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LETTER TO THE EDITOR

New approach to self-avoiding walks as a critical phenomenon

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Abstract. A new approach is developed to self-avoiding walks as a critical phenomenon. The approach is based on a simple assumption made on the step–step correlation function. This leads to a single scaling field related to the degree of polymerisation. As a result, all critical exponents are related to a single exponent. Moreover, the order parameter and critical fields have a clear physical meaning. The present interpretation of self-avoiding walks as critical suggests an additional meaning of the exponent ν in other critical systems.

The phenomenon of long polymer chains is known to be analogous to critical phenomena. A great deal has been learnt in recent years about the universal properties of long polymer chains from the connection between polymer statistics and those of the n-vector model in the $n = 0$ limit (de Gennes 1979, Domb 1972, des Cloizeaux 1974, McKenzie 1976). While this relationship is of great importance for studying the $n = 0$ ferromagnet case, it is not as enlightening from the point of view of a self-avoiding walk (SAW). For instance, the physical meaning of an order parameter or related fields is not clear at all in the context of SAWs (de Gennes 1979).

Recently, Redner and Reynolds (1981) presented an approach to the SAW problem without appeal to the n-vector model. Their approach treats the generating function for SAWs as a grand partition function. They find a single scaling field which is the fugacity per monomer. As a result, all critical exponents are related to a single exponent.

In the present work, we present a different physical approach which considers SAWs as a critical phenomenon on its own, that is, without appeal to the n-vector model or to any other analogue. Our approach is based on a simple assumption made on the step–step correlation function (SSCF). This assumption defines the order parameter and leads to a single scaling field which is related to N_0, the degree of polymerisation. As a result, all critical exponents are related to a single exponent. We believe that our approach gives a clear and simple physical meaning of the different exponents and fields. For instance, it is shown that the Flory (1969) result for ν is equivalent to a Curie–Weiss law for the chain susceptibility χ. The solution of the simple case $d = 1$ is trivial. The exponents suggested by the present theory fit this solution well. Also, the exponents obtained for $d \geq 4$ are the same as those for a ferromagnet in a classical mean field approach.

The present interpretation of SAWs as a critical phenomenon suggests an additional meaning for the exponent ν in other critical systems.

Recently, following Mandelbrot (1977) we defined and measured the local fractal dimensionality, LFD (Havlin and Ben-Avraham 1982a, c) of a single polymer chain.

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The concept was found to be useful for characterising this polymer. LFD is defined as

$$D_{N_0}(N) = \ln\left(\frac{N+1}{N}\right) \Big/ \ln\left(\frac{\langle R^2_{N+1}\rangle_{N_0}}{\langle R^2_N\rangle_{N_0}}\right)^{1/2}, \tag{1}$$

where $D_{N_0}(N)$ is the LFD associated with a 'local' scale of length corresponding to N monomers (the full chain consists of N_0 monomers). The quantity $\langle R^2_N\rangle_{N_0}$ is the mean squared length of a segment of N monomers averaged over the whole polymer chain. LFD is a measure of how winding is the polymer in a certain scale N. As $N_0 \to \infty$, there seems to exist a range of scales (the 'main range') for which LFD tends to be constant (see figure 1), thus resembling a self-similarity property. Then, fractal dimensionality D is defined for the main range by the following equation:

$$[(\langle R^2_N\rangle_{N_0})^{1/2}]^D = AN, \qquad 1 \ll N \ll N_0. \tag{2}$$

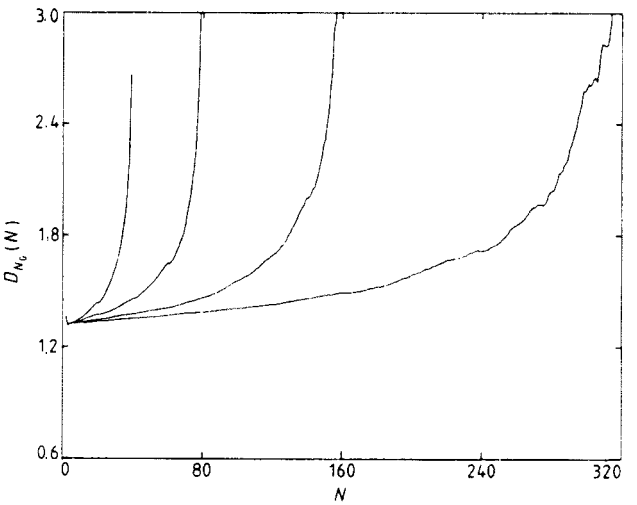

Figure 1. Plot of the local fractal dimensionality $D_{N_0}(N)$ as a function of N for two-dimensional self-avoiding walks, with $N_0 = 40, 80, 160, 320$.

The fractal dimensionality D is shown to be related to the end-to-end exponent ν by $D = 1/\nu$ (Havlin and Ben-Avraham 1982a). The fact that the exponents ν and $1/D$ are equal is by no means obvious. Moreover, the usual end-to-end exponent ν does not represent an *internal* self-similarity of the polymer and therefore it does not have the meaning of fractal dimensionality (FD).

The existence of FD is supported by a Monte Carlo enrichment technique (Wall *et al* 1963). Results are shown in figure 1. It is seen that as N_0 increases, there is a larger range with nearly constant D. This result is not restricted to square planar lattices but is also present for other dimensions and types of lattice (Havlin and Ben-Avraham 1982c).

The mean square length can also be expressed as a sum of correlations in the form

$$\langle R^2_{i,i+N}\rangle_{N_0} = \sum_{j=0}^{N-1}\sum_{k=0}^{N-1} \langle \boldsymbol{u}_{i+j} \cdot \boldsymbol{u}_{i+k}\rangle \tag{3}$$

where $\boldsymbol{u}_i$ is a unit vector representing the ith step. Since there is a range of N with constant fractal dimensionality, (2) must hold. Therefore,

$$\langle \boldsymbol{u}_i \cdot \boldsymbol{u}_{i+N} \rangle_{N_0} = C'/N^{2-2\nu}, \qquad 1 \ll N \ll N_0. \tag{4}$$

Indeed, integration of (4) yields

$$\langle R_N^2 \rangle_{N_0} \cong [C'/\nu(2\nu-1)]N^{2\nu}. \tag{5}$$

We see that the existence of FD implies an algebraic decay law for the SSCF (Domb 1969, Mandelbrot 1977).

The algebraic decay law suggested in (4) is characteristic of a correlation function when criticality is arrived at. Usually, in critical phenomena the pair correlation function that is related to the order parameter is of the form

$$g(\boldsymbol{r}_{ij}) = \frac{f(r_{ij}/\xi)}{r_{ij}^{d-2+\eta}}, \qquad r \gg \text{one lattice separation}. \tag{6}$$

In (6), $\boldsymbol{r}_{ij}$ is the displacement vector between sites i and j, and ξ is a correlation length tending to infinity as $T \to T_c$. Since, for SAWs, $\langle R_N^2 \rangle_{N_0}^{1/2} \equiv r_N \sim N^{\nu}$, (4) is similar to (6) when $\xi \to \infty$.

Following this resemblance, we assume that (4) plays the same role in the SAW problem as (6) in a general critical phenomenon. It should be noted that this is a very restrictive assumption. From this assumption, the physics of the SAW problem can be viewed as a critical phenomenon. For instance, it follows that $\boldsymbol{u}_i$ is analogous to, say, the magnetic moment $\boldsymbol{s}_i$ of a ferromagnet. Also, the relations among exponents are uniquely determined, as we presently show.

Finally, we extend (4) to the non-critical case by writing, in analogy to (6),

$$\langle \boldsymbol{u}_i \cdot \boldsymbol{u}_{i+N} \rangle = \frac{f(r_N/\xi)}{r_N^{d-2+\eta}} \qquad 1 \ll N \ll N_0. \tag{7}$$

If one regards the SAW as critical, then the correlation length appearing in (7) should be of the order of the end-to-end length. That is,

$$\xi \sim \langle R_{N_0}^2 \rangle^{1/2} \sim N_0^{\nu} \tag{8}$$

where ν is the known end-to-end exponent. Usually, in critical phenomena we have

$$\xi \sim t^{-\nu}, \qquad t = |T - T_c|/T_c, \tag{9}$$

where t is the reduced temperature and ν is the correlation length exponent. We make an arbitrary identification of the temperature-like field

$$t \sim 1/N_0 \tag{10}$$

so that ν in (8) keeps its original meaning.

Equation (10) can be interpreted in the following way. In the SAW problem, all physical results are derived solely from entropy considerations. The only parameter which controls entropy and is allowed to change is the degree of polymerisation N_0. Therefore, it is in fact the actual field determining SAW behaviour. We still can say that $1/N_0$ is a temperature-like field because of the similarity between (8) and (9). The fact that all fields are related to a single parameter leads to the peculiar result that all critical exponents are related to a single exponent. Thus our previous assumption contained in (7) relates all critical exponents to ν.

According to (10), criticality is reached when $N_0 \to \infty$. When this happens, SSCF decays in an algebraic form. Comparing (7) and (4) and keeping in mind that $r_N \sim N^{\nu}$, we find that

$$\eta = (2 - d\nu)/\nu = 2D - d. \tag{11}$$

The meaning of the exponent η is easily understood from (7).

The SSCF, as written in (7), suggests identifying an order parameter

$$\langle \boldsymbol{u}_i \rangle_{N_0} \sim \boldsymbol{R}/N_0 \sim N_0^{\nu-1}. \tag{12}$$

The average might be taken over all the configurations of a chain with N_0 steps with an end-to-end vector pointing in a certain direction. The order parameter is a measure of the polymer length per monomer. The ordering means that different steps tend to be aligned. That is, the chain tends to form in a certain direction.

Using (10) and (12), β follows from its definition (the order parameter exponent)

$$\beta = 1 - \nu. \tag{13}$$

We argue that the known scaling laws (i.e. relations between critical exponents) hold in the SAW problem. A general expression for the free energy density might be

$$\mathscr{F} = F/N_0^{d\nu} = N_0^{\alpha-2} g(uN_0^{\beta}) + \boldsymbol{u} \cdot \boldsymbol{h} \tag{14}$$

where F is the total free energy and $N_0^{d\nu}$ is a measure of the system's volume. The factor $N_0^{\alpha-2}$ is required to give the correct meaning of the critical exponent α related to the 'specific heat'. The scaling function $g(uN_0^{\beta})$ is in accordance with the usual form derived for the probability of the end of the SAW being at $\boldsymbol{R} = N_0 \boldsymbol{u}$ (de Gennes 1979). The last term assumes the usual form of interaction with an external field $\boldsymbol{h}$. We can understand the meaning of the external field $\boldsymbol{h}$ by the following argument. The external ordering field tends to align the steps $\boldsymbol{u}_i$ of the walk. Therefore $\boldsymbol{h}$ should be related to a stretching force f applied to the ends of the polymer. The contribution to the energy density from f is $\boldsymbol{R} \cdot f/N_0^{d\nu}$. This yields, when compared with $\boldsymbol{u} \cdot \boldsymbol{h}$,

$$\boldsymbol{h} = fN_0^{1-d\nu}. \tag{15}$$

The Kadanoff and Widom relations (Stanley 1972) follow easily from equation (14):

$$2 - \alpha = \nu d, \tag{16}$$

$$\alpha + 2\beta + \gamma = 2. \tag{17}$$

A relation for the exponent η can be obtained from the sum rule which gives χ,

$$\chi = \frac{\partial u}{\partial h} \propto N_0^{\gamma} \propto \int \langle \boldsymbol{u}_i \cdot \boldsymbol{u}_{i+N} \rangle \, \mathrm{d}^d r. \tag{18}$$

Using (7) there results

$$\gamma = \nu(2 - \eta). \tag{19}$$

Finally we derive a relation for the exponent δ, which is defined by

$$u \propto h^{1/\delta}. \tag{20}$$

From this definition and the one for β it follows that

$$u = N_0^{\nu-1} \phi(N_0^{\delta\beta} h). \tag{21}$$

One the other hand a usual scaling function for u can be obtained (Pincus 1976, de Gennes 1979),

$$u = N_0^{\nu-1}\phi(N_0^{\nu}f) = N_0^{\nu-1}\phi(N_0^{\nu}hN_0^{d\nu-1}). \tag{22}$$

Comparison with (21) yields the usual relation.

$$\delta\beta = \nu(d+1)-1. \tag{23}$$

We emphasise that apart from α and ν all the other critical exponents have neither the same value nor the same interpretation as those of the $n=0$ vector model. Indeed, in the present approach the exponents are related to an order parameter and to critical fields which are not the ones in the $n=0$ vector model.

In contrast to general critical phenomena, all critical exponents are related to a single exponent. In fact the usual scaling relations are supplemented by either (11) or (13), which enables us to express all exponents in terms of ν, say:

$$\alpha = 2-\nu d, \qquad \beta = 1-\nu, \qquad \gamma = 2\nu+\nu d-2, \qquad \delta = \frac{\nu(d+1)-1}{1-\nu},$$
$$\eta = 2/\nu - d. \tag{24}$$

We note that the assumptions leading to (11) and (13) are consistent, for one can derive each of these equations from the other by using scaling relations.

We show now that the scaling laws concerning the elongation R of a chain when an external stretching force f is applied to its ends, both for a weak and a strong f (Pincus 1976, de Gennes 1979), follow immediately from the present approach. Indeed, when f is weak h is weak too. Then using (15), (18) and (24), we obtain

$$u \propto N_0^{\gamma}h = fN_0^{1+\gamma-d} = fN_0^{2\nu-1}, \tag{25}$$

that is

$$R \propto fN_0^{2\nu} \qquad \text{for a weak } f. \tag{26}$$

On the other hand, for a strong f (i.e. a strong h) it follows from equations (20), (21) that u is independent of N_0, so that

$$R \propto N_0 \qquad \text{for a strong } f. \tag{27}$$

Equations (26), (27) are in agreement with Pincus (1976) and de Gennes (1979).

We can restate the relation for γ in (24) as

$$\nu = (\gamma+2)/(d+2). \tag{28}$$

It is interesting to note that the Flory (1969) result for ν

$$\nu = 3/(d+2) \tag{29}$$

follows if $\gamma = 1$ for every lattice dimension d. That is, the Flory result is equivalent, according to the present approach, to the assumption that susceptibility χ follows a Curie–Weiss law, independent of the lattice dimension. It is in this respect that the Flory result is obtained from a mean field approximation (Edwards 1965).

We use the Flory relation (29) or $\gamma = 1$ in order to evaluate all other critical exponents

$$\alpha = 2\nu - 1 = \frac{4-d}{2+d} = \frac{2}{D} - 1, \qquad \beta = 1 - \nu = \frac{d-1}{d+2} = 1 - \frac{1}{D},$$
$$\delta = \frac{2-\nu}{1-\nu} = \frac{2d+1}{d-1} = \frac{2D-1}{D-1}, \qquad \eta = 2 - \frac{1}{\nu} = \frac{4-d}{3} = 2 - D. \tag{30}$$

The numerical values for the critical exponents are calculated from (30) and presented in table 1.

Table 1.

d	ν	$D = 1/\nu$	α	β	γ	δ	η	$d-2+\eta$
1	1	1	1	0	1	∞	1	0
2	$\frac{3}{4}$	$\frac{4}{3}$	$\frac{1}{2}$	$\frac{1}{4}$	1	5	$\frac{2}{3}$	$\frac{2}{3}$
3	$\frac{3}{5}$	$\frac{5}{3}$	$\frac{1}{5}$	$\frac{2}{5}$	1	$\frac{7}{2}$	$\frac{1}{3}$	$\frac{4}{3}$
4	$\frac{1}{2}$	2	0	$\frac{1}{2}$	1	3	0	2

The case $d = 1$ is trivial, with the only possible SAW being a fully stretched chain. The exponents predicted agree with this picture. It is obvious that $R \sim N_0$, implying that $\nu = 1$. The fact that $\beta = 0$ means that there is no difference in the ordering between the cases of finite N_0 and $N_0 \to \infty$. The step–step correlation remains constant, in agreement with $d - 2 + \eta = 0$. The order parameter is constant and cannot depend on any field, a fact that is well represented by $\delta = \infty$.

Also, for $d = 4$ it is interesting to note that the critical exponents are exactly like those derived in a mean field theory. In particular, the fractal dimensionality is $D = 2$, the same as for the 'ideal chain', that is, an unrestricted random walk (Mandelbrot 1977). However, there is a difference between a four-dimensional SAW and a random walk. In the SAW, there are still finite correlations between steps. These correlations give rise to logarithmic corrections to scaling which are known, from the $n = 0$ vector model (Guttmann 1980), to be present (Havlin and Ben-Avraham 1982b).

The present approach predicts the same exponents ν and α as those of the $n = 0$ vector model. This is due to the fact that the only characteristic length in the SAW problem is the end-to-end distance, which must be related to the correlation length ξ, and thus to ν. However, we emphasise that the other exponents are not identical to those of the $n = 0$ vector model. This is because our definition of the order parameter does not seem to be related to the order parameter of the $n = 0$ ferromagnet.

In the present approach, there is a clear physical meaning to the order parameter and to the ordering field. The susceptibility is simply related to the response of the elongation of the chain to a stretching force applied to its ends.

In addition to the usual meaning of the critical exponent ν in general critical phenomena, in the context of the SAW problem, ν is a measure of the fractality of the system. That is, the SAW has a fractal structure with an FD equal to $1/\nu$. This suggests a possible interpretation of ν in other critical phenomena as being an indication of a fractal structure. For example, in the case of a ferromagnet, the length ξ of the patches of spins pointing in a certain direction grows as $t^{-\nu}$ (Ma 1976). But we may

interpret the patches as having a fractal structure. This means that they possess a self-similarity property, as for example in a Sierpinski sponge (Mandelbrot 1977). Moreover, this interpretation explains the scaling law in the Kadanoff (1967) transformation for the order parameter in a ferromagnet

$$L^d\langle\sigma\rangle \sim L^x\langle\mu\rangle. \tag{31}$$

Here, L is the block size, $\langle\sigma\rangle$ is the original magnetisation, and $\langle\mu\rangle$ is the renormalised magnetisation. Each side of (31) displays the total amount of magnetisation in a block. The left-hand term is the usual expression, whereas the right-hand term is calculated assuming that $\langle\mu\rangle$ follows a fractal pattern of dimensionality $x = 1/\nu \equiv D$. Thus, $L^x = L^D$ is the effective volume of the renormalised magnetisation $\langle\mu\rangle$. It is interesting to note that if one accepts the above interpretation, then ν should have a limit

$$\nu \geqslant 1/d. \tag{32}$$

This is due to the fact that the fractal dimensionality cannot exceed the Euclidean dimension of the lattice, d.

Finally, we note that the SAW problem is a finite scaling problem. Indeed, the number of monomers N_0 is finite. We can show the consistency of our model of SAWs with finite scaling by using the above interpretation of ν as fractal dimensionality. For example, the susceptibility in finite scaling theory (Fisher 1971) is given by

$$\chi \sim (n^{1/\nu})^{\gamma} \tag{33}$$

where $n \equiv L$ is the size of the sample. If we understand $1/\nu \equiv D$ as FD, then $L^D \equiv N_0$ is the effective number of spins in the system. Then (33) reads $\chi \sim N_0^{\gamma}$, exactly as does (18). The same argument also applies to other critical exponents. However, there is a difference between the SAW as a critical problem and finite systems. In finite systems, criticality is reached with $N_0 \to \infty$ and $t \to 0$, whereas in a SAW, it suffices that $N_0 \to \infty$ because N_0 is the only parameter governing SAW behaviour.

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