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1995 J. Phys. A: Math. Gen. 28 833

(http://iopscience.iop.org/0305-4470/28/4/010)

J. Phys. A: Math. Gen. 28 (1995) 833–838. Printed in the UK

Survival of self-avoiding walks inside spherical cavities—a Monte Carlo study in two dimensions

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Received 11 April 1994, in final form 16 November 1994

Abstract. We have studied the survival probability $f(N, R)$ of an N-step square lattice self-avoiding walk (SAW), with one end at the centre of an absorbing circular cavity of size R. Our numerical results clearly indicate that the form of $f(N, R)$ depends on the method by which the surviving SAW are generated.

A polymer chain is expected to be shrunk more in a porous medium than in a regular medium [1, 2] as confinement inside a cavity can cost a certain reduction, $-\delta S$, in its configurational entropy, S; the smaller the cavity is, the greater the reduction in S will be. Its size is then decided by the competition between its tendency to maximize $-\delta S$ and the availability of suitably sized pores in the medium.

For a freely jointed chain, without an excluded volume interaction and confined in a spherical cavity of size R, Edwards and Freed [3] have shown that $-\delta S$ is proportional to $-N/R^2$. Together with contributions due to the randomness of the medium and the excluded volume interaction, this form of $-\delta S$ has been used [4, 5] to construct the Flory theory of polymers in a random medium. An alternative approach to this problem, as pointed out by Machta and Guyer [5], is to study the survival fraction, f, of random walks in the presence of traps.

Given a random distribution of traps, the medium may be visualized as consisting of trap-free regions of various shapes and sizes. Assuming that these regions are spherical in shape, Grassberger and Procaccia [6] have shown that it is the maximally sized regions which determine the asymptotic behaviour of f. Honeycutt and Thirumalai [4] have demonstrated that non-spherical shapes could lead to interesting results.

We have studied the survival probability, $f(N, R)$, of an N-step square lattice self-avoiding walk (SAW), with one end at the centre of an absorbing circular cavity of size R. Our numerical results clearly indicate that the form of $f(N, R)$ depends on the method by which the surviving SAWs are generated.

A variety of scaling properties is known to be satisfied by SAWs [7]. For example, Lhuillier [8] has proposed the following scaling form for the distribution, $Q(N, r)$, of the gyration radii of an N-step SAW:

$$Q(N, r) \approx N^{-\nu d} \exp[-(N^{\nu}/r)^{\alpha d} - (r/N^{\nu})^{\delta}] \tag{1}$$

in d dimensions, where $\alpha \equiv 1/(\nu d - 1)$ and $\delta \equiv 1/(1 - \nu)$. For a spherical cavity of size R, we may define and evaluate the integral

$$q(N, R) \equiv \int_{N^{1/d}}^{R} Q(N, r)\, \mathrm{d}r \approx N^{-\nu(d-1)} q(N^{\nu}/R). \tag{2}$$

0305-4470/95/040833+06\$19.50

The lower limit for the integral is set equal to the size of the most compact SAW, which is of the order of $N^{1/d}$ [5]. It is reasonable to expect that $q(N, R)$ will provide an upper limit for $f(N, R)$, and also that the asymptotic decay of $f(N, R)$ can be described in the form of a scaling function:

$$f(N, R) \propto \exp[-c(N^{\nu}/R)^{\Delta}] \qquad N^{\nu} > R \tag{3}$$

where the constant c and the exponent Δ are to be estimated.

We start growing a SAW configuration on a square lattice from the centre of the cavity. The first step is taken at random in one of the four directions. Thereafter, excluding the direction which reverses the walk, all the other steps are taken in one of the available directions with probability 1/3. If at any stage in the generation process, the walk steps into an already occupied site, it is said to suffer 'attrition' [9] and is discarded. It is also discarded when it steps into a site which is at a distance of R or more from the centre of the cavity. Only such walks which do not suffer attrition until either they grow to their full lengths inside the cavity or they encounter the boundary are counted as attempts for the trapping problem. The survival fraction, $f(N, R)$, is then obtained as the ratio of the number of configurations which have successfully remained untrapped inside the cavity to the total number of attempts made.

Table 1. The survival fraction, $f(N, R)$, of N-step SAWs inside a circular cavity of size R. Data obtained using the FPT method represent averages over 10 sets of (+) 100 000 configurations each or (*) 50 000 configurations each; data obtained using the ensemble method represent averages over five sets of 20 000 configurations each.

		$f(N, R)$				$f(N, R)$	
R	N	FPT method	Ensemble method	R	N	FPT method	Ensemble method
8	14	0.7977^{+}	0.8015	12	27	0.5698^{+}	0.6464
	20	0.3242^{*}	0.4019		34	0.2197^{*}	0.3944
	22	0.2183^{+}	0.3104		38	0.1128^{+}	0.2940
	25	0.1151^{*}	0.2120		44	0.0374^{*}	0.1899
	29	0.0461^{+}	0.1281		48	0.0175^{+}	0.1408
	31	0.0279^{*}	0.0993		53	0.0067^{*}	0.0976
	35	0.0106^{+}			57	0.0031^{+}	0.0734
	40	0.0029^{+}	0.0295		65	0.0006^{+}	0.0383
	47	0.0005^{*}	0.0172				
10	20	0.7044^{+}	0.7300	14	36	0.4021^{+}	
	27	0.2642^{*}	0.3876		42	0.1760^{*}	
	30	0.1580^{+}	0.2997		48	0.0658^{+}	
	34	0.0725^{*}	0.2071		54	0.0230^{*}	
	38	0.0317^{+}	0.1416		59	0.0094^{+}	
	41	0.0165^{*}	0.1061		65	0.0032^{*}	
	45	0.0072^{+}	0.0705		69	0.0015^{+}	
	52	0.0015^{+}	0.0360		79	0.0003^{+}	
	54	0.0009^{*}	0.0296				

Because a walk is discarded when it encounters the boundary for the first time, this method of generating SAWs inside a cavity may be called the first passage trapping (FPT) method. Recently, Jaeckel and Dayantis [10] have used this FPT method for studying the concentration profiles of SAWs which survive in the interior of the cavity.

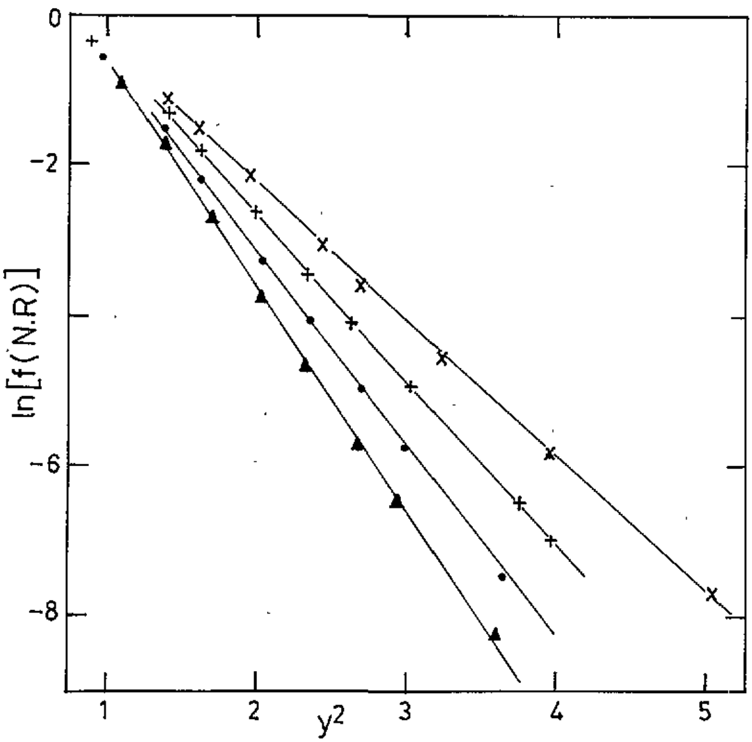

Figure 1. Logarithm of $f(N, R)$, obtained by the FPT method, as a function of y^2, for $R = 8$ (×), 10 (+), 12 (●), 14 (▲). The lines have been drawn to guide the eye.

It should be noted that the variable $y(\equiv N^\nu/R)$ is bounded below by value $R^{\nu-1}$, because the boundary becomes effective only for $N \geqslant R$. However, the longest surviving walk cannot have more steps than the total number of points, N_R, inside the cavity. That is to say, y must be bounded above by $R^{\nu d-1}$, because $N_R \approx R^d$. Therefore, the realizable values of y are in the range, $R^{\nu-1} \leqslant y \leqslant R^{\nu d-1}$. However, numerically probing the entire range will be quite difficult because as the value of the mean radius of gyration of a walk compared to the cavity size increases, the more rapidly it will die. It is reasonable to set the upper limit of y as equal to R itself. Then the numerical results, $\langle r\rangle \approx 0.34N^{0.75}$ in two dimensions and $\langle r\rangle \approx 0.47N^{0.59}$ in three dimensions [9] imply that $y \leqslant 2.94$ in two dimensions and $y \leqslant 2.13$ in three dimensions respectively.

However, the centre of gravity of a SAW will not, in general, coincide with the centre of the cavity from which it has grown. This implies that the numerically realizable value, $y_{\max}$ will be less than 2.94 in two dimensions. Thus, we must be able to probe the range, $R^{\nu-1} \leqslant y \leqslant y_{\max} < 3$, with ease.

For each value of N, we have computed the survival fraction, f_i, by generating 10^5 SAW configurations which have not suffered attrition until either they are trapped in the boundary or they have grown to their full lengths. We have used the standard random number generator, RAN2 [11], for generating the SAWs. We have repeated this process ten times and calculated the mean, $f(N, R)$, of the values f_i (i = 1–10). It is clear that $f(N, R)$ is the same as that obtained from an ensemble of 10^6 configurations.

We have estimated $f(N, R)$ for various values of N and R in the range $0.9 < y(\equiv N^{3/4}/R) < 2.25$. The data are presented in table 1. The standard deviation estimated in the worst case $\approx 7\%$. In figure 1, we have plotted $\ln[f(N, R)]$ as a function of y^2. It is clear that, for a given value of R, the data fall on a straight line, and that the slope of the line increases with increasing values of R.

On the basis of the available data, we could not estimate the functional dependence of the slope on R. However, by trial and error, we drew figure 2 by plotting $\ln[f(N, R)]$ as a function of $y^2 R^{2/3}$. Even though we cannot say that the data have collapsed onto a straight line, there is a clear indication that $f(N, R)$ has the form

$$f(N, R) \propto \exp(-cy^2 R^{\beta}) \tag{4}$$

where $\beta \approx 2/3$ for $1 < y < 2.25$, and $c(\approx 1/2)$ is the slope of the collapsed line in figure 2. The proportionality factor may also, in general, be a function of y and R. However, estimating it will require a much more extensive numerical study.

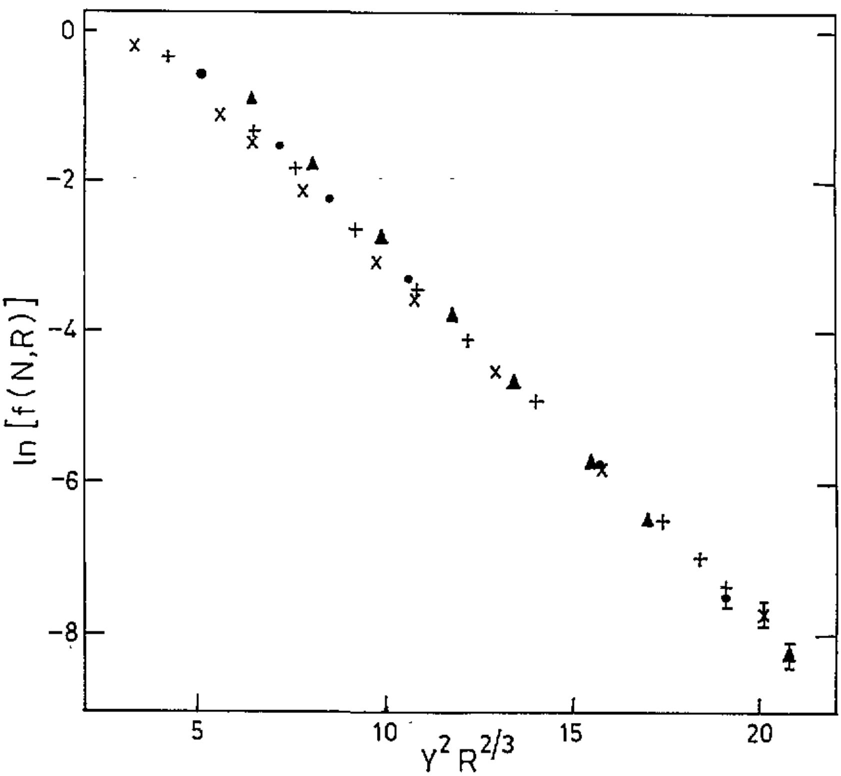

Figure 2. The same data as in figure 1 but plotted as a function of $y^2 R^{2/3}$.

In the FPT method, attrition is taken care of only inside the cavity, and a SAW configuration which has encountered the boundary for the first time is counted as a 'failed' attempt for the trapping problem. In other words, such a configuration is assigned a unit weight. If the walk were allowed to grow to its full length, despite encountering the boundary, it would suffer attrition and consequently acquire a weight less than unity. This will be the case if we first generate a SAW, and then check whether it is inside a cavity centred on one of its ends. For this reason, the latter method which takes care of attrition despite crossing a boundary may be referred to as the 'ensemble' method.

Using this ensemble method, we have generated five sets of 20000 SAW configurations each. We have computed the survival fractions, f_i ($i = 1$–5), and their mean value, $f(N, R)$. The data are presented in table 1. We have plotted $\ln[f(N, R)]$ as a function of N in figure 3. For a given value of R, the data fall on a straight line. In the same figure, we have also plotted $\ln[f(N, R)]$ as a function of $N/R^{4/3}$. It is clear that the data have collapsed onto a single line. So, we have the result

$$f(N, R) \propto \exp(-cN/R^{4/3}) \tag{5}$$

where c is the slope of the collapsed line. There is a slight indication that the slope changes its value from ~ 2 to ~ 2.25 in the neighbourhood $N/R^{4/3} \approx 1.75$. However, we need more accurate data to obtain the scaling function.

To summarize, the survival fraction, $f(N, R)$, of N-step SAWs inside a circular cavity of radius R depends on the method by which these walks were generated. On the basis of the available numerical results (equations (4) and (5)) it is tempting to speculate that

$$\ln[f(N, R)] \propto \begin{cases} -N^{2\nu}/R^{2-\beta} & \text{(FPT method)} \\ -N/R^{1/\nu} & \text{(ensemble method)} \end{cases} \tag{6}$$

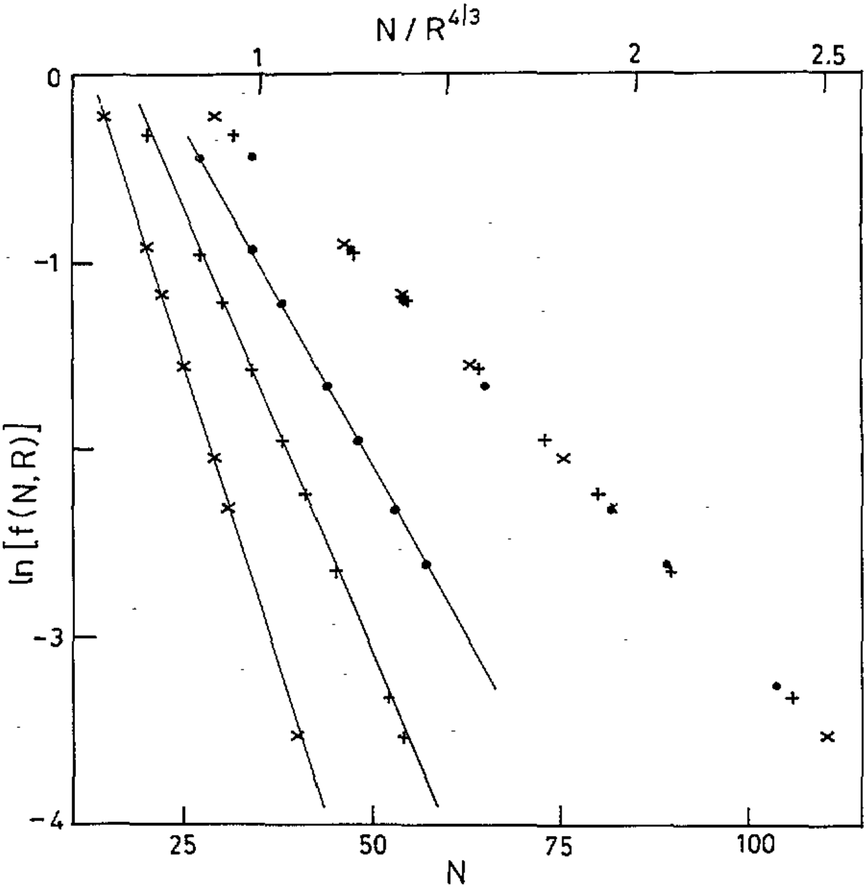

Figure 3. Logarithm of $f(N, R)$, obtained by the ensemble method, as a function of N (marked at the bottom), for $R = 8$ (×), 10 (+), 12 (●). The same data also plotted as a function of $N/R^{4/3}$ (marked at the top). The lines have been drawn to guide the eye.

where ν is the end-to-end distance exponent for the SAW. Simulation data in three dimensions are required to confirm this.

It is not clear to us whether the result obtained by the FPT method, equation (4), points to the correct asymptotic form. In the absence of theoretical reasons, we should hold the view that the ensemble method is better suited for these studies. For purely kinetic walks such as the true SAW [12], however, the FPT method could be the most natural of the two.

It is a pleasure to thank Mr M A Prasad for valuable suggestions. I am thankful to the referees for their comments. I am grateful to Dr K R Rao for support and guidance.

References

[1] Baumgartner A and Muthukumar M 1987 *J. Chem. Phys.* **87** 3082
[2] Honeycutt J D and Thirumalai D 1989 *J. Chem. Phys.* **90** 4542
[3] Edwards S F and Freed K 1969 *J. Phys. A: Math. Gen.* **2** 145
[4] Honeycutt J D and Thirumalai D 1990 *J. Chem. Phys.* **93** 6851
[5] Machta J and Guyer R A 1989 *J. Phys. A: Math. Gen.* **22** 2539
Cates M E and Ball R C 1988 *J. Physique* **49** 2005
Edwards S F and Chen Y 1988 *J. Phys. A: Math. Gen.* **21** 2963
Nattermann T and Renz W 1989 *Phys. Rev.* A **40** 4675
[6] Grassberger P and Procaccia I 1982 *J. Chem. Phys.* **77** 6281
[7] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
[8] Lhullier D 1988 *J. Physique* **49** 705
[9] Wall F T and Erpenbeck J J 1959 *J. Chem. Phys.* **30** 634; 637
[10] Jaeckel A and Dayantis J 1994 *J. Phys. A: Math. Gen.* **27** 2652
[11] Press W H, Flannery B P, Tenkolsky S A and Vetterling W A 1986 *Numerical Recipes: The Art of Scientific Computing* (New York: Cambridge University Press)
[12] Amit D J, Parisi G and Peliti L 1983 *Phys. Rev.* B **27** 1635