Monte Carlo studies of the excluded-volume problem in freely rotating polymer chains

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Monte Carlo studies of the excluded-volume problem in freely rotating polymer chains

Abstract. Results reported in an earlier publication by Fleming have been extended to freely rotating three-dimensional polymer chains of 100 links, using the chain-enrichment procedure of Wall and Erpenbeck. On the assumption that the correct asymptotic value of the index γ in the expression $\langle R_n^2 \rangle = an^\gamma$ relating the mean square end-to-end length $\langle R_n^2 \rangle$ and the number of links n of the chains is $\frac{6}{5}$, the close approach (approximately 1·18) to this value now observed tends to refute a suggestion by Flory and Fisk that asymptotic behaviour would be attained only by very long chains exceeding 10^6 links. On the other hand, values of the ratio $\langle S_n^2 \rangle / \langle R_n^2 \rangle$, where $\langle S_n^2 \rangle$ is the mean square radius of gyration of n-link chains, are, in the neighbourhood of $n = 100$, approximately half the asymptotic figure of 0·157 quoted by Wall *et al.* and by Windwer.

In a recent paper Fleming (1967) has investigated the value of the index γ in the generally accepted formula

$$\langle R_n^2 \rangle = an^\gamma \tag{1}$$

relating the mean square end-to-end length $\langle R_n^2 \rangle$ of three-dimensional freely rotating polymer chains perturbed by excluded-volume effects and the number of links n in the chains. Heavy attrition of the sample due to violation of the excluded-volume conditions was encountered, and the calculations were of necessity limited to chains of not more than 20 links for the largest value of the excluded-volume ratio investigated, namely 0·5. The purpose of this letter is to report the results of extending the calculations to 100-link chains, with the same excluded-volume ratio, using the chain-enrichment (or s, p) procedure introduced by Wall and Erpenbeck (1959). Reference to the attrition rate for the 20-link chains led to a 15, 10 choice of s, p parameters. For this choice the number of samples decreased from 1868 at $n = 30$ to 1331 at $n = 90$. The upper limit on the chain lengths given by $n = 100$ was set by rapidly increasing computer-time requirements, continued use of the chain-enrichment method of generation being assumed.

As in the earlier publication (Fleming 1967), both normal and relative least-square fits of the data to equation (1) were computed. The values of a and γ obtained were $0{\cdot}942 \pm 0{\cdot}017$ and $1{\cdot}173 \pm 0{\cdot}004$ respectively for the normal fit, and 0·914 and 1·180

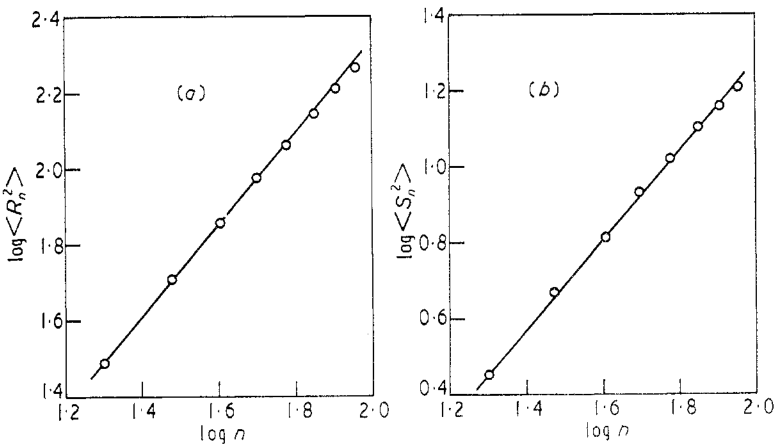

Figure 1. (*a*) Plot of log $\langle R_n^2 \rangle$ against log n; (*b*) plot of log $\langle S_n^2 \rangle$ against log n.

respectively for the relative fit. The quoted standard deviations were calculated from the variances. Graphs of $\log\langle R_n^2\rangle$ against $\log n$, $\log\langle S_n^2\rangle$ against $\log n$, where $\langle S_n^2\rangle$ is the mean square radius of gyration of n-link chains, and $\langle S_n^2\rangle/\langle R_n^2\rangle$ against n are plotted in figures 1(*a*), 1(*b*) and 2, respectively.

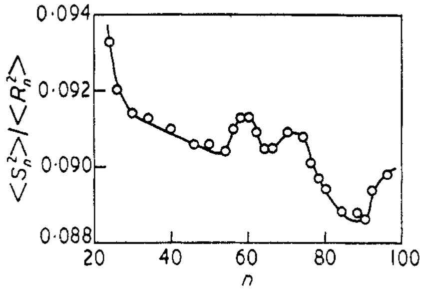

Figure 2. Plot of $\langle S_n^2\rangle/\langle R_n^2\rangle$ against n.

Mazur (1965) has discussed the determination of the distribution function of the chain lengths using extrapolated plots of the fractional variances of $\langle R_n^2\rangle$ against $1/n$, the fractional variances $\delta_n(u, v)$ being defined by

$$\delta_n(u, v) = \frac{\langle r_n^u\rangle}{\langle r_n^v\rangle^{u/v}} - 1.$$

Mazur found a steady increase in $\delta_n(u, v)$ with increasing n for various u/v combinations; in the present work $\delta_n(4, 2)$, $\delta_n(8, 4)$ and $\delta_n(12, 6)$ were investigated, but in no case was a sustained variation with increasing n noted. These three functions assumed values (for $n > 20$) roughly within the ranges 0·5–0·6, 2·6–2·9 and 8·2–9·3, respectively.

The γ values quoted above cannot be considered as evidence either for or against recent suggestions (Windwer 1965, Mark and Windwer 1967, Reiss 1967) that the asymptotic γ value $\frac{6}{5}$ suggested for three-dimensional chains by Domb (1963), Domb *et al.* (1965) and Edwards (1965) is incorrect. The most significant feature of the present results is the overall increase from the figure of 1·155 reported earlier for 20-link chains. Flory and Fisk (1966) have recently supported the asymptotic γ value $\frac{6}{5}$ mentioned above, but have suggested that it would be attained only by very long chains exceeding 10^6 links. On the other hand, Domb *et al.* (1965), using exact enumeration methods, have reported a γ value of $\frac{6}{5}$ for $n > 14$. The present results are therefore more compatible with the findings of the latter authors, on the assumption of course that $\frac{6}{5}$ is the correct asymptotic value.

The absence of a sustained increase in the fractional variances $\delta_n(u, v)$ as n increases is imputed to large statistical fluctuations arising from averaging over relatively small (approximately 1500) numbers of samples. On the other hand, an overall decrease of the ratio $\langle S_n^2\rangle/\langle R_n^2\rangle$ with increasing n can be discerned in figure 2, although there are no unambiguous indications that an asymptotic value has been attained within the range considered. In contrast with this observation, Wall and Erpenbeck (1959) and Wall *et al.* (1963), investigating lattice-constrained chains, have reported asymptotic values of $\langle S_n^2\rangle/\langle R_n^2\rangle$ around 0·157 attained after as few as 40 steps. Windwer (1965) obtained similar values around 30 links in a study permitting freer bond rotation between consecutive links, although Gallacher and Windwer (1966) found an induction length of about 80 links before the value 0·157 was attained by a variety of branched chains generated on a tetrahedral lattice. This limiting value, which is supported by analytical studies of more realistic polymer chain models (Fixman 1955, Yamakawa *et al.* 1966), is roughly twice the values obtained in the present work. In view of the close approach of the γ values around 100 links to the limiting figure $\frac{6}{5}$, it seems unlikely that $\langle S_n^2\rangle/\langle R_n^2\rangle$ will pass through a minimum at larger n and subsequently almost double its value, as would be required to produce agreement with the theory. A study of 60-link chains using five distinct s, p combinations gave essentially the same results, indicating that the present results are not unduly influenced by the quoted s, p choice.

It is clear that an extension of the calculations to treat longer chains is required in order to resolve the differences noted above. A new method of generating freely rotating chains, based on the work of Scott *et al.* (1962) and Bernal (1964) on random packing of spheres, is being investigated, and it is hoped to present additional results in the near future.

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A measurement of optical linewidth by photon-counting statistics

Abstract. An optical linewidth of 20 Hz of laser light scattered by spherical particles undergoing Brownian motion has been measured experimentally by photon-counting statistics using the theory of the intensity-fluctuation distribution of Gaussian–Lorentzian light.

In a recent paper (Jakeman and Pike 1968) we presented the theory of the intensity fluctuations of Gaussian light having a Lorentzian spectrum of finite linewidth, and gave photon-counting distributions for such light as a function of counting rate and linewidth. In this letter we compare our theoretical predictions with experimental results obtained by scattering laser light from 0·6 μm diameter polystyrene spheres undergoing Brownian motion in water at room temperature. Such a system is expected theoretically (Glauber 1963, Pecora 1964) to produce Gaussian–Lorentzian scattered light, and has been used in previous investigations by Cummins *et al.* (1964) who used a heterodyne method to determine the linewidth, and by Dubin *et al.* (1967) and independently by Arecchi *et al.* (1967) who used a homodyne or self-beating method to determine the linewidth and also confirmed the Lorentzian form of the spectrum. The latter authors also verified the Gaussian nature of the scattered light by photon-counting statistics in the Bose limit, that is in the limit γ (= ΓT) tends to zero, where Γ is the half-width at half-height of the spectral line and T is the sampling time.

The predicted theoretical value for the half-width is (Cummins *et al.* 1964)

$$\Gamma = |\mathbf{k}_s - \mathbf{k}_0|^2 \frac{kT_a}{12\pi^2 \eta r} \tag{1}$$