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Examination of the θ-point from exact enumeration of self-avoiding walks

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Abstract. Self-avoiding walks on the square lattice with nearest-neighbour attractive interactions are invesigated as a model for the two-dimensional version of a polymer in dilute solution. Temperature dependences of the exponent ν and the free energy of the chain are estimated from the exact enumeration data for up to 20 steps; the value of ν at the θ-point disagrees with the mean-field theory. The end-distance distribution function at the θ-point is also examined.

1. Introduction

A polymer chain in a good solvent takes the form of an extended coil owing to the excluded volume effect; the end-distance distribution is non-Gaussian. The extension of the chain with length n is characterised by $R_n \sim n^{\nu}$, where R_n is the root-mean-square end-to-end distance; the mean-field theory (e.g. de Gennes 1979) gives $\nu = 3/(d+2)$ for d-dimensional space. When the solvents are changed from good to poor or the temperature is lowered, attractive interactions between monomers become eminent: the chain transforms toward a collapsed coil decreasing in R_n. The excluded volume parameter vanishes around the θ temperature (or θ solvents), where two contributions of repulsion and attraction cancel each other; the chain can be treated as a phantom chain with $\nu = \frac{1}{2}$. The θ region is rather broad for finite n, but as $n \to \infty$, it tends to a unique θ-point, which is regarded as the tricritical point (de Gennes 1975), to coincide with the collapse transition point (Domb 1974). The chain itself is still non-phantom even at the θ-point although the excluded volume effect seems to disappear. As far as we are aware, there is no direct evidence that the polymer chain at the θ-point is *Gaussian*. The amended mean-field theory (de Gennes 1975) leads to $\nu = 2/(d+1)$ at the θ-point; it suggests that a chain at the θ-point is non-Gaussian for $d = 2$, where the three-body interactions become important.

Self-avoiding walks (SAWs) on lattices with an attractive force have been extensively investigated as a model of configurational properties of a polymer in dilute solution. Each pair of non-consecutive monomers occupying nearest-neighbour lattice sites contributes to the energy of the system by $-\varepsilon$. The temperature dependence of the properties is usually expressed in terms of ω, where $\omega = -\varepsilon/kT$. The dependence of ν on ω has been obtained by McCrackin *et al* (1973) by the use of the Monte Carlo method for three-dimensional lattices. Rapaport (1976, 1977) has estimated the value of ν for a relatively narrow range of ω from the exact enumeration of rather short chains ($n \leqslant 8$) on the face-centred cubic lattice. The end-distance distribution of a chain is

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obtained only for $\omega = 0$ from the exact enumerations (Domb 1969, McKenzie 1973). More recently, Kremer *et al* (1982) and Baumgärtner (1982) have investigated the scaling properties around the collapse transition point using the Monte Carlo method for SAWs on the tetrahedral and square (SQ) lattices, respectively.

In this paper, we estimate the respective ω dependences of ν and the free energy of a chain for a wide range of ω, which contains the θ-point, from the exact enumeration of n-step SAWs on the SQ lattice for relatively large size ($n \leqslant 20$). A series analysis technique (Ishinabe 1984) improved for this purpose is used, which was efficient for the estimation of the cross-over exponent for polymer adsorption. We examine, in particular, the end-distance distribution function at the θ-point. The two-dimensional case is thought favourable for examining the θ-point since $d = 3$ is a marginal case and a logarithmic correction term is involved (Moore 1977, de Gennes 1978).

2. Series analysis

Let $C_n(x, m)$ be the number of n-step SAWs having m nearest-neighbour contacts between non-consecutive vertices; x is the integer x component of the end-to-end distance R. We can obtain the mean-square end-to-end distance from

$$\langle R^2 \rangle_n = d \sum_x \sum_m x^2 C_n(x, m)\, \mathrm{e}^{m\omega} \left(\sum_x \sum_m C_n(x, m)\, \mathrm{e}^{m\omega} \right)^{-1}, \tag{1}$$

where d is the spatial dimension, and the end-distance distribution function for the x component from

$$P(x) = \sum_m C_n(x, m)\, \mathrm{e}^{m\omega} \left(\sum_x \sum_m C_n(x, m)\, \mathrm{e}^{m\omega} \right)^{-1} \tag{2}$$

at any given $\omega (= -\varepsilon/kT)$. We introduce the reduced end-distance distribution function (Chikahisa 1984) by

$$P^*(\tilde{x}) = (2/d)^{1/2} R_n P(x), \tag{3}$$

where $\tilde{x} = (d/2)^{1/2} x / R_n$ and $R_n = \langle R^2 \rangle_n^{1/2}$. For random walks of $\omega = 0$, $P^*(\tilde{x})$ can be written as

$$P^*(\tilde{x}) = \pi^{-1/2} \exp(-\tilde{x}^2). \tag{4}$$

We have obtained the first twenty terms in the $C_n(x, m)$ series for the SQ lattice; the values of $C_{n,m} = \Sigma_x\, C_n(x, m)$ and $D_{n,m} = \Sigma_x\, x^2 C_n(x, m)$ are given in tables 1 and 2, respectively. Note that these tables quote the values divided by 2.

The estimation of ν for various ω is performed as follows: we assume that

$$R_n(\omega) \simeq R_0(\omega) n^{\nu(\omega)}, \tag{5}$$

and form ratios of the alternate terms. The Neville tables are constructed for the linear and quadratic extrapolants. Then we plot these extrapolants against $1/n$ and extrapolate to $n \to \infty$ taking into account the curvature of convergence as a whole along with the damping oscillation around it. The last process improves the accuracy of the estimation for such cases as a confluent singularity exists. An example of the estimation for $\omega = 0.75$ is shown in figure 1. For $\omega = 0$, we estimate that $\nu = 0.748 \pm 0.002$ for the

Table 1. Values of $\frac{1}{2}C_{n,m}$ for SAWs on the SQ lattice.

n \ m	0	1	2	3	4	5
1	2					
2	6					
3	14	4				
4	34	16				
5	82	44	16			
6	198	128	64			
7	470	368	172	76		
8	1 122	1 016	536	264	20	
9	2 662	2 688	1 700	692	392	
10	6 334	7 112	4 916	2 304	1 192	192
11	14 970	18 488	13 800	7 776	3 212	1 776
12	35 506	47 752	38 500	22 872	11 320	5 048
13	83 734	121 768	105 868	66 944	38 152	14 888
14	198 086	309 584	286 280	193 808	113 188	54 600
15	466 314	779 584	767 256	553 784	338 428	182 256
16	1 100 818	1 958 480	2 036 332	1 548 080	1 001 852	550 464
17	2 587 634	4 884 536	5 362 712	4 299 548	2 919 288	1 683 780
18	6 097 830	12 160 776	14 017 564	11 789 048	8 336 508	5 075 456
19	14 316 402	30 099 732	36 415 636	32 092 728	23 658 516	15 060 260
20	33 687 146	74 401 912	94 069 808	86 512 192	66 298 236	43 792 632

n \ m	6	7	8	9	10	11	12
11	124						
12	1 468						
13	7 956	1 440					
14	22 620	8 488	568				
15	74 932	34 648	10 820	276			
16	269 220	106 080	43 780	7 560			
17	889 152	379 300	159 264	61 432	6 692		
18	2 725 900	1 317 152	535 716	210 424	60 816	2 176	
19	8 480 992	4 341 420	1937 556	774 756	309 920	68 380	2 012
20	25 824 256	13 526 488	6548 420	2738 832	1037 412	366 344	44 904

SQ lattice. The mean-field value $\frac{3}{4}$ for $d=2$, which is supported by a recent analytic calculation (Nienhuis 1982), is just on the limit of the estimated uncertainty in our estimate.

3. Results and discussion

Figure 2 illustrates the plot of ν for $\omega \geqslant 0$ estimated from the above method as a function of ω; the value of ν is almost constant for small ω, but it decreases as ω increases and seems to converge to a constant value for large ω although error bars enlarge there. An inflection point is found at $\omega = 0.75$ for the plot; we regard it tentatively as the θ-point (tricritical point) ω_t, then we estimate that $\nu_t = 0.503 \pm 0.01$

Table 2. Values of $\frac{1}{2}D_{n,m}$ for SAWs on the SQ lattice.

n \ m	0	1	2	3	4	5
1	1					
2	8					
3	39	2				
4	152	24				
5	529	134	16			
6	1 704	608	140			
7	5 211	2 424	710	102		
8	15 344	8 784	3 224	728	40	
9	43 907	29 808	13 194	3 418	820	
10	122 812	96 592	49 196	15 704	4 564	456
11	337 293	301 644	172 644	65 680	20 118	5 032
12	912 536	914 416	580 840	249 424	90 536	24 456
13	2 437 883	2 705 620	1 884 294	898 256	370 988	107 668
14	6 443 668	7 846 688	5 932 864	3 112 456	1 394 668	485 608
15	16 875 389	22 369 648	18 229 500	10 403 148	5 029 022	1 973 592
16	43 843 784	62 847 320	54 869 544	33 750 304	17 545 608	7 436 552
17	113 113 569	174 334 652	162 228 036	106 868 030	59 214 564	27 049 234
18	290 024 644	478 257 320	472 288 680	331 391 512	194 508 176	95 332 360
19	739 530 889	1299 163 914	1356 422 066	1008 943 132	624 853 266	325 367 266
20	1876 441 960	3498 476 512	3849 256 304	3023 047 520	1968 591 312	1082 288 528

n \ m	6	7	8	9	10	11	12
11	310						
12	4 904						
13	32 610	4 000					
14	145 028	35 408	2 112				
15	637 490	186 156	39 658	698			
16	2 774 880	820 328	237 224	31 440			
17	11 003 144	3 627 570	1 106 576	286 380	24 026		
18	41 148 980	15 339 904	4 906 828	1 414 464	310 680	8 776	
19	149 460 616	59 999 622	21 226 002	6 435 874	1871 808	299 422	6 982
20	527 152 512	224 085 192	86 759 968	28 590 984	8548 784	2261 336	227 672

at $\omega_t = 0.75$ (see figure 1). The value of ω_t is in good agreement with the estimate 0.76 tof Baumgärtner (1982) from the Monte Carlo technique while the estimated ν_t deviates noticeably from the mean-field value $\nu_t = \frac{2}{3}$ for $d = 2$. Our value is, however, consistent with a renormalisation group calculation (Stephen and McCauley 1973, Stephen 1975) to second order in $\varepsilon'(\varepsilon' = 3 - d)$ leading to $\nu_t = 0.506$. Recently, Kholodenko and Freed (1984) have deduced a slightly larger value 0.551 using the conformational space renormalisation group method. Thus the mean-field value for $d = 2$ should be corrected.

In collapsed state for $\omega > \omega_t$, monomer density must be constant on the inside of a coil, so that $\nu_c = 1/d$ is expected. Figure 2 shows that $\nu_c \simeq 0.3$; it is too low compared with the expected value even if we take into account the inaccuracy of the estimation. It seems that the estimated value of ν_c is different from that defined from R_g (radius of gyration); self-avoiding walks on the SQ lattice with maximum m have unexpectedly large numbers of configurations (e.g. 89 808 for $n = 20$ and $m = 12$).

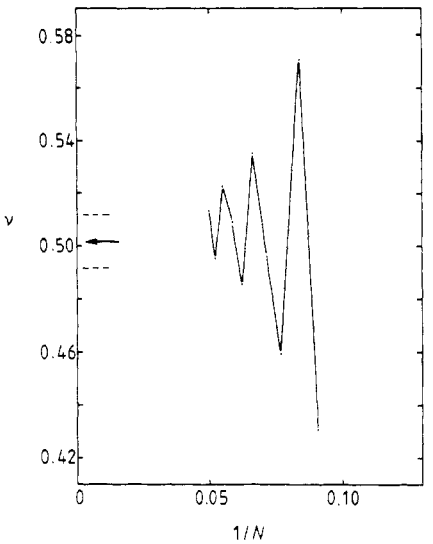

Figure 1. Ratio estimate of ν at $\omega = 0.75$ from the linear extrapolants of alternate terms in series; the arrow indicates $\nu = 0.503$.

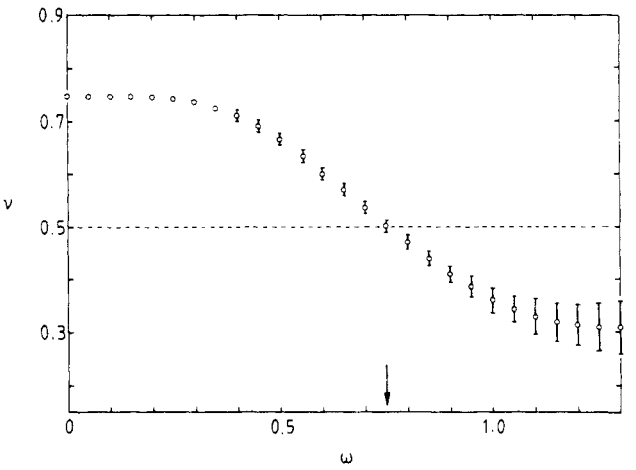

Figure 2. Plot of ν against ω as estimated from the ratio method; the arrow indicates an inflection point.

The partition function of the chain can be written as

$$Z_n(\omega) = \sum_m C_{n,m} \, e^{m\omega}, \tag{6}$$

where $C_{n,m} = \Sigma_x C_n(x, m)$. We assume that

$$Z_n(\omega) \sim n^{\gamma(\omega)-1} \mu(\omega)^n \tag{7}$$

by analogy with the case of $\omega = 0$. We can estimate $\mu(\omega)$ using the ratio method stated

above; this is nothing but the reduced free energy of the chain which is defined by

$$\mu(\omega) = \lim_{n\to\infty} n^{-1} \ln Z_n(\omega). \tag{8}$$

The plot of $\mu(\omega)$ thus obtained as a function of ω is given in figure 3; a slight discontinuous change in the slope is noticeable at the point $\omega = 0.75 \pm 0.005$, i.e. we get the same value of ω_t as before. We define a critical exponent λ by

$$\mu(\omega) - \mu(\omega_t) \sim |\omega - \omega_t|^{\lambda}. \tag{9}$$

The relation $\lambda = 2/\varepsilon$ ($\varepsilon = 4 - d$) is suggested by Moore (1977). The plot of $\mu(\omega)$ in figure 3 supports the relation for $d = 2$ since the estimated values lie on two straight lines with slightly different slopes which cross at ω_t.

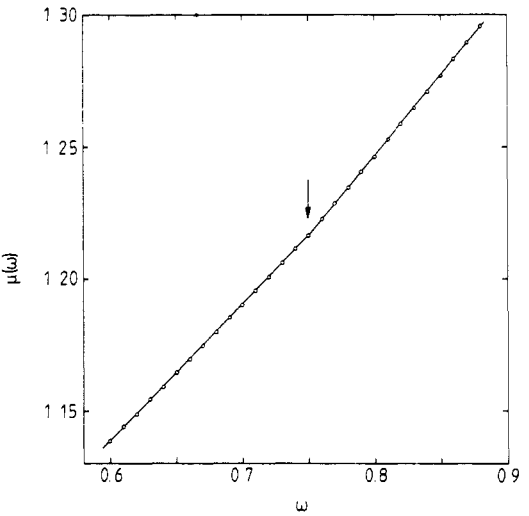

Figure 3. Plot of $\mu(\omega)$ against ω; a discontinuous change in the slope is found at the point ($\omega = 0.75$) indicated by the arrow.

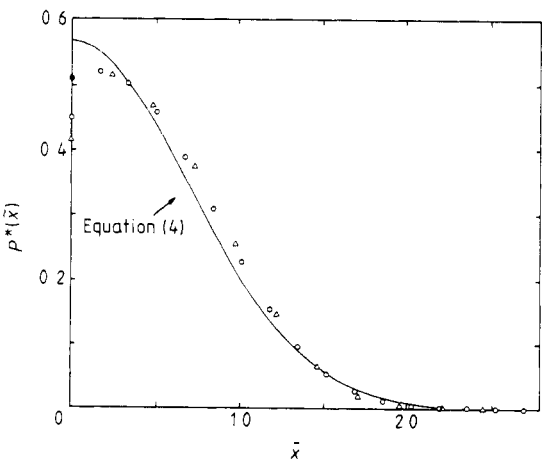

Figure 4. Plot of $P^*(\tilde{x})$ against $\tilde{x}$ at $\omega_t = 0.75$ for $n = 10$ (Δ) and 20 (○). ●: $P^*(0)$ extrapolated to $n \to \infty$. The full curve shows equation (4).

The plot of $P^*(\tilde{x})$ at ω_t against $\tilde{x}(\geq 0)$ for $n = 10$ and 20 is given in figure 4. As n increases, the plot approaches the Gaussian distribution (4). The limiting value of $P^*(0)$ estimated from the Neville tables is 0.51 ± 0.02, which is also shown in the figure. Thus we conclude that for $d = 2$ a polymer chain is almost Gaussian at the θ-point in the limit $n \to \infty$.

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