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LETTER TO THE EDITOR

Real polymer chains: passage from lattice models to the continuum

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Abstract. The 'universal' model of Domb and Barrett is combined with Monte Carlo data of Smith and Fleming to clarify the correspondence between chains confined to a lattice, and chains in the continuum. Lattice walks are classified in terms of the parameter ν = (nearest neighbour distance)/(step length) which is analogous to the excluded volume ratio v for chains in the continuum. Comparisons of results for on-lattice and off-lattice chains should be made only for equivalent values of these two parameters. A theoretical picture of a linear hard-sphere chain is constructed and a comparison is made with the Monte Carlo results.

Recent research has done much to dispel the obscurity shrouding the excluded volume linear chain. Some of the more promising studies have involved the Domb–Joyce model, which attempts to combine in a single picture the well-established features both of continuum models and of lattice models (Domb and Joyce 1972, Domb *et al* 1973, Domb and Barrett 1976). Other studies of an 'experimental' nature include the Monte Carlo research of Alexandrowicz and Accad (1973) on lattice chains with varying excluded volume, and of Smith and Fleming (1975) on hard sphere chains in the continuum. The predictions of the Domb–Joyce model for lattices have been tested against the results of Alexandrowicz and Accad (Domb *et al* 1973); the present work will endeavour to show that the data of Smith and Fleming are not inconsistent with the predictions of the theoretical model.

Consider $N+1$ hard spheres, each of diameter D, linked linearly by N bonds each of length a, the chain being perfectly flexible at each sphere centre. For $D=0$, this is a random flight chain, with a mean-square end-to-end length given by the well-known formula

$$\langle R_N^2 \rangle = Na^2. \tag{1}$$

For $D>0$, the excluded volume of the chain will be characterized by the *excluded volume ratio* v, defined by (Smith and Fleming 1975)

$$v = \frac{D}{a} = \frac{\text{closest approach of two centres}}{\text{bond length}}. \tag{2}$$

Thus, while $v=0$ represents a random flight chain, $v=1$ represents a chain with maximum excluded volume. The expansion factor of the chain is defined by the usual formula

$$\alpha_N^2(v) = \langle R_N^2(v) \rangle / \langle R_N^2 \rangle. \tag{3}$$

Smith and Fleming (1975) have made Monte Carlo measurements of such chains, $N \leqslant 100$, for $v = 0{\cdot}2$ to $v = 1{\cdot}0$. Their results have the form $\alpha^2 = AN^{\gamma}$; values of A and γ for various v are reprinted in table 1.

Table 1.

v	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
γ	0·026	0·089	0·092	0·165	0·186	0·173	0·193	0·243	0·208
A	0·973	0·898	0·967	0·928	0·936	1·105	1·139	1·076	1·210

It is worth noting that this continuum chain is based upon the fixed-bond-length Rayleigh model, rather than upon the Gaussian model. It is difficult to see how the latter could be the basis for such a chain; the location of a hard sphere at each vertex of the walk fundamentally alters the Gaussian distribution of bond lengths. Clearly, no chain exhibiting large excluded volume may have its bond lengths so distributed.

The Domb and Joyce model consists of an N-step walk on a lattice, with an interaction $-\omega\delta_{ij}$ between every pair of vertices of any configuration of the walk. $\delta_{ij} = 1$ if the ith and jth steps of the walk occupy the same lattice site, and is zero otherwise. The effect of this interaction is that each configuration of the chain has an associated Boltzmann factor of

$$\prod_{i=0}^{N-2} \prod_{j=i+2}^{N} (1-\omega\delta_{ij}) = (1-\omega)^k \tag{4}$$

where k is the number of self-intersections of the chain. Each intersection of the chain with itself is thus accorded a statistical weight of $(1-\omega)$. The factor (4) appears in the partition function; for $\omega = 0$ all configurations are permitted, and $\omega = 1$ excludes all but self-avoiding configurations.

Consider such a walk with $\omega = 1$. No two vertices of the chain occupy the same lattice site. In fact, no two vertices may approach more closely than the distance between nearest neighbours. A hard sphere of just this diameter may therefore be located at each vertex of the walk without effect. It is convenient to associate with each lattice walk the parameter

$$\nu = \frac{\text{nearest neighbour distance}}{\text{step length}}. \tag{5}$$

(Here 'nearest neighbour' means the nearest neighbour which it is possible for the walk to visit). ν and v are clearly analogous. However there is an important difference in application. For the continuum walk the excluded volume may be controlled by varying v between 0 and 1, while for the lattice walk the excluded volume is controlled by varying the statistical weight ω. $\omega = 1$ corresponds to an excluded volume ratio of ν. In other words ν is the maximum excluded volume ratio obtainable from a given lattice walk. For any nearest-neighbour walk $\nu = 1$; a walk to fourth nearest neighbours on a BCC lattice has $\nu = 2/\sqrt{11} \sim 0{\cdot}6$. (The idea of controlling the excluded volume by permitting walks to other than nearest neighbours is due to Domb 1970.) Comparison of results, to be meaningful, should be made between measurements of the continuum model at a given v, and the predictions of the lattice model for the particular combination of ν and ω which correspond to this value of v.

Thus far, the principal results for the Domb–Joyce model have been confined to lattices with $\nu = 1$. Expanding α^2 as a perturbation series in ω, for large N, one obtains

the expansion (Domb and Barrett 1976)

$$\alpha^2 = 1 + \tfrac{4}{3}z^* + \cdots. \tag{6}$$

Here, z^* is defined by

$$z^* = \left(\frac{3}{2\pi}\right)^{3/2} \frac{g}{a^3} N^{1/2}\omega \equiv h_0 N^{1/2}\omega. \tag{7}$$

g is the volume per lattice site. The series (6) is identical to the familiar expansion of Zimm (1946), Fixman (1955) and others, except that in this latter case the expansion variable is

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \frac{N^{1/2}\beta}{a^3}. \tag{8}$$

β is the binary cluster integral, defined by (e.g. Fixman 1955)

$$\beta = \int [1 - \exp(-V(\boldsymbol{r}_{ij})/kT)]\, \mathrm{d}^3 r_{ij}. \tag{9}$$

Performing the integration for hard spheres of diameter D, one finds

$$\beta/a^3 = \frac{4\pi}{3} v^3. \tag{10}$$

Comparison of (7) and (8) would seem to suggest

$$\frac{4\pi}{3} v^3 = \frac{g}{a^3}\omega \equiv g^*\omega \tag{11}$$

at least in the region of small v. The binary cluster approximation is justified only in the limit of small β and should not be expected to hold for the entire range of v. From the foregoing it follows that $\alpha^2(v)$ has an expansion of the form

$$\alpha^2(v) = 1 + c_1 v^3 + c_2 v^6 + \cdots. \tag{12}$$

(Incidentally, $\alpha^2(v)$ will have an expansion of the form (12) for any short-range potential $V(\boldsymbol{r}_{ij})$, the coefficients $c_1, c_2, \ldots$ depending on the particular form of V.)

For the lattice walks, Domb and Lax (to be published, see also Domb *et al* 1973) have shown that for $0{\cdot}5 \leqslant \omega \leqslant 1{\cdot}0$, N large, α^2 can be fitted by the relation

$$\alpha^2 \sim A N^{1/5} \tag{13}$$

where A depends on ω and on the particular lattice. Their numerical estimates of A are reasonably well fitted by the relation (Barrett 1975)

$$A = (2\sqrt{\pi} h_0 \omega)^{2/5}. \tag{14}$$

On the basis of (6), (13) and (14), Domb and Barrett (1976) have suggested that α^2 is 'universal', that is, the same function of $h_0 N^{1/2}\omega$ for all lattice models and the continuum, for large N. It may be that this claim is only valid for $\nu = 1$, or perhaps α^2 can be shown to be a universal function of some parameter which includes h_0, $N^{1/2}$, ω and ν. That is a question for future research; it must first be determined whether or not the claim is reasonable for $\nu = 1$. For such a walk $\omega = 1$ corresponds to $v = 1$, the upper limit of excluded volume. This, taken together with (11) would seem to make the

following correspondences reasonable:

$$\begin{aligned} &\omega \leftrightarrow \frac{4\pi}{3g^*}v^3; && v \geqslant 0 \\ &\omega \leftrightarrow v^3; && v \leqslant 1. \end{aligned} \tag{15}$$

One expects, then, the formula (13) to be valid for $0{\cdot}8 \leqslant v \leqslant 1{\cdot}0$, which corresponds roughly to $0{\cdot}5 \leqslant \omega \leqslant 1{\cdot}0$. A glance at table 1 shows that the Monte Carlo exponents for $v = 0{\cdot}8$ and $v = 1{\cdot}0$ do not differ greatly from 1/5; the value quoted for $v = 0{\cdot}9$ is thought by Smith and Fleming to be non-representative. In order to compare the coefficients A of table 1 with those given by (14) it is necessary to obtain the value of h_0 for the continuum model, and this unfortunately is not available. From (7),

$$h_0 = \left(\frac{3}{2\pi}\right)^{3/2} g^*.$$

For the lattice walks studied, g^* is a dimensionless constant, which preliminary research indicates is dependent only on ν and on q, the lattice coordination. A simple calculation shows that for a continuum chain with $v = 1$, the approximate 'coordination' is 16. One therefore expects g^* for the continuum model in this case to have a value close to that for a lattice walk with $\nu = 1$ and $q = 16$. In any case the matter requires further study. For purposes of comparison a tentative value of $g^* = 2$ for the $v = 1$ continuum walk is suggested as being compatible with the Monte Carlo data.

Finally, it is possible to make use of the expansion (12) near $v = 0$, and (13) and (14) near $v = 1$ to construct a plot of α^2 against v for any N over the entire range of v from 0 to 1, interpolating in the region not covered by (12) or (13). This has been done in figure 1 for $N = 100$ with the Monte Carlo data plotted on the same axes. The agreement can be seen to be reasonable over the entire range of v, not only near $v = 1$ where the agreement has been forced somewhat by the speculative choice of g^*. Incidentally, the shape of this curve accords well with that predicted by two parameter theory.

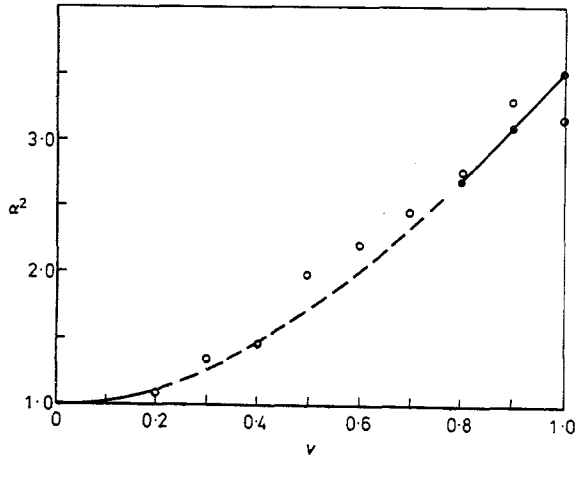

Figure 1. α^2 against v for $N = 100$. – – –, the interpolated portion of the curve; ●, points computed using (13); ○, Monte Carlo data computed using table 1.

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