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1990 J. Phys. A: Math. Gen. 23 3297

(http://iopscience.iop.org/0305-4470/23/14/026)

J. Phys. A: Math. Gen. **23** (1990) 3297–3306. Printed in the UK

Scaling at the rod-to-flexible chain crossover in the stiff limit

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Received 3 April 1990

Abstract. We critically examine the present theoretical understanding of the conformational rod-to-flexible chain crossover of a linear chain polymer in dilute solution with good solvent. There is good evidence for weak universality in this crossover while strong universality seems unlikely from available evidence. In addition, this system should exhibit a second crossover from Gaussian to excluded volume. We present a scaling hypothesis for the behaviour of this second crossover and compare with the initial results of numerical simulations and with the experiment of Murakami *et al.*

1. Rod-to-flexible chain crossover and two scaling limits

In this paper, we review the theoretical understanding of the rod-to-flexible chain crossover in stiff linear polymers in dilute solution and critically examine various arguments and evidence which have been presented to support the scaling ansatz and the nature of the crossover. In addition, a new scaling hypothesis is presented and some experimental and simulation results are analysed in the light of this hypothesis.

A convenient lattice model for studying the rod-to-flexible chain crossover is the persistent self-avoiding walk (PSAW)* introduced by Halley *et al* (1985). In this model the ensemble of stiff chains is obtained by generating self-avoiding walks on a lattice with a probability p of taking a turn (gauche) and $1-p$ of going straight (trans), and removing the walk if it intersects itself. The only variables in this model are N, the number of steps, and p, the gauche probability. While the rod-to-flexible chain crossover has been studied using various other models and approaches as well (see, e.g., Bhattacharjee and Muthukumar 1987 and references therein), we concentrate on the PSAW stiff-chain model here as the main discussion concerns some of the results predicted using this model.

The original scaling ansatz (Halley *et al* 1985) for the PSAW model was written as:

$$\langle R^2 \rangle = N^{2\nu} p^{(2\nu-2)\Delta} F(Np^{\Delta}) \tag{1}$$

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* This model was called the biased self-avoiding walk (BSAW) in previous publications of the current authors. Because of the possible confusion with a walk with a bias in fixed direction, we shall hereafter call it the persistent self-avoiding walk (PSAW). Correspondingly, what used to be called the biased random walk (BRW) will henceforth be called PRW.

0305-4470/90/143297+10$03.50

where R is the end-to-end distance and ν is the Flory exponent (for the definition of ν and other critical exponents, see, e.g., de Gennes (1979) and Yamakawa (1971)). This relation is intended for the asymptotic limit of:

$$N \to \infty \qquad p \to 0 \qquad \text{with } Np = \text{constant}. \tag{2}$$

Let us call this limit the rod-to-flexible chain limit because $F(x)$ then describes the rod-to-flexible crossover as x grows from $x \ll 1$ to $x \gg 1$.

By now many different calculations have been made to check this ansatz and obtain both the value of the crossover exponent Δ and the functional form of $F(x)$. These calculations include Monte Carlo simulations (Halley *et al* 1985, Lee and Nakanishi 1986), mapping to a lattice and continuum spin Hamiltonians (Atkatz *et al* 1987), real space renormalisation (Lee and Nakanishi 1987), exact solution of directed self-avoiding walk models (Glasser *et al* 1986, Privman and Frisch 1988, Privman and Svrakic 1988), series enumeration (Privman and Redner 1987), small-Np expansion (Glasser *et al* 1986), and Flory approximation (Schaefer *et al* 1980, Nakanishi 1987a). While they all support scaling of the form (1) with $\Delta = 1$, there are some substantial disagreements concerning the behaviour of $F(x)$, which will be the subject of section 2.

The scaling ansatz (1) anticipated $F(x) \to$ constant as $x \to \infty$ since this is the flexible (or coil-like) limit in which we expect $\langle R^2 \rangle$ to behave as $N^{2\nu}$. This must certainly be true if p is fixed, however small, and N is then allowed to go to infinity. However, the rod-to-flexible chain limit defined here is a subtle one which does not call for a fixed p. In fact a detailed Monte Carlo study (Lee and Nakanishi 1986) of this problem indicated that, in $d = 3$ dimensions, this limit produces a Gaussian stiff-chain behaviour with no excluded volume effect whereas in $d = 2$ it did yield excluded volume rod-to-flexible chain crossover. In particular, $F(x)$ did not show any sign of saturation but continued to decrease as $x \to \infty$. This feature was studied carefully using a number of alternative forms of the scaling ansatz and for quite long and stiff chains (on the simple cubic lattice, the closest approach to the rod-to-flexible chain limit was for $N = 1600$ and $p = 0.0125$).

Such behaviour was in fact anticipated by Schaefer *et al* (1980) and by Petschek (private communication), and a simple physical picture of why the dimensional differences can arise was given by Halley and quoted in Lee and Nakanishi (1986). A real space renormalisation study (Lee and Nakanishi 1987) later confirmed this behaviour by explicitly including an independent parameter controlling the strength of the excluded-volume effect.

Subsequently, a Flory approximation was applied (Nakanishi 1987a; see also an earlier application by Schaefer *et al* 1980) to the other crossover involved in this problem, the crossover from Gaussian to excluded volume, and suggested that this latter crossover is controlled by the magnitude of $Np^{d/(4-d)}$ (Np^3 in $d = 3$). Thus let us denote by excluded-volume crossover the limit in which the self-avoiding walk behaviour is restored after the first crossover to Gaussian behaviour when $d > 2$. Then, the excluded-volume crossover occurs for $d = 3$ in the limit of

$$N \to \infty \qquad p \to 0 \qquad \text{with } Np^y = \text{constant} \tag{3}$$

for a suitable value of $y > 1$, where $y = 3$ according to the Flory argument. The two limits, rod-to-flexible chain and excluded-volume, are such that in three dimensions, the rod-to-flexible chain limit implies Np^y is small (therefore the chain is Gaussian) and the excluded-volume limit implies Np is large (therefore the chain is coil-like). This situation is somewhat unconventional since both limits concern the same point

in the space of physical parameters $(N^{-1}, p) = (0, 0)$. In two dimensions, the two crossovers are both controlled by Np and the two scaling limits are identical.

The scaling ansatz (1) appears to be confirmed by all available work. In addition to the direct Monte Carlo studies already discussed, exact solutions of directed walks and series enumerations indicate that indeed various quantities, including $\langle R^2 \rangle$ and the number of walks with a given statistical weight w for gauche turns scale in this way with the crossover exponent equal to 1. The statistical weight w is the weight for a given gauche bond when the weight for trans bonds is taken as 1. Taking account of the fact that the relative weight per step of all gauche bonds together in this sense is $p/(1-p)$, our variable p is related to w by $w = p/[4(1-p)]$ on the simple cubic lattice, where the number of possible gauche steps per site is 4.

For example, Glasser *et al* (1986) expand $C(w, N)$, the number of turn-weighted self-avoiding N-step walks on the square lattice, to $O((wN)^3)$. This expansion extends the earlier derivation of the result $\Delta = 1$ in Halley *et al* (1985) which showed that, as long as scaling of the form (1) is assumed, the value of Δ can be obtained from just the $O(p)$ term in, say, $\langle R^2 \rangle / N^2$ (or the $O(w)$ term in $C(w, N)$). Thus Glasser *et al* (1986) reconfirmed that the value of this exponent is the same for the PSAW and PRW (persistent *random* walk with no immediate return) stiff-chain models and further calculated higher-order terms that affect the functional form of the scaling function.

2. Relationship to Gaussian scaling

Privman and Redner (1987) performed and analysed the series enumeration of the turn-weighted self-avoiding walks on the square, triangular and simple cubic lattices. Using the enumeration up to $N = 22$ steps on the square and $N = 16$ steps on the other two lattices, they concluded that, although scaling such as (1) holds, the suppression of excluded-volume effects in the stiff limit is only partial and the three-dimensional scaling function does not have the Gaussian character. On this basis, they argued that the Flory type argument (Schaefer *et al* 1980, Nakanishi 1987a) is likely to be valid only in the limit of $d \to \infty$.

In particular, they studied the scaling of two quantities, the number of walks $C(w, N)$ and the mean-squared end-to-end distance scaled in the way given in (1). In both cases, they form finite-order approximants for the relevant quantities and plot them against known Gaussian results. For example, for the latter, the approximants used for $F(x)$ in (1) are

$$F_{N,k}(x) = x^{2(1-\nu)}[R_N^2(w)/N - R_{N-k}^2(w)/(N-k)]/k \tag{4}$$

where $x = 4wN$, N is the number of steps, and k is an arbitrary integer. As before, w is the statistical weight for gauche turns. These approximants are evaluated for the several largest values of N available and for $k = 1$ (or 2 to avoid even–odd oscillations) and no extrapolation is attempted. We note that the approximants must be calculated with fixed x in order that they serve as approximants for $F(x)$.

Their results for $F(x)$ on the simple cubic lattice are compared in figure 1 with the Gaussian results and the Monte Carlo data from Lee and Nakanishi (1986). The series results are simply taken from figure 6 of Privman and Redner (1987) in which they were compared directly with the Gaussian result obtained in the rod-to-flexible chain limit. This means that, although their variable $4wN$ can be substantially different from

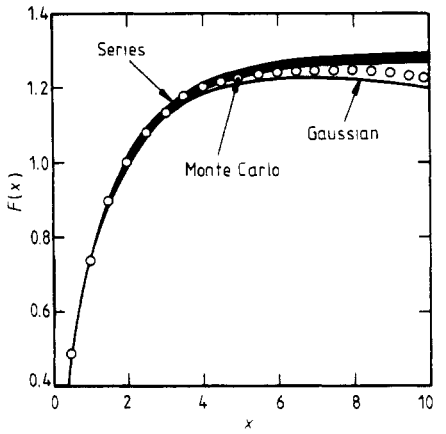

Figure 1. Comparison of the estimates of the scaling function $F(x)$ for the PSAW on the simple cubic lattice from the series enumeration work of Privman and Redner (1987), Monte Carlo results of Lee and Nakanishi (1986), and the Gaussian solution.

$x = Np$ for the range of w and N used in the enumeration work, we regard them to be the same because in the true rod-to-flexible chain limit they must be.

Clearly, the Monte Carlo results for this scaling function are fairly close to the Gaussian ones in this range of $x = Np$, while the series approximants deviate significantly more. In particular, the Monte Carlo and Gaussian results have a maximum in this range while the series results do not. We attribute this difference mainly to the fact that the enumeration was limited to $N = 16$ (thus $w = 0.16$ or $p = 0.38$ approximately) and is simply not probing the rod-to-flexible chain limit (2). In terms of the numerical accuracy it is important to realise that the lack of extrapolation procedures (to $N \to \infty$, $w \to 0$) makes this enumeration approach much less satisfactory than other more standard series enumeration analyses such as the Padé approximant method used to calculate the critical indices from the high-temperature series expansions for thermal critical phenomena.

However, the scaling function $F(x)$ for PSAW stiff chains on the simple cubic lattice is definitely not *identical* to the corresponding Gaussian one:

$$F_0(x) = 2(e^{-x} + x - 1)/x^{2\nu}. \tag{5}$$

(Note that the way we defined $F(x)$ is tuned to the non-Gaussian case, and thus the Flory exponent ν appears even in the corresponding Gaussian scaling function. This is of no consequence to our discussion.) Clearly, excluded volume effects change the values of $\langle R^2 \rangle / N^{2\nu} p^{2\nu-2}$, for example, even in the rod-to-flexible chain limit. The difference as deduced from our numerical results is relatively small in the range of figure 1, but it becomes readily noticeable, although still bounded, for much larger values of Np. The Flory argument refers to the case $x = Np \gg 1$ and implies that the Gaussian and PSAW scaling functions should have the same exponent in that region when $p \to 0$, $N \to \infty$ but not necessarily the same amplitudes.

In order to obtain strong universality (see below) between PSAW stiff chains and the Gaussian counterpart, we would require that the amplitude of the scaling function approach the same value as $Np \gg 1$ for the two cases. The amplitude must be the same because the value of $F(x)$ for small x is the same for the PSAW (on any lattice) and the Gaussian cases, and thus no rescaling to bring the large-x values into coincidence is permitted. Since the available evidence suggests that the amplitudes are in fact different, the scaling functions probably cannot be made identical for the two cases

by simple rescaling using metrical factors alone. This is neither inconsistent nor does it affect other aspects of the scaling ansatz (such as $\Delta = 1$).

Further, it is important to note that the Flory argument concerns only the end-to-end distance. Thus, for example, no suggestion was made about the character of the scaling function for the number of walks in the rod-to-flexible chain limit. The Monte Carlo results (Lee and Nakanishi 1986) studied the scaling behaviour of the attrition rate in sampling the PSAW. From this result, the scaling character of the number of walks can be easily inferred, and the behaviour is not identical to the true Gaussian case for both square and simple cubic lattices. (Note that Gaussian stiff chains have *no* attrition.) Thus there is no disagreement in this regard among our studies and those of the series enumerations (Privman and Redner 1987). It is, however, interesting that this problem seems to yield another example of the very different behaviours associated with the size and number of the walks.

3. Universality

We distinguish weak from strong universality. By weak universality we mean the coincidence of exponents independent of lattice while by strong universality we mean the universality of scaling functions. It is well known that strong universality holds for stiff chains which are not self-avoiding: see for example, for continuum wormlike chains (Kratky and Porod 1949, Landau and Lifshitz 1969, Benoit and Doty 1953), for chains inscribed on a diamond lattice (Schroll *et al* 1982) and for a lattice PRW (Lee and Nakanishi 1986).

In Atkatz *et al* (1987), Halley *et al* (1985), Lee and Nakanishi (1986, 1987) and Nakanishi (1987a), the question of the existence of strong universality in the case of self-avoiding stiff chains was not addressed explicitly. For example, extensive Monte Carlo simulations of the PSAW stiff chains were only for the square lattice in two dimensions and for the simple cubic lattice in three dimensions. So we cannot definitively answer the question of whether the amplitudes of the scaling functions $F(x)$ for different lattices coincide at large x in this rod-to-flexible chain limit. (Such coincidence would be required for strong universality since the small-x behaviour is necessarily identical for all lattices as mentioned earlier.)

This question in the self-avoiding case was investigated by Privman and coworkers: by series enumeration (Privman and Redner 1987), and exact solutions of various directed walk models (Privman and Frisch 1987, Privman and Svrakic 1988). From the series enumeration work on the square and triangular lattices, they conclude that simple rescaling by metrical factors cannot collapse the corresponding scaling functions (such as $F(x)$) for the two lattices into one and the same form over the whole range of $0 < x < \infty$, so that strong universality does not hold. While we have argued by comparison with Monte Carlo data that these series expansions may be too short to give reliable results on the scaling function, they do show quite large lattice dependences. Thus it is rather hard to imagine that strong universality could hold.

Furthermore, from the exact solutions of the directed walk models (Privman and Frisch 1987, Privman and Svrakic 1988), the authors conclude that there is no strong universality between, say, triangular and square lattices and that the strict collapsing of the scaling functions for the hypercubic lattices in d dimensions occurs only in the $d \to \infty$ limit. However, the exact solutions are for a different problem than the one considered here. In particular, the directed walk models reduce to a factor which

describes a self-avoiding one-dimensional walk and a factor describing a Gaussian walk and thus have properties somewhat like a mean-field theory. Deviations from strong universality are not unfamiliar in critical phenomena of systems with mean-field-like behaviour. For example for the cluster number scaling function in the percolation problem the scaling function obtained on a Bethe lattice and that obtained from the molecular field solution of the so-called Potts model agree in the strong sense (i.e. up to metrical factors) only in the $d \to \infty$ limit (Nakanishi and Stanley 1980).

Finally, we note that, for the partially-directed self-avoiding walk, the scaling functions for various quantities are very similar. For example, the scaling functions for the generating function take the form

$$z_{SQ}(x) = \frac{3+4x}{3(1-2x^2)} \tag{6}$$

for the square lattice, and the form

$$z_{TR}(x) = \frac{2+3x}{2(1-x-4x^2)} \tag{7}$$

for the triangular lattice (Privman and Frisch 1987). Other scaling functions show similar differences. This is somewhat similar to other cases of weak universality (see, e.g., Nakanishi 1987b for the so-called AB-percolation problem). In any case it is clear in all cases that *weak* universality holds.

4. Scaling in Gaussian-to-excluded volume crossover

Assuming that the rod-to-flexible chain crossover can be separated from the excluded-volume crossover, we may ask how one can study the latter crossover by itself. We may start, for example, from a form suggested by the Flory approach:

$$\langle R^2 \rangle = \frac{N}{p} a^2 h(Np, Np^y) \tag{8}$$

with $y > 1$ (where $y = 3$ by the Flory argument), and a is the linear size of (isotropic) monomers. If the excluded-volume limit (3) can be taken, then $Np \to \infty$ and thus (8) implies

$$\langle R^2 \rangle = \frac{N}{p} a^2 \bar{h}(Np^y) \tag{9}$$

in the excluded-volume limit. For large x, we are deep in the excluded volume region and thus we expect a behaviour: $\langle R^2 \rangle \propto N^{2\nu}$ (where $\nu \simeq \frac{3}{5}$ in three dimensions). This leads to the asymptotic form of

$$\bar{h}(x) \sim x^{2\nu-1} \qquad x \to \infty \tag{10}$$

which implies

$$\langle R^2 \rangle \sim N^{2\nu} p^{-\alpha} a^2 \qquad x \to \infty \tag{11}$$

where $\alpha = 1-(2\nu-1)y$ ($\alpha = \frac{2}{5}$ in $d = 3$ by Flory approximation).

This is a concrete hypothesis that should be directly testable either using PSAW stiff-chain simulation data or with the results from real experiments on the chain size.

Indeed, light scattering experiments (Murakami *et al* 1980) on polyhexyl-isocyanate polymers in the dilute limit do suggest two crossovers such as would be expected from the sort of scaling behaviour given by (8) and (9). After Murakami *et al* (1980), we show their experimental data in figure 2 by plotting a quantity proportional to $\langle R^2\rangle/N$ against one that is proportional to N in a double logarithmic scale. The initial saturation evident in the figure corresponds to the rod-to-flexible chain crossover and the sharp increase near the highest moelcular weights appears to indicate the departure from the Gaussian flexible chain behaviour toward the excluded-volume chain behaviour. Although a detailed analysis of this and other experiments will not be attempted here, we simply note that the increase at large N appears to be consistent with $\langle R^2\rangle/N \propto N^{2\nu-1}$ (with this exponent approximately equal to $\frac{1}{5}$).

An extensive numerical test of equations (8) and (9) is currently in progress but because of the requirement of large computing resources to probe this crossover, in this paper we present only the initial simulation results available. From (8), we should have scaling as a function of Np in the rod-to-flexible chain limit, while scaling should result as a function of Np^{y} in the excluded-volume limit. In figures 3 and 4, we present the results on PSAW at $p = 0.015$ (up to 160 000 steps), $p = 0.05$ (up to 80 000 steps), and $p = 0.1$ (up to 10 000 steps), first against Np, and next against Np^{y} (where $y = 2.3$ is chosen as a candidate for the crossover exponent purely numerically). The number of walks used for averaging is approximately 10 000 for $p = 0.015$, 30 000 for $p = 0.05$, and 70 000 for $p = 0.1$, even for the longest walks, respectively. The simulation employs a standard enrichment technique and has been carried out using a Cray-2 at the University of Minnesota and ETA-IOP at Purdue for the most part.

In figure 3, the collapsing of the simulation data from the three different values of p is clearly observed for Np up to about 10^2. Thereafter, $p = 0.1$ data deviate first and then $p = 0.05$ data deviate from those of the smallest p (i.e closest to the rod-to-flexible chain scaling limit). The manner of departure also bears qualitative similarity to the experimental results shown in figure 2. The points of departure correspond roughly to the region where Np^{y} begins to be greater than O(1), all in accordance with the scaling

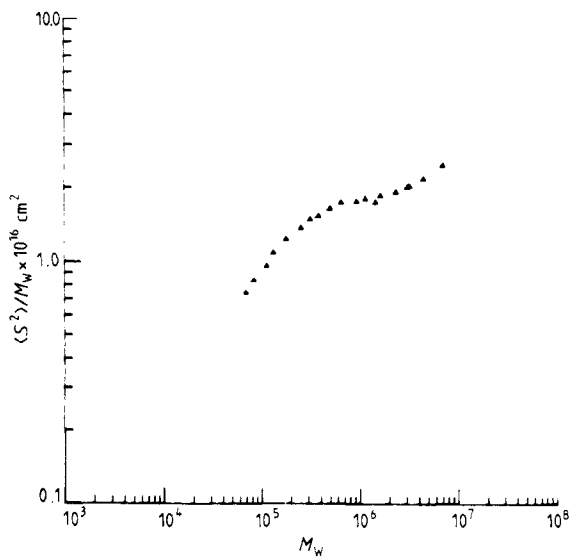

Figure 2. The results of Murakami *et al* (1980) on poly-hexyl-isocyanate polymers. The abscissa is the molecular weight and the ordinate is the z-average of the squared radius of gyration divided by the molecular weight.

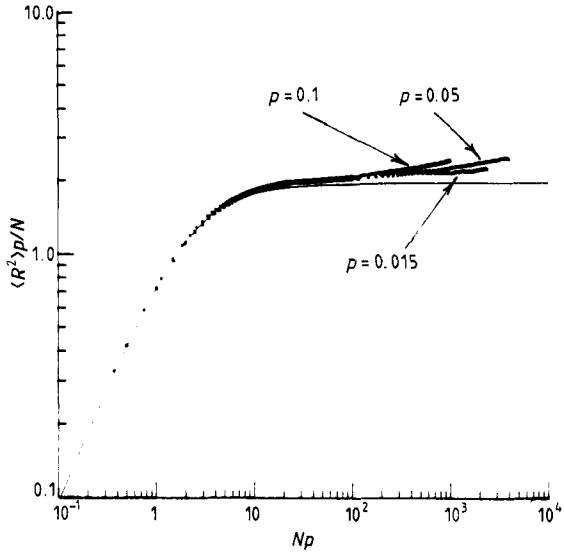

Figure 3. Our PSAW stiff chain simulation results plotted against Np. The Gaussian scaling function is also drawn for comparison.

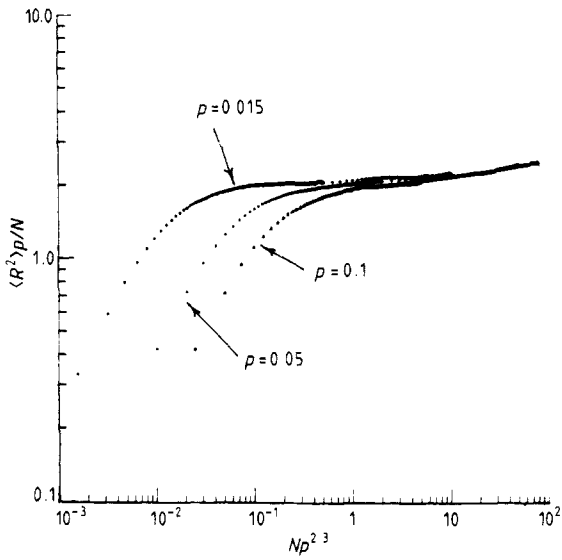

Figure 4. Our PSAW stiff chain simulation results plotted against $Np^{2.3}$.

law (8). We have already discussed the relationship of this scaling function to the Gaussian-chain result (also shown in figure 3 by a continuous curve).

In figure 4, the data are plotted against $Np^{2.3}$. Here, the data for different values of p deviate significantly from each other up to about $Np^{2.3} = O(10)$, but thereafter there is a suggestion of data collapsing. The value $y = 2.3$ is a somewhat arbitrary choice made to obtain best data data collapsing in this large-Np^y region, and it is not to be considered as an accurate estimate. While it appears that $2 < y < 3$, the estimation

of the true value will require much further investigation. However, at least qualitatively, the simulation data are consistent with the scaling law (8).

5. Summary

In summary, all available evidence indicates that there is simple scaling for the rod-to-flexible chain crossover of a linear chain polymer in dilute solution, and, moreover, the crossover exponent within the PSAW stiff-chain model is exactly 1.

While universality for the Gaussian case appears to be valid without a doubt, there may be lattice dependences for the fully excluded-volume case which cannot be removed by metrical factors. Therefore, while weak universality holds for the PSAW, strong universality may not. Also, contrary to other authors' assertions, the series enumeration currently available does not establish that there is only partial suppression of the excluded-volume effect for the three-dimensional chains in the rod-to-flexible chain limit, while theoretical arguments suggest total suppression.

Finally, we present a scaling hypothesis for the second, Gaussian-to-excluded volume crossover and look for its test in numerical and experimental realisations. There is a suggestion of this crossover in an experiment on real stiff polymers, and our own numerical simulation also confirms various aspects of the hypothesis. Although there appear to be substantial quantitative discrepancies between the behaviour of the experimental results and our lattice calculations for corresponding values of p, we believe that they can be ultimately resolved in terms of the anisotropic shape of the monomers used in the experiment of Murakami *et al* (1980).

Acknowledgments

We thank V Privman for informing us of their work on this problem and one of us (HN) thanks him for discussions as well. This work was performed in part while HN was a visitor at the Theoretical Physics Institute of the University of Minnesota and DA was a visitor at the Physics Department of the University of Minnesota; the respective generosity and hospitality are gratefully acknowledged. HN appreciates the partial support of this work by the Donors of the Petroleum Research Fund administered by the American Chemical Society.

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