorname{Im} f(\lambda, Z) =$ constant hold true in the neighbourhood of point β on the line $\lambda = \beta + i\tau$. Hence β is the saddle point of surface $w = \operatorname{Re} f(\lambda, Z)$. Therefore, integrating along the line $\lambda = \beta + i\tau$, which is the steepest descent line in the neighbourhood of β, one can find the asymptotics of W_Z. At this point let us expand $f(\lambda, Z)$ at the point $\lambda = \beta + i\tau$ to the power series with centre β, that is

$$f(\lambda, Z) = f(\beta, Z) - ZL_1\frac{\tau^2}{2} + Z\sum_{\nu \geq 3} L_{\nu-1}\frac{(i\tau)^\nu}{\nu!} = f(\beta, Z) - ZL_1\frac{\tau^2}{2} + Zr(\tau)$$

where $L_\nu = L^{(\nu)}(\beta)$ is the ν fold derivative of the Langevin function at point β. Then

$$W_Z(h) = \frac{\exp f(\beta, Z)}{4\pi^2 b^2 h}\int_{-\infty}^{\infty} (\beta + i\tau)\exp(-\tfrac{1}{2}ZL_1\tau^2)\exp(Zr(\tau))\, d\tau. \tag{8}$$

Because $h/bZ = L(\beta)$ it is obvious that L_ν depends implicitly on Z. From the expansion of $L(\beta)$ in the neighbourhood of zero (which is convergent for $\beta < \pi$)

$$L(\beta) = \coth \beta - \frac{1}{\beta} = \sum_{k=1}^{\infty} \frac{2^{2k}B_{2k}}{(2k)!}\beta^{2k-1} = \tfrac{1}{3}\beta - \tfrac{1}{45}\beta^3 + \tfrac{2}{945}\beta^5 - \tfrac{1}{4725}\beta^7 + \dots$$

and from the inversion function expansion

$$\beta = L^{(-1)}\left(\frac{h}{bZ}\right) = 3\left(\frac{h}{bZ}\right) + \frac{9}{5}\left(\frac{h}{bZ}\right)^3 + \frac{297}{175}\left(\frac{h}{bZ}\right)^5 + \frac{1539}{875}\left(\frac{h}{bZ}\right)^7 + \dots \tag{9}$$

it follows for $\beta \to 0$

$$L^{(\nu)}(\beta) = \begin{cases} O(1) & \text{for odd } \nu \\ O(Z^{-1}) & \text{for even } \nu. \end{cases}$$

Therefore in the τ power expansion of $\exp(Zr(\tau))$ which has to be performed in (8) for the determination of asymptotics it is sufficient to leave only the terms which contain after integration $Z^{-1}, Z^{-2}, \dots, Z^{-k}$ explicitly, when one wishes to find the asymptotics to the order of Z^{-k-1}. In (8) we have after expansion

$$W_Z(h) = \frac{1}{4\pi^2 b^2 h}\exp(-\beta Z L(\beta))\left(\frac{\sinh \beta}{\beta}\right)^Z \int_{-\infty}^{\infty} \exp(-\tfrac{1}{2}ZL_1\tau^2)(\beta + i\tau) \times (1 + Zr(\tau) + \tfrac{1}{2}Z^2 r^2(\tau) + \dots)\, d\tau.$$

Substituting the power series for $r(\tau)$, $r^2(\tau), \ldots$ and integrating with the use of

$$\int_{-\infty}^{\infty} \tau^n \exp(-a\tau^2)\,\mathrm{d}\tau = \begin{cases} 0 & \text{for odd } n \\ \Gamma\left(\dfrac{n+1}{2}\right) a^{-(n+1)/2} & \text{for even } n,\ a > 0 \end{cases}$$

we find the following asymptotical expansion for W_Z

$$W_Z(h) = \frac{1}{(2\pi Z b^2)^{3/2}} \frac{\beta}{L(\beta)(L'(\beta))^{1/2}} \exp(-\beta Z L(\beta)) \left(\frac{\sinh \beta}{\beta}\right)^Z \times \left(1 + \frac{C_1}{Z} + \frac{C_2}{Z^2} + \mathrm{O}\left(\frac{1}{Z^3}\right)\right) \tag{10}$$

or introducing h partially

$$W_Z(h) = \frac{1}{2\pi} \frac{1}{(2\pi Z L'(\beta))^{1/2}} \frac{\beta}{hb^2} \exp\left(-\beta\frac{h}{b}\right) \left(\frac{\sinh \beta}{\beta}\right)^Z \times \left(1 + \frac{C_1}{Z} + \frac{C_2}{Z^2} + \mathrm{O}\left(\frac{1}{Z^3}\right)\right). \tag{11}$$

Here C_1 and C_2 are functions of β; it holds that

$$C_1 = \frac{1}{L_1^2}\left(\frac{L_3}{8} + \frac{L_2}{2\beta} - \frac{5}{24}\frac{L_2^2}{L_1}\right)$$

$$C_2 = -\frac{1}{L_1^3}\left(\frac{L_5}{48} + \frac{L_4}{8\beta} - \frac{35}{384}\frac{L_3^2}{L_1} - \frac{7}{48}\frac{L_2 L_4}{L_1} - \frac{35}{48}\frac{L_2 L_3}{\beta L_1} + \frac{35}{64}\frac{L_2^2 L_3}{L_1^2} + \frac{35}{48} \times \frac{L_2^3}{\beta L_1^2} - \frac{385}{1152}\frac{L_2^4}{L_1^3}\right).$$

The asymptotics of W_Z were evaluated for various Z; results have been compared with ED and its approximations. The following statements hold true:

(i) the main term of asymptotics (MTA) and GD have the same value for $h = 0$;
(ii) in the neighbourhood of $h = 0$ GD is less than MTA and GD is a better approximation here;
(iii) the MTA provides a uniform approximation of ED in the whole extension range of the chain. In the range of small extensions MTA is a better approximation than $\mathscr{L}_Z$ and $\mathscr{L}_Z^*$ (their values being higher) as well as in the range of large extensions (the values of $\mathscr{L}_Z$ and $\mathscr{L}_Z^*$ are on the contrary lower);
(iv) first order asymptotics provide a very accurate approximation over the whole extension range. Agreement is to several decimal places even for small Z;
(v) second order asymptotics give practically complete agreement with ED over the whole extension range.

In applications, the MTA is of major importance (especially for a good approximation in the large extension region) and also the first order asymptotics. The second order correction is too complicated for practical use.

The approximations derived here (MTA and first order asymptotics A1) are not normalized. When one wishes to use them as density distribution functions (DDF) they are to be normalized in agreement with (5). The shift due to normalization makes the approximations provided by MTA or first order asymptotics still closer to the exact DDF.

3. Relation between asymptotics and $W_Z(h)$ approximations

From the asymptotic expansion derived in (10) or (11) it is easy to find the relation of asymptotics to the amended Langevin distribution $\mathscr{L}_Z^*$, given by (6). The difference between them consists in considering $F_Z^*(\beta) = (2\pi Z L'(\beta))^{-1/2}$ as a normalization constant in $\mathscr{L}_Z^*$ whereas it is actually a function of β, namely

$$F_Z^*(\beta) = \frac{1}{(2\pi Z)^{1/2}} \cdot \frac{1}{(\beta^{-2} - \sinh^{-2}\beta)^{1/2}} = \begin{cases} (2\pi Z/3)^{-1/2} & \text{for } \beta \to 0 \\ \sim \beta(2\pi Z)^{-1/2} & \text{for large } \beta. \end{cases}$$

In the original Langevin distribution the normalization constant replaces

$$F_Z(\beta) = \frac{1}{2\pi} \frac{1}{(2\pi Z L'(\beta))^{1/2}} \cdot \frac{\beta}{hb^2} = \frac{1}{2\pi} \frac{\beta}{hb^2} F_Z^*(\beta)$$

making the approximation of W_Z even worse. From the $\mathscr{L}_Z$ derivation it follows:

$$\mathscr{L}_Z(h) = \mathscr{L}_Z(0) \exp\left(-\beta \frac{h}{b}\right) \left(\frac{\sinh \beta}{\beta}\right)^Z.$$

Because the value of $\mathscr{L}_Z(0)$ does not follow from this procedure, it is determined from normalization of $\mathscr{L}_Z$. Similarly A^* is connected with $\mathscr{L}_Z^*(0)$. Having in mind that the asymptotics are a closer approximation of W_Z in the neighbourhood of zero than $\mathscr{L}_Z$ or $\mathscr{L}_Z^*$ one can see by taking the initial value of these distributions to be equal to the value given by asymptotics, one arrives at the approximation, which is better than the one provided by normalization.

This leads to

$$\bar{\mathscr{L}}_Z(h) = \left(\frac{3}{2\pi Z b^2}\right)^{3/2} \exp\left(-\beta \frac{h}{b}\right) \left(\frac{\sinh \beta}{\beta}\right)^Z$$

for the original and

$$\bar{\mathscr{L}}_Z^*(h) = \frac{1}{2\pi} \left(\frac{3}{2\pi Z}\right)^{1/2} \frac{\beta}{hb^2} \exp\left(-\beta \frac{h}{b}\right) \left(\frac{\sinh \beta}{\beta}\right)^Z$$

for the amended Langevin distribution.

MTA also leads simply to GD corrected by power series. For MTA it holds that

$$\mathscr{A}_Z(h) = \frac{1}{(2\pi Z b^2)^{3/2}} \cdot \frac{\beta}{L(\beta)(L'(\beta))^{1/2}} \exp(-\beta Z L(\beta)) \left(\frac{\sinh \beta}{\beta}\right)^Z \sim W_Z(h) \tag{12}$$

and further

$$\lg\left(\frac{\sinh \beta}{\beta}\right) = \int_0^\beta L(\tau)\, d\tau = \beta L(\beta) - \int_0^\beta \tau L'(\tau)\, d\tau.$$

Introducing $\rho = L(\tau)$ into the foregoing relation leads to

$$T = \lg\left(\frac{\sinh \beta}{\beta}\right) - \beta L(\beta) = -\int_0^{L(\beta)} L^{(-1)}(\rho)\, d\rho$$

where $L^{(-1)}$ is the inverse Langevin function. With the use of expansion (9) and

$L(\beta) = h/bZ$ after integration we get

$$T = -\frac{3}{2}\left(\frac{h}{bZ}\right)^2 - \frac{9}{20}\left(\frac{h}{bZ}\right)^4 - \frac{99}{350}\left(\frac{h}{bZ}\right)^6 - \ldots.$$

Further

$$\frac{\beta}{L(\beta)(L'(\beta))^{1/2}} = 3^{3/2}\left\{1 + \frac{3}{2}\left(\frac{h}{bZ}\right)^2 + \ldots\right\}$$

passing to chain length h. Both expansions in h are convergent for $h < bZ$. Hence MTA may be rewritten as follows:

$$\mathscr{A}_Z(h) = \left(\frac{3}{2\pi Zb^2}\right)^{3/2} \exp\left(-\frac{3h^2}{2Zb^2}\right)\left\{1 + \frac{3}{2}\left(\frac{h}{bZ}\right)^2 + \ldots\right\}$$
$$\times \exp\left(-\frac{9}{20}\frac{h^4}{b^4Z^3} - \frac{99}{350}\frac{h^6}{b^6Z^5} - \ldots\right)$$

that is

$$\mathscr{A}_Z(h) = \mathscr{G}_Z(h)\left\{1 + \frac{3}{2}\left(\frac{h}{bZ}\right)^2 + \ldots\right\}\exp\left(-\frac{9}{20}\frac{h^4}{b^4Z^3} - \frac{99}{350}\frac{h^6}{b^6Z^5} - \ldots\right). \quad (13)$$

From (13) it is obvious that GD is obtained from $\mathscr{A}_Z(h)$ by omitting the last two factors there. The deviations of GD from asymptotics or from ED then result because of the omitted terms in (13). The product of these terms equals 1 for $h = 0$, then becomes greater than 1 and again decreases to 1 and further, it is even lower than 1. From this it follows immediately that up to certain value $h = h_m$ GD runs below asymptotics $\mathscr{A}_Z$ and above it for $h > h_m$. The value h_m may well be considered as upper limit of GD applicability, because for $h > h_m$ the difference between GD and ED becomes significant. For $h < h_m$ GD lies between ED and MTA providing the best approximation in this range with the exception of the first and second order asymptotics. h_m may be estimated easily. Owing to the fact that h_m lies in a small-extension range, it may be determined from the term

$$1 = \left\{1 + \frac{3}{2}\left(\frac{h_m}{bZ}\right)^2 + \ldots\right\}\exp\left(-\frac{9}{20}\frac{h_m^4}{b^4Z^3} - \ldots\right) \simeq \frac{1 + (\frac{3}{2}h_m^2/b^2Z^2)}{1 + (\frac{9}{20}h_m^4/b^4Z^3)}$$

whence it follows:

$$h_m \simeq bZ^{1/2}\sqrt{\tfrac{10}{3}}.$$

Therefore the range of extension h/bZ where GD may be used is getting smaller with increasing Z in accordance with the term

$$\frac{h}{bZ} \leqslant Z^{-1/2}\sqrt{\frac{10}{3}}. \quad (14)$$

The result (14) is more precise than the usually mentioned condition $h \ll bZ$ for GD applicability.

4. Numerical evaluation

The comparison of known and newly derived approximations of W_Z is given for $Z = 3$ by figure 2 and for $Z = 6$ by figure 3. The results for $Z = 8$ and $Z = 100$ are given by tables 1, 2 and 3 for the distributions mentioned above. The values of the first order asymptotic are given in table form also for $Z = 200$, 400 and 800 together with exact values of $W_Z(h)$.

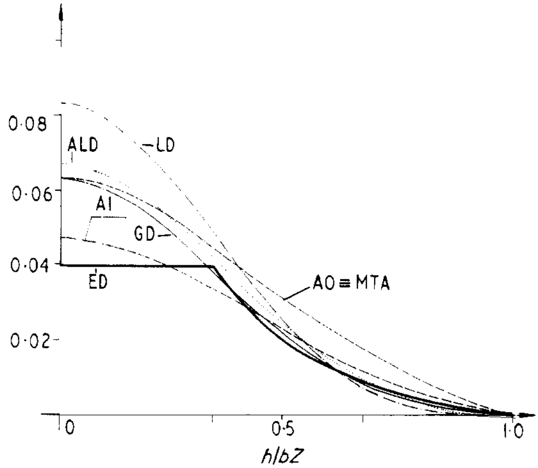


Figure 2. Exact distribution and its approximations for $Z = 3$.

Table 1. Freely jointed chain DDF for $Z = 8$

h/b	Gaussian DDF	MTA	Exact DDF	First order asymptotics	LD	ALD
0·0	1·4581–02	1·4581–02	1·3263–02	1·3214–02	1·6063–02	1·4866–02
0·2	1·4472–02	1·4485–02	1·3175–02	1·3127–02	1·5943–02	1·4760–02
0·4	1·4150–02	1·4203–02	1·2914–02	1·2868–02	1·5588–02	1·4448–02
0·6	1·3629–02	1·3743–02	1·2491–02	1·2449–02	1·5013–02	1·3941–02
0·8	1·2932–02	1·3124–02	1·1923–02	1·1883–02	1·4242–02	1·3260–02
1·0	1·2087–02	1·2366–02	1·1229–02	1·1192–02	1·3305–02	1·2430–02
1·5	9.5622–03	1·0046–02	9·1089–03	9·0780–03	1·0486–02	9·9165–03
2·0	6·8874–03	7·4848–03	6·7696–03	6·7467–03	7·4774–03	7·1957–03
2·5	4·5169–03	5·0934–03	4·5914–03	4·5764–03	4·7972–03	4·7263–03
3·0	2·6972–03	3·1486–03	2·8267–03	2·8174–03	2·7477–03	2·7907–03
3·5	1·4664–03	1·7546–03	1·5668–03	1·5622–03	1·3897–03	1·4671–03
4·0	7·2593–04	8·7213–04	7·7367–04	7·7176–04	6·1105–04	6·7736–04
4·5	3·2720–04	3·8077–04	3·3525–04	3·3461–04	2·2839–04	2·6938–04
5·0	1·3428–04	1·4273–04	1·2451–04	1·2450–04	7·0154–05	8·9621–05
5·5	5·0178–05	4·4293–05	3·8309–05	3·8378–05	1·6779–05	2·3819–05
6·0	1·7072–05	1·0666–05	9·2104–06	9·2078–06	2·8464–06	4·6701–06
6·5	5·2887–06	1·7485–06	1·5131–06	1·5100–06	2·8568–07	5·7832–07
7·0	1·4918–06	1·4245–07	1·2335–07	1·2315–07	1·1148–08	3·1444–08
7·1	1·1452–06	7·4638–08	6·4632–08	6·4530–08	4·7992–09	1·4828–08
7·2	8·7586–07	3·6305–08	3·1438–08	3·1389–08	1·8705–09	6·4111–09
7·3	6·6736–07	1·6070–08	1·3916–08	1·3894–08	6·4270–10	2·4831–09
7·4	5·0659–07	6·2869–09	5·4441–09	5·4356–09	1·8726–10	8·3265–10
7·5	3·8311–07	2·0774–09	1·7989–09	1·7961–09	4·3550–11	2·2928–10
7·6	2·8865–07	5·3741–10	4·6537–10	4·6464–10	7·3065–12	4·7451–11
7·7	2·1666–07	9·4406–11	8·1749–11	8·1622–11	7·3147–13	6·2516–12
7·8	1·6202–07	8·1818–12	7·0849–12	7·0738–12	2·8541–14	3·6120–13
7·9	1·2070–07	1·2622–13	1·0930–13	1·0852–13	1·1148–16	2·7862–15
8·0	8·9587–08	0	0	0	0	0

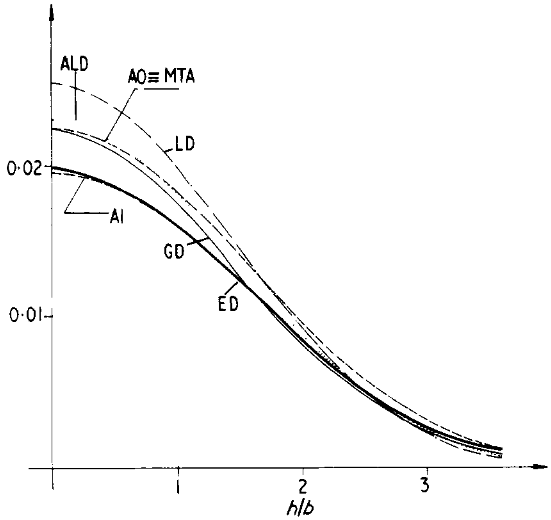


Figure 3. Exact distribution and its approximations for $Z = 6$.

Table 2. Freely jointed chain DDF for $Z = 100$

h/b	Gaussian DDF	MTA	Exact DDF	First order asymptotic	LD	ALD
0·0	3·2992–04	3·2992–04	3·2745–04	3·2745–04	3·3241–04	3·3042–04
0·5	3·2869–04	3·2870–04	3·2624–04	3·2623–04	3·3117–04	3·2919–04
1·0	3·2501–04	3·2506–04	3·2263–04	3·2262–04	3·2746–04	3·2552–04
2·0	3·1071–04	3·1089–04	3·0857–04	3·0856–04	3·1305–04	3·1125–04
3·0	2·8826–04	2·8864–04	2·8648–04	2·8647–04	2·9042–04	2·8884–04
6·0	1·9226–04	1·9319–04	1·9174–04	1·9174–04	1·9360–04	1·9286–04
10·0	7·3616–05	7·4398–05	7·3837–05	7·3836–05	7·3836–05	7·3838–05
15·0	1·1289–05	1·1415–05	1·1329–05	1·1328–05	1·1114–05	1·1200–05
20·0	8·1780–07	8·0785–07	8·0161–07	8·0160–07	7·6530–07	7·7968–07
25·0	2·7983–08	2·5698–08	2·5495–08	2·5495–08	2·3479–08	2·4268–08
30·0	4·5231–10	3·5472–10	3·5187–10	3·5186–10	3·0958–10	3·2589–10
35·0	3·4534–12	2·0275–12	2·0107–12	2·0107–12	1·6721–12	1·8004–12
40·0	1·2455–14	4·5117–15	4·4732–15	4·4732–15	3·4732–15	3·8438–15
45·0	2·1219–17	3·6049–18	3·5730–18	3·5729–18	2·5536–18	2·9213–18
50·0	1·7075–20	9·2900–22	9·2046–22	9·2045–22	5·9528–22	7·0877–22
55·0	6·4908–24	6·6827–26	6·6187–26	6·6186–26	3·7933–26	4·7403–26
60·0	1·1654–27	1·0987–30	1·0877–30	1·0877–30	5·3818–31	7·1343–31
65·0	9·8855–32	3·1016–36	3·0692–36	3·0692–36	1·2671–36	1·8070–36
70·0	3·9607–36	9·7823–43	9·6771–43	9·6771–43	3·1864–43	4·9824–43
75·0	7·4958–41	1·7375–50	1·7185–50	1·7185–50	4·2403–51	7·4726–51
80·0	6·7010–46	5·3168–60	5·2587–60	5·2586–60	8·8951–61	1·8412–60
85·0	2·8297–51	2·8620–72	2·8310–72	2·8310–72	2·8654–73	7·4461–73

5. Conclusions

The asymptotics of W_Z make it possible to understand the character and the course of ED approximations and to determine their mutual relations and their tie-ups to ED. In this way the problem of W_Z approximations has been solved completely; especially, the relation of MTA to GD has been found, which leads directly to power series correction of GD and to the exact determination of GD validity range.

The MTA term derived here is not more complex than the Langevin approximations $\mathscr{L}_Z, \mathscr{L}_Z^*$. MTA itself reproduces correctly the course of W_Z over the whole extension range; especially, it gives good agreement for large extensions, where the other approximations deviate considerably. The first order asymptotics which are already very close to W_Z can be applied easily too. The second order asymptotics are less suitable because of their complicated forms. Moreover, the accuracy provided by the first order asymptotics is quite sufficient in all applications. All asymptotic approximations may be used even for the smallest Z ($Z \geqslant 3$).

Table 3. The exact distribution and first order asymptotics for $Z = 200$, 400 and 800 (the values not written out are of order 10^{-76} or less).

h/b	Z = 200		Z = 400		Z = 800	
	ED	A I	ED	A I	ED	A I
0	1·16208–4	1·16206–4	4·11630–5	4·11582–5	1·45670–5	1·45623–5
1	1·15344–4	1·15343–4	4·10094–5	4·10120–5	1·45397–5	1·45377–5
2	1·12790–4	1·12790–4	4·05517–5	4·05517–5	1·44583–5	1·44584–5
3	1·08659–4	1·08658–4	3·98003–5	3·98003–5	1·43235–5	1·43237–5
4	1·03127–4	1·03127–4	3·87716–5	3·87716–5	1·41370–5	1·41369–5
5	9·64269–5	9·64265–5	3·74880–5	3·74879–5	1·39007–5	1·39007–5
10	5·50681–5	5·50678–5	2·83154–5	2·83154–5	1·20791–5	1·20792–5
20	5·82057–6	5·82054–6	9·20887–6	9·20885–6	6·88644–6	6·88644–6
30	1·34439–7	1·34439–7	1·41239–6	1·41239–6	2·69839–6	2·69839–6
40	6·55024–10	6·55021–10	1·01724–7	1·01724–7	7·26337–7	7·26337–7
50	6·39186–13	6·39183–13	3·41977–9	3·41976–9	1·34206–7	1·34206–7
60	1·16326–16	1·16326–16	5·32416–11	5·32416–11	1·70057–8	1·70057–8
80	1·65957–26	1·65956–26	1·22986–15	1·22987–15	8·76308–11	8·76308–11
100	5·85477–40	5·85476–40	1·12961–21	1·12961–21	9·81925–14	9·81925–14
120	6·25803–58	6·25802–58	3·57431–29	3·57430–29	2·35505–17	2·35505–17
140			3·21900–38	3·21900–38	1·18542–21	1·18542–21
160			6·41939–49	6·41939–49	1·22276–26	1·22277–26
180			2·03818–61	2·03818–61	2·51257–32	2·51257–32
200					9·94937–39	9·94937–39
220					7·30573–46	7·30572–46
240					9·51582–54	9·51581–54
260					2·08931–62	2·08931–62
280					7·29395–72	7·29396–72
300						

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