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Simulations of grafted polymers in a good solvent

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Abstract

We present improved simulations of three-dimensional self-avoiding walks with one end attached to an impenetrable surface on the simple cubic lattice. This surface can either be a-thermal, having thus only an entropic effect, or attractive. In the latter case we concentrate on the adsorption transition. We find clear evidence for the cross-over exponent to be smaller than $1/2$, in contrast to all previous simulations but in agreement with a re-summed field theoretic ϵ -expansion. Since we use the pruned-enriched Rosenbluth method (PERM) which allows very precise estimates of the partition sum itself, we also obtain improved estimates for all entropic critical exponents.

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1. Introduction

Single polymers grafted to a plane impenetrable wall have been studied intensely for a long time. If the surface is energetically neutral, the main effect is a change in the critical exponent governing the scaling of the partition sum. For an attractive surface the situation is more interesting, as there is a second-order adsorption transition at a finite strength of the attraction [1].

Of particular interest is the cross-over exponent at this transition. Early simulations [1, 2] had given $\phi > 0.5$, but it was claimed in [3] that this was due to finite size corrections to scaling, and that ϕ is actually very close to $1/2$ (the best estimated being $\phi = 0.496 \pm 0.004$). Basically the same conclusion was reached recently in [4], where an even smaller error bar was obtained, $\phi = 0.5005 \pm 0.0036$, suggesting that $\phi = 1/2$ exactly. Since $\phi = 1/2$ also in $d = 2$ and $d \geq 4$, this would mean that ϕ is superuniversal, as it is for branched polymers [5, 6]. But a completely different picture was drawn in another recent paper [7], where it was claimed that $\phi = 0.59$. To add to the confusion, we should cite field theoretic results. The ϵ -expansion with $\epsilon = 4 - d$ predicts [8, 9] $\phi = 1/2 - \epsilon/16 + [16\pi^2 - 39]\epsilon^2/512 + \dots$. This would give $\phi = 0.68$, if higher order terms were simply omitted, but Padé–Borel summation gives $\phi = 0.483$ [10]. On the other hand, fixed dimension (massive theory) renormalization

group calculations [10, 11] give $\phi = 0.52$. All these calculations have errors which are difficult to pin down, and the authors of [10] preferred the value 0.52 over 0.483. In any case, these renormalization group calculations strongly suggest that ϕ is not superuniversal.

It is the purpose of the present work to clarify the situation by means of much more precise simulations. We will find that indeed ϕ is definitely smaller than $1/2$ (as predicted by the resummed ϵ -expansion, but not by the supposedly more reliable massive field theory approach). In addition, we shall also provide precise estimates for the location of the adsorption transition and for the entropic exponents. The latter will be done both for thermal surfaces (at the adsorption transition point) and for a-thermal surfaces.

We model the polymer by a self-avoiding walk (SAW) of $N - 1$ steps on a simple cubic lattice with restriction $z \geq 0$. There is an energy $-\epsilon$ for each monomer (site) at $z = 0$, the first monomer is located at $\mathbf{x} = 0$. The temperature is taken to be $T = 1$, so that the Boltzmann factor for each contact with the surface is $q = e^\epsilon$. The adsorption transition is at $q = q_c > 1$. For the simulations we use the pruned-enriched Rosenbluth method (PERM) [12, 13]. This is a recursively (depth-first) implemented sequential sampling algorithm with re-sampling [14]. It is similar to the algorithm used in [3], but it is faster and much easier to use. Its main advantage over conventional Markov chain Monte Carlo (MC) methods is that it gives very precise estimates of the partition sum, without any need for thermodynamic integration or the like. To minimize statistical errors and speed up the algorithm, we use Markovian anticipation [15, 16]. We simulated $\approx 6.6 \times 10^8$ walks with $N = 8000$ for $q = 1$ and $\approx 9.5 \times 10^8$ walks at $q \approx q_c$. In both cases, about 1.6% of these walks were strictly independent. Altogether this needed ≈ 5000 h CPU time on fast (3 GHz) PCs. During the runs with $q > 1$, results at slightly different values of q were obtained by re-weighting on the fly, so that one run made with $q \approx q_c$ gave results at three close values of q . The critical point q_c was then found by interpolation.

The partition sum is written as $Z_1(N, q) = \sum_m C_{Nm} q^m$, where C_{Nm} is the number of configurations with m contacts with the wall, $z_{i_k} = 0$ for $k = 1, \dots, m$, and the subscript '1' indicates that one end is grafted. For $q < q_c$ it scales as

$$Z_1(N, q) \sim \mu^N N^{\gamma_1 - 1} \quad (1)$$

with μ and γ_1 independent of q , but with a q -dependent prefactor.

Near the adsorption transition, $Z_1(N, q)$ should scale as [1]

$$Z_1(N, q) \sim \mu^N N^{\gamma_1 - 1} \Psi[(q - q_c)N^\phi], \quad (2)$$

where $\Psi(z)$ is analytic for finite z and $\lim_{z \rightarrow -\infty} \Psi(z)$ is finite and positive. Note that the dominant exponential growth of $Z_1(N, q)$ with N is the same as for ordinary SAWs, as long as $q \leq q_c$. Taking the derivative of $\ln Z_1(N, q)$ with respect to q and setting $q = q_c$ thereafter, we obtain for the average energy exactly at the critical point

$$E_N(q_c) = \langle \epsilon m \rangle \sim N^\phi. \quad (3)$$

Taking two derivatives we would obtain a scaling ansatz for the specific heat which is often used to estimate ϕ and other aspects of the critical behaviour. We will *not* use it in the present paper, since equations (2) and (3) give much more precise results, as already found in [3, 6]. We refer to [6] (which deals with the analogous problem for branched polymers) for a detailed discussion. Note that equation (2) cannot be used with Markov chain MC methods, since the latter do not give simple and precise estimates of $Z_1(N, q)$ itself.

2. Results: a-thermal walls

From previous simulations [3, 17] we know that $\mu \approx 4.68404$, but the present simulations have higher statistics, therefore we should first estimate the critical exponent γ_1 in such a way

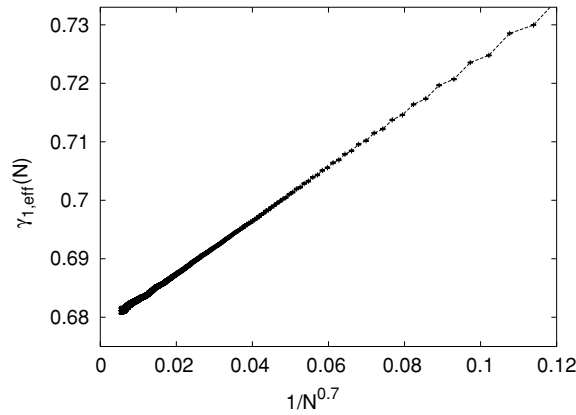


Figure 1. Effective exponents defined by equation (4), plotted against $1/N^{0.7}$.

that neither μ nor the unknown prefactor in equation (1) affect the value. For this we form the triple ratios [17]

$$\gamma_{1,\text{eff}}(N) = 1 + \frac{4 \ln Z_1(N) - 3 \ln Z_1(N/3) - \ln Z_1(3N)}{\ln 9} \quad (4)$$

(with $Z_1(N) \equiv Z_1(N, 1)$), which should tend to γ_1 as $N \rightarrow \infty$. The leading corrections to equation (1) (and thus also to equation (4)) should scale as $1/N^\Delta$ with the same exponent $\Delta \approx 0.5$ holding also for SAWs in absence of a surface [16, 18, 19]. This would suggest that we should get a straight line when plotting $\gamma_1(N)$ against $1/\sqrt{N}$. Unfortunately this is not true, due to the presence of very large analytic corrections $\propto 1/N, 1/N^2, \dots$. As seen from figure 1, they shift the effective correction to scaling exponent to $\Delta_{\text{eff}} \approx 0.7$, and the extrapolation to $N \rightarrow \infty$ gives

$$\gamma_1 = 0.6786 \pm 0.0012. \quad (5)$$

This is in good agreement with the best previous MC estimate 0.679 ± 0.002 [3] and with the field theoretic result 0.680 [10].

Using this value of γ_1 , we next show in figure 2 the quantity $\ln Z_1(N) - aN + (1 - \gamma_1) \ln N$ for different values of a , plotted again versus $1/N^\Delta$. Again these data should extrapolate to $1/N \rightarrow 0$ with a finite slope, if $a = \ln \mu$. From figure 2 we see that

$$1/\mu = 0.213\,490\,98 \pm 0.000\,000\,05 \quad (\mu = 4.684\,0386 \pm 0.000\,0011), \quad (6)$$

where the error includes the uncertainty in the estimate of γ_1 . This is the most precise value of the critical fugacity of SAWs on the simple cubic lattice published up to now. It is about 80 times more precise than the best estimate from exact enumerations [21].

In addition to the partition sum for SAWs grafted at one end to the surface, we can also study the partition sum $Z_{11}(N)$ where both ends are constrained to have $z = 0$. In analogy to equation (1), it should scale as

$$Z_{11}(N, q = 1) \sim \mu^N N^{\gamma_{11}-1}. \quad (7)$$

The exponent γ_{11} should be related to previous exponents by the Barber relation [22]

$$\gamma - 2\gamma_1 + \gamma_{11} + \nu = 0, \quad (8)$$

where γ and ν are the entropy and Flory exponents ($R \sim N^\nu$) for ungrafted SAWs in the bulk. Values of $Z_{11}(N)$ are obtained simply by summing over those walks for which the N th

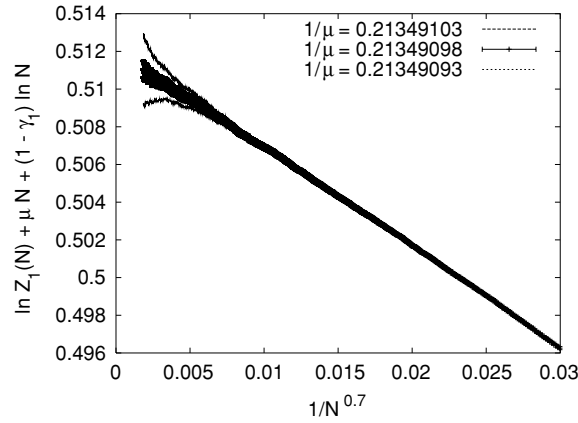


Figure 2. The combination $\ln Z_1(N) - N \ln \mu + (1 - \gamma_1) \ln N$, with γ_1 determined from figure 1 and for three candidate values of μ , plotted against $1/N^{0.7}$. Error bars are plotted only for the central curve, but errors are the same (within the precision of drawing) for all three curves.

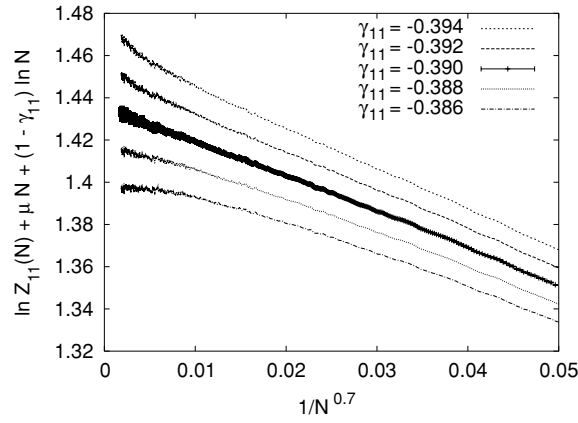


Figure 3. Analogous to figure 2, but for SAWs grafted at both ends to the surface, and with the candidate values of μ replaced by candidate values of γ_{11} . In order to reduce statistical errors, the data are binned with bin width $\Delta N/N \approx 0.01$.

monomer has $z = 0$. Using the above estimate of μ and different candidate values of γ_{11} , we plot in figure 3 the analogous quantity to that shown in figure 2 for singly grafted chains. We find

$$\gamma_{11} = -0.390 \pm 0.002, \quad (9)$$

to be compared to the previous MC estimate -0.383 ± 0.005 [3] and to the field theoretic prediction -0.388 [10]. Using the most precise previous estimates of γ and ν from [20] ($\gamma = 1.1573 \pm 0.0002$ and $\nu = 0.58765 \pm 0.00020$), we see that the Barber relation is indeed perfectly satisfied,

$$\gamma - 2\gamma_1 + \gamma_{11} + \nu = -0.0023 \pm 0.0031. \quad (10)$$

Root mean square end-to-end distances should scale with the same Flory exponent as in the bulk, but with different prefactors and with different corrections to scaling. We measured both the components parallel and perpendicular to the wall for singly grafted SAWs. This

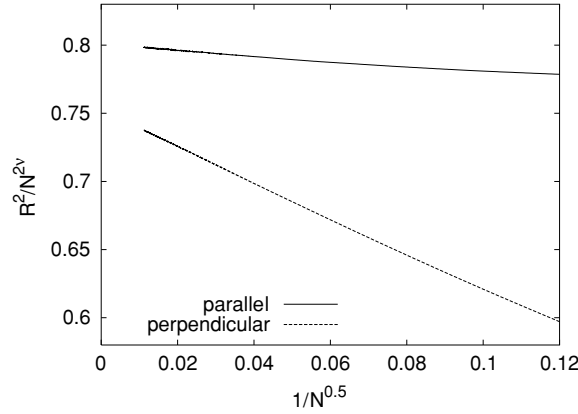


Figure 4. $\langle x_N^2 + y_N^2 \rangle / N^{2\nu}$ (upper curve) and $\langle z_N^2 \rangle / N^{2\nu}$ (lower curve) against $1/\sqrt{N}$. Error bars are smaller than the thickness of the lines.

time the corrections to scaling were $\sim 1/\sqrt{N}$ as expected, i.e. there are much smaller analytic corrections. Results are shown in figure 4, where we divided averaged square distances by $N^{2\nu}$ and plotted them against $1/\sqrt{N}$. The ratio $\langle z_N^2 \rangle / \langle x_N^2 + y_N^2 \rangle$ increases with N as also found in [23], but it converges for $N \rightarrow \infty$ to a finite value, 0.938 ± 0.002 . In contrast to [23] we see no indication that either $\langle z_N^2 \rangle$ or $\langle x_N^2 + y_N^2 \rangle$ scales with an exponent different from the bulk Flory exponent.

3. Results: attractive walls

According to equation (2), the exponential growth of the partition sum with N is the same at q_c as at $q = 1$, i.e. we do not need the triple ratio equation (4) to estimate $\gamma_1^s(N)$. Instead we can use

$$\gamma_{1,\text{eff}}^s(N, q) = 1 + \frac{\ln[Z_1(2N, q)/Z_1(N/2, q)]/\mu^{3N/2}}{\ln 4} \quad (11)$$

where the ratio between the two partition sums eliminates the unknown prefactor. The critical point is characterized by the fact that $\gamma_{1,\text{eff}}^s(N, q)$ diverges for $q > q_c$ when $N \rightarrow \infty$, converges slowly to γ_1 for $q < q_c$ and converges to a constant value larger than γ_1 exactly at q_c . Values of $\gamma_{1,\text{eff}}^s(N, q)$ obtained by means of equation (11) are shown in figure 5. As in the next figures to follow, we plotted it against $1/\sqrt{N}$ since there was no different unique value of Δ which fitted all observables, and $\Delta = 1/2$ was not worse overall than other values.

From figure 5, we see that $q_c \approx 1.3307$ and $\gamma_1^s \approx 1.23$, in good agreement with the estimates of [3]. More precise values will result by combining also the information from other observables.

The next quantity we looked at is the average energy, or rather the average number of sites in contact with the wall. Plotting simply $\langle m \rangle / N^\phi$ would suggest $\phi = 1/2$ and $q_c = 1.331$, see figure 6. But this does not take into account the fact that corrections to scaling are very large and should still be important even for the largest N . Indeed, when defining an effective exponent by $\phi_{\text{eff}}(N, q) = (\ln 4)^{-1} \ln[E_{2N}(q)/E_{N/2}(q)]$ and plotting it against $1/\sqrt{N}$ (figure 7), we see that it extrapolates clearly to a value $< 1/2$, and that q_c is closer to the value 1.3307 found from figure 5.

Instead of the effective exponent $\gamma_{11,\text{eff}}^s(N, q)$ defined in complete analogy to equation (11), we show in figure 8 the difference $\gamma_{1,\text{eff}}^s(N, q) - \gamma_{11,\text{eff}}^s(N, q)$. This is obtained

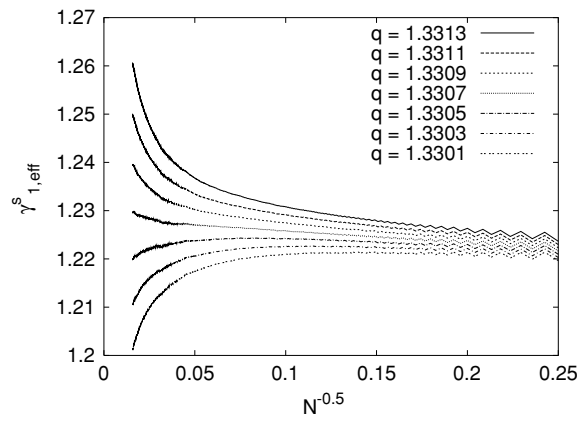


Figure 5. Effective exponents $\gamma_{1,eff}^s(N, q)$, plotted versus $1/\sqrt{N}$, for several values of q .

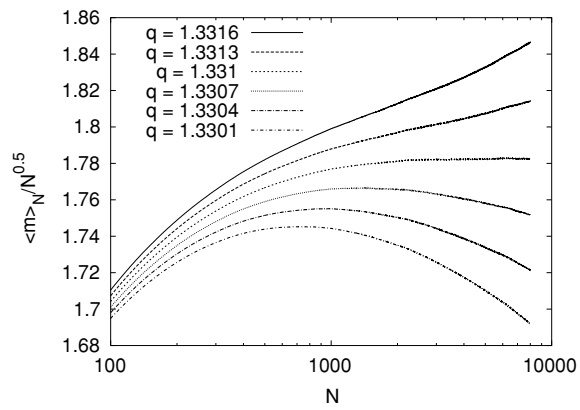


Figure 6. Average number of contacts with the wall, divided by \sqrt{N} . This would suggest $\phi \approx 1/2$, if we would assume that corrections to scaling are negligible for $N > 4000$.

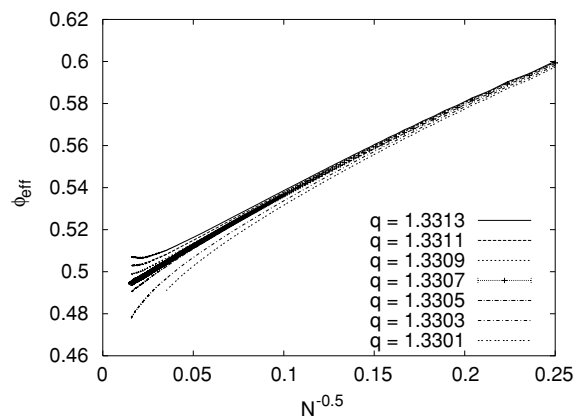


Figure 7. Effective cross-over exponent as defined in the text, plotted versus $1/\sqrt{N}$.

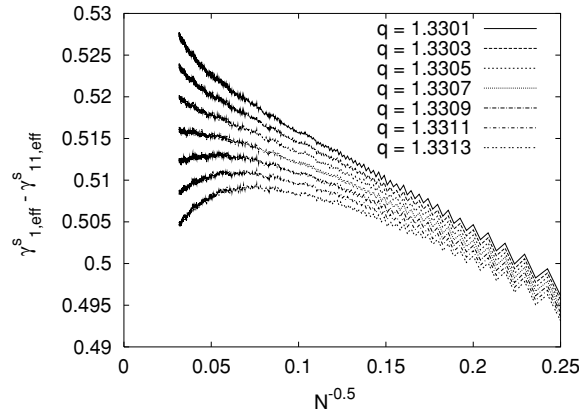


Figure 8. Difference between the effective entropic exponent for polymers grafted at one end, and the exponent for polymers grafted at both ends, again plotted versus $1/\sqrt{N}$.

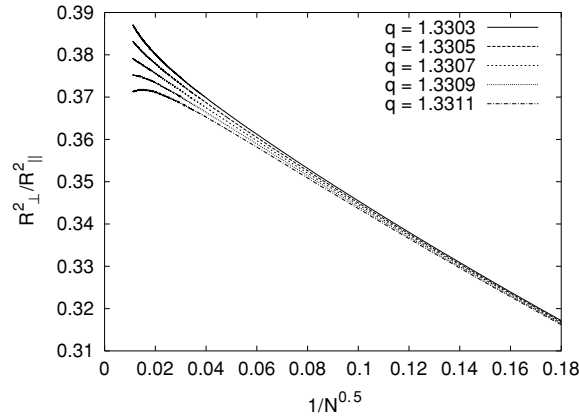


Figure 9. Ratio $\langle z^2 \rangle / \langle x^2 + y^2 \rangle$ between mean square end-to-end distances perpendicular and parallel to the wall.

from the ratio between the partition sums for singly and doubly grafted polymers, and is independent of the precise value of μ . Finally, we show in figure 9 the ratio between the mean square end-to-end distances perpendicular and parallel to the wall.

Comparing figures 5–9, we see that all of them (except of course figure 6) give the same value for q_c . Thus we obtain our precise estimate

$$q_c = 1.33065 \pm 0.00010. \quad (12)$$

This is in agreement with the value 1.3310 ± 0.0003 of [3], and with the recent estimate 1.334 ± 0.026 of [4]. For the anisotropy of infinitely long chains at the adsorption transition this gives $\langle z^2 \rangle / \langle x^2 + y^2 \rangle = 0.3845 \pm 0.0010$. The best estimates of the critical exponents are then

$$\phi = 0.484 \pm 0.002, \quad \gamma_1^s = 1.226 \pm 0.002, \quad (13)$$

and

$$\gamma_1^s - \gamma_{11}^s = 0.519 \pm 0.003. \quad (14)$$

These values are in less agreement with previous estimates. First, the entropic exponents are slightly smaller (by about 2 standard deviations) than the values given in [3], although these were already lower than all previous MC estimates. While γ_1^s agrees roughly with the field theoretic prediction 1.207 of [10], γ_{11}^s is quite a bit larger (0.707 as opposed to ≈ 0.666). Second, and more importantly, the cross-over exponent is now clearly less than $1/2$, by some 8 standard deviations. The closest previous MC estimate was 0.496 ± 0.004 [3], which is off by three sigma. The estimate 0.5005 ± 0.0036 of [4] seems clearly excluded by our data. It is based on very high statistics of very short ($N \leq 200$) chains, which suggests that the corrections to scaling were not taken fully into account in [4]. As mentioned above, $\phi < 1/2$ is predicted by the first-order term of the ϵ -expansion, but not when terms up to $O(\epsilon^2)$ are included and not by fixed dimension renormalization group methods. But the resummation of the ϵ -expansion done in [10] gave $\phi = 0.483$, in surprisingly good (and presumably fortuitous) agreement with our result. At least, our estimate is comfortably larger than the first-order epsilon expansion result, $\phi > 1/2 - \epsilon/16 = 0.4375$.

4. Conclusion

In this paper, we have presented Monte Carlo simulations of single grafted 3D polymers in a good solvent, both for attractive and for a-thermal walls. The sample seems to be the biggest studied so far, both concerning the number of chains simulated and their lengths. By using PERM which gives precise estimates of the partition sum, we could use the partition sum itself (instead of the specific heat) to locate the critical adsorption point and the critical exponents. Our estimates continue the decrease with increased statistics observed already in [3]. Our most interesting result is that the cross-over exponent is clearly less than $1/2$, in contrast to all previous simulations and to the best estimates from field theory.

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References

- [1] Eisenriegler E, Kremer K and Binder K 1982 *J. Chem. Phys.* **77** 6296
- [2] Meirovitch H and Livne S 1988 *J. Chem. Phys.* **88** 4507
- [3] Hegger R and Grassberger P 1994 *J. Phys. A: Math. Gen.* **27** 4069
- [4] Janse van Rensburg E J and Rechnitzer A R 2004 *J. Phys. A: Math. Gen.* **37** 6875
- [5] Janssen H K and Lyssy A 1995 *Europhys. Lett.* **29** 25
- [6] Hsu H-P, Nadler W and Grassberger P 2004 *Preprint cond-mat/0408061*
- [7] Descas R, Sommer J-U and Blumen A 2004 *J. Chem. Phys.* **120** 8831
- [8] Diehl H-W and Dietrich S 1981 *Phys. Rev. B* **24** 2878
- [9] Diehl H-W 1986 *Phase Transitions and Critical Phenomena* vol 10 ed C Domb and J L Lebowitz (New York: Academic)
- [10] Diehl H-W and Shpot M 1998 *Nucl. Phys. B* **528** 595
- [11] Diehl H-W and Shpot M 1994 *Phys. Rev. Lett.* **73** 3431
- [12] Grassberger P 1997 *Phys. Rev. E* **56** 3682
- [13] Grassberger P 2002 *Comput. Phys. Commun.* **147** 64
- [14] Liu J S 2001 *Monte Carlo Strategies in Scientific Computing (Springer Series in Statistics)* (New York: Springer)
- [15] Frauenkron H, Grassberger P and Walter N 1998 *Preprint cond-mat/9806321*
- [16] Hsu H-P and Grassberger P 2004 *J. Chem. Phys.* **120** 2034
- [17] Grassberger P, Sutter P and Schäfer L 1997 *J. Phys. A: Math. Gen.* **30** 7039

-
- [18] Li B, Madras N and Sokal A D 1995 *J. Stat. Phys.* **80** 661
 - [19] Belohorec P and Nickel B G 1997 Accurate universal and two-parameter model results from a Monte-Carlo Renormalization Group Study *Preprint* Guelph University
 - [20] Hsu H-P and Grassberger P 2004 *Macromolecules* **37** 4658
 - [21] MacDonald D, Joseph S, Hunter D L, Moseley L L, Jan N and Guttman A 2000 *J. Phys. A: Math. Gen.* **33** 5973
 - [22] Barber M N 1973 *Phys. Rev. B* **8** 407
 - [23] Odenheimer J and Heermann D W 2004 Statistics of a polymer grafted to a repulsive wall *Preprint* University of Heidelberg