Examination of the theta -point from exact enumeration of self-avoiding walks. II

1987 J. Phys. A: Math. Gen. 20 6435

(http://iopscience.iop.org/0305-4470/20/18/041)

J. Phys. A: Math. Gen. **20** (1987) 6435-6453. Printed in the UK

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

T Ishinabe

Faculty of Engineering, Yamagata University, Yonezawa 992, Japan

Received 2 February 1987, in final form 24 April 1987

Abstract. The θ-point (collapse transition) is examined using a series analysis method for self-avoiding walks on the tetrahedral and square lattices. The results are, as a whole, compatible with Moore's conjecture that the order of transition is first in two dimensions while second in three dimensions. The temperature dependence of an exponent δ for the end-distance distribution is estimated together with those of exponents ν and γ. In particular, we have obtained that δ is 2.22 ± 0.05 at the θ-point in two dimensions and 2.06 ± 0.04 in three dimensions.

1. Introduction

In a good solvent a polymer chain is swollen as compared to an ideal chain on account of the excluded volume effect. When the temperature is reduced or the solvent is changed towards poor, the chain contracts as a result of increasing attractive force. The excluded volume effect is considered to vanish at the θ-point, which is originally defined as the vanishing of the second virial coefficient. For a temperature below the θ-point, a so-called collapse transition takes place, which is often referred to as the coil–globule transition in the connection with the problem of the denaturation of a protein globule (e.g., Lifshitz *et al* 1978). In the limit of infinite chain length ($n \to \infty$) the θ-point coincides with the collapse transition point (Domb 1974); it is regarded as the tricritical point (de Gennes 1975).

The nature of the transition is still controversial although much theoretical effort has been devoted to this problem. Some mean-field theories (Sanchez 1979, DiMarzio 1984) indicate that the transition is second-order while it becomes first-order as the stiffness of a chain increases (de Gennes 1975, Lifshitz *et al* 1978, Allegra and Ganazzoli 1983, 1985, Muthukumar 1984). Such tendency has been demonstrated by a Monte Carlo study (Kolinski *et al* 1986) whereas Domb (1974) and Oyama and Oono (1977) suggest that the transition is always first-order for $n \to \infty$. Kholodenko and Freed (1984a) have shown that the order of the transition is dependent on the magnitude of a three-body interaction parameter using a field theoretical approach; it exhibits a contrast to a similar treatment (Moore 1977) which gives the second-order transition. However, the renormalisation group calculations (Burch and Moore 1976, Moore 1977, de Gennes 1978, Duplantier 1980) predict the second-order transition with logarithmic divergence.

The correlation length exponent ν at the θ-point can be given in terms of the Flory type mean-field theory (Ptitsyn and Eizner 1965, de Gennes 1975, Marqusee and Deutch 1981) incorporating two- and three-body interactions: $\nu_t = 2/(d+1)$ for d-dimensional

0305-4470/87/186435+20$02.50

space. This implies that a θ-chain is non-Gaussian for $d = 2$. The ε expansion to the next-to-zeroth order (de Gennes 1975, Stephen 1975) yields $\nu_t = 0.506$ for $d = 2$ while the three-parameter calculation in conformational space formulation by Kholodenko and Freed (1984b, c) leads to a different value $\nu_t = 0.551$; Derrida and Saleur (1985) obtain $\nu_t = 0.55 \pm 0.01$ from a transfer matrix method combined with finite-size scaling. These results, as a whole, deviate considerably from the mean-field value. However, the three-parameter-renormalisation calculation by Douglas *et al* (1985) suggests that ν_t should be between 0.5 and 0.55; it is dependent on the strength of the three-body interaction. They also indicate that a generalisation of the self-consistent field theory (Edwards and Singh 1979) gives a similar result.

Since the pioneer work of Fisher and Hilley (1961), there have been a number of numerical attempts to examine the θ-point by exploiting n-step self-avoiding walks (SAW) on lattices with the attractive nearest-neighbour interaction ε. Baumgärtner (1982) has performed a Monte Carlo calculation for SAW on the square (SQ) lattice and confirmed the tricriticality by testing $\omega(=-\varepsilon/kT)$ and n dependences of the finite-size scaling relations assuming de Gennes–Stephen value. In a previous paper (Ishinabe 1985, hereafter referred to as I) we have obtained the ω dependence of the free energy together with that of ν from the exact enumeration of SAW on the SQ lattice; we estimate $\nu_t = 0.503 \pm 0.01$, which is consistent with the de Gennes–Stephen value. Recently, Privman (1986) has obtained $\nu_t = 0.535 \pm 0.025$ from the exact enumeration for the triangular lattice. The non-ideal behaviour at the θ-point is suggested from a Monte Carlo method (Tobochnik *et al* 1982) for the off-lattice model in $d = 2$.

For three-dimensional lattices the ω dependence of ν has been estimated by McCrackin *et al* (1973) by the use of the Monte Carlo technique. Rapaport (1974, 1977) has carried out the exact enumeration for the face-centred cubic lattice; he suggests a transition point at which the specific heat diverges as $n \to \infty$. The Gaussian behaviour of the θ chain has been demonstrated by Monte Carlo simulations (Webman *et al* 1981, Fixman and Mansfield 1984). However, the self-consistent field theory by Oono (1976) and the conformational space renormalisation theory by Oono and Freed (1981) indicate that $\nu_t = \frac{1}{2}$ and the end-point distribution of the θ chain is asymptotically Gaussian but not exactly. Baumgärtner (1980) has shown that $\nu_t = \frac{1}{2}$ but the detailed structure is different from a random walk shape using a Monte Carlo technique of freely jointed chain with Lennard-Jones type interactions. The perturbation theory by Martin (1984) also suggests that the chain is non-Gaussian. The tricriticality of the θ-point is confirmed by Kremer *et al* (1982) from a Monte Carlo calculation of SAW on the tetrahedral (TET) lattice while the experimental evidence is given by Duplantier *et al* (1986).

The purpose of this paper is to re-examine the critical behaviours of a flexible chain in a dilute solution from exact enumerations of SAW on the TET and SQ lattices (these lattices were chosen on account of some resemblance to the polymer chain structure). First, we estimate the ω dependence of the free energy on the basis of a ratio method associated with the Neville table to assess the order of the collapse transition, especially for $d = 3$. Then, the values of ν and γ (the susceptibility exponent) are estimated similarly for a wide range of ω including the θ-point. Finally, we obtain δ, an exponent characterising the end-distance distribution, as a function of ω using various moments of the distribution extrapolating to $n \to \infty$ for each ω. This is the first attempt both for $d = 2$ and 3 as far as we are aware although the moments are already evaluated for some selected value of ω from a Monte Carlo approach for the simple cubic lattice (McCrackin *et al* 1973).

2. Exact enumerations

We have obtained the series of $C_n(x, m)$, the number of n-step SAW with m nearest-neighbour contacts between nonconsecutive vertices, for the TET ($n \leqslant 22$) and SQ ($n \leqslant 22$) lattices, x being the end-point distance in the x direction. For the SQ lattice we have added two more terms to the series expansions in I. The values of $C_n(x, m)$ for $x \geqslant 0$ for the TET lattice are listed in table 1, where the length of the step vector is taken as $\sqrt{3}$. The total number C_n of walks for each n can be obtained from $C_n = 2\Sigma_m \Sigma'_x C_n(x, m)$ for odd n and $C_n = 2\Sigma_m \Sigma'_x C_n(x, m) + \Sigma_m C_n(0, m)$ for even n, where Σ' means the exclusion of $x = 0$. For the SQ lattice, only the result for $n = 22$ is given in table 2 (but full data are available upon request) since the values for $n \leqslant 20$ are partly listed in I and those for $n \leqslant 21$ are already obtained (but not published) by Privman (1986). Note that these tables quote the values divided by two.

3. Order of the transition

The partition function of a chain with attractive nearest-neighbour pair interaction $\varepsilon(\leqslant 0)$ can be written as

$$Z_n(\omega) = \sum_m C_{n,m} \, \mathrm{e}^{m\omega} \tag{1}$$

where $C_{n,m} = \Sigma_x C_n(x, m)$ and $\omega = -\varepsilon/kT$. We define the reduced free energy per monomer by

$$A(\omega) = \lim_{n\to\infty} n^{-1} \ln Z_n(\omega) \tag{2}$$

and assume the form

$$Z_n(\omega) \sim n^{\gamma(\omega)-1} \mu(\omega)^n \tag{3}$$

where $\mu(\omega)$ and $\gamma(\omega)$ correspond to the connective constant and susceptibility exponent, respectively. The value of $\mu(\omega)$ can be estimated for given ω using the ratio method associated with the Neville table in the same manner as in I. Accordingly, we obtain $A(\omega)$ since $A(\omega) = \ln \mu(\omega)$ as $n \to \infty$ (the logarithm in front of $\mu(\omega)$ is dropped by mistake in (8) and (9) in I). The ω dependence of $A(\omega)$ thus estimated is shown in figure 1 as a function of ω in the range $0.3 \leqslant \omega \leqslant 0.68$. $A(\omega)$ increases progressively with ω, but no noticeable change in the curvature is recognised in contrast with the case of the SQ lattice (see I), probably because it is masked by a logarithmic term as will be mentioned later.

The mean contact number $\langle m \rangle$ for given ω is evaluated from

$$\langle m \rangle = \left(\sum_m m C_{n,m} \, \mathrm{e}^{m\omega} \right) (Z_n(\omega))^{-1}. \tag{4}$$

We expect that

$$E(\omega) = \lim_{n\to\infty} \langle m \rangle / n \tag{5}$$

by analogy with the case of $\omega = 0$ (Ishinabe and Chikahisa 1986); $E(\omega)$ is nothing but the reduced energy of a chain since $E(\omega) = \mathrm{d}A(\omega)/\mathrm{d}\omega$. Figure 2 illustrates the plot of $E(\omega)$, which was estimated from Neville tables, as a function of ω for the TET

Table 1. Values of $\frac{1}{2}C_n(x, m)$ for $x \geqslant 0$ for the TET lattice.

n	m	x	C_n	n	m	x	C_n
1	0	1	1	10	1	4	1 148
2	0	0	2	10	1	6	528
2	0	2	2	10	2	0	416
3	0	1	5	10	2	2	408
3	0	3	4	10	2	4	104
4	0	0	14	10	2	6	24
4	0	2	12	11	0	1	8 961
4	0	4	8	11	0	3	8 820
5	0	1	31	11	0	5	7 824
5	0	3	28	11	0	7	5 920
5	0	5	16	11	0	9	3 328
5	1	1	6	11	0	11	1 024
6	0	0	78	11	1	1	4 284
6	0	2	78	11	1	3	3 898
6	0	4	64	11	1	5	2 850
6	0	6	32	11	1	7	1 184
6	1	0	16	11	2	1	1570
6	1	2	16	11	2	3	1 112
7	0	1	193	11	2	5	284
7	0	3	190	11	2	7	64
7	0	5	144	11	3	1	142
7	0	7	64	11	3	3	54
7	1	1	66	11	3	5	2
7	1	3	42	12	0	0	23 882
8	0	0	506	12	0	2	23 684
8	0	2	500	12	0	4	22 424
8	0	4	458	12	0	6	19 008
8	0	6	320	12	0	8	13 600
8	0	8	128	12	0	10	7 168
8	1	0	192	12	0	12	2 048
8	1	2	176	12	1	0	12 192
8	1	4	100	12	1	2	12 048
8	2	0	16	12	1	4	10 288
8	2	2	8	12	1	6	6 936
8	2	4	2	12	1	8	2 624
9	0	1	1 301	12	2	0	4 720
9	0	3	1 274	12	2	2	4 348
9	0	5	1 088	12	2	4	2 830
9	0	7	704	12	2	6	736
9	0	9	256	12	2	8	160
9	1	1	528	12	3	0	616
9	1	3	452	12	3	2	576
9	1	5	232	12	3	4	236
9	2	1	138	12	3	6	8
9	2	3	34	12	4	0	64
9	2	5	8	12	4	2	32
10	0	0	3 442	12	4	4	8
10	0	2	3 414	13	0	1	62 633
10	0	4	3 180	13	0	3	61 810
10	0	6	2 552	13	0	5	56 292
10	0	8	1 536	13	0	7	45 664
10	0	10	512	13	0	9	30 976
10	1	0	1 496	13	0	11	15 360
10	1	2	1 464	13	0	13	4 096

Table 1. (continued)

n	m	x	C_n	n	m	x	C_n
13	1	1	35 130	15	0	3	437 566
13	1	3	32 770	15	0	5	405 296
13	1	5	26 554	15	0	7	343 416
13	1	7	16 600	15	0	9	256 000
13	1	9	5 760	15	0	11	157 184
13	2	1	14 140	15	0	13	69 632
13	2	3	11 938	15	0	15	16 384
13	2	5	7 116	15	1	1	284 320
13	2	7	1 840	15	1	3	269 294
13	2	9	384	15	1	5	230 142
13	3	1	4 002	15	1	7	167 228
13	3	3	2 056	15	1	9	91 296
13	3	5	740	15	1	11	27 136
13	3	7	24	15	2	1	126 814
13	4	1	136	15	2	3	114 114
13	4	3	80	15	2	5	84 666
13	4	5	24	15	2	7	43 300
13	5	1	6	15	2	9	10 688
13	5	3	4	15	2	11	2 048
13	5	5	2	15	3	1	44 502
14	0	0	167 458	15	3	3	33 800
14	0	2	166 500	15	3	5	15 960
14	0	4	159 168	15	3	7	5 052
14	0	6	139 754	15	3	9	160
14	0	8	108 608	15	4	1	7 808
14	0	10	70 016	15	4	3	4 744
14	0	12	32 768	15	4	5	1 458
14	0	14	8 192	15	4	7	276
14	1	0	99 856	15	5	1	762
14	1	2	98 380	15	5	3	290
14	1	4	87 604	15	5	5	64
14	1	6	67 180	15	5	7	24
14	1	8	39 168	16	0	0	1 186 530
14	1	10	12 544	16	0	2	1 180 516
14	2	0	41 288	16	0	4	1 136 944
14	2	2	40 564	16	0	6	1 021 752
14	2	4	32 124	16	0	8	836 000
14	2	6	17 692	16	0	10	598 528
14	2	8	4 480	16	0	12	350 720
14	2	10	896	16	0	14	147 456
14	3	0	12 704	16	0	16	32 768
14	3	2	12 068	16	1	0	803 488
14	3	4	5 928	16	1	2	794 048
14	3	6	1 988	16	1	4	725 928
14	3	8	64	16	1	6	594 672
14	4	0	1 064	16	1	8	410 400
14	4	2	1 046	16	1	10	210 560
14	4	4	420	16	1	12	58 368
14	4	6	90	16	2	0	374 124
14	5	0	24	16	2	2	368 824
14	5	2	16	16	2	4	314 402
14	5	4	12	16	2	6	218 656
14	5	6	8	16	2	8	104 496
15	0	1	442 239	16	2	10	25 088

Table 1. (continued)

n	m	x	C_n	n	m	x	C_n
16	2	12	4 608	17	4	9	1 920
16	3	0	137 000	17	5	1	19 354
16	3	2	129 424	17	5	3	11 700
16	3	4	91 752	17	5	5	4 034
16	3	6	41 720	17	5	7	668
16	3	8	12 416	17	5	9	160
16	3	10	384	17	6	1	822
16	4	0	29 136	17	6	3	604
16	4	2	28 196	17	6	5	274
16	4	4	15 900	17	6	7	16
16	4	6	4 316	18	0	0	8 469 530
16	4	8	752	18	0	2	8 431 524
16	5	0	3 160	18	0	4	8 161 180
16	5	2	2 592	18	0	6	7 457 426
16	5	4	1 044	18	0	8	6 318 416
16	5	6	216	18	0	10	4 831 456
16	5	8	64	18	0	12	3 202 048
16	6	0	264	18	0	14	1 718 272
16	6	2	180	18	0	16	655 360
16	6	4	68	18	0	18	131 072
16	6	6	4	18	1	0	6 400 024
17	0	1	3 149 201	18	1	2	6 344 652
17	0	3	3 119 624	18	1	4	5 914 220
17	0	5	2 924 912	18	1	6	5 050 588
17	0	7	2 551 886	18	1	8	3 808 216
17	0	9	2 017 712	18	1	10	2 383 936
17	0	11	1 389 056	18	1	12	1 090 560
17	0	13	778 240	18	1	14	266 240
17	0	15	311 296	18	2	0	3 323 412
17	0	17	65 536	18	2	2	3 273 702
17	1	1	2 271 974	18	2	4	2 893 464
17	1	3	2 181 346	18	2	6	2 235 134
17	1	5	1 928 458	18	2	8	1 384 944
17	1	7	1 514 602	18	2	10	587 456
17	1	9	994 640	18	2	12	133 120
17	1	11	481 152	18	2	14	22 528
17	1	13	124 928	18	3	0	1 306 824
17	2	1	1 132 158	18	3	2	1 282 692
17	2	3	1 043 626	18	3	4	1 036 972
17	2	5	846 400	18	3	6	645 020
17	2	7	554 618	18	3	8	266 944
17	2	9	249 104	18	3	10	70 080
17	2	11	58 112	18	3	12	2 048
17	2	13	10 240	18	4	0	422 408
17	3	1	431 452	18	4	2	405 794
17	3	3	369 426	18	4	4	259 176
17	3	5	245 184	18	4	6	122 422
17	3	7	106 586	18	4	8	29 936
17	3	9	29 776	18	4	10	4 704
17	3	11	896	18	5	0	76 544
17	4	1	133 982	18	5	2	72 380
17	4	3	90 660	18	5	4	40 304
17	4	5	45 638	18	5	6	12 876
17	4	7	11 648	18	5	8	1 864

Table 1. (continued)

n	m	x	C_n	n	m	x	C_n
18	5	10	384	19	6	7	3 272
18	6	0	9 488	19	6	9	128
18	6	2	8 620	19	7	1	5 414
18	6	4	3 920	19	7	3	2 638
18	6	6	1 100	19	7	5	552
18	6	8	48	19	7	7	60
19	0	1	22 561 441	20	0	0	60 788 010
19	0	3	22 373 338	20	0	2	60 545 236
19	0	5	21 161 140	20	0	4	58 839 376
19	0	7	18 853 048	20	0	6	54 424 620
19	0	9	15 518 684	20	0	8	47 283 654
19	0	11	11 484 928	20	0	10	37 830 448
19	0	13	7 335 936	20	0	12	27 117 312
19	0	15	3 776 512	20	0	14	16 711 680
19	0	17	1 376 256	20	0	16	8 265 728
19	0	19	262 144	20	0	18	2 883 584
19	1	1	18 039 976	20	0	20	524 288
19	1	3	17 474 468	20	1	0	50 728 712
19	1	5	15 829 516	20	1	2	50 364 996
19	1	7	13 058 316	20	1	4	47 568 404
19	1	9	9 463 960	20	1	6	41 840 564
19	1	11	5 657 280	20	1	8	33 371 064
19	1	13	2 454 016	20	1	10	23 271 584
19	1	15	565 248	20	1	12	13 305 856
19	2	1	9 862 440	20	1	14	5 486 592
19	2	3	9 260 168	20	1	16	1 196 032
19	2	5	7 876 308	20	2	0	28 742 276
19	2	7	5 806 964	20	2	2	28 397 436
19	2	9	3 412 048	20	2	4	25 776 780
19	2	11	1 372 224	20	2	6	21 092 928
19	2	13	302 080	20	2	8	14 867 146
19	2	15	49 152	20	2	10	8 306 688
19	3	1	4 148 638	20	2	12	3 178 240
19	3	3	3 721 714	20	2	14	679 936
19	3	5	2 841 676	20	2	16	106 496
19	3	7	1 665 674	20	3	0	12 514 400
19	3	9	656 904	20	3	2	12 334 416
19	3	11	162 496	20	3	4	10 550 160
19	3	13	4 608	20	3	6	7 625 048
19	4	1	1 468 858	20	3	8	4 231 512
19	4	3	1 184 456	20	3	10	1 592 544
19	4	5	713 828	20	3	12	372 224
19	4	7	318 396	20	3	14	10 240
19	4	9	74 580	20	4	0	4 571 024
19	4	11	11 200	20	4	2	4 393 216
19	5	1	369 088	20	4	4	3 347 278
19	5	3	261 464	20	4	6	1 926 404
19	5	5	125 304	20	4	8	810 080
19	5	7	36 822	20	4	10	181 520
19	5	9	4 864	20	4	12	26 112
19	5	11	896	20	5	0	1 271 128
19	6	1	52 260	20	5	2	1 225 128
19	6	3	31 784	20	5	4	804 908
19	6	5	12 768	20	5	6	353 160

Table 1. (continued)

n	m	x	C_n	n	m	x	C_n
20	5	8	97 628	21	3	15	22 528
20	5	10	12 160	21	4	1	14 937 492
20	5	12	2 048	21	4	3	12 967 348
20	6	0	223 256	21	4	5	9 308 716
20	6	2	208 396	21	4	7	5 095 464
20	6	4	117 316	21	4	9	2 021 724
20	6	6	40 476	21	4	11	433 840
20	6	8	9 124	21	4	13	59 904
20	6	10	320	21	5	1	4 894 974
20	7	0	23 488	21	5	3	3 771 110
20	7	2	20 668	21	5	5	2 277 768
20	7	4	10 536	21	5	7	944 758
20	7	6	2 364	21	5	9	248 284
20	7	8	264	21	5	11	29 504
20	8	0	1 288	21	5	13	4 608
20	8	2	964	21	6	1	1 102 914
20	8	4	412	21	6	3	770 970
20	8	6	44	21	6	5	380 922
21	0	1	162 403 037	21	6	7	117 212
21	0	3	161 193 910	21	6	9	23 980
21	0	5	153 504 926	21	6	11	768
21	0	7	138 896 010	21	7	1	155 440
21	0	9	117 702 844	21	7	3	103 200
21	0	11	91 576 848	21	7	5	42 838
21	0	13	63 627 520	21	7	7	8 214
21	0	15	37 871 616	21	7	9	832
21	0	17	18 022 400	21	8	1	8 112
21	0	19	6 029 312	21	8	3	4 890
21	0	21	1 048 576	21	8	5	1 824
21	1	1	142 576 214	21	8	7	222
21	1	3	138 924 782	21	9	1	68
21	1	5	128 008 602	21	9	3	36
21	1	7	109 331 436	21	9	5	24
21	1	9	84 373 412	21	9	7	4
21	1	11	56 675 040	22	0	0	438 212 210
21	1	13	31 043 840	22	0	2	436 652 910
21	1	15	12 195 840	22	0	4	425 720 592
21	1	17	2 523 136	22	0	6	397 523 244
21	2	1	84 410 652	22	0	8	351 882 012
21	2	3	80 378 644	22	0	10	290 939 112
21	2	5	70 656 232	22	0	12	220 234 368
21	2	7	55 667 048	22	0	14	148 427 264
21	2	9	37 570 156	22	0	16	85 409 792
21	2	11	20 009 792	22	0	18	39 157 760
21	2	13	7 305 472	22	0	20	12 582 912
21	2	15	1 519 616	22	0	22	2 097 152
21	2	17	229 376	22	1	0	400 227 104
21	3	1	38 909 728	22	1	2	397 781 700
21	3	3	35 760 316	22	1	4	379 212 168
21	3	5	29 228 730	22	1	6	340 662 228
21	3	7	20 095 300	22	1	8	282 688 492
21	3	9	10 596 240	22	1	10	211 235 208
21	3	11	3 811 424	22	1	12	136 813 952
21	3	13	844 032	22	1	14	71 900 160

Table 1. (continued)

n	m	x	C_n	n	m	x	C_n
22	1	16	26 968 064	22	5	2	15 127 260
22	1	18	5 308 416	22	5	4	10 975 552
22	2	0	244 754 636	22	5	6	6 232 252
22	2	2	242 510 726	22	5	8	2 453 176
22	2	4	224 391 788	22	5	10	614 264
22	2	6	190 920 158	22	5	12	70 016
22	2	8	144 965 148	22	5	14	10 240
22	2	10	93 836 296	22	6	0	3 917 948
22	2	12	47 746 304	22	6	2	3 749 266
22	2	14	16 677 888	22	6	4	2 456 952
22	2	16	3 375 104	22	6	6	1 122 754
22	2	18	491 520	22	6	8	318 264
22	3	0	116 463 256	22	6	10	60 224
22	3	2	114 802 760	22	6	12	1 792
22	3	4	101 535 728	22	7	0	690 472
22	3	6	79 497 616	22	7	2	651 248
22	3	8	52 140 820	22	7	4	377 264
22	3	10	26 197 808	22	7	6	137 696
22	3	12	9 020 160	22	7	8	24 172
22	3	14	1 897 472	22	7	10	2 304
22	3	16	49 152	22	8	0	75 264
22	4	0	46 059 700	22	8	2	67 488
22	4	2	45 173 048	22	8	4	33 432
22	4	4	37 325 552	22	8	6	9 240
22	4	6	25 383 932	22	8	8	876
22	4	8	13 223 184	22	9	0	2 936
22	4	10	4 963 712	22	9	2	2 820
22	4	12	1 021 824	22	9	4	1 200
22	4	14	135 680	22	9	6	268
22	5	0	15 628 640				

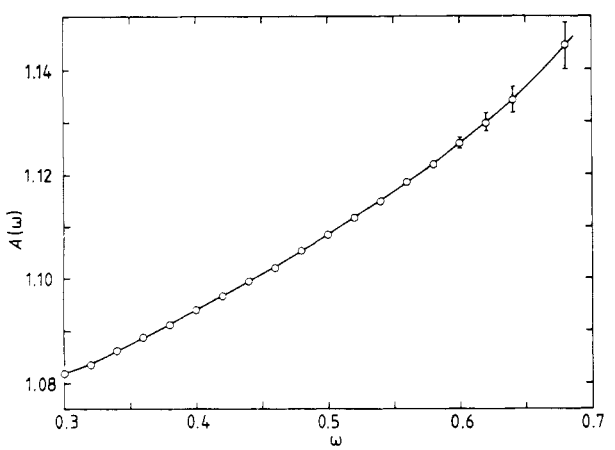

Figure 1. $A(\omega)$ as a function of ω for the TET lattice.

Table 2. Values of $\frac{1}{2}C_{22}(x, m)$ for $x \geq 0$ for the SQ lattice.

N	M	X	C_n	n	m	x	C_n
22	0	0	12 830 842	22	2	12	23 035 812
22	0	1	13 020 920	22	2	13	12 572 124
22	0	2	13 481 386	22	2	14	5 130 202
22	0	3	13 770 876	22	2	15	1 462 196
22	0	4	13 992 620	22	2	16	271 198
22	0	5	14 146 252	22	2	17	29 992
22	0	6	14 202 966	22	2	18	1 714
22	0	7	14 136 144	22	2	19	36
22	0	8	13 936 164	22	3	0	52 392 320
22	0	9	13 623 028	22	3	1	54 715 844
22	0	10	13 190 600	22	3	2	56 167 760
22	0	11	12 446 560	22	3	3	57 667 080
22	0	12	10 974 312	22	3	4	58 711 500
22	0	13	8 522 404	22	3	5	59 107 832
22	0	14	5 502 326	22	3	6	58 602 272
22	0	15	2 818 044	22	3	7	56 789 060
22	0	16	1 102 508	22	3	8	53 162 124
22	0	17	318 612	22	3	9	47 113 436
22	0	18	65 704	22	3	10	38 110 772
22	0	19	9 272	22	3	11	26 659 764
22	0	20	842	22	3	12	15 059 252
22	0	21	44	22	3	13	6 351 492
22	0	22	1	22	3	14	1 843 076
22	1	0	33 465 040	22	3	15	338 168
22	1	1	34 305 884	22	3	16	35 484
22	1	2	35 456 840	22	3	17	1 820
22	1	3	36 357 604	22	3	18	32
22	1	4	37 033 620	22	4	0	46 653 084
22	1	5	37 457 264	22	4	1	49 162 628
22	1	6	37 537 636	22	4	2	50 333 742
22	1	7	37 176 112	22	4	3	51 547 208
22	1	8	36 250 112	22	4	4	52 282 804
22	1	9	34 573 708	22	4	5	52 269 076
22	1	10	31 846 060	22	4	6	51 086 800
22	1	11	27 615 148	22	4	7	48 344 584
22	1	12	21 557 480	22	4	8	43 516 364
22	1	13	14 279 808	22	4	9	35 990 808
22	1	14	7 548 324	22	4	10	25 950 062
22	1	15	3 008 012	22	4	11	15 216 760
22	1	16	856 944	22	4	12	6 679 258
22	1	17	165 196	22	4	13	2 004 320
22	1	18	20 104	22	4	14	373 538
22	1	19	1 376	22	4	15	38 620
22	1	20	40	22	4	16	1 862
22	2	0	48 866 500	22	4	17	28
22	2	1	50 570 448	22	5	0	36 191 136
22	2	2	52 086 772	22	5	1	38 527 720
22	2	3	53 501 612	22	5	2	39 360 336
22	2	4	54 538 874	22	5	3	40 142 168
22	2	5	55 116 824	22	5	4	40 413 568
22	2	6	55 047 058	22	5	5	39 839 148
22	2	7	54 102 568	22	5	6	38 104 832
22	2	8	51 993 914	22	5	7	34 712 296
22	2	9	48 311 340	22	5	8	29 172 884
22	2	10	42 430 386	22	5	9	21 544 924
22	2	11	33 796 668	22	5	10	13 078 540

Table 2. (continued)

n	m	x	C_n	n	m	x	C_n
22	5	11	6 003 868	22	9	4	4 787 008
22	5	12	1 887 436	22	9	5	3 859 996
22	5	13	363 356	22	9	6	2 699 524
22	5	14	37 628	22	9	7	1 553 840
22	5	15	1 736	22	9	8	672 772
22	5	16	24	22	9	9	186 884
22	6	0	25 086 420	22	9	10	26 444
22	6	1	27 066 092	22	9	11	1 344
22	6	2	27 554 186	22	9	12	8
22	6	3	27 901 976	22	10	0	2 347 736
22	6	4	27 756 718	22	10	1	2 741 852
22	6	5	26 810 916	22	10	2	2 712 634
22	6	6	24 739 460	22	10	3	2 480 816
22	6	7	21 227 024	22	10	4	2 027 152
22	6	8	16 132 720	22	10	5	1 455 604
22	6	9	10 192 760	22	10	6	885 952
22	6	10	4 948 544	22	10	7	423 088
22	6	11	1 663 184	22	10	8	134 620
22	6	12	340 520	22	10	9	22 656
22	6	13	36 628	22	10	10	1 450
22	6	14	1 682	22	10	11	4
22	6	15	20	22	11	0	993 296
22	7	0	15 886 680	22	11	1	1 200 272
22	7	1	17 316 708	22	11	2	1 153 664
22	7	2	17 614 296	22	11	3	968 884
22	7	3	17 645 580	22	11	4	714 208
22	7	4	17 141 456	22	11	5	455 868
22	7	5	16 022 332	22	11	6	234 816
22	7	6	13 986 792	22	11	7	84 248
22	7	7	10 850 164	22	11	8	16 448
22	7	8	7 090 820	22	11	9	1 152
22	7	9	3 644 008	22	12	0	412 620
22	7	10	1 322 884	22	12	1	518 776
22	7	11	292 908	22	12	2	454 610
22	7	12	33 100	22	12	3	350 300
22	7	13	1 492	22	12	4	230 416
22	7	14	16	22	12	5	126 376
22	8	0	9 096 520	22	12	6	49 924
22	8	1	10 186 764	22	12	7	10 976
22	8	2	10 225 402	22	12	8	928
22	8	3	10 027 928	22	13	0	102 800
22	8	4	9 523 816	22	13	1	130 784
22	8	5	8 460 324	22	13	2	109 736
22	8	6	6 718 552	22	13	3	80 232
22	8	7	4 572 000	22	13	4	45 224
22	8	8	2 506 774	22	13	5	18 208
22	8	9	997 576	22	13	6	4 152
22	8	10	246 842	22	13	7	256
22	8	11	31 144	22	14	0	4 752
22	8	12	1 502	22	14	1	5 472
22	8	13	12	22	14	2	4 785
22	9	0	4 932 424	22	14	3	3 524
22	9	1	5 547 976	22	14	4	1 878
22	9	2	5 541 024	22	14	5	300
22	9	3	5 342 208				

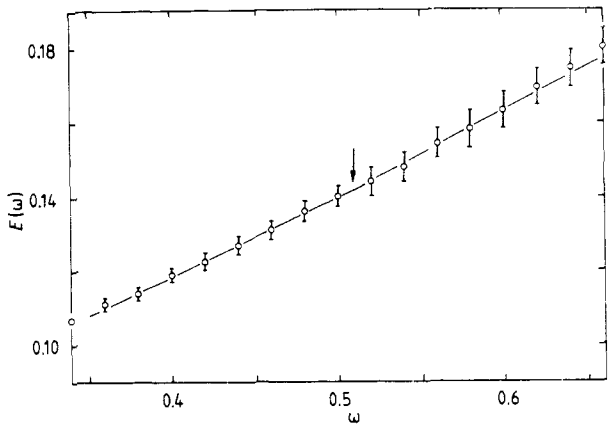

Figure 2. $E(\omega)$ as a function of ω for the TET lattice; the arrow indicates a point of discontinuous change in slope.

lattice; $E(\omega)$ increases almost linearly with ω. A slight but fairly distinct discontinuous change in the slope is noticed at $\omega = 0.51$. We regard it tentatively as the transition point, which will be confirmed in the next section.

A logarithmic correction term may be included in the θ-point quantities for $d = 3$ since the marginal dimension is three (see, e.g., Pfeuty and Toulouse 1978). The reduced free energy A^* around the θ-point is taken to be

$$A^* \sim \tau^q |\ln|\tau||^p \tag{6}$$

where $A^* = |A - A_0|/A_0$ (A_0 is A at $\omega = \omega_t$) and $\tau = (\omega - \omega_t)/\omega_t$. For exponent p, different values $p = 1$ (Moore 1977) and $p = \frac{3}{11}$ (de Gennes 1978) are proposed from renormalisation group calculations while $q = 2$ in both cases. Equation (6) turns out to be

$$q = \lim_{|\tau| \to 0} [\ln(A^*/|\ln|\tau||^p)/\ln|\tau|]. \tag{7}$$

We will estimate q by calculating $q_i = \ln(A_i^*/|\ln|\tau_i||^p)/\ln|\tau_i|$ for appropriate interval $|\tau_i|$ and extrapolating to $|\tau_i| \to 0$. The values of A_i^* and q_i for $p = 1$ and $\frac{3}{11}$ are given in table 3 for the TET lattice with the interval $\omega_i - \omega_{i-1} = 0.01$ in each case of $\tau_i > 0$ and

Table 3. Values of $q_i \equiv \ln(A_i^*/|\ln|\tau_i||^p)/\ln \tau_i$ ($i = 1$–8) for the TET lattice.

		$A_i^*(\times 10^2)$		$q_i(p=1)$		$q_i(p=\frac{3}{11})$	
i	$\lvert\tau_i\rvert$	$\tau_i > 0$	$\tau_i < 0$	$\tau_i > 0$	$\tau_i < 0$	$\tau_i > 0$	$\tau_i < 0$
1	0.0196	0.15	0.14	2.00	2.01	1.74	1.76
2	0.0392	0.31	0.28	2.15	2.18	1.89	1.92
3	0.0588	0.44	0.42	2.28	2.30	2.01	2.03
4	0.0784	0.61	0.57	2.37	2.40	2.10	2.13
5	0.0980	0.77	0.71	2.46	2.49	2.20	2.23
6	0.1176	0.92	0.84	2.55	2.59	2.29	2.33
7	0.1373	1.08	0.95	2.63	2.69	2.37	2.44
8	0.1569	1.26	1.10	2.69	2.77	2.45	2.53

$\tau_i < 0$. The plots of q_i against $|\tau_i|$ are shown in figure 3; we have

$$q = 1.90 \pm 0.10 \qquad \text{for } p = 1 \tag{8a}$$

and

$$q = 1.60 \pm 0.10 \qquad \text{for } p = \tfrac{3}{11} \tag{8b}$$

in both the cases of $\tau_i > 0$ and $\tau_i < 0$. The estimate (8*a*) is almost consistent with $q = 2$ (the second-order transition), which is also recognised from the dependence of $E(\omega)$ on ω in figure 2. Therefore, our numerical results, together with $q = 1$ for $d = 2$ (in I), are in favour of Moore's conjecture $q = 2/\varepsilon$ ($\varepsilon = 4 - d$); recently, this relation has been deduced by Douglas *et al* (1986) and Douglas (1987) from a scaling argument.

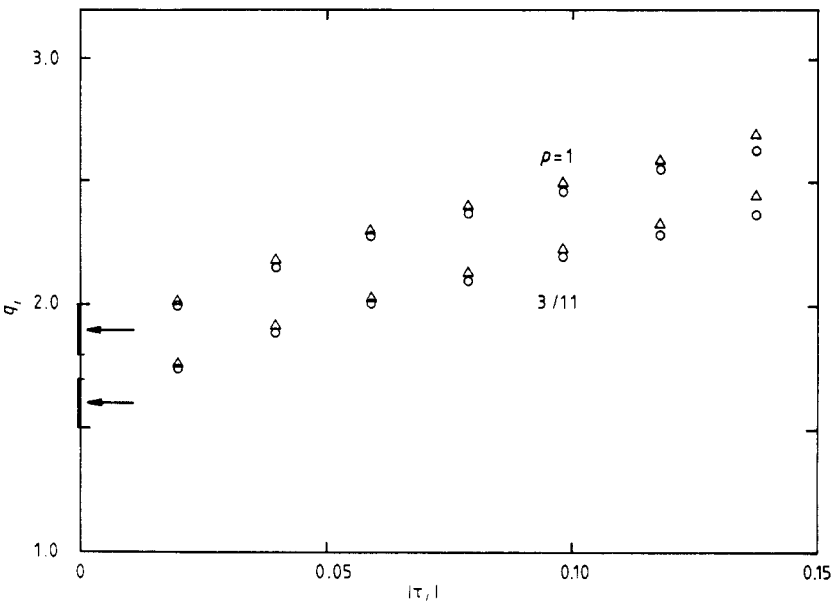

Figure 3. Estimation of q from plots of q_i against $|\tau_i|$ assuming $p = 1$ (upper) and $p = \frac{3}{11}$ (lower) for the TET lattice.

4. Estimation of ν and γ

The mean-square end-to-end distance for any given ω can be evaluated from

$$\langle R_n^2 \rangle = \mathrm{d}\left(\sum_m \sum_x x^2 C_n(x, m)\, \mathrm{e}^{m\omega} \right) (Z_n(\omega))^{-1} \tag{9}$$

by considering the spherical (and circular) symmetry of the distribution. We assume that

$$R_n(\omega) \equiv \langle R_n^2 \rangle^{1/2} \simeq R_0(\omega) n^{\nu(\omega)} \tag{10}$$

and form ratios

$$\nu_n = n(R_n / R_{n-2} - 1)/2. \tag{11}$$

Neville tables for linear, quadratic and cubic extrapolants

$$\nu_n^{(r)} = [n\nu_n^{(r-1)} - (n-2r)\nu_{n-2}^{(r-1)}]/2r \tag{12}$$

are constructed for $r = 1$-3, with $\nu_n^{(0)} \equiv \nu_n$. We then estimate $\nu(\omega)$ by plotting these extrapolants against $1/n$ and extrapolating to $n \to \infty$.

The values of ν thus obtained for the TET lattice are given in figure 4 as a function of ω for $0 \leqslant \omega \leqslant 0.9$; ν decreases from 0.592 ± 0.007 at $\omega = 0$ to 0.31 ± 0.06 at $\omega = 0.9$ taking the value $\nu = \frac{1}{2}$ around $\omega = 0.51$ as ω increases. No inflection point is noticeable in this case in contrast with the SQ lattice. We plot $\nu_n^{(1)}$ at $\omega = 0.51$ against $1/n$ in figure 5 in order to estimate ν_t. The value $\nu_t = 0.500 \pm 0.008$ is obtained, which shows an excellent agreement with the ideal chain value, that is, it confirms the transition point $\omega_t = 0.51$ for the TET lattice provided that $\nu_t = \frac{1}{2}$ whereas Kremer *et al* (1982) suggest $\omega_t = 0.44$ from a Monte Carlo technique. The corresponding plot for the SQ lattice yields $\nu_t = 0.508 \pm 0.008$ at the inflection point $\omega = 0.75$; it revises the previous result $\nu_t = 0.503 \pm 0.01$ based on the data for $n \leqslant 20$.

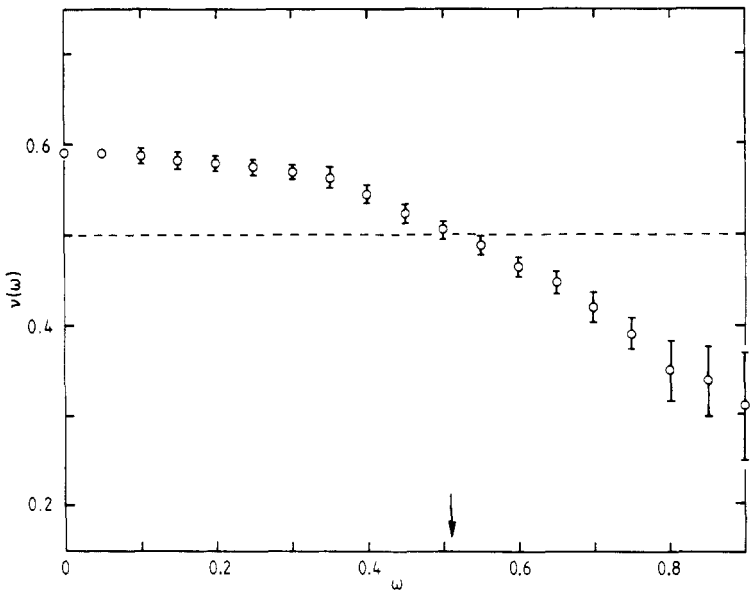

Figure 4. $\nu(\omega)$ as a function of ω for the TET lattice.

We estimate γ similarly as a function of ω using the values of μ obtained for each ω in the preceding section by forming

$$\gamma_n = n(\mu^{-2} Z_n / Z_{n-2} - 1)/2 + 1 \tag{13}$$

where Z_n is given by (1). Figure 6 shows the plots of γ against ω for the TET and SQ lattices; γ is nearly constant for small ω while it decreases abruptly for large ω as ω increases although error bars become larger there. The error bars were determined by considering also the accuracy of the estimation of $\mu(\omega)$. A few values selected from among Monte Carlo data given by Kremer *et al* (1982) are also shown in the figure for the sake of comparison. We estimate $\gamma_t = 1.00 \pm 0.03$ for $d = 3$ and $\gamma_t = 0.93 \pm 0.05$ for $d = 2$, the former being in good agreement with the ideal chain value

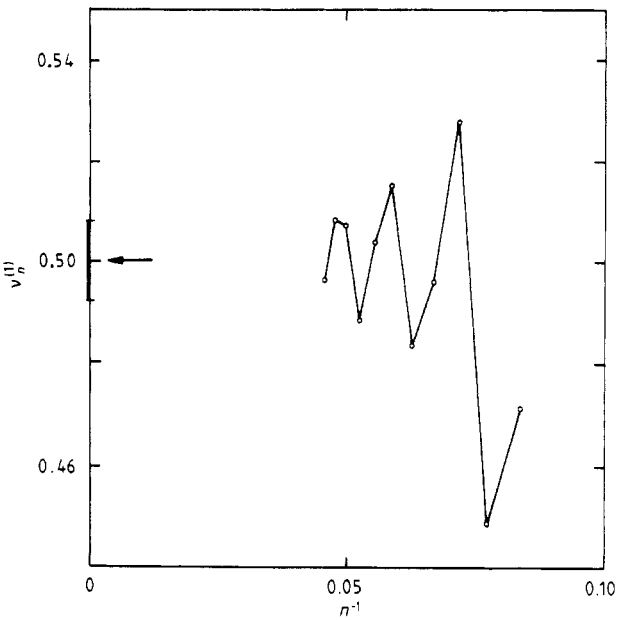

Figure 5. Estimation of ν at $\omega = 0.51$ for the TET lattice.

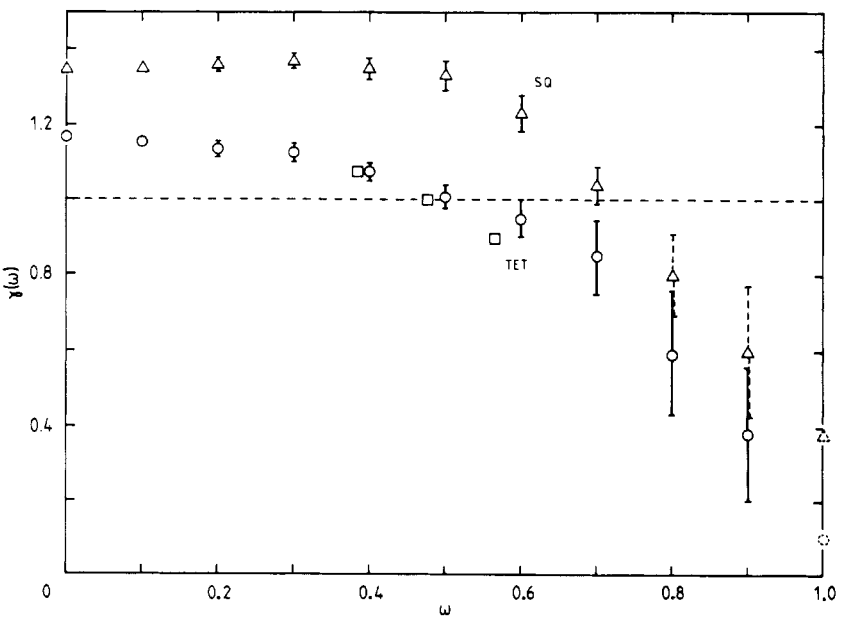

Figure 6. $\gamma(\omega)$ as a function of ω for the TET and SQ lattices. Monte Carlo values (□) are also given.

while the latter can be compared with the results $\gamma_t = 1.010$ of the ε expansion to the next-to-zeroth order (Stephen and McCauley 1973) and $\gamma_t = 1.025$ of the Monte Carlo calculation (Lyklema 1985) for the growing self-avoiding trail, which can be thought of as a model of the θ polymer. The relation $\gamma_t = 2(2 - \nu_t d)$ was proposed by Pietronero and Peliti (1985) using a generalised Flory approach; our values are consistent with it for $d = 3$, but far from it for $d = 2$.

5. End-distance distribution

We define the probability distribution function $P_n(x, \omega)$ for the x-component end-to-end distance at any given ω by

$$P_n(x, \omega) = (A/R_n(\omega)) \exp(|x_n|/R_n(\omega))^{\delta(\omega)} \tag{14}$$

for sufficiently large n in view of the spherical (circular) symmetry for $\omega = 0$ (Domb *et al* 1965, Wall and Hioe 1970). To estimate the exponent $\delta(\omega)$, we consider the reduced moment $m_{2k}^{(n)}$ of the distribution defined by

$$m_{2k}^{(n)} = \langle x_n^{2k} \rangle / \langle x_n^2 \rangle^k \tag{15}$$

where $\langle x_n^{2k} \rangle$ is the mean $2k$th power of $|x_n|$ for n-step walks. The reduced moment for (14) can be expressed in terms of gamma functions

$$m_{2k} = \frac{\Gamma((2k+1)/\delta)}{\Gamma(1/\delta)} \left(\frac{\Gamma(1/\delta)}{\Gamma(3/\delta)} \right)^k . \tag{16}$$

We evaluate $m_{2k}^{(n)}$ for $k = 2$–5 from our data for various values of ω and estimate the limiting values $m_{2k}^{(\infty)}$ by the use of the Neville table. Exponent δ is estimated for given ω as follows. First the table of m_{2k} for each k is constructed from (16) for appropriate values of δ. Then we compare this table with the values of estimated $m_{2k}^{(\infty)}$ to find a region of δ such that each value of $m_{2k}^{(\infty)}$ ($k = 2$–5) is contained in the corresponding region of m_{2k}; error limits are determined by taking account of estimated errors in $m_{2k}^{(\infty)}$. The values of δ thus obtained are shown in figure 7 as a function of ω for the TET and SQ lattices; δ decreases as ω increases in both cases, but the change is more eminent for the SQ lattice and it seems to converge to the Gaussian value $\delta = 2$ for large ω. We estimate the θ-point values

$$\delta_t = 2.06 \pm 0.04 \qquad \text{at } \omega = 0.51 \qquad \text{(TET)} \tag{17a}$$

and

$$\delta_t = 2.22 \pm 0.05 \qquad \text{at } \omega = 0.75 \qquad \text{(SQ)}. \tag{17b}$$

In table 4 we reproduce the values $m_{2k}^{(\infty)}$ ($k = 2$–5) estimated for the TET and SQ lattices at each θ-point and a point where δ is very close to $\delta = 2$; Gaussian values of $m_{2k}^{(\infty)}$ are also listed there for the sake of comparison. For the TET lattice the end-distance distribution is almost Gaussian at the θ-point ($\omega = 0.51$), but it is further close to the Gaussian behaviour at $\omega = 0.6$; this is consistent with Oono's indication (1976) that a chain is not Gaussian at the θ-point even when $\nu = \frac{1}{2}$. Martin (1984) also has demonstrated that the θ chain is always swollen relative to its unperturbed reference state. For the SQ lattice the chain at the θ-point is evidently not Gaussian and it seems that a point ($\omega = 1.0$) in a collapsed state yields the value of δ very close to 2.

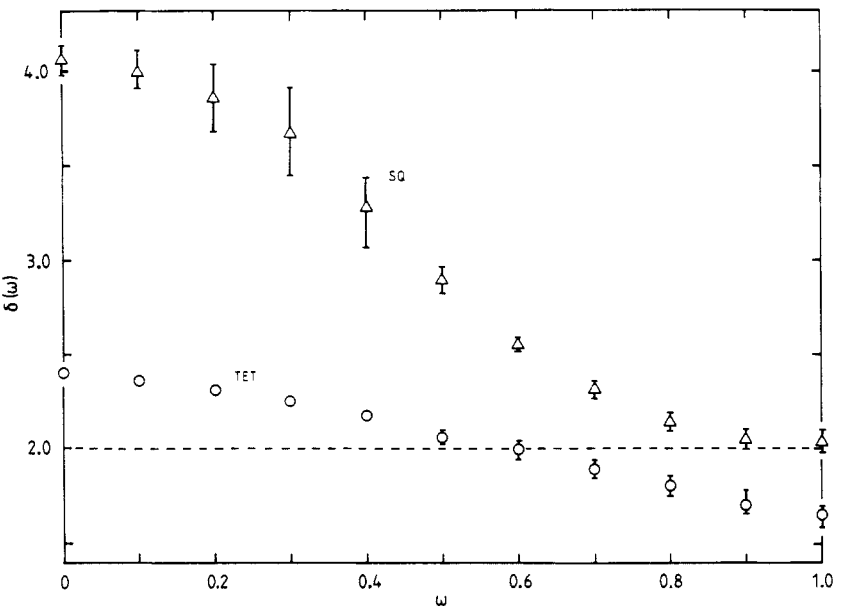

Figure 7. $\delta(\omega)$ as a function of ω for the TET and SQ lattices.

Table 4. Values of $m_{2k}^{(\infty)}(k=2\text{-}5)$ at some selected ω for the TET and SQ lattices.

ω	m_4	m_6	m_8	m_{10}
TET $0.51(\omega_t)$	2.94 ± 0.03	14.2 ± 0.4	93 ± 3	790 ± 40
0.6	3.02 ± 0.05	15.2 ± 0.6	105 ± 7	940 ± 50
SQ $0.75(\omega_t)$	2.81 ± 0.02	12.65 ± 0.10	77 ± 2	590 ± 30
1.0	2.93 ± 0.03	14.4 ± 0.4	100 ± 4	920 ± 50
Gaussian	3	15	105	945

6. Discussion and conclusion

For a chain in a very good solvent, exponents δ and ν are related through (Fisher 1966)

$$\delta = 1/(1-\nu). \tag{18}$$

We shall examine the validity of (18) when the solvent is changed toward poor using values of δ and ν estimated above. Figure 8 illustrates plots of $(1-\nu)\delta$ against ω for $0 \leqslant \omega \leqslant 1.0$; the scaling relation (18) holds for the good-solvent region of $\omega < \omega_t$ in both cases of the TET and SQ lattices. However, the plots deviate largely from (18) for $\omega > \omega_t$, i.e. (18) is untenable in the collapsed region although error bars enlarge there.

We have carried out exact enumerations of SAW with nearest-neighbour attractive interactions on the TET and SQ lattices to examine the θ-point. The following results have been obtained.

(i) The exponent q for the free energy is estimated as $q = 1.9\pm0.10$ for $d=3$ by assuming a logarithmic correction term, and $q=1$ for $d=2$. These results are, as a whole, reconciled with Moore's conjecture $q = 2/\varepsilon$ ($\varepsilon = 4\text{-}d$), i.e. the order of the collapse transition becomes first or second for a flexible chain depending on d.

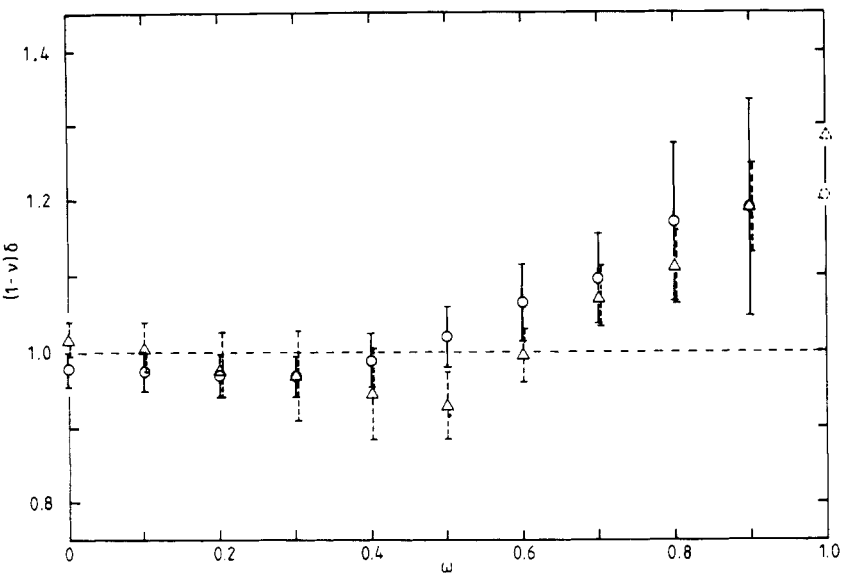

Figure 8. Examination of the relation $\delta = 1/(1-\nu)$ from estimated values of δ and ν.

(ii) The θ-point exponents ν_t and γ_t are in agreement with the ε expansion results by de Gennes-Stephen and Stephen and McCauley, respectively, for $d = 2$ while they are compatible with Gaussian values for $d = 3$.

(iii) The first attempt to estimate the ω dependence of exponent δ is done; δ_t is very close to the Gaussian value for $d = 3$ but still non-Gaussian. For $d = 2$ it deviates largely from the Gaussian value.

The values of ν_t, γ_t and δ_t estimated for $d = 2$ and 3 are listed in table 5.

Table 5. Values of critical exponents at the θ-point.

	$d = 3$(TET)	$d = 2$(SQ)
δ_t	2.06 ± 0.04	2.22 ± 0.05
ν_t	0.500 ± 0.008	0.508 ± 0.008
γ_t	1.00 ± 0.03	0.93 ± 0.05

Acknowledgment

I should like to thank S Miura for assistance with computational work.

References

Allegra G and Ganazzoli F 1983 *Macromol.* **16** 1311
—— 1985 *J. Chem. Phys.* **83** 397
Baumgärtner A 1980 *J. Chem. Phys.* **72** 871
—— 1982 *J. Physique* **43** 1407

Burch D J and Moore M A 1976 *J. Phys. A: Math. Gen.* **9** 435
de Gennes P G 1975 *J. Physique Lett.* **36** 55
—— 1978 *J. Physique Lett.* **39** 299
Derrida B and Saleur H 1985 *J. Phys. A: Math. Gen.* **18** L1075
DiMarzio E 1984 *Macromol.* **17** 969
Domb C 1974 *Polymer* **15** 259
Domb C, Gillis J and Wilmers G 1965 *Proc. Phys. Soc.* **85** 625
Douglas J F 1987 private communication
Douglas J F, Cherayil B J and Freed K F 1985 *Macromol.* **18** 2455
Douglas J F, Wang S Q and Freed K F 1986 *Macromol.* **19** 2207
Duplantier B 1980 *J. Physique Lett.* **41** 409
Duplantier B, Jannink G and des Cloizaux J 1986 *Phys. Rev. Lett.* **56** 2080
Edwards S F and Singh P 1979 *J. Chem. Soc. Faraday Trans.* II **75** 1001
Fisher M E 1966 *J. Chem. Phys.* **44** 616
Fisher M E and Hilley B 1961 *J. Chem. Phys.* **34** 1253
Fixman M and Mansfield M L 1984 *Macromol.* **17** 522
Ishinabe T 1985 *J. Phys. A: Math. Gen.* **18** 3181
Ishinabe T and Chikahisa Y 1986 *J. Chem. Phys.* **85** 1009
Kholodenko A L and Freed K F 1984a *J. Phys. A: Math. Gen.* **17** 2703
—— 1984b *J. Chem. Phys.* **80** 900
—— 1984c *J. Phys. A: Math. Gen.* **17** L191
Kolinski A, Skolnick J and Robert Y 1986 *J. Chem. Phys.* **85** 3585
Kremer K, Baumgärtner A and Binder K 1982 *J. Phys. A: Math. Gen.* **15** 2879
Lifshitz I M, Grosberg A Yu and Khokhlov A R 1978 *Rev. Mod. Phys.* **50** 683
Lyklema J W 1985 *J. Phys. A: Math. Gen.* **18** L617
Marqusee J A and Deutch J A 1981 *J. Chem. Phys.* **75** 5179
Martin J E 1984 *Macromol.* **17** 1263
McCrackin F L, Mazur J and Guttman C M 1973 *Macromol.* **6** 859
Moore M A 1977 *J. Phys. A: Math. Gen.* **10** 305
Muthukumar M 1984 *J. Chem. Phys.* **81** 6272
Oono Y 1976 *J. Phys. Soc. Japan* **41** 228
Oono Y and Freed K F 1981 *J. Chem. Phys.* **75** 993
Oyama T and Oono Y 1977 *J. Phys. Soc. Japan* **42** 1348
Pfeuty P and Toulouse G 1978 *Introduction to the Renormalization Group and to Critical Phenomena* (New York: Wiley)
Pietronero L and Peliti L 1985 *Phys. Rev. Lett.* **55** 1479
Privman V 1986 *J. Phys. A: Math. Gen.* **19** 3287
Ptitsyn O B and Eizner Yu Ye 1965 *Biophizika* **10** 3
Rapaport D C 1974 *Phys. Lett.* **48** 339
—— 1977 *J. Phys. A: Math. Gen.* **10** 637
Sanchez I C 1979 *Macromol.* **12** 980
Stephen M J 1975 *Phys. Lett.* **53A** 363
Stephen M J and McCauley J L 1973 *Phys. Lett.* **44A** 89
Tobochnik J, Webman I, Lebowitz J L and Kalos M H 1982 *Macromol.* **15** 549
Wall F T and Hioe F T 1970 *J. Phys. Chem.* **74** 4410
Webman I, Lebowitz J L and Kalos M H 1981 *Macromol.* **14** 1495