Examination of the Series Analysis Method for Adsorption of a Polymer

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(Received April 12, 1986)

ABSTRACT: A series analysis method to estimate the critical point and exponents for adsorption of a polymer was tested using the non-reversal random walk model, for which analytical values are available. The values estimated from the exact enumeration data for up to 18 steps on the tetrahedral lattice are in good agreement with the expected ones for both cases having penetrable and impenetrable interface planes. The result suggests the possibility that for the self-avoiding walk model in penetrable case the estimate of crossover exponent φ is different between two methods; one uses the relation $\varphi = 1/q$ (q : the exponent for the free energy) and the other uses the scaling relation $\varphi = \theta - 1$ (θ : the exponent for the energy).

KEY WORDS Adsorption of a Polymer / Series Analysis / Critical Point /
Critical Exponent / Crossover Exponent / Non-Reversal Random Walk /

Adsorption of polymers at surfaces has attracted the attention of a large number of investigators. The treatments based on the random walk (RW) model have been reviewed by Barber and Ninham.¹ Recently the problem incorporating the excluded volume effect has been treated prevalently by the methods of Monte Carlo and exact enumeration for self-avoiding walks (SAWs) interacting with surfaces.^{2,3} Such a problem is closely related with the surface magnetism for a semi-infinite system of n -component spins.^{4–6} The adsorption transition point is essentially equivalent to the multicritical surface-bulk point for the spin system⁷; the critical exponent q for the free energy of an adsorbed chain corresponds to the inverse of a surface crossover exponent φ , *i.e.*, $q = 1/\varphi$ ($n \rightarrow 0$).^{7,8}

de Gennes⁴ has predicted the relation $\varphi = 1 - \nu$ (ν , the correlation length exponent) from the scaling argument of polymer adsorption. This relation is equivalent to the Bray and Moore conjecture⁹ for the $O(n)$ model obtained from the renormalization

group calculation of φ to first order in ε ($\varepsilon = 4 - d$; d , the spatial dimension). However, Diehl and Dietrich's calculation¹⁰ to second order in ε is incompatible with the relation. In previous papers,¹¹ we estimated that $q = 1.7 \pm 0.3$ ($d = 3$) and $q \simeq 1.9$ ($d = 2$) for the adsorption of a polymer at an impenetrable surface from a series analysis of the exact enumeration data for SAWs. These results are in conflict with the de Gennes–Bray–Moore conjecture since¹² $\nu = 3/(d+2)$. Eisenriegler *et al.*⁷ obtained the value $\varphi = 0.59 \pm 0.02$ for $d = 3$, which supports our estimate, from the Monte Carlo result for SAWs combined with the concept of critical phenomena. For $d = 2$, a real space renormalization group study¹³ has yielded $\varphi = 0.55 \pm 0.15$, which also supports our estimate. After consideration of these results, de Gennes and Pincus¹⁴ has modified the previous scaling theory¹⁵ introducing the “proximal exponent.”

On the other hand, Hammersley *et al.*¹⁶ have treated SAWs interacting with a penetrable plane as a model of polymer adsorption

at a liquid-liquid surface; it is closely connected with the critical behavior of the spin system near a plane of defects.¹⁷ They have shown rigorously that there exists a transition point in this case as well as in a semi-infinite system. We estimated the same values⁸ of q for $d=2$ and 3 as those for the semi-infinite case from exact enumerations of SAWs. The breakdown of the de Gennes-Bray-Moore conjecture has been suggested also in this case while the conjecture is thought valid in general for such an infinite system.^{17,18} More recently, Kremer¹⁹ estimated φ for the infinite system which supports the conjecture $\varphi = 1 - \nu$ using a Monte Carlo simulation of SAWs on the tetrahedral lattice. Consequently, it seems worthwhile to test the validity of series analysis technique for the adsorption of a polymer chain using a walk such as non-reversal random walk (NRRW) for which rigorous results are known although the validity has been established for the two-dimensional Ising model²⁰; NRRW is RW for which direct reversal is not allowed.

ADSORPTION TRANSITION OF A NON-REVERSAL RANDOM WALK CHAIN

Consider N -step NRRWs on a lattice which interact with the interfacial plane either penetrable or impenetrable. Taking into account interaction energy ε for a vertex in the plane (liquid-liquid or solid-liquid surface), we can write the partition function of such a chain as

$$Q_N(\omega) = \sum_{m=1} C_N(m) e^{m\omega} \quad (1)$$

where $C_N(m)$ is the number of walks with m vertices in the plane and $\omega = -\varepsilon/kT$. Introducing the reduced free energy

$$A(\omega) = \lim_{N \rightarrow \infty} N^{-1} \log Q_N(\omega) \quad (2)$$

it is shown that²¹ there exists a critical value, *i.e.*, an adsorption transition point

$$\omega_c = \sup \{ \omega : A = A_0 \} \quad (3)$$

where A_0 is a constant. For weak adsorption the critical exponent q can be defined by

$$A - A_0 \sim (\omega - \omega_c)^q, \quad \omega \rightarrow \omega_c + 0 \quad (4)$$

For the infinite system with penetrable plane, we have $\omega_c = 0$, *i.e.*, the adsorption transition occurs at an infinitely small monomer-interface interaction as is seen for the SAW model.^{8,16} The value of ω_c , however, depends on the type of lattice for the semi-infinite system. Rubin²² has shown for the RW model,

$$\omega_c = \log \frac{2z}{z + z_0} \quad (5)$$

z being the coordination number of a lattice and z_0 that of a (two-dimensional) surface lattice. Although a rigorous value of ω_c has not been obtained for the NRRW model, we can get the conjecture of ω_c by the substitution: $z \rightarrow z - 1$ and $z_0 \rightarrow z_0 - 1$ in eq 5. The RW value^{12,21,22} of $q = 2$, which is irrespective of d , is also valid for NRRWs, in both cases penetrable and impenetrable, since RW and NRRW belong to the same class of universality.

The mean fraction of monomers in an interfacial plane, *i.e.*, the energy of an adsorbed chain per monomer is given by

$$f_N(\omega) = \frac{\sum_m m C_N(m) e^{m\omega}}{N \sum_m C_N(m) e^{m\omega}} \quad (6)$$

and for sufficiently large N

$$f_N(\omega) \sim \begin{cases} N^{-1}, & \omega < \omega_c \\ N^{-\theta}, & \omega = \omega_c \\ \text{const}, & \omega > \omega_c \end{cases} \quad (7)$$

It is shown that²² $\theta = 1/2$ for the RW model in a semi-infinite case. In general, the relation $\theta = 1 - \varphi$ holds for NRRWs in both infinite and semi-infinite systems since the scal-

ing arguments^{7,8} predict $\theta = v$ and $\varphi = 1 - v$.

EXACT ENUMERATION

We obtained exact values of $C_N(m)$ for $N \leq 18$ for NRRWs on the tetrahedral lattice in two cases of penetrable and impenetrable interfacial planes. The computations were performed on the ACOS 1000 computer at the Tohoku University. In the infinite system

with a penetrable interface, all walks originate in the plane $z=0$ while in the semi-infinite system the walks are restricted to the half-space $z \geq 0$ and have at least one vertex in the plane $z=0$. The interfacial planes¹¹ are chosen to contain lattice points in the planar zig-zag conformation such as $\alpha\bar{\beta}\alpha\bar{\beta}\dots$, where $\alpha=(1,1,1)$ and $\bar{\beta}=(\bar{1},1,1)$. The values of $C_N(m)$ for semi-infinite system are given in Table I; those for the infinite system are

Table I. Values of $C_N(m)/2$ for the tetrahedral lattice in a semi-infinite system

<i>N</i>	<i>m</i>						
	1	2	3	4	5	6	7
1	1	1					
2	3	2	1				
3	7	8	2	1			
4	19	21	11	2	1		
5	53	63	28	15	2	1	
6	147	192	85	40	19	2	1
7	411	578	258	133	52	23	2
8	1163	1735	775	414	193	64	27
9	3313	5221	2316	1283	610	269	76
10	9475	15722	6925	3956	1931	870	361
11	27207	47312	20722	12125	6076	2851	1194
12	78419	142325	61987	37034	18901	9204	4091
13	226709	428127	185372	112871	58354	29245	13548
14	657043	1287696	554405	343328	179411	91946	43973
15	1908459	3872322	1658354	1042565	549764	287087	140898
16	5554347	11642863	4960959	3161798	1679609	891576	446923
17	16193409	35001981	14841964	9578779	5119378	2756493	1406380
18	47283843	105213762	44408445	28992972	15575179	8491438	4398225

<i>N</i>	<i>m</i>										
	8	9	10	11	12	13	14	15	16	17	18 19
7	1										
8	2	1									
9	31	2	1								
10	88	35	2	1							
11	469	100	39	2	1						
12	1582	593	112	43	2	1					
13	5715	2034	733	124	47	2	1				
14	19428	7787	2550	889	136	51	2	1			
15	64557	27164	10371	3130	1061	148	55	2	1		
16	211226	92661	37076	13531	3774	1249	160	59	2	1	
17	681895	309970	130205	49484	17331	4482	1453	172	63	2	1
18	2178208	1019459	445706	179365	64708	21835	5254	1673	184	67	2 1

eliminated to save space and paper. Note that the table values are divided by 2.

SERIES ANALYSIS

We assume that

$$Q_N(\omega) \sim N^{\lambda(\omega)} \mu(\omega)^N \quad (8)$$

by analogy with the RW and/or SAW of $\omega=0$, and form ratios of the alternate terms of Q_N in order to reduce the marked odd-even oscillation characteristic of a loose-packed lattice:

$$Q_N/Q_{N-2} = [1 + 2\lambda/N + O(N^{-2})]\mu^2. \quad (9)$$

Then we construct Neville tables²⁰ for the

Figure 1. Estimation of μ from linear ($r=1$) and quadratic ($r=2$) extrapolants $\mu_N^{(r)}$ for $\omega=0.45$ in a semi-infinite case.

Figure 2. $A(\omega)$ as a function of ω for the semi-infinite system. The arrow indicates the transition point, ω_c .

linear and quadratic extrapolants of $\mu_N = (Q_N/Q_{N-2})^{1/2}$:

$$\mu_N^{(r)} = [N\mu_N^{(r-1)} - (N-2r)\mu_{N-2}^{(r-1)}]/2r \quad (10)$$

for $r=1$ and 2, with $\mu_N^{(0)} \equiv \mu_N$. We plot these extrapolants against $1/N$ and estimate μ by extrapolating to $N \rightarrow \infty$ taking into account the curvature of convergence as a whole along with the damping oscillation around it. The last process is efficient when a confluent singularity exists. Thus we obtain $A(\omega)$ for given ω since $\log \mu = \lim_{N \rightarrow \infty} N^{-1} \log Q_N$ from eq 8.

Figure 1 illustrates an example of the plot of linear ($r=1$) and quadratic ($r=2$) extrapolants $\mu_N^{(r)}$ against $1/N$ which are calculated for $\omega=0.45$ from our data for the semi-infinite

Figure 3. The same as Figure 2 but for the infinite system.

Table II. The values of $q_i \equiv \log \Delta A_i / \log \Delta \omega_i$ ($i=1-10$) for the semi-infinite system; $\Delta A_i = A(\omega_i) - A_0$ and $\Delta \omega_i = \omega_i - \omega_c$

i	$\Delta \omega_i$	$\Delta A_i (\sim \pm 0.0002)$	q_i
1	0.01	0.0001	2.000
2	0.02	0.0003	2.074
3	0.03	0.0006	2.116
4	0.04	0.0010	2.146
5	0.05	0.0015	2.171
6	0.06	0.0020	2.209
7	0.07	0.0026	2.238
8	0.08	0.0032	2.274
9	0.09	0.0038	2.314
10	0.10	0.0045	2.347

system; we estimate $\mu = 3.003 \pm 0.001$. The values of $A(\omega)$ obtained for the semi-infinite system are plotted in Figure 2 as a function of ω ; the arrow indicates $\omega_c = 0.405$, which is in good agreement with the conjecture $\omega_c = \log(6/4) = 0.4054\dots$, and it confirms $A = A_0 = \log 3$ for $\omega \leq \omega_c$. The analogous plot for the infinite system is shown in Figure 3; it reproduces the expected value of $\omega_c = 0$ and $A_0 = \log 3$.

Equation 4 turns out to be

$$q = \lim_{\Delta\omega \rightarrow +0} \frac{\log \Delta A}{\log \Delta\omega} \quad (11)$$

where $\Delta A = A - A_0$ and $\Delta\omega = \omega - \omega_c$. We can estimate q by calculating $\log \Delta A / \log \Delta\omega$ for different values of $\Delta\omega$ with an appropriate interval and extrapolating to $\Delta\omega \rightarrow 0$. The values of ΔA and $q_i = \log \Delta A_i / \log \Delta\omega_i$ for the semi-infinite system are given in Table II with the interval of $\Delta\omega_i - \Delta\omega_{i-1} = 0.01$. The plot of q_i against $\Delta\omega_i$ is shown in Figure 4; we estimate that $q = 2.0^{+0.15}_{-0.10}$. The corresponding plot for the infinite system, which is shown in Figure 5, gives the estimate $q = 2.0^{+0.13}_{-0.08}$. These estimates are in excellent agreement with the theoretical value of $q = 2$.

We then estimate the exponent θ in eq 7 from the ratios

$$\theta_N = N(1 - f_N/f_{N-2})/2 \quad (12)$$

and using the method stated above. Figure 6 shows a plot of linear and quadratic extrapolants $\theta_N^{(r)}$ against $1/N$ obtained for $\omega = 0.45$ in a semi-infinite system; the value $\theta = 0.390 \pm 0.015$ was estimated. Figures 7 and 8 illustrate the plots of θ thus obtained as a function of ω for the semi-infinite and infinite systems, respectively. In both cases, θ decreases with increasing ω , approaching unity for $\omega \ll \omega_c$ but still less than unity while it becomes negative for $\omega \gg \omega_c$ contrary to expectation although the error bars enlarge there. We have the respective estimates $\theta = 0.52$ and 0.51 at $\omega_c = 0.405$ and 0 for the semi-infinite and infinite systems; these values are

Figure 4. The plot of q_i vs. $\Delta\omega_i$ for the semi-infinite system. The arrow indicates the extrapolated value of q .

Figure 5. The same as Figure 4 but for the infinite system.

Figure 6. Estimation of θ from linear and quadratic extrapolants $\theta_N^{(r)}$ for $\omega = 0.45$ in a semi-infinite case.

Figure 7. The plot of θ as a function of ω for the semi-infinite system. The arrow indicates an inflection point.

Figure 8. The same as Figure 7 but for the infinite system.

compatible with the theoretical result $\theta = 0.5$.

DISCUSSION

We have shown in the preceding section that our series analysis method is very reliable for the estimation of the transition point and critical exponents for the adsorption of a NRRW chain. In Figures 7 and 8, an inflection point is noted around the points indicated by arrows; $\theta = 0.4$ is found at the inflection point in both plots. However, the point should not be regarded as a transition

point since the values of ω and θ in this case are inconsistent with the expected values. A similar plot of f_N in our previous paper⁸ for SAWs in the infinite system gives $\theta = 0.585$ (*i.e.*, $\varphi = 0.415$) for the choice of $\omega_c = 0$ instead of the inflection point $\omega = 0.20$. This value is inconsistent with the corresponding estimate $\varphi = 0.40 \pm 0.02$ given by Kremer¹⁹ using a Monte Carlo method. Hence, for SAWs, we notice a discrepancy between values of respective φ obtained through q and θ although the reason is not clear. It suggests that the scaling theory for critical behavior at a defect plane deserves further examination, at least for

Figure 9. Location of the zeros of the partition function for semi-infinite system; $N=14$ ($\odot$), 15 ($+$), 16 ($\triangle$), 17 ($\square$), 18 ($\circ$), and the largest real part ($\bullet$) for $N=7-18$.

Figure 10. The same as Figure 9 but for the infinite system.

the $n=0$ model.

Zeros of the Partition Function

We rewrite eq 1 as

$$Q_N(x) = \sum_m C_N(m) x^m \quad (13)$$

where x is real and positive. Equation 13 can be represented as

$$Q_N(x) = C_N(1) \prod_{j=1}^{m_N} (1 - x/z_j) \quad (14)$$

Figure 11. Plots of the real part x_N of the zeros with largest real value and its linear extrapolant $x_N^{(1)}$ against $1/N$ for the semi-infinite system.

Figure 12. The same as Figure 11 but for the infinite system.

using the roots z_j ($j=1, \dots, m_N$) of $Q_N(z)=0$. None of the roots z_j lies on the real positive axis of the complex z plane since all coefficients $C_N(m)$ are positive. However, the zeros of $Q_N(z)$ must approach the positive real axis at $x=x_c$ ($=e^{\omega_c}$) as $N \rightarrow \infty$, seeing that $\lim_{N \rightarrow \infty} N^{-1} \log Q_N(x)$ is nonanalytic at $x=x_c$ as expected from the Yang-Lee theory.²³ Hence the location of the transition point can be estimated also from the zeros of the partition function,²⁴ but the value seems¹¹

always fairly larger than that estimated from the $A(\omega)$ vs. ω plot.

Figures 9 and 10 show the plots of the location of zeros close to the origin obtained for the semi-infinite and infinite systems, respectively. Black dots represent the zeros with the largest real part for $N=7-18$. The location of zeros is symmetric about the real axis but not the imaginary axis, and lies approximately on circles except for values on the negative real axis in the semi-infinite system. The circles for $\text{Re } z > 0$ cross at the point on the real axis. It is interesting to compare our results with the corresponding ones for the two-dimensional Ising model,^{25,26} where such zeros lie nearly on simple loci, often on circles.

In Figure 11, we plot the real part x_N of the zeros with the largest real value in the semi-infinite system against $1/N$ along with its linear extrapolant $x_N^{(1)}$. The latter gives $x_c = 1.52 \pm 0.08$, which coincides with the expected value $x_c = 1.5$ and is in agreement with the crossing point on the real axis in Figure 9, while the former gives a much larger value. Similar plots for the infinite system are given in Figure 12. Almost the same situation is seen although the plot of $x_N^{(1)}$ yields $x_c = 1.09 \pm 0.09$ a little larger than the theoretical value $x_c = 1$.

Acknowledgements. I am grateful to Mr. H. Ishikawa for assistance with computational work, and to Dr. K. Kremer for sending me his preprint prior to publication.

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