INSTITUTO DE FÍSICA
Universidade Federal Fluminense

# Pressure exerted by a grafted polymer on the limiting line of a semi-infinite square lattice

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Effect of excluded volume interactions: end-grafted SAWs on a semi-infinite square lattice, using exact enumerations. Guttmann, Jensen,... Exact enumerations of SAW's on square lattice: $c_{71} = 4\,190\,893\,020\,903\,935\,054\,619\,120\,005\,916$.

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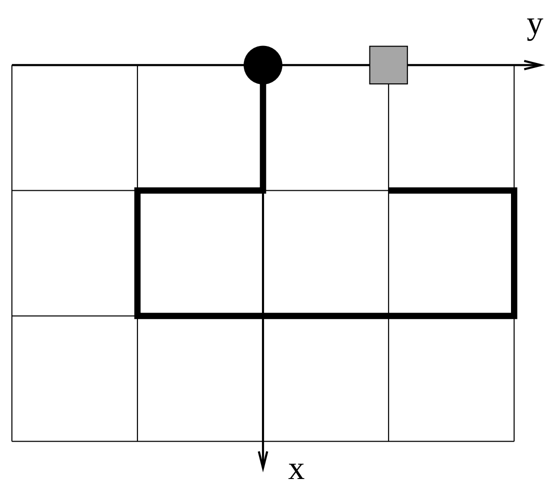
SAW grafted at origin $(0, 0)$ to a rigid wall placed at $x = 0$:



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$$p_n(r) = \frac{P_n(r) a^2}{k_B T} = -\ln \frac{c_n^{(1)}(r)}{c_n^{(1)}},$$

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Thermodynamic limit $p(r) = \lim_{n\to\infty} p_n(r)$. Density of monomers at $(0,r)$: $\rho(r) = 1 - \lim_{n\to\infty} c_n^{(1)}(r)/c_n^{(1)}$, therefore:

$$p(r) = -\ln[1 - \rho(r)].$$

# Exact enumerations

SAW's are counted using a transfer matrix formalism in suitable chosen rectangles. Details in I. Jensen, J. Phys. A **37**, 5503 (2004). Actually, the generating function of the SAW's $G(x) = \sum_n c_n^{(1)} x^n$ is calculated up to a certain order.

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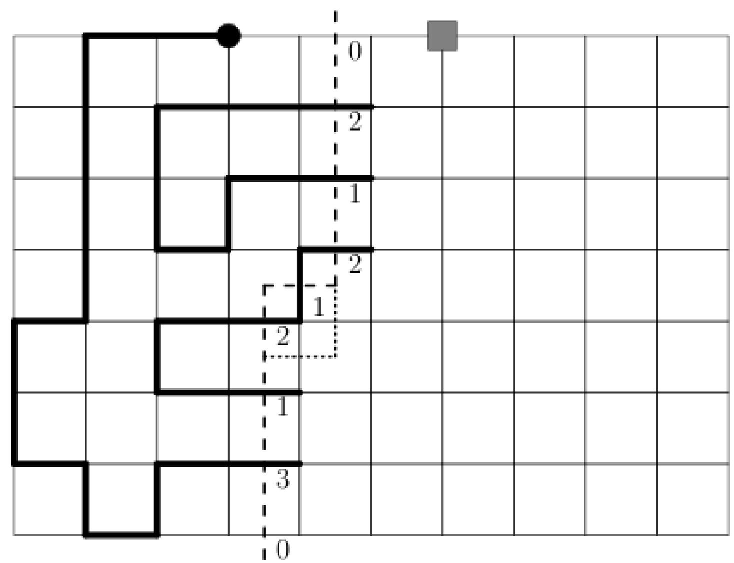

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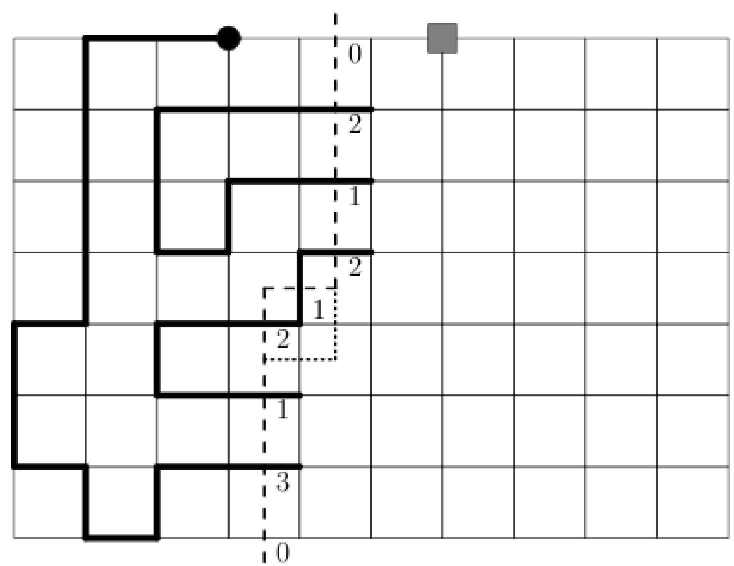


Update of the generation functions, indexed by signature $S$, when boundary is moved one step:
$G_{S'}^{new}(x) = G_{S'}^{old}(x) + x^m G_S(x)$.

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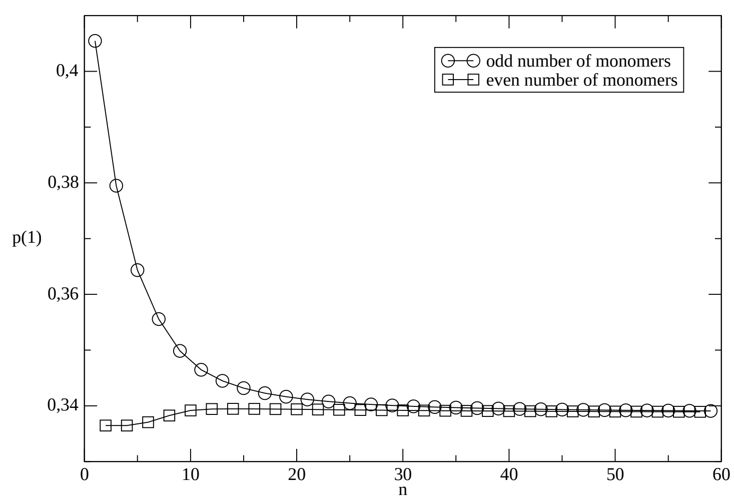
Direct calculation of the pressures:



# Analysis and results

Critical behavior of the generating function:

(1) $$G(x) = \sum_n c_n^{(1)} x^n \sim A(1-\mu x)^{-\gamma_1},$$

with $\gamma_1 = 61/64$. Parity effect: besides the physical singularity $x_c = 1/\mu$ there is another singularity at $x = x_- = -x_c$, with exponent $\gamma_-$.

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Series analysis: differential approximants (A. J. Guttmann in *Phase Transitions and Critical Phenomena*, vol. 13, Academic Press (1989)). Some results:

# Analysis and results

| $r$ | $L$ | $x_c$ | $\gamma$ |
|---|---|---|---|
| 0 | 0 | 0.379052260(64) | 0.953097(70) |
| 0 | 4 | 0.379052241(20) | 0.953072(17) |
| 0 | 8 | 0.379052243(14) | 0.953071(15) |
| 1 | 0 | 0.3790522582(30) | 0.9530884(24) |
| 1 | 4 | 0.3790522575(38) | 0.9530879(30) |
| 1 | 8 | 0.379052257(11) | 0.953090(14) |

# Analysis and results

| $r$ | $L$ | $x_-$ | $\gamma_-$ |
|---|---|---|---|
| 0 | 0 | -0.3790526(38) | 1.5002(19) |
| 0 | 4 | -0.3790492(30) | 1.5023(13) |
| 0 | 8 | -0.3790498(21) | 1.5016(12) |
| 1 | 0 | -0.3790425(97) | 1.5074(74) |
| 1 | 4 | -0.379030(26) | 1.523(29) |
| 1 | 8 | -0.379058(16) | 1.4988(69) |

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Conclusion: $x_c$, $\gamma$, and $\gamma_-$ are the same.

# Analysis and results

Amplitudes: fit of the enumeration data to asymptotic form:

$$c_n^{(1)}(r) = \mu^n \left[ n^{\gamma_1 - 1} \left( A(r) + \sum_{j=2} a_j(r)/n^{j/2} \right) + \right.$$

$$\left. (-1)^n n^{-\gamma_- - 1} \sum_{k=0} b_k(r)/n^k \right],$$

with $\mu = 2.63815853035(2)$, $\gamma_1 = 61/64$ and $\gamma_- = 3/2$.
Evidence for this behavior comes from detailed studies with unconstrained SAWs enumerations: (S. Caracciolo, A. J. Guttmann, I. Jensen, A. Pelissetto, A. N. Rogers, and A. D. Sokal, J. Stat. Phys. **120**, 1037 (2005))

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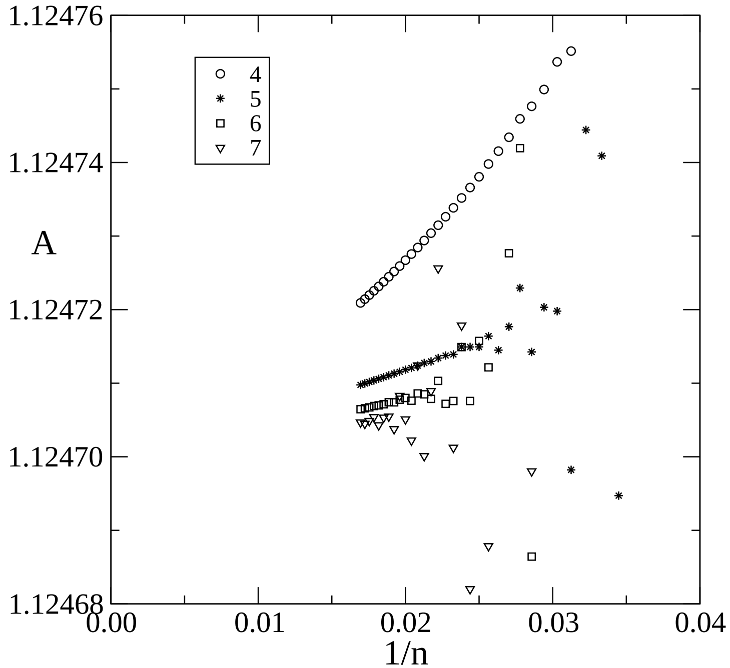


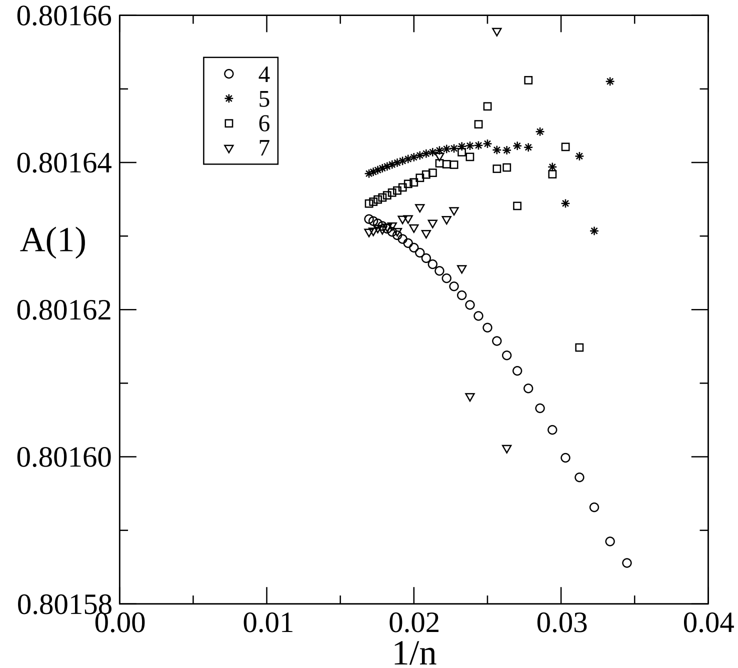

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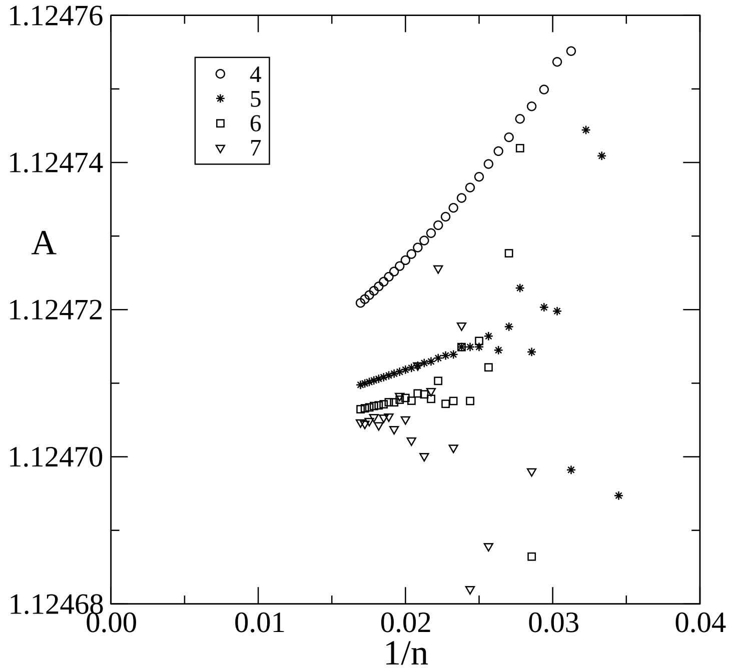


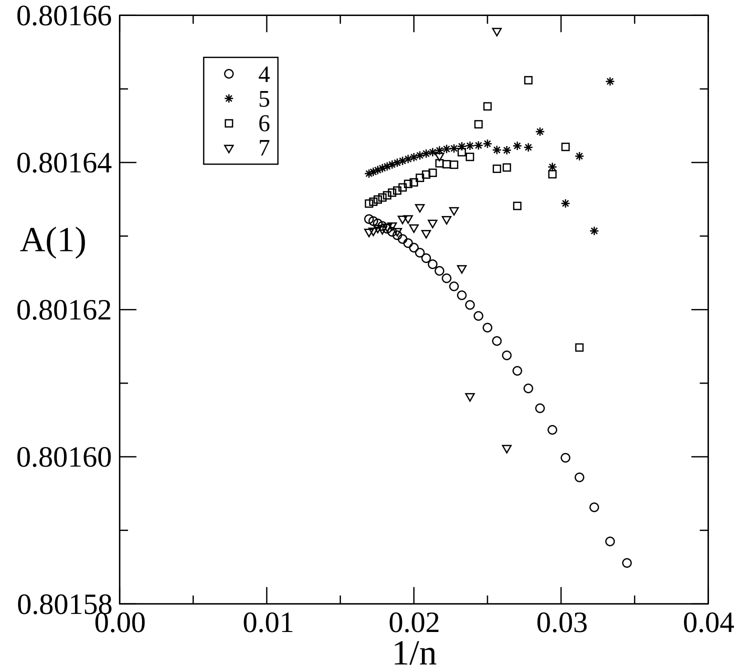


This leads to estimates for the amplitudes and, therefore, for the pressures. For example: $A = 1.124705(5)$, $A(1) = 0.801625(5)$, $A(2) = 0.97564(2)$ and $A(5) = 1.09325(10)$.

# Analysis and results

Pressures:

| $r$ | $p(r) - SAWs$ | $p(r)$-gaussian |
|---|---|---|
| 1 | 0.33863 | 0.15915 |
| 2 | 0.14218 | 0.06366 |
| 3 | 0.07334 | 0.03183 |
| 4 | 0.04347 | 0.01872 |
| 5 | 0.02844 | 0.01224 |
| 10 | 0.00735 | 0.00315 |

# Analysis and results

The result is compared with exact values for gaussian chains:

$$p_G(r) = \frac{P_G(r)a^d}{k_B T} = \frac{\Gamma(d/2)}{\pi^{d/2}} \frac{1}{(r^2+1)^{d/2}},$$

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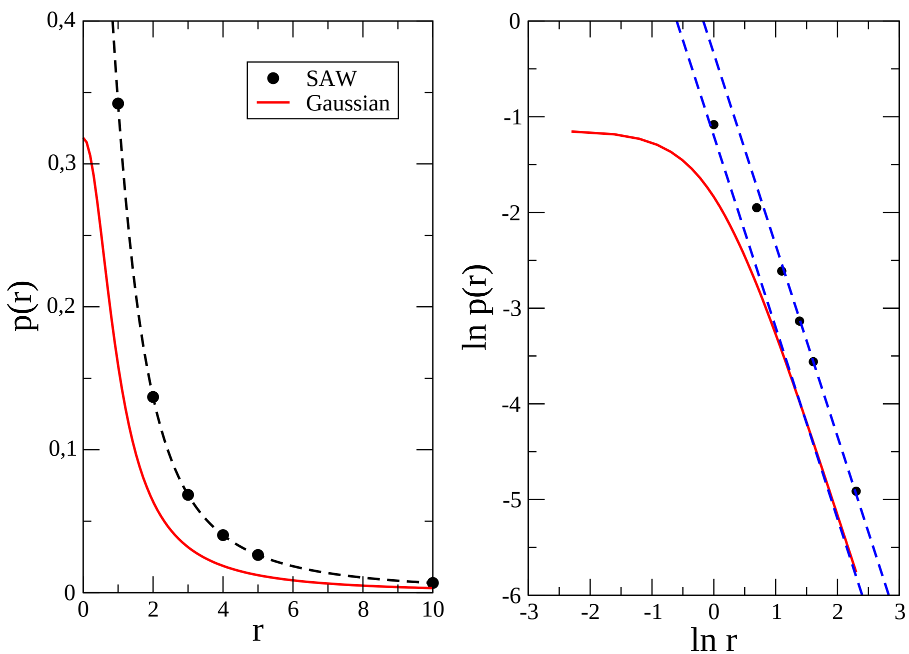


(a) (b)

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No direct comparison between athermal SAW's on a lattice and gaussian chains in the continuum. Possible reason for no effect of self-avoidance constraint: low densities of monomers.

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Force on polymer at grafting point:

$$f = \frac{\mathcal{F} a}{k_B T} = 2 \sum_{r=1}^{\infty} p(r).$$

Gaussian chains: $f_G = 1$. SAWs: $f_{SAW} \approx 1.533$

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Ideal chains (RW): Force on the grafting point may be calculated using an image walker. The result is: $f_{RW} = \ln 2 \approx 0.6931$.

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Work in progress: 1) Adsorbing wall, energy $-\epsilon$ associated to each monomer on wall. 2) Solution on semi-infinite Bethe lattice, exponential decay of $p(r)$.

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Reference: J. Phys. A **46** 115004 (2013); arXiv:1301.3432.