

A SINGLE POLYMER CHAIN ON A LATTICE - SOME QUERIES

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Towards the end of the CCP5 workshop of polymer simulation (15th November, 1989), there was granted an opportunity for the participants to raise queries and questions about polymers and I duly displayed my ignorance about lattice chains. Many comments were made by the audience, so now that I have been asked to reveal my confusions to even more people, I hope I can incorporate some of the points made then. At the outset, though, I would like to make the disclaimer that I am fairly new to the polymer field, so many of my problems and arguments will doubtless either be old chestnuts or, as likely as not, just simply wrong! In any case, I would like to learn more about the subject, so any suggestions, references, etc., would be most welcome.

In this article I would like to consider single lattice chains in good solvent conditions. I thus begin with a rapid outline of two-parameter theory, then give a brief account of self-avoiding walks on a lattice (SAW's) and finally consider SAW's but with nearest neighbour attractions. Finally I try to summarize what I do not understand.

1 Two-Parameter Theory

It is commonly assumed [1] that the behaviour of sufficiently long chains in good solvents is predicted by a Hamiltonian, \mathcal{H} , given by

$$\mathcal{H} = -\frac{3}{2l^2} \int_0^N dn \left(\frac{\partial \mathbf{r}(n)}{\partial n} \right)^2 - \frac{v}{2} \int_0^N dn_1 \int_0^N dn_2 \delta(\mathbf{r}(n_1) - \mathbf{r}(n_2)), \quad (1)$$
$$|n_1 - n_2| > a$$

where the chain is represented by a continuous curve of contour length Nl and $\mathbf{r}(n)$ is a point a contour length nl along the chain. The excluded volume parameter is v , l is the Kuhn persistence length and a is a cut-off to rule out segments interacting with themselves. In the limit $a \rightarrow 0$ one obtains the result

$$\frac{\langle R^2 \rangle}{Nl^2} = F(z); \quad F(0) = 1, \quad (2)$$

where $\langle R^2 \rangle$ is the mean squared end-to-end distance and

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \frac{v}{l^3} N^{1/2} \quad (3)$$

Similarly, $\langle S^2 \rangle / Nl^2$, where $\langle S^2 \rangle$ is the mean squared radius of gyration, is also simply a function of the single variable, z .

The most recent calculation I know of $F(z)$ is due to Muthukumar and Nickel [2], and their results are fitted extremely well by

$$F(z) = (1 + 7.524z + 11.06z^2)^{0.1772} \quad (4)$$

Another recent formula due to Douglas and Freed [3] is

$$F(z) = 1.732z^{0.1772} \quad (z > 0.75) \quad (5)$$

and many other formulae have been proposed.

We can now ask whether lattice chains obey two parameter theory, and, if so, how we get values for v , l , and N ? Then one could attempt to verify the various approximate formulae for $F(z)$. We first consider the most studied lattice model of SAW's without attractions.

2 Potted History of SAW's

For a walk of N steps, each of length l , Domb and Barrett [4] noted that

$$\lim_{N \rightarrow \infty} \frac{\langle R \rangle^2}{Nl^2} \sim 1.64z_{DB}^{0.4} \quad (6)$$

for many types of three dimensional lattices, where

$$z_{DB} = \frac{\sqrt{N}}{3} \left(\frac{3}{2\pi}\right)^{3/2} v_{cell}, \quad (7)$$

v_{cell} being the volume per lattice point of the unit cell (for a diamond lattice $v_{cell} = 1.54l^3$). The denominator in eq. (6), Nl^2 , is the mean square end-to-end distance for a random walk with immediate reversals allowed.

Some theoretical basis for this form for z came from studies of the Domb-Joyce model [5], where intersections of the chain are permitted with a non-zero probability, a configuration

being weighted by the factor $\prod_{i,j}(1 - w\delta_{ij})$. $w = 0$ corresponds to a random walk without reversals and $w = 1$ corresponds to a SAW.

It was found by carrying out an expansion in w that

$$\frac{\langle R \rangle^2}{Nl^2} = 1 + A_1w + A_2w^2 + \dots, \quad (8)$$

where $A_1 = (4/3)z_{DB}(1 + O(N^{-0.5}))$ and so on. Thus if, in each term, one kept only the leading power of N , one regains the two-parameter theory with $z = z_{DB}$, N and l being simply the number of steps and the step length respectively i.e.

$$\frac{\langle R \rangle^2}{Nl^2} = F(wz_{DB}) \quad (9)$$

Yamakawa [6] compared this prediction against computer simulation, finding plots of $\langle R \rangle^2 / Nl^2$ vs. z_{DB} gave a smooth curve for results from many different lattices. On the diamond lattice, with $42 < N < 240$ Yuan [7] found $\langle R \rangle^2 / Nl^2$ fitted eq. (5) very well with $z = z_{DB}$ but agreed very poorly with eq. (4).

Not all lattices fitted this picture, though, but Tanaka [8] showed that if v was treated as a parameter to be fixed empirically for each type of lattice, a smooth master curve could be obtained for $\langle R^2 \rangle / \langle R^2 \rangle_0$ where $\langle R^2 \rangle_0$ is the value of $\langle R^2 \rangle$ for a random walk in which immediate reversals were forbidden (e.g. for large N on a diamond lattice, $\langle R^2 \rangle_0 = 2Nl^2$). Furthermore, having now determined z , Tanaka showed a plot of $\langle S^2 \rangle / \langle S^2 \rangle_0$ vs. z (where again $\langle S^2 \rangle_0$ corresponds to a random walk without immediate reversals) gave a smooth curve for all the lattices considered.

The questions now arise as to whether one can calculate the value of v theoretically and as to why the Yamakawa and Domb-Barrett form of two-parameter theory, obtained from consideration of eq. (8), seems to fail. We now pursue these points a little further in the course of considering attractive potentials.

3 Attractive Potentials

A typical simulation might take the pair potential, $v(r)$, between two segments to be

$$v(r) = \begin{cases} \infty, & r = 0 \\ \frac{\epsilon}{kT}, & r = 1 \\ 0 & r > 1 \end{cases} \quad (10)$$

At $\epsilon = 0$ we regain the SAW, but there is a theta point, where $\epsilon = \epsilon_0$, when

$$\lim_{N \rightarrow \infty} \langle R^2 \rangle = C_\infty Nl^2 \quad (11)$$

- i.e. the random walk without immediate reversals result.

Two-parameter theory would suggest an ϵ -dependent volume, $v(\epsilon)$, should exist, where $v(\epsilon_0) = 0$. Within the Domb-Barrett approach, one would presumably use eq. (7) replacing v_{cell} by $v(\epsilon)$ and having $v(0) = v_{cell}$. This fails, though, at the theta-point, for eq. (8) would then incorrectly predict $\langle R^2 \rangle_0 = Nl^2$ instead of the result given by eq. (11). Thus modifications must be made to the Domb-Joyce model if it is to have any hope of describing the variation of $\langle R^2 \rangle$ with ϵ .

The obvious approach is simply to forbid immediate reversals in the original model, in which case one finds

$$\frac{\langle R^2 \rangle}{\langle R^2 \rangle_0} = B_0 + B_1 w + B_2 w^2 + \dots \quad (12)$$

where $B_0 = 1 + O(N^{-1})$ and $B_1 = (4/3)z'_{DB}(1 + O(N^{-1/2}))$, etc. with z'_{DB} containing an excluded volume different from v_{cell} . If one is permitted to keep only the leading powers of N in each term (as before in the original model), one obtains

$$\frac{\langle R^2 \rangle}{\langle R^2 \rangle_0} = F(wz'_{DB}) \quad (13)$$

with the same function F as in eqs. (2) and (9).

As $w \rightarrow 1$, however, both models reduce to the same SAW and then eqs. (9) and (13) are clearly incompatible. Evidently the problems have arisen from dropping the lower order powers of N in the expansion coefficients - in a way that I do not see, the sum of these neglected terms must be of the same order of magnitude as the terms retained. In fact, looking at the problem this way, I find it hard to see how, in the $w = 1$ limit, the series in eqs. (8) and (12) can agree and still obey two parameter theory!

On the more practical side, preliminary studies suggest that eq. (13) also fails. It appears that a plot of $\langle R^2 \rangle / \langle R^2 \rangle_0$ vs. z'_{DB} gives anything but a smooth curve for all the different lattices, and, for the diamond lattice, the results disagree strongly both with eqs. (4) and (5).

I also attempted, for the diamond lattice, to determine directly $v(\epsilon)/v(0)$ by requiring a plot of $\langle R^2 \rangle / \langle R^2 \rangle_0$ vs. $(v(\epsilon)/v(0))N^{1/2}$ to yield as smooth a curve as possible ($42 < N < 220$). The results are shown in fig. (1). The full curve is the best fit to the data from eq. (4), using $v(0)$ as the fitting parameter. Close inspection reveals that points for a given ϵ cross the master curve, and clearly eq. (4) fits the data poorly. Furthermore a plot of $\langle S^2 \rangle / \langle S^2 \rangle_0$ vs. $(v(\epsilon)/v(0))N^{1/2}$, with $v(\epsilon)/v(0)$ determined from the $\langle R^2 \rangle$ data, shows no smooth curve. Evidently, for this range of chain lengths on a diamond lattice, two parameter theory is not working too well.

4 Final Comments

Ideally one would like to use the computer simulation of lattice chains to test theories, such as two parameter theory. The work of Tanaka suggests that if the excluded volume parameter is fitted empirically, then $\langle R^2 \rangle / \langle R^2 \rangle_0$ and $\langle S^2 \rangle / \langle S^2 \rangle_0$ for SAW's for many different lattices fall onto a single master curve when plotted against z . So far our attempts to extend this analysis to include walks with attractive potentials have failed - studies on chains much longer than $N = 210$ would probably be needed.

The problem in testing theories such as the one given by eq. (4) lies in determining v . The original and modified Domb-Joyce models give different predictions for v , and indeed, in the SAW limit and for large N , it is hard to see how the two expansions contrive to sum to the same result, which they evidently must do.

These, then, are my difficulties. The theoretical ones being a failure to properly understand the relationship between two parameter theory and the Domb-Joyce models and the practical ones being an inability to get two parameter theory to agree well with simulation results obtained for a chain with attractive potentials on a diamond lattice. The latter problem might be helped by simulations of longer chains or else by having some theoretical idea as to the form of corrections to two parameter theory. For example studies based on the full Hamiltonian in eq. (1), retaining the cut-off a might prove enlightening. For a diamond lattice and without immediate reversals, it takes six steps or more for a chain to return to its starting point, and if $a \sim 6$, then a chain might have to be very long before neglecting a becomes a good approximation.

Acknowledgements

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References

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Figure Caption

Plot of $\langle R^2 \rangle / \langle R^2 \rangle_0$ vs. z , the points from computer simulation of a chain on a diamond lattice and the solid curve from eq. (4). The key is : \square , $\epsilon = -0.4$; \times , $\epsilon = -0.3$; $+$, $\epsilon = -0.2$; ∇ , $\epsilon = -0.1$; and Δ , $\epsilon = 0.0$. N ranges between 42 and 210, and the method for calculating z is outlined in the text.