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COMMENT

Polymer conformations through 'wiggling'

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Abstract. A new Monte Carlo method is proposed which allows for the efficient generation of equilibrium conformations of polymer chains in two and three dimensions. The method treats each site (monomer) as a potential pivot around which a new conformation may be generated by rotating a portion of the chain. The method does not suffer from the severe attrition associated with the simple sampling of self-avoiding walks and may be extended to treat the interacting polymer chain. We find in two dimensions that $\nu = 0.748 \pm 0.005$ (exact = 0.750) and in three dimensions $\nu = 0.595 \pm 0.005$ (series expansion and renormalisation group predict $\nu \sim 0.588$). The end-end distances calculated for shorter chains are in good agreement with the exact values from enumeration techniques.

The interacting polymer chain is a problem that has received attention from several groups (see, e.g., Vilanove and Rondelez (1980) for recent experimental results and Kremer *et al* (1982) for recent theoretical work) and the determination of the critical properties at the θ point remains an unresolved problem in two dimensions (Kholodenko and Freed 1984, Stephen 1975, Marquese and Deutch 1981). At temperatures lower than the θ temperature the polymer chain exists in the collapsed phase whilst at temperatures above θ the polymer chain has the critical characteristics of a self-avoiding walk (SAW). Thus

$$\langle R_N^2 \rangle \sim N^{2\nu} \quad (1)$$

where R is the end-end distance or radius of gyration of the chain and N is the number of links.

We find for a polymer embedded in a three-dimensional lattice that $\nu \sim 0.333$ for temperatures less than θ whilst $\nu \sim 0.59$ for temperatures greater than θ and $\nu \sim 0.5$ at the θ temperature (de Gennes 1979). However, if the chain is embedded in a two-dimensional lattice we expect the following: $\nu = 0.5$ for temperatures less than θ , $\nu = 0.75$ for temperatures greater than θ (Nienhuis 1982) and ν somewhere in the range 0.51 to 0.67 (Stephen 1975, Flory 1969, Kholodenko and Freed 1984) at the θ temperature.

Monte Carlo techniques for generating polymer chains have been limited to simple sampling, 'reptation', '3-4' bond motions (Kremer *et al* 1981), the scanning-ahead (Meirovitch 1982) and dimerisation approach (Alexandrowicz 1969). In the simple sampling method a chain is generated through the random-walk algorithm and the growth process terminated whenever the excluded volume condition is violated. This leads to an unbiased sample of SAW or equivalently conformations of polymer chains of varying lengths at high temperatures. In order to determine the low-temperature

properties these chains are weighted by their respective Boltzmann factors $\exp(\eta\varepsilon/k_B T)$ to take into account the η interactions each of energy $-\varepsilon$ between neighbouring segments of the chain. The severe attrition rate limits the method to chains of ~ 100 monomers and an extremely large number of conformations are needed to ensure adequate sampling of the collapsed phase. The 'reptation' method introduced by Wall and Mandell (1975) and used subsequently by Kremer *et al* (1982) and Baumgärtner (1982) does not suffer from the 'attrition' effect. The polymer chain is placed in an initial conformation. One end is labelled the head and a direction is selected at random and a link removed from the tail and added to the head. This conformation is selected with a probability $p \propto \exp(-\Delta E/k_B T)$ where ΔE is the energy change between the initial and final conformation, provided that excluded volume effect is not violated by the movement of the link. This method suffers from the disadvantage that $\sim \frac{1}{2}N$ successful moves are required before a significantly distinct conformation is observed, and Kremer *et al* (1982) reported that the method was unsatisfactory for determining the low-temperature properties of the interacting chain for N greater than 100. A new innovation was introduced by Kremer *et al* (1982) which allowed for internal rotation of the chain—the so-called '3-4' bond motion. This is an extension of a technique introduced by Gény and Monnerie (1979) which led to a more accurate analysis of the collapsed phase than was possible with reptation or simple sampling techniques. Two further attempts have been made to circumvent the severe attrition in the generation of SAW or interacting SAWs—the scanning ahead method of Meirovitch (1982) and the dimerisation approach of Alexandrovicz (1969). Briefly, the scanning ahead technique avoids attrition by constructing the walks from *only* the unvisited sites. These walks are generated with different weights than an identical SAW and thus these weights have to be taken into account in the subsequent analysis, e.g. in the determination of the average end-to-end distance, etc. The dimerisation method of Alexandrovicz generates segments via the normal SAW algorithms and then segments are randomly selected and fused together to form longer chains which are accepted if the excluded volume constraint is met. Both these approaches yield satisfactory results for the SAW critical properties but suffer from the disadvantage that the configurations generated may not be the 'important' conformations at low temperatures.

We consider in this comment an extension of the reptation method—the 'wobble' method. The polymer chain is embedded in an initial state in the lattice. We usually start with a straight chain. A monomer on the chain is selected at random and an available direction at this local site is selected at random. The shorter portion (to reduce computation) is moved to this new direction. We treat at this instant the rest of the chain as a rigid structure and only consider the rotation about the selected monomer. The new conformation is accepted if the excluded volume criterion is satisfied—if not the old conformation is retained. A few rotations are shown in figure 1 starting from an initial straight chain on a square lattice. The process is continued by the selection of another monomer which now becomes the pivot and the whole process is repeated. Conformations are accepted after a preset number of attempted rotations (~ 60 for the longer chains where we note that on average there were 15 successful rotations).

We have applied this technique to polymer chains of lengths varying from $N = 10$ to $N = 1000$ on the 2D square lattice and the average end-end distances are shown in table 1 together with the available exact values. The agreement with the exact results is excellent for small chains. Figure 2 shows a plot of $\langle R^2 \rangle$ against N for chains varying from 20 to 1000 links. From a least squares fit of the data and from the slope of the

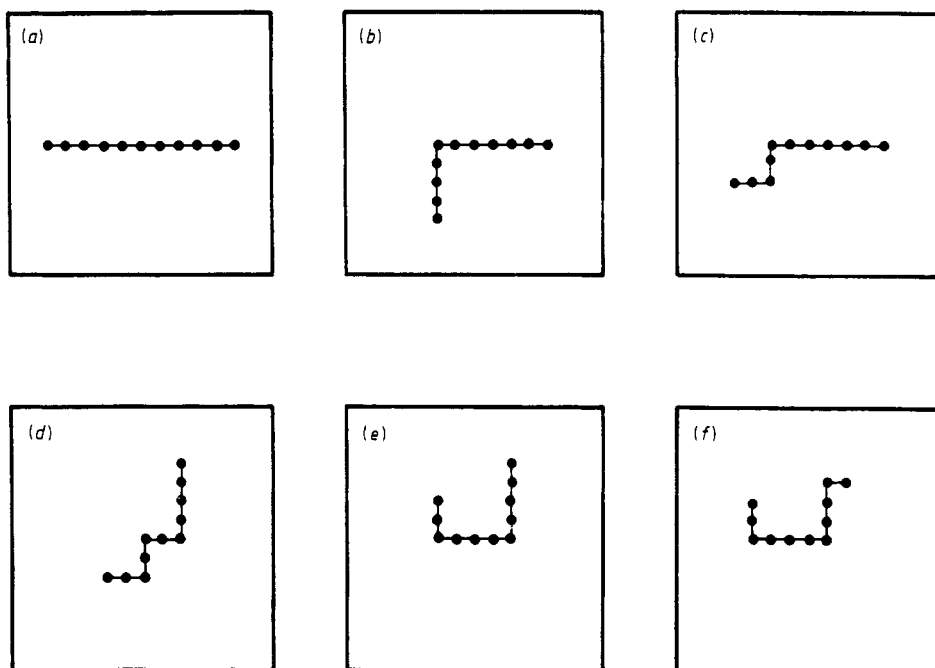


Figure 1. The initial stages indicated in ascending order of a polymer chain of 11 monomers as a result of successive rotations about various monomers.

Table 1. The end-to-end distance obtained by the 'wiggle' method for polymer chains of length 10 to 1000 links on the 2D square lattice. The results obtained from exact enumeration are shown in column 4. A least squares fit of the data gives $\nu = 0.748$.

Monomers	Links	Conformations	Exact results ^(a) $\langle R^2 \rangle$	Mean squared end-end distance $\langle R_{\infty}^2 \rangle$
11	10	275 000	26.2425	26.200
16	15	20 000	47.218	47.215
17	16	20 000	51.993	51.943
21	20	20 000		72.309
31	30	8 000		132.03
41	40	6 000		202.18
61	60	6 000		364.34
81	80	6 000		555.7
101	100	6 000		783.1
201	200	6 000		2 201
301	300	3 000		3 975
441	440	2 000		7 225
601	600	2 000		11 586
801	800	1 600		17 631
1001	1000	1 100		25 394

^(a) Domb (1963).

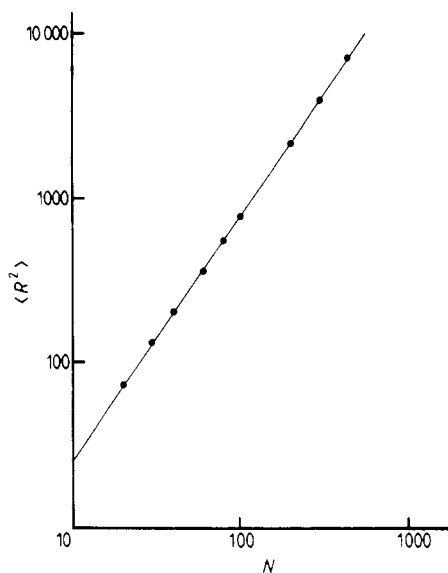


Figure 2. A log-log plot of the results listed in table 1. The straight line has a slope of $2\nu = 1.50$ or $\nu = 0.75$.

graph we conclude that $\nu = 0.748 \pm 0.005$. This result is close to the exact value of 0.75. The 3D results are shown in table 2 and figure 3. We note that the overall agreement is quite good although our value of $\nu = 0.595 \pm 0.005$ cannot exclude the Flory result of 0.6. The value obtained from series expansion (Majid *et al* 1983) and renormalisation group (Le Guillou and Zinn-Justin 1980) is ~ 0.589 which is the lower bound of our result. Perhaps the consideration of longer chains may resolve this discrepancy but this requires a major reconstruction of our program which is in progress.

Table 2. The end-end distance obtained by the 'wiggle' method for polymer chains of varying length on the simple cubic lattice. The result obtained from exact enumeration is shown in column 4. A least squared fit of the data gives $\nu = 0.594$.

Monomers	Links	Conformations	Exact results ^(a) $\langle R_N^2 \rangle$	Mean-squared end-end distance $\langle R_N^2 \rangle$
11	10	14 000	16.817	16.913
21	20	10 000		38.825
31	30	6 000		63.896
41	40	6 000		88.88
50	49	10 000		113.924
61	60	6 000		145
76	75	6 000		189
90	89	6 000		230
126	125	6 000		342
151	150	10 000		429
200	199	6 000		610
221	220	5 800		674
251	250	8 000		783

^(a) Domb (1963).

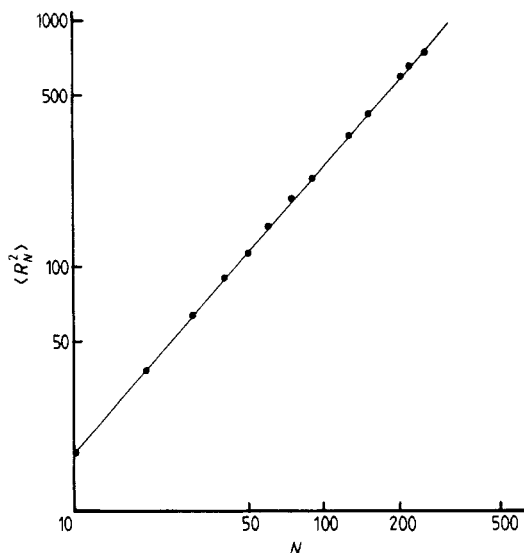


Figure 3. A log-log plot of the results listed in table 2. The straight line has a slope of $2\nu = 1.183$ or $\nu = 0.591$.

In summary, we have introduced a new method which is able to produce efficiently the conformations of a polymer chain in two and three dimensions. The method is efficient and we were able to calculate the average end-end distance of chains of lengths ranging to 1000 links in two dimensions and 250 links in three dimensions. We are modifying our algorithm to allow for the consideration of longer chains in three dimensions and also to take into account interaction between nearest-neighbour monomers. We find ν equal to 0.748 ± 0.005 and 0.595 ± 0.005 in two and three dimensions respectively.

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