Location of the Adsorption Transition for Polymers with Excluded Volume

Monte Carlo and Enumeration Results

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The temperature dependence of the limiting reduced free energy per step for self-avoiding walks on the cubic and face centred cubic lattices, interacting with a plane (square lattice) surface, is studied by exact enumeration and extrapolation techniques as well as by Monte Carlo methods. These data, together with the locations of the zeros of the partition functions, are used to estimate the locations of the adsorption transitions.

The problem of excluded volume effects in the adsorption of a polymer molecule at an interface [1, 2] has attracted a considerable amount of attention. Most recent work has been of a numerical nature and both Monte Carlo [3-6] and exact enumeration and extrapolation [7-16] approaches have been used. In addition, a few rigorous results on the existence of limits [14] and on bounds on the partition function [14, 16] have appeared. The model which has been used for most of this work is a self-avoiding walk on a lattice, terminally attached to a plane which represents the interface, confined to lie in, or on one side of, this plane and interacting with the plane via a short range attractive or repulsive potential. (There have also been some modifications and extensions in which the walk is not necessarily terminally attached to the interface [5, 16] and in which solvent effects are included in various ways.[5-7])

Some of the general features of the behaviour are now fairly clear. For a repulsive potential, the limiting value of the partition function per step is independent of temperature while, for an attractive potential, there is a phase transition at which adsorption begins to occur.[14] The location of the phase transition is lattice dependent and has been examined by Padé and other methods.[15, 16] However, these estimates are based on extrapolation of exact enumeration data for short walks and rely on the form chosen for the extrapolating function. There are a few rigorous results [14, 16] which give some guidance as to an appropriate function but it would be useful to have some independent estimate of the large n behaviour. This paper is concerned with obtaining Monte Carlo data on this problem for two lattices. One, the simple cubic lattice with the interface represented by a square lattice, has already been studied by exact enumeration for walks of up to thirteen edges.[15, 16] The second is the face centred cubic lattice, again with the surface represented by a square lattice, which we refer to as f.c.c.sq. We have extended the series on this lattice to $n = 9$. If the extrapolations based on enumeration data for $n \lesssim 10$ and on Monte Carlo data for $n \lesssim 100$ agree, our confidence in the overall results would be enhanced. In addition, the zeros of the partition function from enumeration data have proved useful in estimating the location of the transition. Monte Carlo estimates of the zeros for longer walks have been obtained which allow more precise estimates to be made by this approach.

MONTE CARLO APPROACH

The Monte Carlo scheme used in this work was based on a method proposed by Hammersley and Morton [17] and by Rosenbluth and Rosenbluth,[18] and later extended by Mazur, McCrackin and others.[19-21] The advantages of this method are that it partially compensates for the sample attrition inherent in all "walk growing" schemes for self-avoiding walks and it is easily modified to incorporate a form of importance sampling necessary when the walk interacts strongly with the interface.

We are concerned with self-avoiding walks on a regular lattice beginning at the origin and confined to the half space defined by the plane $z = 0$. The potential function for interaction with the interface is chosen so that a walk with m vertices in the interfacial plane has energy $m\varepsilon$ and corresponding Boltzmann factor $\lambda^m \equiv \exp(-m\varepsilon/kT)$. The partition function for walks with n steps will be

$$Z_n(\lambda) = \sum_{m=1}^{n+1} (n, m)_s \lambda^m \tag{1}$$

where $(n, m)_s$ is the number of n-step walks, with a vertex of unit degree at the origin, no vertices with negative z-coordinate and a total of m vertices having zero z-coordinate. We shall be concerned with the regime $\lambda \geqslant 1$, *i.e.*, either no interaction or an attractive interaction with the interface.

Clearly, as λ becomes larger, coefficients $(n, m)_s$ with large m will become increasingly important in determining the value of $Z_n(\lambda)$. When n is large as well, however, these walks with a large number of vertices in the adsorbing plane form a very small fraction of the total number of walks; to estimate their number accurately we have used the following biased Monte Carlo sampling procedure.

A sample of N walks with n steps was obtained by growing the walks step by step. Suppose that at the addition of the jth step in the kth walk a_{jk} different step vectors can be added without passing through the interface or intersecting the previous part of the walk. Instead of choosing the next step of the walk from among these a_{jk} possibilities with uniform probability the step vector to be added is chosen with probability

$$p_i = b_i \Big/ \sum_{j=1}^{a_{jk}} b_j \tag{2}$$

where $b_i = \lambda$ or 1 depending on whether the new vertex is in or out of the interfacial plane.

The step weight w_{jk} is the reciprocal of the probability for the step chosen and the n-step walk (with m vertices in the plane $z = 0$) so generated contributes to the estimate of $(n, m)_s$ with a weight equal to the product of the individual step weights. An unbiased estimate of the partition function is then given by

$$\hat{Z}_n(\lambda) = N^{-1} \sum_{k=1}^{N} \lambda^{m_k} \prod_{j=1}^{n} w_{jk} \tag{3}$$

where m_k is the number of vertices in the interface for the kth walk in the sample.

EXACT ENUMERATIONS

We consider the number (per site of the square lattice) of simple chains, with a total of n edges, having m vertices in the plane $z = 0$, $(n, m)_c$, and the corresponding number which are terminally attached, *i.e.*, have at least one vertex of unit degree in $z = 0$, $(n, m)_s$. For the cubic lattice some entries in the appropriate tables have

been given elsewhere.[14, 16, 22] For the f.c.c.sq. the terminally attached chains were previously enumerated for $n \leqslant 7$, though the detailed results were not reported. We have added two extra terms ($n = 8$ and 9) and the complete results are given in table 1. In addition we have obtained exact values of $(n, m)_c$ for $n \leqslant 9$. These results are given in table 2.

TABLE 1.—VALUES OF $(n, m)_s$ FOR THE f.c.c.sq. LATTICE

$n\backslash m$	1	2	3	4	5	6	7	8	9	10
2	8	7	3							
3	72	55	32	9						
4	672	479	287	124	25					
5	6 348	4 409	2 589	1 298	432	71				
6	60 588	41 315	24 158	12 631	5 230	1 450	195			
7	582 268	392 575	228 550	122 321	55 642	19 814	4 656	543		
8	5 625 476	3 761 663	2 186 957	1 185 903	567 361	229 860	71 226	14 670	1 479	
9	54 578 380	36 261 983	21 070 697	11 544 947	5 692 271	2 483 208	898 186	247 582	45 028	4 067

TABLE 2.—VALUES OF $(n, m)_c$ FOR THE f.c.c.sq. LATTICE

$n\backslash m$	1	2	3	4	5	6	7	8	9	10
2	38	22	6							
3	376	220	88	18						
4	3 778	2 212	990	320	50					
5	37 972	22 548	10 468	4 072	1 064	142				
6	382 278	229 618	109 714	46 122	15 268	3 468	390			
7	3 850 344	2 338 524	1 140 744	502 440	187 000	55 064	10 872	1 086		
8	38 789 078	23 792 136	11 808 896	5 365 948	2 139 170	726 412	190 240	33 684	2 958	
9	390 816 860	241 793 780	121 766 672	56 672 708	23 633 428	8 752 144	2 699 512	641 836	101 888	8 134

TEMPERATURE DEPENDENCE OF THE PARTITION FUNCTION

For the partition function defined by eqn (1) it has been shown elsewhere [14] that

$$\lim_{n\to\infty} n^{-1} \ln Z_n(1) = \ln \mu_3 \tag{4}$$

where $\ln \mu_3$ is the connective constant of the appropriate three dimensional lattice (the " self-avoiding walk limit "). By analogy, we assume that

$$Z_n(\lambda) \sim n^{\sigma(\lambda)} \mu(\lambda)^n \tag{5}$$

for all values of λ. The value of $\ln \mu(\lambda)$ can be estimated directly from the Monte Carlo data as the intercept in a plot of $n^{-1} \ln Z_n(\lambda)$ against $n^{-1} \ln n$. The samples extended up to $n = 100$ with sample sizes typically of 10 000. Each λ-value was sampled separately to avoid the problems with reweighting the data which would otherwise occur for the larger values of λ. The Monte Carlo estimates of $\ln \mu(\lambda)$ are given in tables 3 and 4.

TABLE 3.—THE CUBIC LATTICE

$\ln \lambda$	$(n, m)_c$	$(n, m)_s$	Monte Carlo	lower bound
0.1	1.543	1.549	1.538±0.001	1.5440
0.2	1.543	1.537	1.538±0.001	1.5440
0.3	1.548	1.547	1.542±0.001	1.5440
0.4	1.565	1.570	1.562±0.001	1.5440
0.5	1.604	1.613	1.606±0.002	1.5440
0.6	1.663	1.675	1.640±0.005	1.5702
0.7	1.730	1.749	1.730±0.005	1.6702

TABLE 4.—THE f.c.c.sq. LATTICE

	$(n, m)_c$		$(n, m)_s$			
ln λ	(3, 4)	(4, 4)	(3, 4)	(4, 4)	Monte Carlo	lower bound
0.2	2.306	2.305	2.306	2.304	2.304±0.002	2.306
0.4	2.309	2.306	2.235	2.294	2.304±0.002	2.306
0.6	2.323	2.315	2.299	2.301	2.304±0.001	2.306
0.7	2.338	2.327	2.318	2.318	2.320±0.003	2.306
0.8	2.361	2.347	2.342	2.342	2.333±0.005	2.306
1.0	2.435	2.417	2.423	2.516	2.420±0.005	2.306
1.2	2.544	2.527	2.540	2.572	2.53 ±0.01	2.306
1.4	2.677	2.662	2.678	2.703	2.65 ±0.01	2.370

To extract corresponding estimates from the exact enumerations it is convenient to define the generating function, $G(x, \lambda)$, of the partition functions

$$G(x, \lambda) = 1 + \sum_{n \geqslant 1} Z_n(\lambda) x^n. \tag{6}$$

G will have a singularity at $x = \mu(\lambda)^{-1}$ and, close to this point, will behave as

$$G(x, \lambda) \sim A[1 - x\mu(\lambda)]^{-(1+\sigma)}. \tag{7}$$

Since the singularity is not a simple pole we form the logarithmic derivative

$$\mathcal{G}(x, \lambda) = (\partial/\partial x) \ln G(x, \lambda) \tag{8}$$

and then form Padé approximants to $\mathcal{G}$. Estimates of ln $\mu(\lambda)$ from the (6, 6) Padés for the cubic lattice and the (3, 4) and (4, 4) Padés for the f.c.c.sq. lattice are given in Tables 3 and 4. The lower bound given in ref. (14) is also included.

The agreement amongst the various estimates is generally quite good. However, the differences are sufficiently significant that it is very difficult to decide upon the location of the transition from desorbed to adsorbed behaviour. [This occurs at the point at which ln $\mu(\lambda)$ first deviates from the lower bound given.] *E.g.*, in table 4

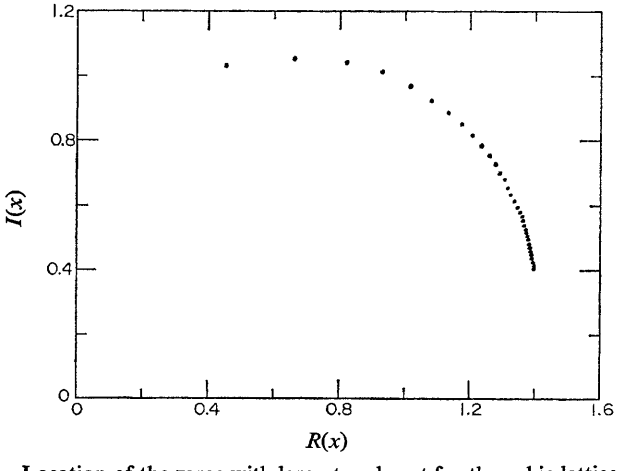

FIG. 1.—Location of the zeros with largest real part for the cubic lattice: $n < 40$.

any value between ln $\lambda = 0.4$ and 0.7 seems to be possible. This is unfortunate since the location of the transition is required accurately before one can begin to compare these results with recent scaling arguments.[23] (Actually, the situation isn't quite so dismal since the behaviour of the complete Padé tables enable us to rule out some of

the lower estimates.) An alternative way to approach the problem is to examine the zeros of the partition function.[24] The zeros of $Z_n(\lambda)$ must approach the positive real axis (as $n \to \infty$) at $\lambda = \lambda_c$ where λ_c is the location of the transition. Unfortunately the zeros for values of n amenable to exact enumeration do not give rise to very precise estimates of λ_c.[15, 16] We have estimated the coefficients, $(n, m)_s$, in $Z_n(\lambda)$ for intermediate values of n using Monte Carlo data. (Finding the zeros of a high degree polynomial is always a difficult numerical problem and one needs to pay considerable attention to the possibility of ill-conditioning. The coefficients need to be known rather precisely and we have therefore confined our attention to $n < 40$ for the simple cubic lattice and $n < 15$ for the f.c.c.sq. case. Even with these very short walks, the sample sizes needed were of the order of 10^5.) The location in the complex plane of the zeros with largest real part are given in fig. 1 and 2. For the simple cubic lattice, it is fairly certain that $\lambda_c > 1.4$ and probably lies between 1.4 and 1.5. A tentative estimate of $\lambda_c = 1.45$ ($\ln \lambda_c \simeq 0.37$) appears quite reasonable. This is in good agreement with the exact enumeration results of table 3 which suggest a value between 0.3 and 0.4 for $\ln \lambda_c$. The situation is more difficult for the f.c.c.sq. lattice, but the plot of the zeros suggests $\lambda_c > 1.6$ and a value as high as 1.8 (*i.e.*, $\ln \lambda_c \simeq 0.6$) is quite consistent with the data. (The Monte Carlo data in table 4 suggest that $\ln \lambda_c < 0.7$.)

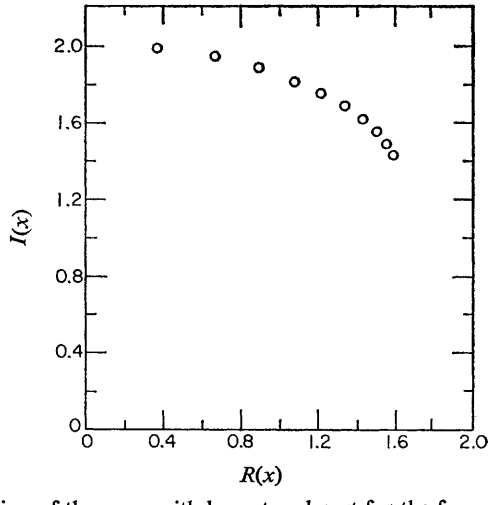

FIG. 2.—Location of the zeros with largest real part for the f.c.c.sq. lattice: $n < 15$.

CONCLUSIONS

The estimates of $n^{-1} \ln Z_n(\lambda)$ (in the limit $n \to \infty$) obtained from Monte Carlo data and from the combination of exact enumerations and Padé methods are very similar. However, the differences which remain are sufficient to make it difficult to estimate the location of the transition from desorbed to adsorbed behaviour, from inspection of these estimates. The behaviour of the zeros of the partition function gives rise to a reasonably precise estimate of the location of the transition, at least for the cubic lattice. We intend to return to a detailed investigation of the λ-dependence of $n^{-1} \ln Z_n(\lambda)$ (for $n \to \infty$) near the transition in a future publication.

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[1] A. Silberberg, *J. Chem. Phys.*, 1967, **46,** 1105.
[2] M. N. Barber and B. W. Ninham, *Random and Restricted Walks* (Gordon and Breach, New York, 1970), chap. 11.
[3] E. J. Clayfield and E. C. Lumb, *J. Colloid and Interface Sci.*, 1966, **22,** 285.
[4] F. L. McCrackin, *J. Chem. Phys.*, 1966, **47,** 1980.
[5] M. Lal, K. A. Richardson, D. Spencer and M. A. Turpin in *Colloidal Dispersions and Micellar Behaviour*, ed. K. L. Mittal, ACS symposium series No. 9.
[6] A. T. Clark, M. Lal, M. A. Turpin and K. A. Richardson, *Disc. Faraday Soc.*, **59,** 189.
[7] M. Lax, *J. Chem. Phys.*, 1974, **60,** 1931, 2245, 2627.
[8] M. Lax, *J. Chem. Phys.*, 1974, **61,** 4133.
[9] M. Lax, *Macromol.*, 1974, **7,** 660.
[10] P. Mark and S. Windwer, *Macromol.*, 1974, **7,** 690.
[11] P. Mark, S. Windwer and M. Lax, *Macromol.*, 1975, **8,** 946.
[12] M. Lax, *Macromol.*, 1975, **8,** 947.
[13] M. Lax, *Chem. Phys.*, 1975, **10,** 285.
[14] S. G. Whittington, *J. Chem. Phys.*, 1975, **63,** 779.
[15] K. M. Middlemiss and S. G. Whittington, *J. Chem. Phys.*, 1976, **64,** 4684.
[16] G. M. Torrie, K. M. Middlemiss, S. H. P. Bly and S. G. Whittington, *J. Chem. Phys.*, 1976 **65,** 1867.
[17] J. M. Hammersley and K. W. Morton, *J. Roy. Stat. Soc. B*, 1954, **16,** 23.
[18] M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.*, 1955, **23,** 356.
[19] J. Mazur and F. L. McCrackin, *J. Chem. Phys.*, 1968, **49,** 648.
[20] F. L. McCrackin, *J. Res. Nat. Bur. Stand. B*, 1972, **76,** 193.
[21] F. L. McCrackin, J. Mazur and C. M. Guttman, *Macromol.*, 1973, **6,** 859.
[22] K. M. Middlemiss, G. M. Torrie and S. G. Whittington, *J. Chem. Phys.*, 1977, **66,** 3227.
[23] P. G. deGennes, *J. Physique*, 1976, **37,** 1445.
[24] R. Finsy, M. Janssens and A. Bellemans, *J. Phys.* (*A*), 1975, **8,** L106.

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