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Structure function of linear polymers in a good solvent: A self-avoiding-walk model

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The fourth moment $\langle r^4 \rangle$ of the average monomer-monomer separation is calculated in a self-avoiding-walk model on a lattice in two and three dimensions. The universal ratio $\zeta = \langle r^4 \rangle / (R_g^2)^2$, with R_g^2 the averaged squared radius of gyration of the polymer, is found to be 0.606±0.003 and 0.690±0.007 in two and three dimensions, respectively, which are both smaller than the ideal Gaussian-chain value of 0.75 in all dimensions, with the deviation being stronger in the lower-dimensional case. Using the result for ζ, the scaled structure function for small values of the momentum transfer can be calculated and compared with that of the ideal chain.

I. INTRODUCTION

Information about the spatial monomer distribution in polymers is contained in the structure function $S(k)$, which is defined as the Fourier transform of the density-density autocorrelation function $\langle \rho(0)\rho(r) \rangle - \langle \rho \rangle^2$. Just as in other areas of condensed matter physics, the structure function can be measured by light[1] or neutron[2] scattering. For a noninteracting Gaussian chain of N monomers, the structure function is known as the Debye function[3]

$$S(Q) = 2[\exp(-Q^2) - 1 + Q^2]/Q^4 , \tag{1}$$

where $Q^2 \equiv Nb^2k^2/(2d)$, with b the monomer length, d the spatial dimension, and k the momentum transfer in a scattering experiment. Expanding (1) one obtains

$$S(x) = 1 - x^2 + \zeta x^4 + O(x^6) \tag{2}$$

with $x^2 \equiv Q^2/3$. The coefficient ζ of the x^4 term in (2) has the value $\zeta = \frac{3}{4}$ in the case of a Gaussian chain in all dimensions.

For an interacting chain, the structure function is defined as

$$S(k) = N^{-2} \sum_{m,n}^{N} \langle \exp[i\mathbf{k}\cdot(\mathbf{R}_n - \mathbf{R}_m)] \rangle , \tag{3}$$

where the average is taken over the configurations of the polymer, and $\mathbf{R}_n$ denotes the position of the nth monomer. Averaging over the angle between $\mathbf{k}$ and $(\mathbf{R}_{\mathrm{n}} - \mathbf{R}_{\mathrm{m}})$ one obtains

$$S(k) = N^{-2} \sum_{m,n}^{N} \langle J_0(k|\mathbf{R}_m - \mathbf{R}_n|) \rangle \quad d=2 , \tag{4a}$$

$$S(k) = N^{-2} \sum_{m,n}^{N} \langle \sin(k|\mathbf{R}_m - \mathbf{R}_n|)/[k|\mathbf{R}_m - \mathbf{R}_n|] \rangle \quad d=3 , \tag{4b}$$

where J_0 is the zeroth-order Bessel function. Expanding J_0 and the sine functions one obtains exactly Eq. (2) with

$$x^2 = \begin{cases} k^2R_g^2/2 & \text{for } d=2 , \\ k^2R_g^2/3 & \text{for } d=3 , \end{cases} \tag{5}$$

$$\zeta = \begin{cases} \frac{1}{8}\langle r^4 \rangle/(R_g^2)^2 & \text{for } d=2 , \\ \frac{3}{20}\langle r^4 \rangle/(R_g^2)^2 & \text{for } d=3 , \end{cases} \tag{6}$$

$$R_g^2 = (2N^2)^{-1} \sum_{m,n}^{N} \langle (\mathbf{R}_m - \mathbf{R}_n)^2 \rangle , \tag{7}$$

$$\langle r^4 \rangle = (2N^2)^{-1} \sum_{m,n}^{N} \langle (\mathbf{R}_m - \mathbf{R}_n)^4 \rangle . \tag{8}$$

The expansion of $S(x)$ in (2) was introduced by Witten and Schäfer[4] who also calculated ζ using renormalization group with ϵ expansion. Their result for ζ depends on two exponents ν and γ. Using the best available estimates for ν and γ,[5] they obtained $\zeta = 0.690 \pm 0.007$ in three dimensions. The resulting structure function calculated with this value of ζ differs very little both from the calculated with the ideal Gaussian value $\zeta = 0.75$ and from the Debye function (1). This was confimed by Ohta, Oono, and Freed[6] who directly calculated $S(k)$ using the renormalization group with ϵ expansion, and by experimental result.[7] The closeness of the ideal Debye function to experimental data in three dimensions suggests that the coefficient ζ is a more sensitive test of the polymer excluded volume effect than direct calculation of the structure functon itself. Since so far there has been no numerical calculation of the universal ratio, it is the purpose of this paper to perform such a calculation, using a recently developed Monto Carlo method[8,9] that is an extension of the exact enumeration method for linear and branched polymers.[10] Using this method one obtains simultaneously exact results for small monomer numbr N and Monte Carlo data for large N.

Since fluctuation is stronger in lower dimensions, one expects larger deviations from the Gaussian value for ζ in two dimensions. Experiments have already been performed on linear polymers in two dimensions, for quantities such as the exponent characterizing the radius of gyration.[11,12] One can imagine that similar experiments

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on the structure function of linear polymers can also be carried out in two dimensions. Therfore a Monte Carlo calculation of the coefficient ζ is also performed in two dimensions, on the square and triangular lattices. Both the data on the square and triangular lattices are extrapolated to the same asymptotic value $\zeta=0.606\pm0.003$. This confirms the universal nature of the ratio ζ. In three dimensions the calculation is performed on the simple cubic lattice. The data can be extrapolated to the asymptotic value $\zeta=0.690\pm0.007$, in very good agreement with that of Ref. 4.

II. MONTE CARLO METHOD FOR SERIES EXPANSIONS

A new Monte Carlo method, called the incomplete enumeration method, had been described before.[8,9] It can be used to enumerate the configurations of lattice animals and self-avoiding walks (SAW's) on lattices. It is essentially based on the exact series expansion method,[10] which is a very powerful technique for obtaining physical quantities such as the critical exponents. However, the computational effort needed to calculate the Nth order term by exact enumeration increases exponentially with N. The exact enumeration method is based on a well-known deterministic algorithm using backtracking.[10] One starts with an N-step configuration Γ. Deleting the last step from Γ one obtains an $(N-1)$-step SAW Γ' called the parent of Γ. The SAW configurations are then classified into a tree structure according to their lineage. The unique one-step walk forms the root of the tree. The N-step configuration of height $(N-1)$ is connected to their parents at height $(N-2)$. The exhaustive enumeration of all SAW's having N steps proceeds by a systematic exploration of the genealogical tree to height $(N-1)$.

In the incomplete enumeration method, one arbitrarily chooses a set of $(N-1)$ real numbers p_i with $0<p_i\leq 1$ and $i=2,\ldots,N$. One deletes with probability $(1-p_r)$ all r-step configurations and their descendants from the genealogical tree. One then systematically enumerates the remaining N-step configurations in the genealogical tree. This can be done very efficiently using backtracking. When a particular r-step SAW is first generated, one chooses to ignore it and all its descendants in the enumeration with probability $(1-p_r)$. The probability that a particular r-step SAW will be enumerated in a given trial is $p_2p_3\cdots p_r\equiv P_r$, and is the same for all configurations with the same r. The algorithm thus generates an unbiased sample of configurations. In the calculation p_i is chosen to be $p_1=1, p_i=\mu^{-1}$ for $i\geq 2$, where $\mu=2.5$, 4.0, and 4.5 for the square, triangular, and simple cubic lattices, respectively. By setting $p_i=1$ for all i one obtains exact enumeration, which is possible only for small N. The results for R_g^2, $\langle r^4\rangle$, and the ratio $\langle r^4\rangle/(R_g^2)^2$, obtained by exact enumeration, are shown in Table I for the three lattices. The values of R_g^2 have been obtained before by Domb and Hioe[13] with N up to 15, 10, and 10 for the square, triangular, and simple cubic lattices, respectively. The R_g^2 values given here are obtained using Eq. (7). This checks the values for $\langle r^4\rangle$, since these are obtained directly by squaring the individual terms of $(\mathbf{R}_m-\mathbf{R}_n)^2$ before doing the summation over m and n as indicated in Eq. (8).

The Monte Carlo result for the ratio $\langle r_4\rangle/(R_g^2)^2$ is shown in Fig. 1 for the square and triangular lattices and in Fig. 2 for the simple cubic lattice. In both figures this ratio is plotted against $1/N$. The exact values for small N are denoted by crosses, and the dots represent Monte Carlo data, up to $N=50$ for the three lattices. These data are obtained using 6000, 12 000, and 72 000 trials for the square, triangular, and simple cubic lattices, respectively. The error bars are obtained by dividing the data into ten samples and then calculating the standard devia-

TABLE I. Exact values of R_g^2, $\langle r^4\rangle$ and their ratio $\langle r^4\rangle/(R_g^2)^2$ as functions of N for the square, triangular, and simple cubic lattices.

N	R_g^2	$\langle r^2\rangle$	$\langle r^4\rangle/(R_g^2)^2$
		Square	
1	0.250 000	0.250 000	4.000 000
2	0.518 518	1.111 111	4.132 652
3	0.805 556	2.805 555	4.323 422
4	1.155 199	5.871 999	4.400 198
5	1.520 735	10.353 285	4.476 835
6	1.936 996	16.946 518	4.516 720
7	2.364 180	25.502 289	4.562 660
8	2.839 589	36.979 095	4.586 118
9	3.323 222	50.973 663	4.615 588
10	3.850 145	68.659 668	4.631 771
11	4.385 065	89.454 590	4.652 114
12	4.959 219	114.703 842	4.663 921
13	5.541 065	143.656 784	4.678 855
14	6.159 132	177.831 955	4.687 816
15	6.784 321	216.296 722	4.699 343
16	7.443 557	260.763 428	4.706 364
		Triangular	
1	0.250 000	0.250 000	4.000 000
2	0.488 889	1.022 222	4.276 857
3	0.766 304	2.592 391	4.414 666
4	1.078 835	5.231 067	4.494 491
5	1.422 771	9.208 116	4.548 837
6	1.795 774	14.798 120	4.588 840
7	2.196 823	22.289 520	4.618 601
8	2.623 858	31.958 969	4.642 072
9	3.075 659	44.091 721	4.661 016
10	3.551 116	58.973 557	4.676 569
11	4.049 143	76.889 252	4.689 637
		Simple cubic	
1	0.250 000	0.250 000	4.000 000
2	0.488 889	0.933 333	3.904 959
3	0.730 000	2.129 999	3.996 995
4	0.989 752	3.990 082	4.073 139
5	1.255 093	6.523 533	4.142 248
6	1.537 535	9.902 144	4.188 701
7	1.824 327	14.080 074	4.230 578
8	2.124 458	19.236 099	4.262 069
9	2.428 013	25.295 334	4.290 801
10	2.742 711	32.446 579	4.313 291
11	3.060 200	40.590 088	4.334 314

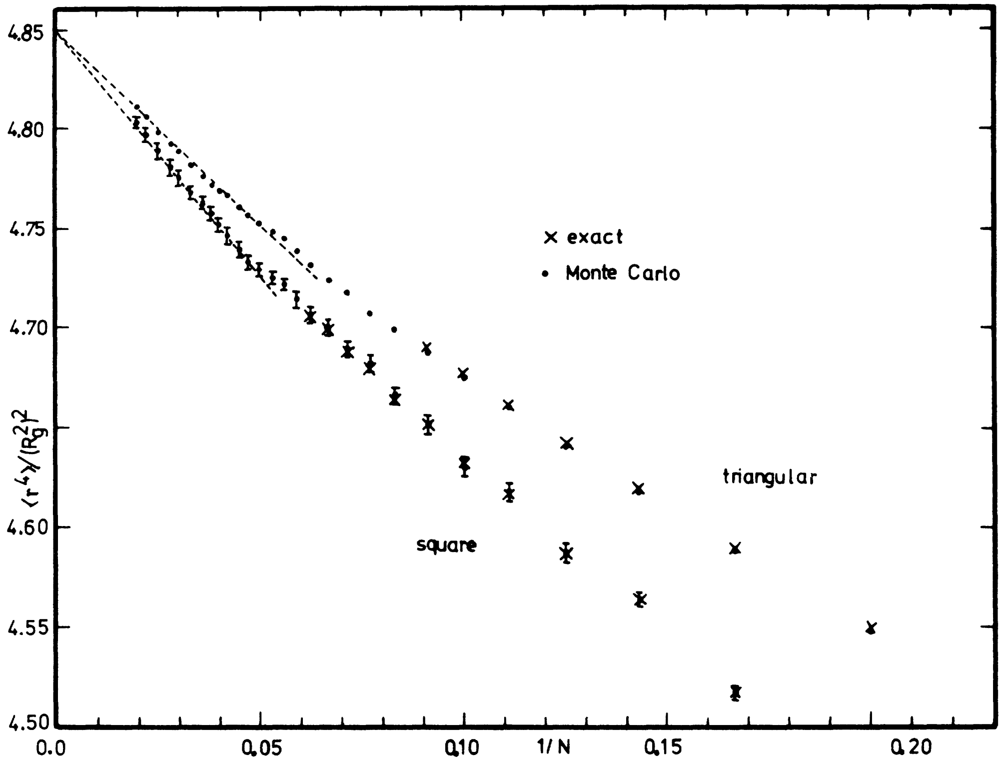

FIG. 1. The ratio $\langle r^4 \rangle/(R_g^2)^2$ vs $1/N$ for the square and triangular lattices. The crosses and dotes denote exact enumeration and Monte Carlo data, respectively.

tions. The error bars for the triangular lattice are of the same order of magnitude as those for the square lattice and, for the sake of clarity, are not shown in the figure. From both figures one sees that the Monte Carlo data agree very well with exact enumeration data at small N and that they approach a straight line for large N. From Fig. 1 the extrapolated value for the ratio $\langle r^4 \rangle/(R_g^2)^2$ is found to be 4.85±0.02 for both the square and triangular lattices. This confirms universality for the ratio. From (6) one obtains $\zeta=0.606\pm0.003$ in two dimensions. Similarly from Fig. 2 one obtains $\langle r^4 \rangle/(R_g^2)^2=4.61 \pm0.04$ and $\zeta=0.691\pm0.007$ in three dimensions. This is

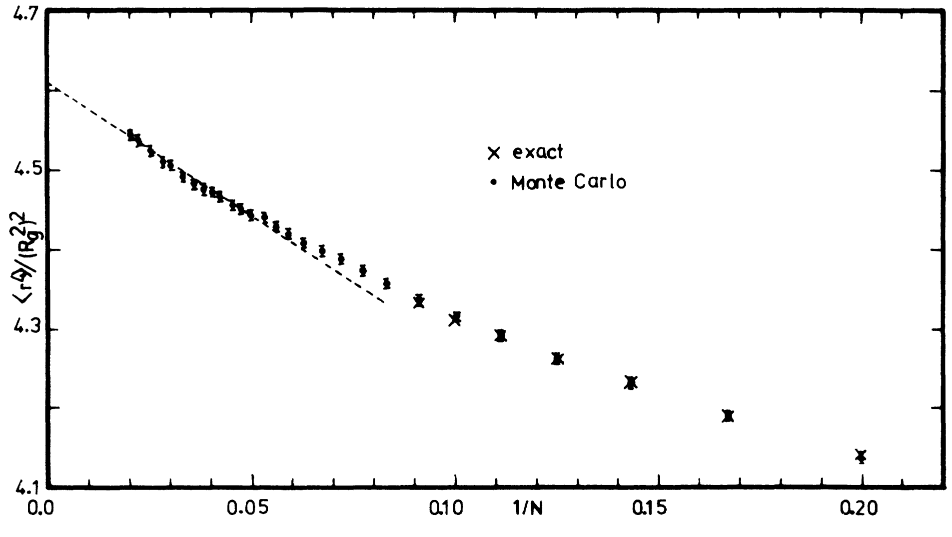

FIG. 2. Same as Fig. 1, but for the simple cubic lattice.

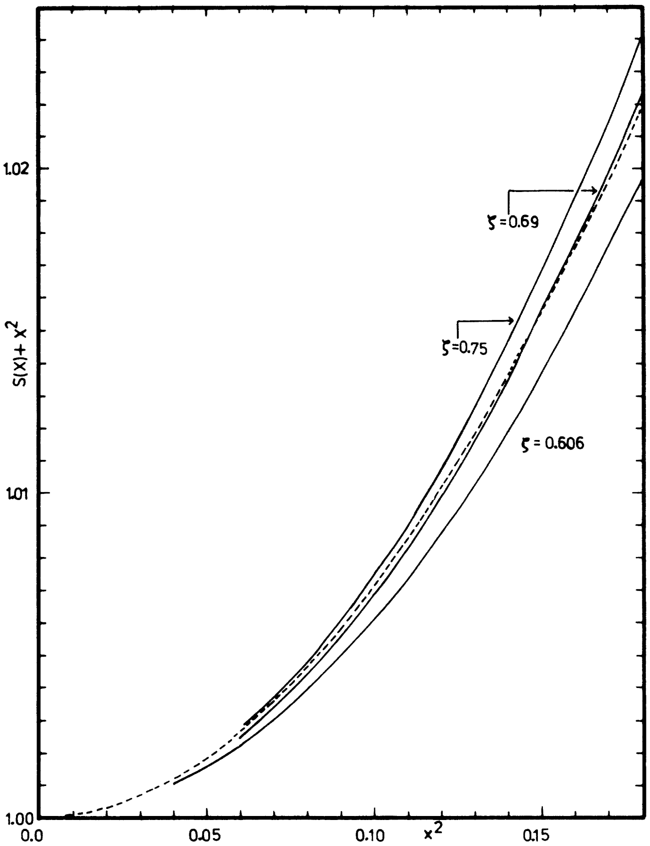

FIG. 3. The function $S(x)+x^2$ vs x^2 calculated using Eq. (2) up to order x^4, with different values of ζ. The dashed line represents results obtained using the exact Debye function, Eq. (1).

in very good agreement with the result of Ref. 4.

The scaled structure function with the x^2 term subtracted, i.e., the function $[S(x)+x^2]$ calculated using (2) with $\zeta=0.75$, 0.690, and 0.606 are plotted versus x^2 in Fig. 3. The result obtained using the exact Debye function (1) is also shown in the same figure with a dashed line. One sees that the deviation from the ideal Gaussian chain result is significant in two dimensions. The same plot for the three-dimensional case had already been shown in Fig. 3 of Ref. 4.

III. CONCLUSION

In conclusion, the coefficient of the x^4 term in the expansion of the scaled structure function $S(x)$ of linear polymers has been calculated using both exact enumeration and the Monte Carlo method in two and three dimensions. Significant deviation from the ideal chain result is found in the two-dimensional case. This suggests that experments should be done in this lower dimension to study the excluded volume effect on the structure function of linear polymers. From (2) and (4) one sees that the (x^6) term in (2) has a negative coefficient in both two and three dimensions just like that of the x^2 term. That means that the exact result, obtained by including the higher-order terms in (2) in two and three dimensions, will with all likelihood, at least for small values of x^2, lie below their respective curves in Fig. 3, which are calculated using only the x^4 term. This will give even stronger deviation from the ideal Gaussian value in two dimensions.

The calculations done here for linear polymers are based on Eqs. (3)–(8). Since these equations hold both for linear and branched polymers, this suggests that similar calculations can also be carried out for the latter case. Work on this problem has begun and will be reported elsewhere.

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