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Study of the θ point by enumeration of self-avoiding walks on the triangular lattice

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Abstract. We report series expansion analyses of the self-avoiding walks with nearest-neighbour bond interactions. The estimates $2\nu_t = 1.07 \pm 0.05$ and $\phi = 0.64 \pm 0.05$ for the correlation and crossover exponents at the θ point were obtained by examining the number of walks and the end-to-end distance data up to 16 steps on the triangular lattice.

1. Introduction

The collapse transition of linear polymers has been subject to numerous theoretical investigations: see a review in de Gennes' (1979) book (more recent literature will be cited below). Specifically, let us concentrate on the standard lattice model of this phenomenon. An N-step self-avoiding walk (SAW) connects $N+1$ lattice sites. Let B denote the number of nearest-neighbour pairs among these $N+1$ sites and assign a Boltzmann factor ε per pair. Usually, only an excess number of nearest-neighbour bonds, $B-N$, is counted (see, e.g., Baumgärtner 1982) and with

$$\varepsilon = \exp(-E/kT) \tag{1.1}$$

the energy E models repulsion ($E>0$, $0<\varepsilon<1$) or attraction ($E<0$, $\varepsilon>1$) at every contact of the chain with itself. However, we will not expand on the details of the interpretation: we assign a factor ε^B with $0<\varepsilon<\infty$.

For a given SAW, w, let $r(w)$ denote the end-to-end distance, $|w|$ denote the number of steps and $B(w)$ the number of nearest-neighbour pairs of sites as described above. Then we can form a weighted RMS end-to-end distance of N-step walks, $\langle R_N^2\rangle^{1/2}$, via

$$\langle R_N^2\rangle \equiv \left(\sum_{|w|=N} r^2(w)\varepsilon^{B(w)}\right)\left(\sum_{|w|=N} \varepsilon^{B(w)}\right)^{-1}. \tag{1.2}$$

For convenience, we will omit $\langle\ \rangle$ in the remainder of the paper.

It is generally believed that for large N,

$$R_N^2 \sim N^{2\nu} \tag{1.3}$$

where

$$\nu = \nu(\text{SAW}) \qquad \text{for } 0<\varepsilon<\varepsilon_t \tag{1.4}$$

$$\nu = \nu_t \qquad \text{at } \varepsilon = \varepsilon_t \tag{1.5}$$

$$\nu = 1/d \qquad \text{for } \varepsilon > \varepsilon_t. \tag{1.6}$$

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The range (1.4) corresponds to the 'excluded volume' regime of repulsion or weak attraction. The range (1.6) corresponds to a 'collapsed' strongly self-attracting chain. On the borderline (1.5), a special θ point growth exponent ν_t is expected. Near ε_t, a 'tricritical' scaling behaviour of R_N^2 is anticipated:

$$R_N^2 \approx N^{2\nu_t} F(\Delta\varepsilon N^{\phi}) \tag{1.7}$$

where $\Delta\varepsilon = \varepsilon - \varepsilon_t$.

Verification of the above 'maximal' set of theoretical predictions by approximation methods or numerical techniques encountered substantial difficulties. Let us mention first the issue of the nature of the collapsed phase. Several authors attempted to understand the properties of the most compact walks which dominate for $\varepsilon \gg \varepsilon_t$. Studies by Nagle (1974, 1985), Gujrati (1982) and Schmalz *et al* (1984) (see also references cited therein) indicate that the collapsed walks have a finite entropy (per step) and may have non-trivial properties which are not fully understood. Unfortunately, our series analysis study reported in the next two sections produces no useful results in the 'collapsed' regime.

In the θ regime, one is interested in validating the scaling relation (1.7) and estimating ν_t and ϕ. In three dimensions, scaling behaviours are complicated by logarithmic corrections since $d = 3$ is the upper critical dimensionality for 'tricriticality': for numerical work see Rapaport (1974, 1977), Webman *et al* (1981), Kremer *et al* (1982), Bishop and Michels (1986) and references therein. However, we consider the two-dimensional θ point model here. ε expansions to the next-to-zeroth order by Stephen and McCauley (1973) and Stephen (1975) gave

$$2\nu_t \simeq 1.01 \qquad \phi \simeq 0.636 \tag{1.8}$$

in $d = 2$. Kholodenko and Freed (1984) arrived at a different result, namely

$$2\nu_t \simeq 1.10. \tag{1.9}$$

Ishinabe (1985) estimated

$$2\nu_t \simeq 1.006 \pm 0.02 \tag{1.10}$$

by series analysis of the square lattice endpoint distribution data. However, Derrida and Saleur (1985) proposed

$$2\nu_t \simeq 1.10 \pm 0.02 \tag{1.11}$$

from finite-size scaling studies of lattice strips. Monte Carlo work by Tobochnik *et al* (1982) and Baumgärtner (1982) did not lead to definitive exponent estimates. Baumgärtner (1982) reports consistency with the scaling form (1.7) provided exponent values (1.8) are used.

Our study was motivated in part by the above uncertainty in the θ point exponent values. In §§ 2 and 3, we report series analyses leading to

$$2\nu_t = 1.07 \pm 0.05 \qquad \phi = 0.64 \pm 0.05. \tag{1.12}$$

However, it should be pointed out that the experimental ν value of Vilanove and Rondelez (1980) for $d = 2$ linear polymers which are *probably* in a semi-collapsed state is

$$2\nu = 1.12 \pm 0.02. \tag{1.13}$$

Furthermore, Coniglio *et al* (1985) recently advanced some non-rigorous arguments for ν_t being equal to ν(IGSAW). The value of the latter exponent is

$$2\nu(\text{IGSAW}) = 1.134 \pm 0.006 \tag{1.14}$$

according to Kremer and Lyklema (1985). Finally, note that some further concluding discussion may be found in § 3.

2. Triangular lattice series

We describe here the derivation of the series and also analyses of the global features of the data. The calculation involved a computer enumeration of the number, $c(N, B)$, and the sum of the squared end-to-end distances, $s(N, B)$, of all N-step SAW having exactly B nearest-neighbour pairs. Relation (1.2) reduces to

$$R_N^2 \equiv \left(\sum_B s(n, B)\varepsilon^B\right)\left(\sum_B c(N, B)\varepsilon^B\right)^{-1}. \tag{2.1}$$

The values of $c(N, B)$ and $s(N, B)$ for $N \leqslant 16$ are listed in table 1 for the triangular lattice. We have similar data for $N \leqslant 21$ for the square lattice (not reported here, but available upon request). However, due to the usual strong even–odd oscillations in various estimates, we found the square lattice data of this length unsuitable for an unambiguous analysis. While our work was in progress, we learned that Ishinabe (1985) enumerated a related distribution of the end-to-end distances, to order $N = 20$, on the square lattice. His ν_t estimate (1.10) is reasonably consistent with (1.8) and (1.12). Let us focus on the triangular lattice data from now on.

We form effective exponent estimates:

$$2\nu(N) = \ln(R_N^2/R_{N-1}^2)/\ln(N/N-1). \tag{2.2}$$

These are plotted for $0 < \varepsilon < 4$ in figure 1. The curves for $N = 13, 14, 15, 16$ are very close. However, in figure 2, we plotted the deviations from the average:

$$\Delta\nu(N) = \nu(N) - \tfrac{1}{4}\sum_{K=13}^{16} \nu(K) \tag{2.3}$$

for $0 < \varepsilon < 3$. For $\varepsilon \leqslant 1$, the effective exponent values are close to

$$2\nu(\text{SAW}) = 1.5 \tag{2.4}$$

which value is believed to be exact (Nienhuis 1982). There are two intersection regions of the $2\nu(N)$ curves: at $\varepsilon \simeq 0.9$ and slightly below 1.5. We will discuss the intersections in detail in a moment. For $\varepsilon \geqslant 1.7$, one would anticipate some manifestation of the 'collapsed' behaviour. However, the $2\nu(N)$ curves show no trend towards $2\nu = 2/d = 1$ (this includes $\varepsilon > 4$, not shown in figure 1). Furthermore, the values of $2\nu < 1$ are unphysical since asymptotically they would imply an infinite density. Thus, the $N \leqslant 16$ data are far from the regime of the asymptotic simple power-law behaviour (1.3) with (1.6). The same is true for the $N \leqslant 21$ square lattice data, in the 'collapsed' regime (see also Ishinabe 1985).

Since $\nu(\text{SAW}) > \nu_t > 1/d$, the $N \to \infty$ limit of the $\nu(N)$ in (2.2) is, ideally, a step function. The curves in figure 1 indeed resemble a rounded step, at least for $\varepsilon < 2.3$. It is well known that the intersections of the finite-N curves approximate ν_t and ε_t. If relation (1.7) were exact, the $\nu(N)$ would intersect *at* (ε_t, ν_t). However, (1.7) is

Table 1. The values of $c(N, B)$ and $s(N, B)$ for the triangular lattice (definitions are given in the first paragraph of § 2).

N	B	$c(N, B)/6$	$s(N, B)/6$
1	1	1	1
2	2	3	10
2	3	2	2
3	3	9	59
3	4	8	28
3	5	6	10
4	4	27	280
4	5	32	218
4	6	24	110
4	7	20	46
5	5	79	1 179
5	6	122	1 282
5	7	108	874
5	8	76	440
5	9	70	202
6	6	233	4 614
6	7	422	6 416
6	8	470	5 472
6	9	366	3 512
6	10	264	1 778
6	11	216	798
6	12	20	34
7	7	679	17 145
7	8	1 458	29 148
7	9	1 766	29 356
7	10	1 746	22 666
7	11	1 322	14 274
7	12	848	6 756
7	13	672	3 068
7	14	156	408
8	8	1 983	61 398
8	9	4 824	123 198
8	10	6 758	143 892
8	11	6 902	126 198
8	12	6 536	93 608
8	13	4 642	55 602
8	14	2 760	25 336
8	15	2 060	11 912
8	16	890	2 938
9	9	5 759	213 705
9	10	15 824	494 610
9	11	24 290	654 390
9	12	28 310	648 270
9	13	26 898	533 360
9	14	23 400	371 234
9	15	16 478	213 284
9	16	9 000	96 004
9	17	6 808	48 080
9	18	3 532	14 724
9	19	390	1 078
10	10	16 717	727 506
10	11	50 898	1 907 224
10	12	86 396	2 820456

Table 1. (continued)

N	B	$c(N,B)/6$	$s(N,B)/6$
10	13	107 900	3 092 612
10	14	114 940	2 823 622
10	15	101 628	2 170 648
10	16	82 360	1 438 478
10	17	58 074	814 108
10	18	31 770	380 694
10	19	22 100	187 298
10	20	12 606	65 282
10	21	3 472	12 720
11	11	48 387	2 432 583
11	12	162 158	7 124 122
11	13	299 210	11 637 124
11	14	406 820	13 996 112
11	15	457 252	13 912 864
11	16	448 830	11 812 076
11	17	376 962	8 609 946
11	18	288 266	5 504 916
11	19	205 522	3 155 826
11	20	116 108	1 512 224
11	21	71 966	714 902
11	22	42 944	281 012
11	23	19 414	86 854
11	24	984	3 296
12	12	139 897	8 014 812
12	13	510 966	25 930 666
12	14	1 021 548	46 357 226
12	15	1 489 314	60 608 222
12	16	1 796 284	65 162 520
12	17	1 857 536	59 881 630
12	18	1 708 278	47 958 262
12	19	1 377 572	33 571 350
12	20	1 024 262	21 207 402
12	21	720 920	12 190 756
12	22	428 574	5 967 984
12	23	239 660	2 757 352
12	24	150 838	1 211 560
12	25	78 336	427 044
12	26	15 216	63 454
13	13	403 771	26 082 721
13	14	1 597 412	92 378 774
13	15	3 435 010	179 367 758
13	16	5 359 986	253 158 606
13	17	6 855 400	292 266 230
13	18	7 555 808	288 770 016
13	19	7 318 950	249 227 882
13	20	6 385 058	190 558 434
13	21	5 025 528	130 606 314
13	22	3 666 222	81 666 880
13	23	2 524 966	46 790 946
13	24	1 555 802	23 432 180
13	25	861 174	11 046 444
13	26	516 332	4 963 332
13	27	286 056	1 902 572
13	28	103 164	523 272
13	29	5 142	21 026

Table 1. (continued)

N	B	$c(N, B)/6$	$s(N, B)/6$
14	14	1 164 057	83 994 856
14	15	4 957 204	323 205 792
14	16	11 413 472	677 195 416
14	17	18 960 690	1 025 865 544
14	18	25 681 992	1 264 787 622
14	19	29 875 510	1 333 923 906
14	20	30 682 280	1 232 690 046
14	21	28 185 274	1 011 553 284
14	22	23 711 714	750 394 112
14	23	18 301 294	506 326 906
14	24	13 140 314	313 400 192
14	25	8 899 388	179 106 248
14	26	5 597 540	92 487 766
14	27	3 193 382	44 486 780
14	28	1 786 220	19 951 430
14	29	1 007 908	8 226 906
14	30	495 932	2 983 856
14	31	77 704	382 760
15	15	3 351 801	268 058 345
15	16	15 289 564	1 113 468 250
15	17	37 520 218	2 503 765 484
15	18	66 121 822	4 050 807 564
15	19	94 507 440	5 309 582 442
15	20	115 778 668	5 945 584 376
15	21	125 093 030	5 841 698 720
15	22	121 351 606	5 114 269 874
15	23	107 169 414	4 047 955 194
15	24	87 694 004	2 935 087 140
15	25	66 494 840	1 953 540 554
15	26	47 101 304	1 199 211 312
15	27	31 745 210	689 498 134
15	28	20 026 096	363 448 246
15	29	11 808 450	178 109 300
15	30	6 421 932	80 982 364
15	31	3 579 698	35 048 326
15	32	1 949 932	13 991 636
15	33	587 184	3 405 708
15	34	35 384	173 532
16	16	9 641 893	848 778 926
16	17	46 899 988	3 785 135 088
16	18	122 202 704	9 091 075 422
16	19	227 692 466	15 642 072 152
16	20	342 473 560	21 712 426 778
16	21	440 443 600	25 705 217 072
16	22	499 333 190	26 713 469 364
16	23	508 231 584	24 784 985 438
16	24	471 901 204	20 830 892 272
16	25	404 056 292	16 036 287 726
16	26	323 099 256	11 408 053 556
16	27	241 147 298	7 504 464 182
16	28	169 487 916	4 598 991 504
16	29	113 922 336	2 658 209 098
16	30	71 780 088	1 420 524 978
16	31	43 086 988	709 751 386

Table 1. (continued)

N	B	$c(N, B)/6$	$s(N, B)/6$
16	32	23 985 674	333 080 874
16	33	12 803 518	145 981 378
16	34	7 139 838	61 304 358
16	35	3 043 860	20 594 620
16	36	515 134	2 974 792

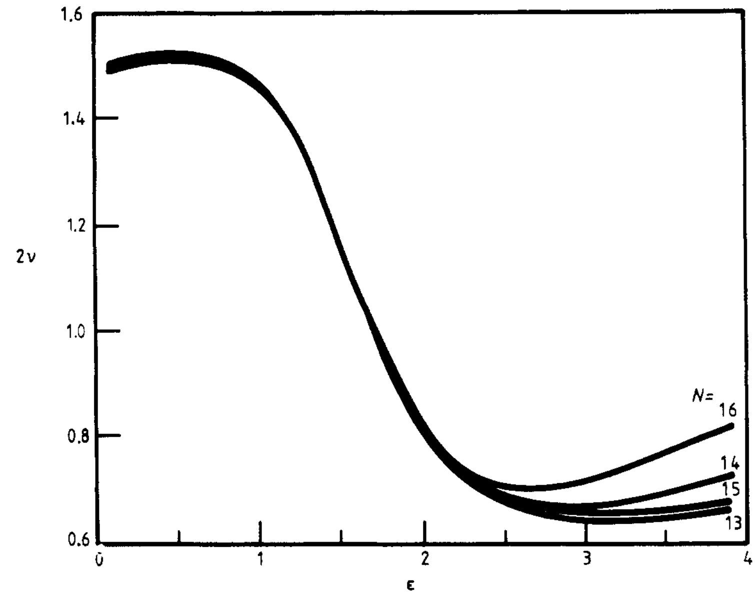

Figure 1. Effective 2ν estimates as functions of ε for $N = 13, \ldots, 16$ (see relation (2.2)).

only approximate for finite N. A natural interpretation is to identify the intersection region at $\varepsilon > 1$ with the centre of the θ region. Thus

$$\varepsilon_t \simeq 1.5(\pm 0.1) \tag{2.5}$$

for the triangular lattice. The appropriate intersection points of $\nu(N)$ with $\nu(N-1)$ are listed in table 2, for $N = 8, 9, \ldots, 16$. The sequences of this sort are frequently used in ratio-type series analyses and in phenomenological renormalisation calculations. In the present case, however, the behaviour is not regular so that the conventional extrapolation methods cannot be employed. We will devise an appropriate procedure in § 3, to accurately estimate ν_t (and also ϕ).

Intersections at $\varepsilon < 1$ occur well within the self-avoiding regime, at least for $N \leq 16$. A possible interpretation is that one or several correction-to-scaling terms change sign at $\varepsilon \simeq 0.9$. There is an ambiguity, however, because the 2ν coordinates of the intersection points, listed in table 2, drift monotonically *away* from the conjectured exact value (2.4) $2\nu = 1.5$, as N increases. At $\varepsilon \equiv 1$, for ordinary SAW, elaborate series analyses (Djordjevic *et al* 1983, Privman 1984) of the triangular lattice data, with allowance for corrections to scaling, found no inconsistency with $2\nu \equiv 1.5$. We conclude that the intersection region at $\varepsilon \simeq 0.9$ *may* be an artificial feature. It may disappear

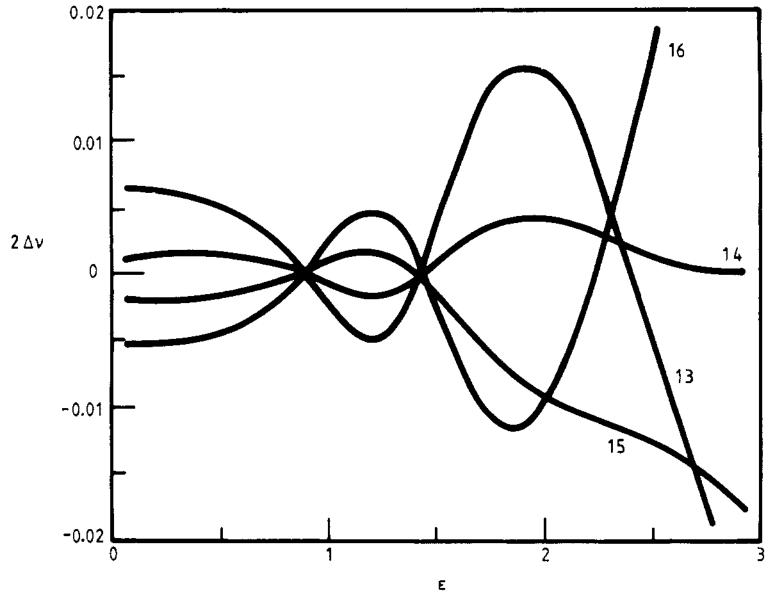

Figure 2. Deviations $2\Delta\nu$ (defined by (2.3)) as functions of ε for $N = 13, \ldots, 16$.

Table 2. $(\varepsilon, 2\nu)$ coordinates at the intersections of $\nu(N)$ and $\nu(N-1)$ curves (defined by relation (2.2)).

N	ε	2ν	ε	2ν
8	1.299 979	1.310 288	0.799 248	1.510 766
9	1.255 858	1.333 753	0.824 721	1.505 114
10	1.503 892	1.180 515	0.851 098	1.499 420
11	1.345 913	1.283 589	0.865 564	1.496 375
12	1.378 098	1.262 038	0.876 563	1.494 153
13	1.449 901	1.209 753	0.884 996	1.492 527
14	1.416 490	1.235 155	0.890 724	1.491 476
15	1.438 220	1.218 080	0.895 131	1.490 711
16	1.469 684	1.192 091	0.898 298	1.490 191

or drift into the θ region for higher N values: further numerical studies are needed to clarify this issue. Let us point out that previous studies in $d = 2$ (Baumgärtner 1982, Derrida and Saleur 1985, Ishinabe 1985) explored only the region $\varepsilon > 1$, corresponding to negative energy E in (1.1).

3. θ point exponents

The 2ν sequence corresponding to $\varepsilon > 1$ in table 2 is rather irregular. The overall trend is toward 2ν values below 1.2. However, the oscillations show no definite pattern. By the well known principle, since we cannot 'beat' the irregularities by conventional extrapolation techniques, let us 'join' them! We adopt the strategy of calculating a very large number of approximants to $2\nu_t$, with an expectation that what was an irregularity in a particular sequence will become a spread in the values of 2ν. Thus we generalise (2.2) to

$$2\nu(N, k) = \ln(R_N^2/R_{N-k}^2)/\ln(N/N-k). \tag{3.1}$$

We then calculate the 2ν coordinate of the appropriate intersection point (if it exists) of $2\nu(N, k)$ with $2\nu(N', k')$, for *all* possible combinations of different (N, k) pairs with N', $N = 12, \ldots, 16$ and k', $k = 1, \ldots, 4$. In figure 3 more than 200 such points are plotted against $1/N_{\text{eff}}$, where

$$N_{\text{eff}} \equiv \tfrac{1}{2}(N + N'). \tag{3.2}$$

This choice is the simplest symmetric combination. We use N, but not k, in (3.2) because empirically the $2\nu(N, k)$ curves are much less sensitive to k than to N, provided $k \ll N$.

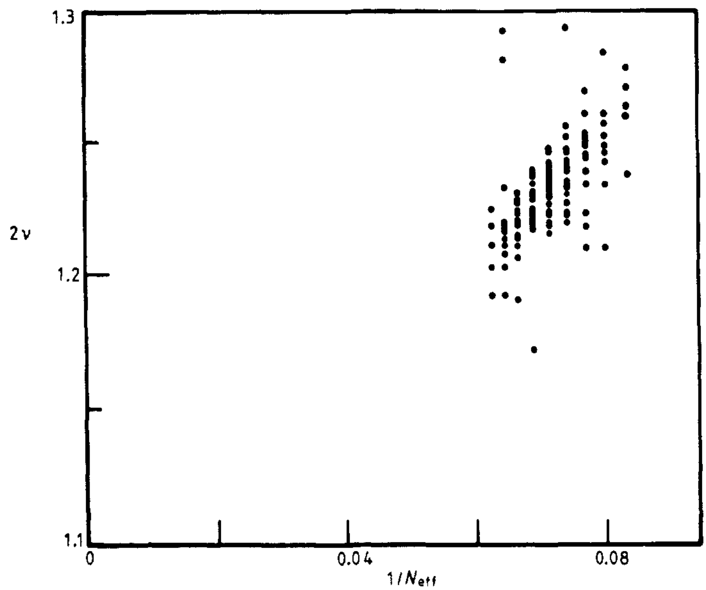

Figure 3. Estimates of $2\nu_t$ against $1/N_{\text{eff}}$ defined in § 3.

Figure 3 is rather difficult to read in detail because the points are very close. However, we examined a considerably enlarged version of it; we located the most populated range of 2ν for each $1/N_{\text{eff}}$ value and extrapolated linearly to $1/N_{\text{eff}} = 0$. We propose

$$2\nu_t = 1.07 \pm 0.05. \tag{3.3}$$

In order to estimate the crossover exponent ϕ in (1.7), we consider the derivative $\partial R_N^2/\partial\varepsilon$ which obeys the scaling law

$$\partial R_N^2/\partial\varepsilon \approx N^{2\nu_t+\phi} G(\Delta\varepsilon N^{\phi}). \tag{3.4}$$

Since, by all the estimates described in § 1, $2\nu_t + \phi > 1.6$, the effective exponent values defined in analogy with (3.1) now approximate not a rounded step, but a rounded non-symmetric peak. This expectation is, indeed, confirmed by plotting several $(2\nu_t + \phi)(N, k)$ against ε curves. (This plot is not presented here.) However, these peaked effective exponent curves, for different (N, k), typically do not intersect for $N \leqslant 16$ and when they do, regarding the intersection coordinates as an approximation to $2\nu_t + \phi$ is ambiguous. In view of the above, we used the intersection points of $\nu(N, k)$, the same as in figure 3. At the ε value of the intersection of $\nu(N, k)$ with $\nu(N', k')$, where now $N \geqslant N'$ is imposed, we calculated

$$\ln\left(\frac{\partial R_N^2/\partial\varepsilon}{\partial R_{N-k}^2/\partial\varepsilon}\right)\left[\ln\left(\frac{N}{N-k}\right)\right]^{-1} - 2\nu(N, k) \tag{3.5}$$

which approximates the exponent ϕ. Here $N \geqslant N'$ is needed explicitly since we preferred to use non-symmetric approximants giving more weight to less truncated series. The resulting ϕ values are plotted against $1/N_{\text{eff}}$ in figure 4. As with $2\nu_t$, we actually used an enlarged version to extrapolate towards $1/N_{\text{eff}} = 0$: we get

$$\phi = 0.64 \pm 0.05. \tag{3.6}$$

In summary, we have demonstrated that series enumerations can be used to study the θ point phenomena. Our results are conclusive in the SAW and θ regimes, confirming the 'tricritical' theoretical picture (de Gennes 1979). We reported the first numerical estimation of the exponent ϕ in $d = 2$. Our $2\nu_t$ and ϕ ranges are close to the ε expansion values. The $2\nu_t$ estimate is consistent with those of Ishinabe (1985) and Derrida and Saleur (1985).

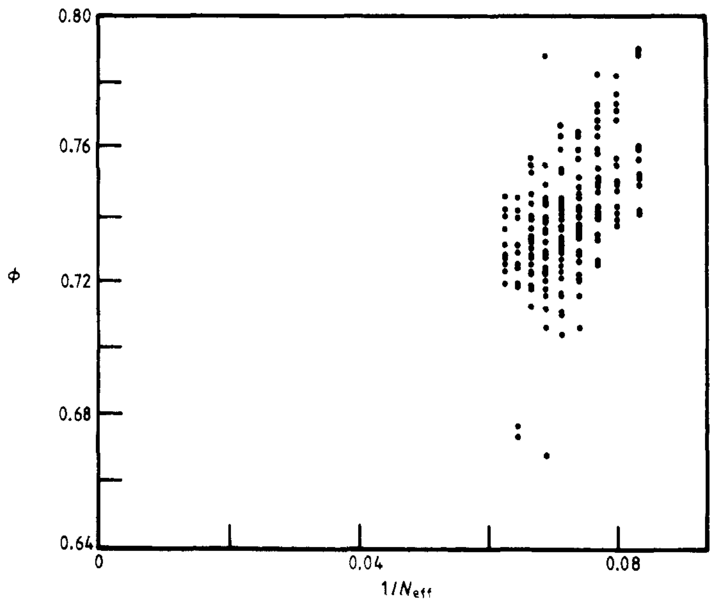

Figure 4. Estimates of ϕ against $1/N_{\text{eff}}$, see (3.5).

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References

Baumgärtner A 1982 *J. Physique* **43** 1407-11
Bishop M and Michels J P J 1986 *J. Chem. Phys.* in press
Coniglio A, Jan N, Majid I and Stanley H E 1985 *Preprint*
de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
Derrida B and Saleur H 1985 *J. Phys. A: Math. Gen.* **18** L1075-9
Djordjevic Z V, Majid I, Stanley H E and dos Santos R J 1983 *J. Phys. A: Math. Gen.* **16** L519-23
Gujrati P D 1982 *J. Stat. Phys.* **28** 441-72
Ishinabe T 1985 *J. Phys. A: Math. Gen.* **18** 3181-7
Kholodenko A L and Freed K F 1984 *J. Chem. Phys.* **80** 900-24
Kremer K, Baumgärtner A and Binder K 1982 *J. Phys. A: Math. Gen.* **15** 2879-97
Kremer K and Lyklema J W 1985 *J. Phys. A: Math. Gen.* **18** 1515-31
Nagle J F 1974 *Proc. R. Soc.* A **337** 569-89
—— 1985 *J. Stat. Phys.* **38** 531-40
Nienhuis B 1982 *Phys. Rev. Lett.* **49** 1062-5
Privman V 1984 *Physica* **123A** 428-42
Rapaport D C 1974 *Phys. Lett.* **48A** 339-40
—— 1977 *J. Phys. A: Math. Gen.* **10** 637-47
Schmalz T G, Hite G E and Klein D J 1984 *J. Phys. A: Math. Gen.* **17** 445-53
Stephen M J 1975 *Phys. Lett.* **53A** 363-4
Stephen M J and McCauley J L 1973 *Phys. Lett.* **44A** 89-90
Tobochnik J, Webman I, Lebowitz J L and Kalos M H 1982 *Macromol.* **15** 549-53
Vilanove R and Rondelez F 1980 *Phys. Rev. Lett.* **45** 1502-4
Webman I, Lebowitz J L and Kalos M H 1981 *Macromol.* **14** 1495-501