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COMMENT

Perturbation series for a polymer chain—why the logarithms cancel

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Abstract. In this note we comment upon a remarkable cancellation which occurs when the logarithm of the configurational partition function is taken. This little-known fact has interesting consequences for the form of the partition function. Indeed, it may explain why there are no logarithmic terms in the perturbation series for the expansion factor of the chain.

1. Introduction

One of the few rigorous results long available on excluded volume polymer chains has been the perturbation series for the mean square length of a chain (Fixman 1955, Barrett and Domb 1979):

$$\alpha_N^2(z) = \langle R_N^2 \rangle / N = 1 + C_1 z + C_2 z^2 + \ldots$$

where $z = h_0 N^{1/2} w$ (in three dimensions), and w is a measure of the strength of volume exclusion. All the coefficients studied so far, C_1, C_2, C_3, are simple constants in the limit of large N and small w. This is curious, since a straightforward expansion of the partition function yields a series in w whose coefficients contain terms in $\log N$, $(\log N)^2, \ldots$. The cancellation of these logarithmic terms has been commented upon (Chikahisa 1970, Domb and Joyce 1972, Edwards and Singh 1979). Indeed Edwards and Singh found it sufficiently remarkable to justify checking.

An equally remarkable cancellation has gone largely without notice (see however Domb and Joyce 1972). The logarithm of the partition function may be expanded in a series whose rth coefficient is of the form

$$a_r N + b_r N^{r/2} + c_r N^{r/2} \log N + O(N^{r/2-1}).$$

This can be understood as a consequence of the form of the partition function, and it is this particular form which explains the absence of logarithms in the series for α_N^2.

The remarks which follow are somewhat conjectural, and depend upon the supposed form of the expansion coefficients. There is, for instance, no proof that the fourth term C_4 does not contain logarithms. However, even if it does, the consequences may well be better understood within the framework presented here.

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2. The characteristic function

Let a random walk, on a lattice or in the continuum, be characterised by the distribution function $p_N(\boldsymbol{l})$. This function represents the probability that the random walker, having taken N steps, is at the position $\boldsymbol{l}=(l_1, l_2, l_3)$ with respect to his starting point. A statistical weight $1-w$ is associated with each self-intersection of the walk, where $0\leq w\leq 1$. Random walk statistics correspond to $w=0$ and self-avoiding walk statistics to $w=1$. The function $p_N(\boldsymbol{l})$ for random walks is thus generalised to $p_N(\boldsymbol{l}, w)$. Summation over all possible configurations yields a partition function

$$p_N(w)=\sum_{\boldsymbol{l}} p_N(\boldsymbol{l}, w).$$

Now define the function

$$P(\boldsymbol{l}; x, w)=\sum_N p_N(\boldsymbol{l}, w)x^N$$

and its Fourier transform

$$Q(\boldsymbol{k}; x, w)=\sum_{\boldsymbol{l}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{l}}P(\boldsymbol{l}; x, w)=\sum_N \zeta_N(\boldsymbol{k}, w)x^N$$

where

$$\zeta_N(\boldsymbol{k}, w)=\sum_{\boldsymbol{l}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{l}}p_N(\boldsymbol{l}, w).$$

The mean square length of walks is defined by

$$\langle R_N^2(w)\rangle=\sum_{\boldsymbol{l}} l^2 p_N(\boldsymbol{l}, w)/p_N(w)\equiv p_N^{(2)}(w)/p_N(w)$$

and its expansion factor by

$$\alpha_N^2(w)=\langle R_N^2(w)\rangle/\langle R_N^2(0)\rangle.$$

Define two more functions,

$$P(x, w)=\sum_{\boldsymbol{l}} P(\boldsymbol{l}; x, w)=Q(\boldsymbol{0}; x, w),$$

$$P^{(2)}(x, w)=\sum_{\boldsymbol{l}} l^2 P(\boldsymbol{l}; x, w)=-\nabla_k^2 Q(\boldsymbol{k}; x, w),$$

so that α_N^2 is the ratio of the coefficients of x^N in $Q(\boldsymbol{0})$ and $-\nabla^2 Q(\boldsymbol{0})$, divided by N, respectively.

It is simple to show that for any reasonable choice of $p_N(\boldsymbol{l}, w)$,

$$\zeta_N(\boldsymbol{k}, w)=p_N(w)-k^2 p_N^{(2)}(w)/3!+k^4 e_N(w)+\ldots.$$

If one substitutes into this expression the known forms of $p_N(1)$ and $\langle R_N^2(1)\rangle$ for self-avoiding walks (Domb 1969)

$$p_N(1)=A\mu^N N^g, \qquad \langle R_N^2(1)\rangle=BN^\gamma,$$

one finds

$$Q(\boldsymbol{k}; x, 1)=C(1-\mu x)^{-g-1}-(k^2/3!)D(1-\mu x)^{-g-\gamma-1}+k^4E(x)+\ldots$$

whence

$$P(x, 1)=C(1-\mu x)^{-g-1}, \qquad P^{(2)}(x, 1)=D(1-\mu x)^{-g-\gamma-1}.$$

Studies of self-avoiding walks under differing excluded volume conditions (Barrett and Pound 1980) indicate that near $w = 1$, the correct forms may be

$$P(x, w) \sim [1 - \mu(w)x]^{-g-1}, \qquad P^{(2)}(x, w) \sim [1 - \mu(w)x]^{-g-\gamma-1}.$$

Less well understood is the form of Q near $w = 0$. A perturbation series has been developed for both $p_N(w)$ and $p_N^{(2)}(w)$ about the random walk limit (Domb and Joyce 1972, Barrett and Domb 1979). The form of the expansion is complicated, to say the least. If

$$p_N(w) = \rho_0 + \rho_1 w + p_2 w^2 + \ldots, \qquad p_N^{(2)}(w) = \rho_0^{(2)} + \rho_1^{(2)} w + \rho_2^{(2)} w^2 + \ldots,$$

then

$$\rho_r(N) = aN^r + bN^{r-1/2} + \ldots + cN^{r/2} + \ldots + dN^{r/2}\log N + \ldots + eN^{r/2}(\log N)^2 + \ldots$$

and similarly for $p_r^{(2)}(N)$. However, an enormous simplification occurs if we follow a suggestion of Domb (1960), originally made with respect to the partition function of the Ising model, and applied to the polymer problem by Domb and Joyce (1972). By formally taking the logarithm of the partition function, we obtain an almost magical cancellation of logarithmic terms. Thus

$$\ln p_N(w) = \tau_1 w + \tau_2 w^2 + \ldots, \qquad \ln p_N^{(2)}(w) = \tau_i^{(2)}(w) + \tau_2^{(2)} w^2 + \ldots,$$

where

$$\tau_1 = a_r N + b_r N^{r/2} + c_r N^{r/2}\log N + \mathrm{O}(N^{r/2-1}) + \mathrm{O}(N^{r/2-1}\log N),$$
$$\tau_1^{(2)} = a_r N^2 + b_r N^{r/2+1} + c_r N^{r/2+1}\log N + \mathrm{O}(N^{r/2}) + \mathrm{O}(N^{r/2}\log N).$$

This has been explicitly verified to $r = 4$. If these relations are supposed true for all r, then

$$\log p_N(w) = (a_1 w + a_2 w^2 + \ldots)N + (b_1 N^{1/2} w + b_2 N w^2 + \ldots) + (c_1 N^{1/2} w + c_2 N w^2 + \ldots)\log N$$

which suggests

$$p_N(w) = \mu(w) C(N^{1/2} w) N^{\psi(N^{1/2}\omega)}, \qquad p_N^{(2)}(w) = \mu^{(2)}(w) D(N^{1/2} w) N^{\psi^{(2)}(N^{1/2}\omega)}. \quad (1)$$

It has been verified to $r = 4$ that $\mu = \mu^{(2)}$, and to $r = 3$ that $\psi = \psi^{(2)}$. If these identities are exact, then

$$\alpha_N^2(w) = p_N^{(2)}(w)/Np_N(w) = D(N^{1/2}w)/C(N^{1/2}w) = \alpha^2(N^{1/2}w).$$

It is clear that while $p_N(w)$ and $p_N^{(2)}(w)$ have series expansions which involve $\log N$ in a natural way, no such logarithmic terms will appear in the expansion of α^2.

Near $w = 0$, and with $N^{1/2}w$ fixed,

$$P(x, w) = C(N^{1/2}w)[1 - \mu(w)x]^{-\psi-1}, \qquad P^{(2)}(x, w) = D(N^{1/2}w)[1 - \mu(w)x]^{-\psi-2},$$

which differ from the corresponding expressions for $w \leqslant 1$ primarily in the nature of the exponent, and the prefactors. As w increases from 0 to 1, the correction terms which have been ignored in the small-w expressions become increasingly significant, indeed changing dramatically the character of the functions. For $w \geqslant 0$ it is the structure of the prefactors which determines α^2, whereas for $w \leqslant 1$ it is the singularity at $\mu x = 1$ which determines α^2.

If we relax the requirement that $\psi(N^{1/2}w)=\psi^{(2)}(N^{1/2}w)$, then it is evident that logarithmic terms will appear in the series expansion for α^2 as well. The implications of the existence of such terms for two-parameter theory are a matter for study. It is proposed to deal with the fourth-order logarithmic term in a forthcoming communication.

3. Conclusions

Some comments have been made concerning the function $Q(\boldsymbol{k}, x, w)$, which contains all the configurational details of chains with excluded volume. Particular attention has been paid to the limiting case of a self-avoiding walk, and to the region of small excluded volume. In this latter region, a conjectured form (equation (1)) of the partition function is used to explain the absence of logarithms in the virial series.

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