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From Random to Self-Avoiding Walks

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A brief review will be given of the current situation in the theory of self-avoiding walks (SAWs). The Domb–Joyce model first introduced in 1972 consists of a random walk on a lattice in which each N step configuration has a weighting factor $\prod_{i=0}^{N-2}\prod_{j=i+2}^{N}(1-\omega\delta_{ij})$. Here **i** and **j** are the lattice sites occupied by the ith and jth points of the walk. When $\omega = 0$ the model reduces to a standard random walk, and when $\omega = 1$ it is a self-avoiding walk. The universality hypothesis of critical phenomena will be used to conjecture the behavior of the model as a function of ω for large N. The implications for the theory of dilute polymer solutions will be indicated.

KEY WORDS: Self-avoiding walk (SAW); generating function; lattice Green's function; universality; polymer chain expansion factor.

1. REVIEW OF PROPERTIES OF SELF-AVOIDING WALKS (SAWs)

I should like to begin with a brief review of the properties of SAWs. In 1969 in a Conference on "Stochastic Processes in Chemical Physics" I described the current situation as follows.[1] By rigorous mathematical analysis it has been possible to derive only very primitive properties of SAWs. However, conjectures based on Monte Carlo simulations and extrapolations from exact enumerations of short chains have indicated a number of interesting features in which SAWs differ radically from normal random walks.

For example, if C_N is the total number of walks of N steps, for a random walk

$$C_N = q^N \tag{1}$$

where q is the coordination number of the lattice, whereas for an SAW

$$C_N \sim A\mu^N N^\gamma \tag{2}$$

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numerical values of the exponent γ being about $1/6$ in three dimensions and $1/3$ in two dimensions. Similarly, if u_N is the number of walks at the origin after N steps, for a random walk

$$u_N \sim C q^N N^{-d/2} \tag{3}$$

whereas for an SAW[2]

$$u_N \sim E \mu^N N^{-\alpha} \tag{4}$$

numerical values of α being about $7/4$ in three dimensions, and $3/2$ in two dimensions.

When we come to consider the mean square end-to-end length, $\langle R_N^2 \rangle$, we again find significant differences. For a random walk

$$\langle R_N^2 \rangle = N \tag{5}$$

whereas for an SAW

$$\langle R_N^2 \rangle \sim F N^{\nu} \tag{6}$$

numerical values of ν being about $6/5$ in three dimensions, and $3/2$ in two dimensions. Finally, $P_N(\mathbf{x})$ the probability distribution of the end-to-end distance is asymptotically Gaussian for a random walk

$$P_N(\mathbf{x}) \sim \left(\frac{d}{2\pi} \right)^{d/2} \exp\left(-\frac{d}{2} x^2 \right) \tag{7}$$

whereas it is non-Gaussian for an SAW

$$P_N(\mathbf{x}) \sim K x^{\theta} \exp(-L|x|^{\delta}) \tag{8}$$

numerical values of δ being about $5/2$ in three dimensions and 4 in two dimensions (θ is less well established).

In the above-mentioned review I drew attention to the further important features: the distinction between "local" properties such as μ and E in formula (4) which vary from one lattice to another in a given dimension, and "long-range properties" like exponents α, γ, δ, ν which depend on dimension but not on lattice structure in a given dimension; and the close analogy between the properties of SAWs and those of the Ising model of ferromagnetism.

I should now like to summarize briefly the great progress in our knowledge of SAWs which has taken place since 1969. The analogy with the Ising model has been made precise. If we define an n-vector model of ferromagnetism in which the interacting spins are vectors in n-dimensional space, $n = 1$ corresponds to the Ising model and $n = 0$ to an SAW. This was discovered by de Gennes,[2] who showed that if n is put equal to zero in a

[2] The definition is modified slightly to allow a return to the origin at the final step.

diagrammatic expansion of the model, the only diagrams which survive correspond to SAWs.

The "long-range" or "universality" concepts have been justified by the use of the renormalization group[3] (RG). Exponents can be calculated directly as asymptotic series expansions in ϵ $(= 4 - d)$, and these series can be resummed to great accuracy by means of Borel transformations.[4] It now seems clear that the rational fraction estimates in three dimensions are not exact but approximations. Better estimates are 0.162 for γ (instead of $1/6$), 1.764 for α (instead of $7/4$), and 1.176 for ν (instead of $6/5$).

In two dimensions there has been significant exact progress largely by B. Nienhaus,[5] who has investigated some special models whose critical properties should be identical with those of SAWs. He has concluded that the value of μ for the honeycomb lattice should be $(2 + \sqrt{2})^{1/2} = 1.847759065$. (The estimate of Guttman and Sykes[5a] based on the ratio method of analysis had been 1.8481 ± 0.0010, and that of M. F. Watts[5b] based on a Padé approximant analysis 1.8478 ± 0.0002.) Nienhaus has shown that the value of α in (4) is exactly $3/2$ and that of ν in (6) is also exactly $3/2$; he has been unable to calculate γ with the same confidence, but suggests that the value of $1/3$ is incorrect and should be replaced by $11/32$.

Another approach to SAWs which has borne fruit recently is that of Mandelbrot,[6] who showed how to apply the concepts of self-similarity and fractal dimensions inherent in the mathematical work of Hausdorff and Besicovitch to real systems in nature. Recent analysis of Monte Carlo simulations by Havlin[7] has made effective use of these concepts.

The RG analysis indicates that the SAW exponents in any dimension $\geqslant 4$ will have the random walk values, but in four dimensions there will be logarithmic correction terms which can be calculated from field theory.[8] The results are as follows:

$$\begin{aligned} C_N &\sim Q\mu^N (\ln N)^{1/4} \\ u_N &\sim R\mu^N N^{-2} (\ln N)^{1/2} \\ \langle R_N^2 \rangle &\sim SN (\ln N)^{1/4} \end{aligned} \tag{9}$$

Finally the RG indicates that the first correction term to the asymptotic formulas (2), (4), and (6) is a factor of the form

$$(1 + a/N^{\theta}) \tag{10}$$

with θ about $1/2$ in three dimensions. Previously it had been assumed that the corrections were of Darboux form

$$(1 + a/N) \tag{11}$$

Formulas (9) have been checked by exact enumerations[9] and Monte Carlo simulations,[7] and the confluent correction (10) has been observed in Monte Carlo simulations.[7]

2. THE DOMB–JOYCE MODEL[10]

Shortly after the 1969 Conference Professor W. H. Stockmayer suggested to me that it might be of interest to consider a "soft" adaptation of an SAW with a nonzero probability of revisiting a site which has already been visited. The model which resulted, and whose properties I investigated with the help of Dr. G. S. Joyce, weights each configuration of a random walk with a factor

$$\prod_{i=0}^{N-2} \prod_{j=i+2}^{N} (1 - \omega\delta_{ij}) \tag{12}$$

Here **i** and **j** are the lattice sites occupied by the ith and jth points of the walk, and a walk with s contacts will have weight $(1-\omega)^s$. When $\omega = 0$ the model gives a standard random walk, and when $\omega = 1$ all configurations with nonzero contacts are eliminated, and an SAW results.

One can clearly define the quantities $C_N(\omega)$, $u_N(\omega)$, $\langle R_N^2(\omega)\rangle$, $P_N(\mathbf{x}, \omega)$ for a Domb–Joyce walk. If C_{Ns} is the number of random walks with exactly s contacts

$$\begin{aligned} C_N(\omega) &= \sum_s C_{Ns}(1-\omega)^s \\ &= \sum_s C_{Ns}\left[1 - s\omega + \frac{s(s-1)}{2!}\omega^2 \right. \\ &\qquad \left. + \cdots \frac{s(s-1)\cdots(s-r+1)}{r!}\omega^r \cdots\right] \end{aligned} \tag{13}$$

and hence $C_N(\omega)$ is a factorial m.g.f. for the number of contacts in a random walk. The C_{Ns} can be enumerated exactly on a computer for small N using a similar program to that for SAW enumerations, and this was done by M. Lax.[11] If we write $v = (1-\omega)$, an expansion in powers of v is an expansion about the SAW limit, to be contrasted with the ω expansion about the random walk limit.

The model is the lattice analog of a continuum random walk model with a Dirac δ-function interaction which has been widely used in polymer theory.[12] The lattice model has a number of advantages: the behavior of an SAW at $\omega = 1$ is quite well established; numerical computations and Monte Carlo simulations are much easier than for a continuum model; and

by considering different lattices in a given dimension it is much easier to separate universal from nonuniversal properties.

3. PERTURBATION EXPANSION

A formal series expansion in the powers of ω was developed by Domb and Joyce.[10] The terms in the expansion can conveniently be represented diagrammatically, and their evaluation is facilitated by the use of appropriate generating functions (g.f.'s). The first term in the expansion of $C_N(\omega)$ is represented diagrammatically in Fig. 1, and one must sum over all random walks with a single loop. If $P(x)$ is the g.f. for chains ($\sum C_N x^N$) and $R(x)$ the g.f. for closed loops ($\sum u_N x^N$), it is easy to show that the g.f. for the class of walks represented in Fig. 1 is $P(x)^2 R(x)$.

There are four types of diagram contributing to the coefficient of ω^2 and these are illustrated in Fig. 2. Diagrams 2a, 2b, and 2c can be expressed in terms of $P(x)$ and $R(x)$. They are "collapsible" or "bubble" diagrams but we called them ladder diagrams following the terminology introduced previously by Chikahisa[13] for the continuum problem.

For higher-order terms Joyce and I found that we were able to calculate the ladder contributions exactly. However, the nonladder dia-

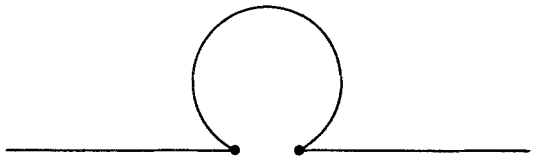

Fig. 1.

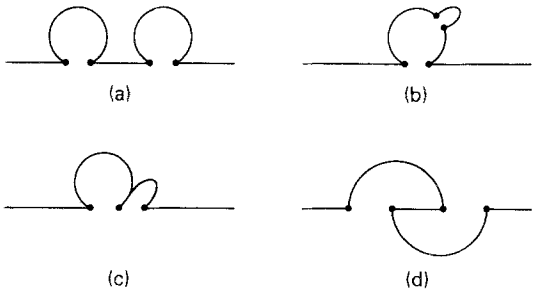

Fig. 2.

grams are much more difficult to deal with, and their calculation up to the third order was undertaken in collaboration with A. J. Barrett.[14]

For the expansion of $\langle R_N^2(\omega)\rangle$ we need to evaluate $\sum l^2 C_N(\mathbf{l})$, where $C_N(\mathbf{l})$ is the number of walks terminating at $\mathbf{l}$, and this is best done by means of the g.f.

$$P(\mathbf{l}, x) = \sum C_N(\mathbf{l}) x^N \tag{14}$$

$P(\mathbf{l}, x)$ is the standard lattice Green's function whose asymptotic behavior for large l has been studied in some detail.[15] In three dimensions $R(x)$ can be written in the form

$$R(x) = e(x) + f(x)(1 - x)^{1/2} \tag{15}$$

where $e(x)$ and $f(x)$ are analytic functions which can conveniently be expanded as Taylor series near $x = 1$; the dominant term is $f_0(1 - x)^{1/2}$. In two dimensions the corresponding expression is

$$R(x) = e(x) + f(x)\ln(1 - x) \tag{16}$$

For the first nonladder diagram Fig. 1d a new type of Green's function is required:

$$W_3(x) = \sum_{\mathbf{l}} P(\mathbf{l}, x)^3 \tag{17}$$

On the basis of numerical investigations we would expect that

$$W_3(x) = e_3(x) + f_3(x)\ln(1 - x) + g_3(x)(1 - x)^{1/2} \tag{18}$$

and we have calculated the important coefficient $f_3(1)$ by approximating to $P(\mathbf{l}, x)$ by its asymptotic form, and replacing the sum in (17) by an integral. But we feel that there is scope for a cleaner mathematical evaluation of $e_3(x)$, $f_3(x)$, and $g_3(x)$.

Each new type of nonladder diagram introduces a new type of Green's function. At the third order, one of these diagrams contributes a coefficient which cannot be calculated exactly but must be evaluated numerically.

4. FORM OF THE ω-EXPANSION COEFFICIENTS

From our experience of C_N and u_N for self-avoiding walks it would appear to be convenient to evaluate $\ln\{C_N(\omega)/C_N\}$ and $\ln\{u_N(\omega)/u_N\}$. These should contain a "bulk" contribution analogous to $N \ln \mu$ and an "exponent" contribution analogous to $\alpha \ln N$. If we write

$$\ln\{C_N(\omega)/C_N\} = g_1\omega + g_2\omega^2 + g_3\omega^3 + \cdots \tag{19}$$

we find, in three dimensions, that for ladder graphs g_r has a bulk contribution of the form $a_r N + b_r$ and an exponent contribution of the form

$$f_0^r\left(C_{0r}N^{r/2} + C_{1r}N^{r/2-1} + \cdots\right) \tag{20}$$

For nonladder graphs, however, even terms in the exponent contribution contain logarithmic factors,

$$\begin{aligned} g_2 &= d_{02}N\ln N + h_{02}N \\ g_4 &= d_{04}N^2(\ln N)^2 + d_{14}N^2\ln N + d_{24}N \end{aligned} \tag{21}$$

In two dimensions it is the *ladder* graphs which give rise to logarithmic terms which can be calculated to all orders

$$g_r = N^r\left[a_{0r}(\ln N)^r + a_{1r}(\ln N)^{r-1} + \cdots\right] \tag{22}$$

We have observed empirically that if we calculate universal quantities like the expansion factor,

$$\alpha^2 = \left\langle R_N^2(\omega)\right\rangle / N = C_N^{(2)}(\omega)/C_N(\omega) \tag{23}$$

where

$$C_N^{(2)}(\omega) = \sum_{\mathbf{l}} l^2 C_N(\mathbf{l},\omega) \tag{24}$$

or the probability of ring closure,

$$\sigma_N(\omega) = u_N(\omega)/C_N(\omega) \tag{25}$$

then the logarithmic terms all cancel in the expansion.[3] In three dimensions this has been established only at the second term,[16] but in two dimensions it has been established to all orders.[17]

Let us now consider the ω expansion of a universal quantity, e.g.,

$$\alpha^2 = 1 + k_1\omega + k_2\omega^2 + k_3\omega^3 + \cdots \tag{26}$$

If we retain only the leading terms in powers of N, we find

$$k_r \sim h_0^r N^{r/2} k_{r0} \tag{27}$$

in three dimensions and

$$k_r \sim h_0^r N^r k_{r0} \tag{27a}$$

in two dimensions. Here h_0 is a characteristic constant for each lattice, related to the volume of unit cell, and k_{r0} is universal. This suggests the

[3] A. J. Barrett has suggested recently[16a] that in expansions like (21) only terms *linear* in $(\ln N)$ survive, i.e., d_{04} is zero.

following functional form:

$$\alpha^2 = \phi_3(h_0 N^{1/2}\omega) \qquad \text{in three dimensions} \tag{28}$$

$$\alpha^2 = \phi_2(h_0 N\omega) \qquad \text{in two dimensions} \tag{29}$$

It is not possible to establish results (28) and (29) rigorously since the series (26) is asymptotic rather than convergent.[18]

5. RELATIONSHIP TO CRITICAL PHENOMENA

We shall now see how the above results can be interpreted in the general framework of critical phenomena. We first summarize briefly the major conclusions which have emerged during the past decade or two on critical behavior of magnetic models. We consider a lattice of interacting spins which are classical vectors in n dimensions. Near a critical point, thermodynamic quantities are characterized by critical exponents, e.g., specific heat,

$$C_H \sim a(T - T_c)^{-\alpha} \tag{30}$$

initial magnetic susceptibility

$$\chi \sim b(T - T_c)^{-\gamma} \tag{31}$$

Critical exponents do not vary continuously but change discontinuously when there is a change in the interaction of (i) dimension d, (ii) symmetry n, (iii) range character σ. We shall consider only short-range forces and shall therefore consider only d and n. A particular set of (d, n) defines a *universality class*; they are in a sense analogous to quantum numbers.

We must remember that every thermodynamic quantity is derived from a partition function; for example for the Ising model

$$\chi = \sum_{N=1}^{\infty} \phi(N)\exp(-\beta NJ) = \sum_{N=1}^{\infty} \phi(N) y^N \qquad (y = \exp - \beta J, \beta = 1/kT) \tag{32}$$

Hence to each $(T - T_c)$ exponent there is an analogous N-exponent, and if

$$\phi(N) \sim d\mu^N N^h$$

then

$$\chi(T) \sim e(1 - \mu y)^{-h-1} \simeq f(1 - T_c/T)^{-h-1} \tag{33}$$

This shows the relationship between $(T - T_c)$ exponents (30), (31), (33) and the N-exponents which we have defined for SAWs [e.g., (2), (4), (6)]. By universality the exponent h does not vary from lattice to lattice in a given dimension.

Amplitudes like a, b do vary from lattice to lattice but can be scaled. If appropriate scaling constants are introduced for each lattice then *universal functions* can be defined which characterize critical behavior (this is usually known as lattice–lattice scaling[19]). For example, the magnetic equation of state in the critical region can be written in the form

$$M = \psi(t_0 T, h_0 H) \tag{34}$$

where t_0 and h_0 vary from one lattice to another, but ψ is a universal function.

We now consider the crossover from one universality class to another. Consider a simple cubic lattice with interactions J in the x and y directions, and J' in the z direction. When $J' = 0$ critical exponents change from those of $d = 3$ to those of $d = 2$. But if we wish to consider the behavior in the transition region of small J', we must introduce another constant γ_0, and we can write

$$M = F(\gamma_0 J', t_0 T, h_0 H) \tag{35}$$

where F is a universal function called the crossover function.

We have suggested that $\omega = 0$ for the Domb–Joyce model is analogous to $J' = 0$ in the above magnetic model, i.e., it is the point at which the sharp change of exponents occurs between random walk and SAW behavior. Hence the functions ϕ_3 and ϕ_2 in (28) and (29) have the nature of crossover functions. The powers of N by which ω is multiplied are analogous to what are called "crossover exponents" in critical phenomena.

On the other hand we suggested that $\omega = 1$ is a point at which nothing dramatic happens, and is analogous to a nonzero positive value of J'. The critical exponents remain unchanged as ω changes, and the amplitudes change smoothly. We tested this conjecture on the numerical data produced by exact enumerations, and found that it fitted the data well.

We have already mentioned that the value $n = 0$ for the n-vector model characterizes an SAW. Correspondingly it has been shown that the value $n = -2$ characterizes a random walk,[20] and the functions which we are seeking to evaluate in (28) and (29) are crossover functions from $n = -2$ to $n = 0$.

6. CALCULATION OF UNIVERSAL FUNCTIONS

Universal functions like (28) and (29) are of great importance in polymer physics,[12] since they represent the effect of the excluded volume on polymer chain dimensions. Many approximations of mean field type were devised, giving results which differed very substantially from one another. The model used was a continuum Gaussian chain with the

Domb–Joyce interaction (12) replaced by $-\omega\delta(\mathbf{r}_{ij})$, where ω is the second virial coefficient of the intermolecular forces. The lattice model analysis readily extends to this continuum model with an appropriate modification of the Green's function $R(x)$, and formulas like (27) remain valid with a suitable definition of h_0.

The great advantage of the lattice model is the possibility of exploiting the reservoir of information about SAWs. Direct use of the ω expansion is limited to a small region which is unlikely to be extended significantly even if additional terms are calculated (a very formidable task) (see Fig. 3). But once the assumption of "smoothness" in the neighborhood of $\omega = 1$ has been accepted, standard methods of extrapolation can be used on exact enumerations for the Domb–Joyce model, and a reasonable estimate of asymptotic behavior can be derived for all standard lattices from $\omega = 0.5$ to $\omega = 1.0$. The range of values up to $\omega = 0.5$ can later be derived by interpolation. Results for a typical lattice are shown in Fig. 4.

By comparing such calculations for different lattices the universal functions can be determined, and the range of validity of the two-parameter approximation can be assessed. In principle this validity should be restricted to large N and small ω, but in practice it is found that the useful range extends very much further. This can be well illustrated by taking only the dominant asymptotic term in $\phi_3(z)$ in (28)

$$\phi_3(z) \sim 1.64 z^{2/5} \tag{36}$$

and looking at the error in using the two-parameter formula at $\omega = 1$. For

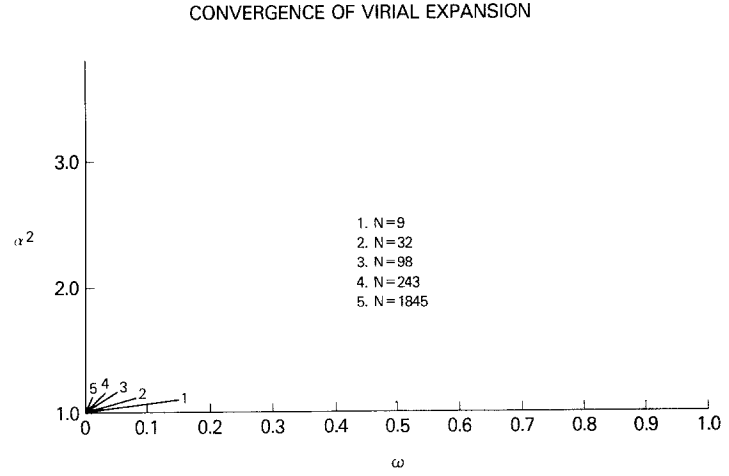

Fig. 3. Region of applicability of three terms of virial expansion for different N.

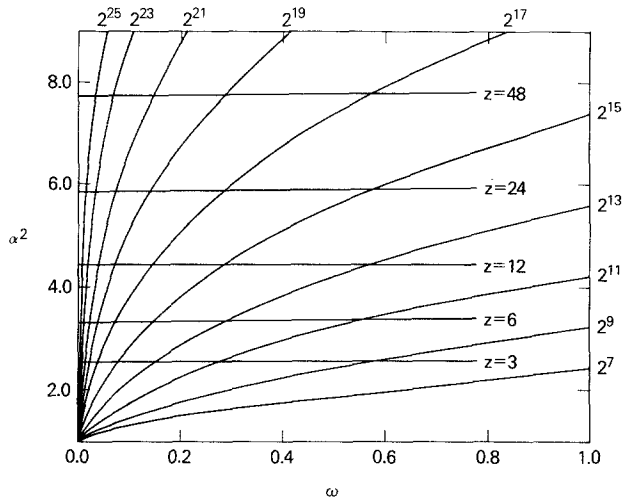

Fig. 4. FCC Lattice. Estimates of α^2 based on (i) virial expansion near $\omega = 0$, (ii) SAW and exact enumerations between $\omega = 0.5$ and $\omega = 1$, (iii) interpolation for the intermediate region. For the two-parameter approximation lines $z = \text{const}$ should be horizontal.

the diamond sc, bcc, and fcc lattices the amplitudes F in (6) give rise to values 1.682, 1.663, 1.659, 1.648 respectively, so that the deviations are of the order of a few per cent.

7. CONCLUSIONS

Our discussion has aimed at providing a bridge between the theory of random walks and critical phenomena. We should like to suggest that each of these disciplines has something to learn from the other. The fruitful developments of recent years in critical phenomena have enabled us to interpret the nature of the transition from random to self-avoiding walks. And for the research worker in critical phenomena a model has been provided of a crossover from one universality class to another which can be explained in considerable mathematical detail.

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