

## Peculiar Scaling of Self-Avoiding Walk Contacts

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The nearest neighbor contacts between the two halves of an  $N$ -site lattice self-avoiding walk offer an unusual example of scaling random geometry: for  $N \rightarrow \infty$  they are strictly finite in number but their radius of gyration  $R_c$  is power law distributed  $\propto R_c^{-\tau}$ , where  $\tau > 1$  is a novel exponent characterizing universal behavior. A continuum of diverging length scales is associated with the  $R_c$  distribution. A possibly superuniversal  $\tau = 2$  is also expected for the contacts of a self-avoiding or random walk with a confining wall.

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The self-avoiding walk (SAW) is a classical problem in statistical mechanics, playing a central role in our understanding of polymer statistics and intimately related to magnetic critical phenomena and percolation [1]. In its most simple version the SAW amounts to the statistical characterization of equally probable single chain conformations, with no overlaps or intersections. These conformations are made by  $N - 1$  successive nearest neighbor (nn) steps ( $N$  sites) on a lattice in  $d$  dimensions. For  $N \rightarrow \infty$ , quantities like the radius of gyration with respect to the center of mass of SAW configurations,  $R_g$ , have an average  $\langle R_g \rangle \sim N^{\nu_{\text{SAW}}}$ , where  $\nu_{\text{SAW}}$  is the SAW metric exponent. When  $d > 1$  self-avoidance does not prevent the conformations from involving close approaches of different parts of the chain: here we generally count as contacts the pairs of nn lattice sites which are visited, not consecutively, by the SAW. The totality of such contacts grows on average proportional to  $N$  [2] and possesses the same fractal dimension ( $\equiv 1/\nu_{\text{SAW}}$ ) as the whole SAW.

In the present Letter we discuss so far unexplored features of a particular subset of SAW contacts. Such features represent an unusual example of how scale invariance can manifest itself in a finite, nonextensive portion of an infinite fractal set. The scaling exponent  $\tau$  of the probability distribution of the gyration radius of such a subset represents a novel characterization of SAW universal behavior. The fact that  $\tau > 1$  implies the existence of a whole continuum of diverging characteristic lengths in the SAW problem, in addition to the length  $\langle R_g \rangle$ .

The subset on which we focus here is that of the contacts between the two halves of a SAW (Fig. 1). Counting such contacts alone allows one to get rid of less interesting effects, which are extensive in  $N$ . Being related to problems like network formation, transport, or intramolecular reactions, these contacts can be of particular interest for applications in which the two half chains are made of different monomers, as for diblock copolymers [3]. When the chain represents a homopolymer, the subset we consider is particularly significant in relation to the effect of nearest neighbor interactions on the SAW [4]. This is the case of models of the polymer  $\Theta$  collapse [1,5,6], where

an attractive nn energy  $\epsilon < 0$  is associated to each contact. In this case a Boltzmann factor  $e^{-\epsilon/T}$  weighs each contact occurring in a configuration at temperature  $T$ . If for such a model one counts contacts only between the two halves of the SAW, the average number of them is of the order  $N^0$  in the high  $T$  regime, increases as  $N^\phi$ , with  $0 < \phi < 1$ , at the  $\Theta$  point, and scales as  $N$  at low  $T$ .  $\phi$  turns out to coincide with the crossover exponent  $\phi_\Theta$  at  $T = T_\Theta$ , where  $\langle R_g \rangle \sim N^{\nu_\Theta}$ , with  $\nu_\Theta \neq \nu_{\text{SAW}}$  [7]. Similar behaviors occur if the attractive interactions are associated exclusively with this subset of contacts, and the model describes a diblock copolymer zipping transition [7,8]. In different  $T$  regimes of the  $\Theta$  and zipping transitions the contacts between the two halves of the SAW behave in a way analogous to the monomers adhering to a wall in polymer adsorption [7]. Most recently it has also been found that in  $d = 2$  the fractal dimensions of the contacts between the two half chains are the same at the homopolymer  $\Theta$  point and at the diblock copolymer zipping transition [8]. Thus, intriguing universality aspects can be expected to underlie the geometry of SAW contacts.

The contacts between the two halves of a polymer have already been studied by renormalization group methods [9] in the high  $T$  regime controlled by excluded volume. The focus there was on the scaling of their average number,  $\langle N_c \rangle$ , and precisely on the scaling correction exponent describing its approach to a finite limit for  $N \rightarrow \infty$ . This finite limit shows that only a vanishing fraction of the

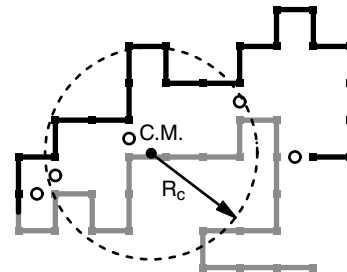


FIG. 1. SAW in two dimensions: the contacts between its two halves (light and dark, respectively) are indicated by open circles. c.m. is the center of mass of these contacts and  $R_c$  is their radius of gyration.

total number of contacts pertains to approaches of remote portions of the chain. In fact,  $\langle N_c \rangle$  gives only limited information on the contact statistics. The full probability distribution function (PDF) for  $N_c$ ,  $P(N_c, N)$ , could in principle have higher moments diverging with  $N \rightarrow \infty$ , and we devote a first effort to check this possibility, which is normally not considered in polymer statistics. We perform several Monte Carlo simulations to investigate this PDF and its moments in various dimensions and for  $80 \leq N \leq 2000$ . Since the configurations with many contacts are very rare, we employ a pruned-enriched Rosenbluth method [6] tuned to increase the sampling of configurations with a high number of contacts. This enables us to obtain good statistics also in the tail of the PDF, which for all  $d$  turns out to be a negative exponential without substantial dependence on  $N$ , as displayed in Fig. 2 for SAW on a cubic lattice.

These results show that this set of contacts is strictly finite in the  $N \rightarrow \infty$  limit. In spite of this, one can still ask whether these contacts have interesting geometrical scaling properties, not just reducing to those of a spatially bounded random set. If we indicate by  $P_{\text{rad}}(R_c, N)$  the cumulative PDF of  $R_c$  (Fig. 1) over all SAW configurations, strict boundedness would mean that the moments  $\langle R_c^q \rangle \sim \int dR_c R_c^q P_{\text{rad}}(R_c, N)$  remain finite, for  $N \rightarrow \infty$ ,  $\forall q$ . We extrapolate the moments in the form  $\langle R_c^q \rangle \sim N^{\sigma_q}$ . The data are generated by sampling SAW of fixed length with a Monte Carlo algorithm based on pivot moves [10], which have been proved to be very efficient for SAW's [11]. Since the contacts between the two halves of the SAW are mainly located close to the junction point, local moves [12] are also attempted in this region. We consider hypercubic lattices and the fcc lattice in  $d = 3$ . Contrary to what happens for  $P(N_c, N)$ , for all  $d$  we find that  $\sigma_q$  is positive and grows linearly with  $q$ , at sufficiently high  $q$ . The data are consistent with a behavior

$$\sigma_q = \begin{cases} 0 & \text{if } q \leq \tau - 1, \\ \nu[q - (\tau - 1)] & \text{if } q > \tau - 1, \end{cases} \quad (1)$$

where  $\sigma_q = 0$  may represent logarithmic divergences for  $0 < q \leq \tau - 1$ . In  $d = 2$ , for example (see Fig. 3),

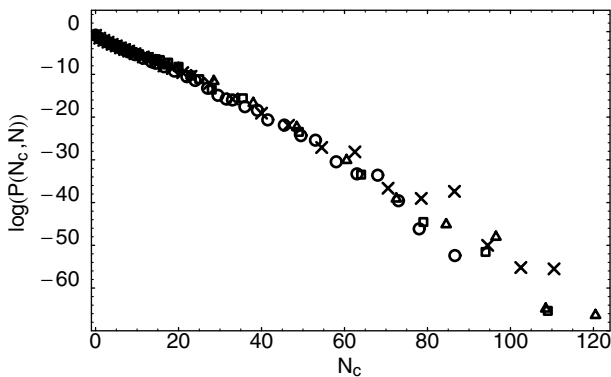


FIG. 2. Histograms of  $\ln[P(N_c, N)]$  for SAW on a cubic lattice, with  $N = 200$  ( $\circ$ ),  $400$  ( $\times$ ),  $800$  ( $\triangle$ ), and  $1600$  ( $\square$ ).

we find  $\tau = 1.93(2)$  and  $\nu = 0.76(1)$ , consistent with  $\nu = \nu_{\text{SAW}} = 3/4$  [13]. The form (1) is compatible with a PDF having a scaling form  $P_{\text{rad}}(R_c, N) \approx R_c^{-\tau} f(R_c/N^\nu)$ . That  $\nu = \nu_{\text{SAW}}$  is quite plausible since  $N^{\nu_{\text{SAW}}}$  is the only expected characteristic length in the problem. However, as discussed below,  $P_{\text{rad}}$  itself introduces a multiplicity of new length scales for the SAW. The fact that the moments do not approach zero for  $q < \tau - 1$  (i.e.,  $\sigma_q$  does not become negative) should be due to the circumstance that  $f(x)$  is not converging to zero for  $x \rightarrow 0$ . In other terms, the scaling function  $g$ , if we write  $P_{\text{rad}} \approx N^{-\tau\nu} g(R_c/N^\nu)$ , is singular for its argument approaching zero,  $g(x) \sim x^{-\tau}$ . We verify these assumptions on the structure of  $P_{\text{rad}}$  by scaling collapse plots for various  $d$ . For example, Fig. 4 shows the data collapse of  $\ln[f(x)]$  for  $d = 3$ . A similar collapse plot for  $\ln[g(x)]$  is reported in the inset.

It is indeed the singular character of  $g(x)$  for  $x \rightarrow 0$ , which allows the exponent  $\tau$  to take a nontrivial value  $> 1$ , while maintaining the zeroth, normalization moment of the PDF equal to 1. The lower length cutoff  $l$  (lattice spacing in this case) is crucial to obtain a finite integral, in  $dx = d(R_c/N^\nu)$ , of the PDF in the continuum limit, because the main contribution comes from small values of  $x$ , close to  $x_- \equiv l/N^\nu$ . This contribution has an  $N$  dependence which compensates the diverging factor  $N^{-\nu(\tau-1)}$  extracted in front of the integral.  $\tau > 1$  means that we cannot associate with the  $R_c$  PDF a unique characteristic length. Indeed, putting  $\xi_q \equiv \langle R_c^q \rangle^{1/q}$  we find  $\xi_q \sim N^{\nu_q}$  with  $\nu_q \equiv \sigma_q/q$ , for  $q \in [\tau - 1, +\infty)$ . This means that the self-similarity of contacts has an intrinsic multiscaling character.

The  $\tau$  found here is a novel exponent for the SAW [14]. It is a measure of the spread of the region within which one-half of the chain feels the presence of the other one in the SAW configurations. A higher  $\tau$  (see Table I) indicates more localized contacts. Like the global geometry of the SAW, the spread of contacts is determined by the interplay between entropic and excluded volume effects. The nonmonotonic behavior of  $\tau$  is remarkable, which takes minimum values in  $d = 3$  and  $d = 4$ , indicating these dimensionalities as the optimal ones for a broad

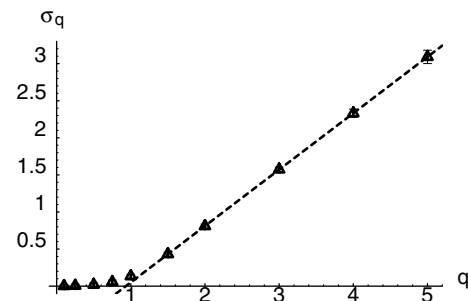


FIG. 3.  $\sigma_q$  vs  $q$  and extrapolation of  $\tau - 1$  for  $d = 2$ . We expect  $\sigma_q = 0$  for  $q \leq \tau - 1$ . Numerically a logarithmic divergence cannot be easily distinguished from a power law one with  $\sigma_q \geq 0$ .

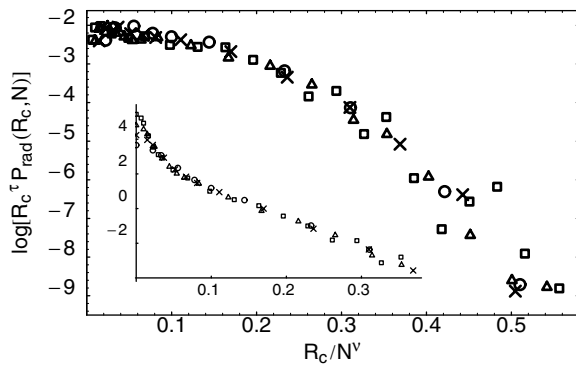


FIG. 4. Collapses of  $\ln[f(x)]$  (see text) and  $\ln[g(x)]$  (inset) for SAW on cubic lattice, with  $N = 200$  ( $\circ$ ),  $400$  ( $\times$ ),  $800$  ( $\triangle$ ), and  $1600$  ( $\square$ ).

interpenetration of the two half chains. At high  $d$  there is soon much room for the two branches of the SAW to develop without giving rise to contacts, and this tends to localize them more.  $\tau$  is rather high in  $d = 2$ : we interpret this as a consequence of the peculiar topology of the two-dimensional lattice, which makes it more difficult than, e.g., in  $d = 3$  for the two half chains to approach each other at large length scales. The dependence of  $\tau$  on  $d$ , also above the upper critical dimension  $d_u = 4$ , is a further indication of the peculiar novel character of this exponent.

In  $d = 2$  and  $d = 3$  we also investigate the behavior of the contacts between the two half chains in the presence of nn attractive interactions ( $\Theta$  point model). While for  $T > T_\Theta$  the behaviors of their PDF's appear the same as at  $T = \infty$ , at the  $\Theta$  point the moments of  $P$  diverge as those of  $P_{\text{rad}}$ , while  $\tau$  becomes equal to 1 and  $\sigma_q/q = \nu_\Theta$  for the latter PDF. This suggests that the disappearance of the singular scaling function in  $P_{\text{rad}}$  could be a good criterion for locating the transition point. This is illustrated in Fig. 5, referring to the  $\Theta$  point in  $d = 3$ , simulated as in Ref. [6] with chains up to  $N = 2000$ . We collect data from two runs at  $-\epsilon/T = 0.25, 0.27$ , and we use the multiple histogram method [15] to calculate the moments in the surrounding interval of temperatures. The result from the values of  $q$  examined is  $-\epsilon/T_\Theta = 0.274(4)$ , consistent with accurate estimates by other methods: for example,  $0.275(8)$  in [5] and  $0.2690(3)$  in [6]. Similar results are valid for models of the diblock copolymer zipping transition [16].

TABLE I. Extrapolated values of  $\tau$  and  $\nu$  for various lattices, using SAW with length from  $N_{\text{min}}$  to  $N_{\text{max}}$ .

Lattice	$\tau$	$\nu$	$\nu_{\text{SAW}}$	$N_{\text{min}}$	$N_{\text{max}}$
$2d$	1.93(2)	0.76(1)	3/4 [13]	1000	10 000
$3d$	1.51(2)	0.595(5)	0.5877(6) [11]	1000	10 000
fcc	1.52(2)	0.594(5)	0.5877(6)	3000	6000
$4d$	1.51(3)	0.52(2)	1/2	1500	8000
$5d$	2.0(2)	0.49(2)	1/2	1000	8000
$6d$	2.9(1)	0.49(1)	1/2	1000	5000

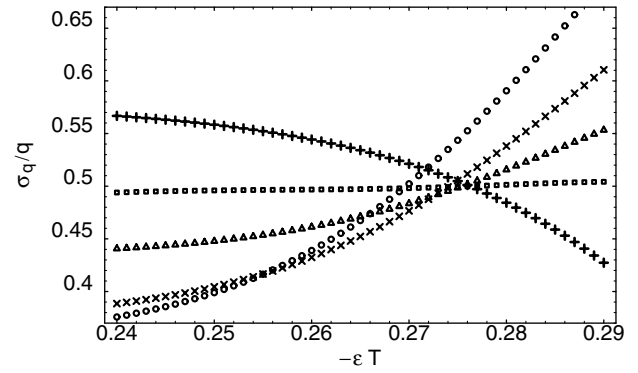


FIG. 5. Extrapolation of  $\sigma_q/q$  close to  $T_\Theta$  in  $d = 3$ , for  $q = 0.5$  ( $\circ$ ),  $q = 1$  ( $\times$ ),  $q = 2$  ( $\triangle$ ), and  $q = 4$  ( $\square$ ). The crossings are consistent with the expectation to find  $\tau = 1$  and  $\sigma_q/q = \nu_\Theta = 1/2$  right at  $T = T_\Theta$ . The curve with the opposite trend (+) refers to the effective  $\nu$  exponent of the SAW radius of gyration.

For SAW with attractive interactions the average number of contacts between the two half chains behaves in the various temperature ranges as the mean number of SAW-wall contacts in a polymer adsorption transition. Thus, it makes sense to check whether also in the adsorption process the high  $T$  ordinary regime is characterized by peculiar scaling features of the kind described above. To this purpose we study the PDF's of the number and the radius of SAW-wall contacts at  $T = \infty$ , where the wall exerts only a geometrical confinement effect on the chain. Here we consider as radius the mean distance  $R_c^*$  of a contact from the point where the SAW is grafted to the wall [17]. Also in this case all the moments of the PDF of  $N_c$  appear to remain finite for  $N \rightarrow \infty$ . The PDF's of  $R_c$  show singular scaling functions with an exponent  $\tau \simeq 2$ , in  $d = 2$  and  $d = 3$  (Table II).

We study also the case of a random walk (RW) confined by a wall, for which we are able to compute exactly  $\tau$ . Consider first a RW on a square lattice tilted at  $45^\circ$  with respect to the coordinate axes, in such a way that the nn of a site have coordinates  $\{(1, 1), (-1, 1), (-1, -1), (1, -1)\}$ . In this way a nn step moves the RW with nonzero and independent displacements along both coordinate directions. This simplifies the calculations, but we expect the final results to be valid for every lattice model, because independence is asymptotically recovered for long RW. The generalization to  $d$  dimensions gives  $2^d$  nn vectors of the form  $(1, 1, \dots, 1), (-1, 1, \dots, 1), \dots, (-1, -1, \dots, -1)$  and, for example, in  $d = 3$  one obtains the bcc lattice. Let the walk start from the origin, near a  $d - 1$ -dimensional hard wall perpendicular to the  $x$  coordinate: the problem in the  $x$  direction is equivalent to a one-dimensional RW which steps

TABLE II. As in Table I, but for SAW-wall contacts.

Lattice	$\tau$	$\nu$	$N_{\text{min}}$	$N_{\text{max}}$
$2d$	1.99(3)	0.744(5)	1000	6000
$3d$	1.968(34)	0.58(1)	1000	8000

to  $nn$  sites with equal probability. The probability to be again at  $x = 0$  after  $n$  steps is given by  $P_n(0) = 2^{-n} \binom{n}{n/2}$ . The effect of the impenetrable wall is represented by forbidden sites located at  $\bar{x} = -1$ . So one has to subtract the probability to travel through this point. The method of images [18] in this simple case says that this is equal to the probability to go from  $x = 0$  to its mirror image with respect to  $\bar{x}$ ,  $x = -2$ . So  $\bar{P}_n(0) = P_n(0) - P_n(-2) = P_n(0)2(n+2)^{-1}$  is the probability to be on the surface. The  $q$ th moment of the average distance of a contact from the origin is thus

$$\langle R_c^*(N)^q \rangle \sim \frac{\sum_{n=2,4,6,\dots}^N \bar{P}_n(0) (n^{1/2})^q}{\sum_{n=2,4,6,\dots}^N \bar{P}_n(0)}, \quad (2)$$

where  $n^{1/2}$  is the root mean square displacement after  $n$  steps. Using  $n! \approx \sqrt{2\pi} n^{n+1/2} e^{-n}$  for the binomials, one recovers that the denominator is finite for  $N \rightarrow \infty$ , while the numerator is equivalent to a sum of the type  $\sum_{n=2}^N n^{(q-3)/2}$ , diverging as  $N^{(q-1)/2}$  if  $q > 1$ . This means  $\tau = 2$  for RW near a wall, in any  $d$ . The exact result for RW suggests that, in any dimension, for SAW confined by a wall, the scaling of the contacts is the same as for RW. Thus, excluded volume effects seem to play no role in determining  $\tau$  for the contacts of the SAW with a confining wall.

In summary, the contacts discussed above represent a very peculiar example of scaling random set: in fractal physics we are familiar with sets in which the number of elements is growing to infinity together with their average radius of gyration, and criticality implies a nontrivial scaling for the PDF's of both quantities. A typical example is percolation clusters [19], whose size PDF has a singular scaling function with nontrivial  $\tau$ , as we instead find here for  $P_{\text{rad}}$ . In the case considered here the scale invariance of the set is not accompanied by its number of elements being broadly, power law distributed. The criticality is in fact triggered by the length of the whole chain,  $N$ , becoming infinite, while  $N_c$  remains finite. A  $\tau$  exponent, possibly superuniversal, can also be defined for the contacts between a SAW and a  $d - 1$ -dimensional confining wall in the ordinary regime. The case of a RW in the presence of a wall can also be treated, yielding the exact classical value  $\tau = 2$ , which could apply also to SAW, independent

of  $d$ . Exact determinations of these exponents for SAW in low ( $d = 2$ ) or high dimensionality and the possible descriptions of the new scalings within the renormalization group framework remain a challenge for the future.

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