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LETTER TO THE EDITOR

Virial expansion of a two-dimensional polymer chain: cancellation of logarithmic terms

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Abstract. A virial expansion is developed for a two-dimensional polymer chain in the two-parameter approximation. Logarithmic terms in the partition function arise from ladder graphs, in contrast to the three-dimensional chain where they are due to non-ladder graphs. It has been possible to show that when the mean square end-to-end distance $\langle R_N^2\rangle$ is calculated the logarithmic terms cancel to all orders, thus verifying universality.

The virial expansion of a polymer chain in dilute solution has attracted the attention of a number of investigators (see e.g. Yamakawa 1971). It has been usual in polymer theory to approximate the intramolecular forces by means of a pseudopotential, i.e. a δ-function interaction of appropriate strength. If $V(\boldsymbol{r})$ represents the intramolecular potential, the forces are replaced by $-\nu\delta(\boldsymbol{R}_{ij})$ where $\boldsymbol{R}_{ij}$ is the distance between the ith and jth steps of the walk, and

$$\nu = \int \{1-\exp[-\beta V(\boldsymbol{r})]\}\,\mathrm{d}\boldsymbol{r} \qquad (\beta = 1/kT). \tag{1}$$

The bonds of the chain are taken to be steps of length a in a continuum gaussian random walk, and a virial series is developed in powers of ν for quantities like $\langle R_N^2\rangle$, the mean square end-to-end length, or $\langle S_N^2\rangle$, the mean square radius of gyration.

In 1972 Domb and Joyce introduced a lattice analogue of the above model in which the interaction is replaced by $-w\delta_{ij}$ where $\boldsymbol{i}$ and $\boldsymbol{j}$ are the lattice sites occupied by the ith and jth points of the walk. They were able to establish a parallelism between the properties of lattice and continuum walks. This was further developed by Barrett and Domb (1979) who calculated three terms of the virial expansion of $\langle R_N^2\rangle$ for a general lattice model of a three-dimensional chain in the form

$$\alpha_N^2(w) = \langle R_N^2\rangle/Na^2 = 1 + k_1 w + k_2 w^2 + k_3 w^3 + \ldots. \tag{2}$$

The k_r are functions of N, and the leading term is of order $N^{r/2}$. Neglecting all but this leading term, they derived a virial series in the 'two-parameter' approximation

$$\alpha^2(z) = 1 + A_1 z + A_2 z^2 + A_3 z^3 + \ldots \tag{3}$$

which had previously been obtained for the continuum gaussian model with

$$z = (3/2\pi a^2)^{3/2} N^{1/2}\nu. \tag{4}$$

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They showed that for the terms which they had calculated expansion (3) is valid for *any* lattice model if an appropriate scale factor h_0 is introduced for each lattice, and

$$z = h_0 N^{1/2} w. \qquad (5)$$

Hence in the two-parameter approximation the series expansion (3) applies to continuum and lattice models, and has universal validity. However, it has been shown that the series is not convergent but asymptotic (Edwards 1975, Oono 1975). The first three coefficients A_1, A_2 and A_3 have been calculated, and Barrett and Domb (1979) introduced a correction to the accepted value for A_3.

Chikahisa (1970) first drew attention to the logarithmic terms which arise in the virial expansion for the partition function of a chain. Writing $c_N(w)$ for this partition function, and expanding the function in the form

$$c_N(w)/c_N(0) = 1 + \tau_1 w + \tau_2 w^2 + \tau^3 w^3 + \ldots, \qquad (6)$$

the even terms τ_{2r} contain factors of the form $\ln N$, $(\ln N)^2$ etc. Similarly, if we denote by $c_N(\boldsymbol{l}, w)$ the partition function of all chains with endpoint $\boldsymbol{l}$, and write

$$c_N^{(2)}(w)/c_N^{(2)}(0) = \sum \boldsymbol{l}^2 c_N(\boldsymbol{l}, w) / \sum \boldsymbol{l}^2 c_N(\boldsymbol{l}, 0) = (1 + \nu_1 w + \nu_2 w^2 + \nu_3 w^3 + \ldots), \qquad (7)$$

the even terms of the form ν_{2r} contain factors $(\ln N)$, $(\ln N)^2$ etc. In forming the expansion for

$$\alpha^2 = c_N^{(2)}(w)/Na^2 c_N(w), \qquad (8)$$

it is easy to show that the logarithmic terms cancel in the first even coefficient k_2. But Chikahisa expressed doubt as to whether they would necessarily cancel in higher orders. Such a cancellation is essential if the universality property described above in (5), and accepted nowadays by most polymer theorists, is to be valid.

In describing the configurational structure of the contributions to τ_r, ν_r, Chikahisa differentiated between *ladder graphs* which do not involve any crossed bonds, and *non-ladder graphs* which do, and are analogous to irreducible cluster integrals in the standard virial expansion for a condensing gas. The former can be tackled with relative ease, and Domb and Joyce obtained a closed form expression from which they can be derived. The non-ladder graphs are much more difficult to handle. Unfortunately, for the three-dimensional model it is these configurations which give rise to the logarithmic terms, and not much progress has been made in finding whether the cancellation occurs even at the second order.

The virial expansion for a two-dimensional chain has received less attention, and only one coefficient with series (3) has been calculated. A lattice model can again be used, and to achieve universality, relation (5) must be replaced by

$$z = h_0 N w. \qquad (9)$$

Logarithmic terms arise in the coefficients τ_r and ν_r in (6) and (7), and they enter at both odd and even orders. But it is now *the ladder graphs which give rise to the logarithmic terms*, the non-ladder graphs giving simple powers of N.

Using an algorithm introduced by Barrett and Domb (1979) based on Lagrange's reversion of series, we have been able to calculate the contribution to τ_r, ν_r of the ladder graphs for general r, and to show that the logarithmic terms in A_r cancel to all orders. It is quite remarkable that this cancellation occurs only for universal quantities like $\langle R_N^2 \rangle$ and not for $c_N(w)$ and $c_N^{(2)}(w)$. There must be some fundamental reason why such a cancellation should occur, but we have been able to demonstrate it pragmatically only.

In addition to the ladder graph contribution for general r, we have calculated the non-ladder graph contributions to the first three coefficients, and hence we find for the two-dimensional virial coefficients

$$A_1 = -\tfrac{1}{2}, \qquad A_2 = \tfrac{1}{256}, \qquad A_3 = -0.204\,473. \tag{10}$$

Expansion (3) describes a crossover from the random-walk universality class ($n = -2$) to the self-avoiding-walk universality class ($n = 0$) (Domb 1974). The features which we have outlined (asymptotic series, and logarithmic terms which cancel for universal quantities) may be characteristic of general crossover behaviour from one universality class to another.

Full details of the calculations described above will be published elsewhere.

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