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LETTER TO THE EDITOR

On the probability distribution of the end-to-end vector of a polymer chain

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Abstract. We calculate the fourth and sixth moments of the probability distribution of the end-to-end vector of a polymer chain, close to the critical dimensionality 4. The results support that the excluded volume interactions do not change the Gaussian structure of the probability for large distances. Depending on the value of the excluded volume parameter u', an expansion or a shrinkage to this probability occurs even for the dimensionality 4.

For a linear flexible polymer chain consisting of $N+1$ beads joined with N bonds, the probability distribution $P(\{\boldsymbol{r}_i\})$ for the positions $\boldsymbol{r}_i$ $(i=1,2,\ldots,N+1)$ of the beads can be written in d dimensions as

$$P(\{\boldsymbol{r}_i\}) = \left[\frac{d}{(2\pi l^2)}\right]^{Nd/2} \exp\left(-\left(\frac{d}{2l^2}\right)\sum_{i=1}^{N}(\boldsymbol{r}_i-\boldsymbol{r}_{i+1})^2 - u'\sum_{\substack{i=1\\ i\neq j}}^{N+1}\sum_{j=1}^{N+1}\delta^d(\boldsymbol{r}_i-\boldsymbol{r}_j)\right). \tag{1}$$

In (1), l is an effective unit length and the prefactor $[d/(2\pi l^2 N)]^{Nd/2}$ comes from the normalisation constants of the ideal distributions of the N bonds. The excluded volume parameter u' can be written in terms of the mean potential between the beads (Yamakawa 1971), and it can take zero, positive or negative values depending on whether we are in an ideal, a good or a poor solvent respectively. The probability distribution $P(\boldsymbol{R}, N)$ for the end-to-end vector $\boldsymbol{R}$ can be taken from $P(\{\boldsymbol{r}_i\})$ if we integrate in the positions $\boldsymbol{r}_i$ of all beads, except the first and the last ones which we fix, say, at the origin $\boldsymbol{r}_1=\boldsymbol{0}$ and at the position $\boldsymbol{R}$, $\boldsymbol{r}_{N+1}=\boldsymbol{R}$,

$$P(\boldsymbol{R}, N) = \int \prod_{i=1}^{N+1} \mathrm{d}^d\boldsymbol{r}_i\, P(\{\boldsymbol{r}_i\})\delta^d(\boldsymbol{r}_1)\delta^d(\boldsymbol{R}-\boldsymbol{r}_{N+1}). \tag{2}$$

In the absence of excluded volume effects ($u'=0$), the model is exactly solvable and yields for the probability $P(\boldsymbol{R}, N)$ the Gaussian form

$$P_0(\boldsymbol{R}, N) = [d/(2\pi l^2 N)]\exp[-dR^2/(2l^2N)]. \tag{3}$$

Turning on the excluded volume interactions ($u'\neq 0$), the conformational behaviour of the chain is changed, and an interesting question is how the excluded volume parameter u' affects the structure of the probability. Previous studies for the good solvent region where $u'>0$ (Fisher 1966, McKenzie 1973, Des Cloizeaux 1974, Oono *et al* 1981) were based on the assumption that the probability is not Gaussian and calculated the characteristic of such distributions. We are going to chase an analogous task in this work and determine the structure of the probability for both good and poor solvents, close to the dimensionality 4.

Recently we have used second-order perturbation theory (Kosmas 1981) and we have calculated the zeroth and second moments of the probability $P(\boldsymbol{R}, N)$, close to the critical dimensionality $d=4$, as

$$C=\mu_0^N \int \mathrm{d}^d\boldsymbol{R}\, P(\boldsymbol{R}, N)=\mu_0^N \exp(-2uN)\{1+2u \ln N+[(u\varepsilon/2)-6u^2]\ln^2 N+\ldots\}, \quad (4)$$

$$\langle R^2\rangle=\int \mathrm{d}^d\boldsymbol{R}\, P(\boldsymbol{R}, N) R^2 \Big/ \int \mathrm{d}^d\boldsymbol{R}\, P(\boldsymbol{R}, N)$$

$$=Nl^2\{1+2u \ln N+[(u\varepsilon/2)-6u^2]\ln^2 N+\ldots\},$$

$$\varepsilon=4-d, \qquad u=[d/(2\pi l^2)]^{d/2} u'. \quad (5)$$

The exponentiation of these series gave the fixed point value of u as $u^*=\varepsilon/16$, so that the average quantities can be written at the fixed point as

$$C=\mu_0^N \exp(-\varepsilon N/8) N^{\varepsilon/8}, \quad (6)$$

$$\langle R^2\rangle \sim N^{1+\varepsilon/8}. \quad (7)$$

In this way the critial exponents can be found to order ε. By means of third-order calculations (Kosmas 1982) we have realised that the infinite series sum up to known analytical expressions, capable of being determined from second-order perturbation theory. The analytical expressions for C and $\langle R^2\rangle$ are

$$C=\mu_0^N \exp(-2uN)(1+8u \ln N)^{1/4}, \quad (8)$$

$$\langle R^2\rangle=Nl^2(1+8u \ln N)^{1/4}, \qquad \ln N=\lim_{\varepsilon\to 0}(2/\varepsilon)(N^{\varepsilon/2}-1), \quad (9)$$

and describe properly both the good solvent region ($u>0$), where the meaning of the critical exponents is valid, and also the poor solvent region ($u<0$), where the shrinkage of the chain starts. In this work we calculate the next two moments $\langle R^4\rangle$ and $\langle R^6\rangle$ in an effort to see the structure of the probability close to the critical dimensionality 4, for large distances and for both the good and the poor solvents.

Combining (1) with (2) we can write for the probability $P(\boldsymbol{R}, N)$, up to second order in u' and in the Fourier $\boldsymbol{K}'$ space, the expression

$$\tilde{P}(\boldsymbol{K}', N)=(1/2\pi)^{d/2}\int \mathrm{d}^d\boldsymbol{R} \exp(\mathrm{i}\boldsymbol{K}'\boldsymbol{R}) P(\boldsymbol{R}, N)$$

$$=(1/2\pi)^{d/2}\Big[\exp(-Nl^2K'^2/2d)-2u'\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}[d/2\pi l^2(j-i)]^{d/2}$$

$$\times\exp[-(N-j+i)l^2K'^2/2d]$$

$$+4u'^2\sum_{i=1}^{N-3}\sum_{j=i+1}^{N-2}\sum_{k=j+1}^{N-1}\sum_{m=k+1}^{N}\{[d/2\pi l^2(j-i)]^{d/2}$$

$$\times[d/2\pi l^2(m-k)]^{d/2}\exp[-(N-m+k-j+i)l^2K'^2/2d]$$

$$+[d/2\pi l^2(k-j)]^{d/2}$$

$$\times[d/2\pi l^2(m-k+j-i)]^{d/2}\exp[-(N-m+i)l^2K'^2/2d]+(d/2\pi l^2)^d$$

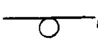
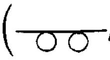
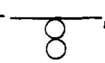
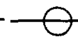
$$\times (l_1 l_2 + l_1 l_3 + l_2 l_3)^{-d/2} \exp[-(N - l_1 - l_2 - l_3 + l_{ef}) l^2 K'^2/2d]\}\Big],$$

$$l_1 = j - i, \qquad l_2 = k - j, \qquad l_3 = m - k, \qquad l_{ef}^{-1} = l_1^{-1} + l_2^{-1} + l_3^{-1}. \quad (10)$$

The K'^{2n}th component of $\tilde{P}(\boldsymbol{K}', N)$ yields the $2n$th moment of the probability $P(\boldsymbol{R}, N)$. $\tilde{P}(\boldsymbol{K}', N)$ can be written in a diagrammatic language as

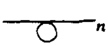
$$\tilde{P}(\boldsymbol{K}, N) = (1/2\pi)^{d/2} \sum_{n=0}^{\infty} (-1)^n K^{2n} C_{2n}/n!, \quad (11)$$

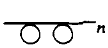
with

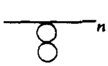
$C_{2n} =$ $_n = 2u$  $_n + 4u^2\Big($  $_n +$  $_n +$  $_n\Big)$, (12)

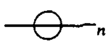
where $u = (d/2\pi l^2)^{d/2} u'$, $K^2 = K'^2 l^2/2d$. The diagrams of (12) are defined as:

 $_n = N^n$, (13a)

 $_n = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} (j-i)^{-d/2} (N - j + i)^n$, (13b)

 $_n = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{m=k+1}^{N} (j-i)^{-d/2} (m-k)^{-d/2} (N - m + k - j + i)^n$, (13c)

 $_n = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{m=k+1}^{N} (k-j)^{-d/2} (m - k + j - i)^{-d/2} (N - m + i)^n$, (13d)

 $_n = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{m=k+1}^{N} (l_1 l_2 + l_1 l_3 + l_2 l_3)^{-d/2} (N - l_1 - l_2 - l_3 + l_{ef})^n$. (13e)

The values of these diagrams have been calculated up to $n = 3$ in the same way as before (Kosmas 1981). Their values are quoted in table 1. Substituting these expressions in (12) we take for the coefficients C_{2n} the following expressions:

$$C_0 = \exp(-2uN)\{1 + 2u \ln N + [(u\varepsilon/2) - 6u^2] \ln^2 N + \ldots\}, \quad (14a)$$

$$C_2 = C_0 N\{1 + 2u \ln N + [(u\varepsilon/2) - 6u^2] \ln^2 N + \ldots\}, \quad (14b)$$

$$C_4 = C_0 N^2 [1 + 4u \ln N + (u\varepsilon - 8u^2) \ln^2 N + \ldots], \quad (14c)$$

$$C_6 = C_0 N^3 \{1 + 6u \ln N + [(3u\varepsilon/2) - 6u^2] \ln^2 N + \ldots\}. \quad (14d)$$

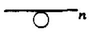
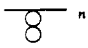
The first thing to notice is that the exponentiation condition, that is the requirement that the half of the square of the first term be equal to the second-order term, yields the same fixed point value $u^* = \varepsilon/16$ for all four series. Using this value for u, the critical exponents for these four moments can be determined to order ε as

$$C_0 = \exp(-\varepsilon N/8) N^{\varepsilon/8}, \qquad C_2 \sim C_0 N^{1+\varepsilon/8}, \quad (15a,b)$$

$$C_4 \sim C_0 N^{2+2\varepsilon/8}, \qquad C_6 \sim C_0 N^{3+3\varepsilon/8}. \quad (15c,d)$$

These expressions reveal that the exponents of the higher moments are multiples of the exponent of the second moment. The knowledge of the coefficients of the first- and second-order terms (14) is capable of determining the closed analytical expressions

Table 1.

n				
0	$N-\ln N-\frac{1}{4}\varepsilon\ln^2 N$	$\frac{1}{2}N^2-2N\ln N+\ln^2 N$	$N\ln N-\ln^2 N$	$-\frac{3}{2}\ln^2 N$
1	$N^2-2N\ln N-\frac{1}{2}\varepsilon N\ln^2 N$	$\frac{1}{2}N^3-3N^2\ln N+3N\ln^2 N$	$N^2\ln N-2N\ln^2 N$	$-3N\ln^2 N$
2	$N^2-3N^2\ln N-\frac{3}{4}\varepsilon N^2\ln^2 N$	$\frac{1}{2}N^4-4N^3\ln N+6N^2\ln^2 N$	$N^3\ln N-3N^2\ln^2 N$	$-\frac{9}{2}N^2\ln^2 N$
3	$N^4-4N^3\ln N-\varepsilon N^3\ln^2 N$	$\frac{1}{2}N^5-5N^4\ln N+10N^3\ln^2 N$	$N^4\ln N-4N^3\ln^2 N$	$-6N^3\ln^2 N$

of these moments (Kosmas 1982) as

$$C_0=\exp(-2uN)(1+8u\ln N)^{1/4}, \qquad C_2=C_0N(1+8u\ln N)^{1/4}, \tag{16a,b}$$

$$C_4=C_0N^2(1+8u\ln N)^{2/4} \tag{16c}$$

$$C_6=C_0N^3(1+8u\ln N)^{3/4}, \qquad \ln N=\lim_{\varepsilon\to 0}(2/\varepsilon)(N^{\varepsilon/2}-1). \tag{16d}$$

These analytical expressions describe both the good solvent region ($u>0$) where the meaning of the exponents is valid (15), but also the poor solvent region where the chain collapses. Substituting these results in (11) we take that $\tilde{P}(\boldsymbol{K},N)$ is Gaussian up to order K^6:

$$\tilde{P}(\boldsymbol{K},N)=(1/2\pi)^{d/2}C_0\exp[-K^2N(1+8u\ln N)^{1/4}], \qquad K^2=K'^2l^2/2d. \tag{17}$$

The probability $P(\boldsymbol{R},N)$ for large $|R|$'s is given by the inverse Fourier transform of (17) as

$$\begin{aligned} P(\boldsymbol{R},N)&=(1/2\pi)^{d/2}\int \mathrm{d}^d\boldsymbol{K}'\exp(-\mathrm{i}\boldsymbol{K}'\boldsymbol{R})\tilde{P}(\boldsymbol{K}',N) \\ &=C_0[d/2\pi l^2N(1+8u\ln N)^{1/4}]^{d/2}\exp[-dR^2/2l^2N(1+8u\ln N)^{1/4}] \\ &=C_0(d/2\pi\langle R^2\rangle)^{d/2}\exp(-dR^2/2\langle R^2\rangle), \qquad \text{large } |R|. \end{aligned} \tag{18}$$

This Gaussian structure is determined from the sole knowledge of its second moment $\langle R^2\rangle$, equation (9), and is expanded or shrunk depending on whether $u>0$ or $u<0$. This character persists even for the critical dimensionality $d=4$.

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