

FRACTIONAL BROWNIAN POLYMERS - SOME FIRST RESULTS

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Recently the Edwards model for chain polymers in good solvents has been extended to include fractional Brownian motion trajectories as a description of polymer conformations. This raises in particular the question of the corresponding Flory formula for the end-to-end length of those molecules. A generalized Flory formula has been proposed, and there are some first results of numerical validations.

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1. The Edwards Model for Chain Polymers in Solvents

Brownian motion paths $x(t)$, $0 \leq t \leq N$, provide a useful model for the conformation of chain polymers in good solvents and have been extensively studied in $d = 1, 2$, and 3 dimensions. Their self-crossings, however, are uncharacteristic for such conformations and should be suppressed (“excluded volume effect”). In the Edwards model⁶ this is done using the self-intersection local time

$$L = \int \int ds dt \delta(x(s) - x(t))$$

of Brownian motion; formally we modify the Wiener measure $d\mu(x)$ by a density function $Z^{-1} \exp(-gL)$, $g > 0$, where the normalization

$$Z = \mathbb{E} \left(\exp \left(-g \int_0^N ds \int_0^N dt \delta(x(s) - x(t)) \right) \right) = \int \exp(-gL) d\mu$$

should be chosen so that $Z^{-1} \exp(-gL)d\mu$ is a probability measure. Mathematically this is tricky: The above expressions can be made well-defined,⁹ e.g. as limit of suitably regularized versions with

$$Z = \lim_{\varepsilon} \int \exp(-gL_{\varepsilon}) d\mu$$

in the unphysical case of $d = 1$. This is not so in higher dimensions. For $d = 2$ the expectation of the local time is divergent, and we need to “center” the local time by subtracting its expectation, i.e. we need to replace

$$L_{\varepsilon} \rightarrow L_{\varepsilon} - \mathbb{E}(L_{\varepsilon})$$

before taking the limit. In three dimensions an additional multiplicative renormalization is required.

2. Fractional Brownian Motion Models

A more general class of models is obtained if we model the conformations $x(t)$ by fractional Brownian motion (fBm) paths. Fractional Brownian motion with “Hurst parameter” $H \in (0, 1)$ can be characterized^{2,12} as a centered Gaussian process with covariance

$$\mathbb{E}(B_i^H(s)B_j^H(t)) = \frac{\delta_{ij}}{2} (t^{2H} + s^{2H} - |t - s|^{2H}), \quad i, j = 1, \dots, d, \quad s, t \geq 0. \quad (1)$$

(We see that $H = 1/2$ is standard Brownian motion.)

More realistically, instead of just using fBm, the excluded volume should again be introduced as above. Of course then the question of mathematical existence arises again, and a (partial) answer has recently been given in:⁸

Theorem 2.1.

The Edwards model is well defined for $x = B^H$ whenever $H \leq 1/d$.

It is important to note that fBm is a process with stationary increments, in keeping with chain polymer homogeneity, contrary to models using e.g.

$$x(t) = B(t^H).$$

On the other hand, fBm is not Markovian, a fact which complicates considerably the mathematical analysis of the corresponding polymer models.

2.1. The interaction between monomers

Usually, infinite dimensional path integrals are defined via finite dimensional approximations, but in the present context the situation is the opposite: the path integral model is an idealization of the finite dimensional integration over all monomer positions x_k . For N monomers we set

$$x_k = x(k) = B^H(k), \quad k = 0, \dots, N - 1$$

$$\int d\mu(x) \approx \text{const.} \prod_{k=0}^{N-1} \int dx_k \exp(-H_0(x)).$$

It is easy to determine the quadratic form $H_0(x) \equiv \frac{1}{2} (x, h_0 x)$, since for any positive matrix h_0 we have

$$\begin{aligned} \mathbb{E}(\exp(x, b)) &= ((2\pi)^n \det h_0)^{-1/2} \int d^n x \exp\left(-\frac{1}{2}(x, h_0 x) + (b, x)\right) \\ &= \exp\left(\frac{(b, h_0^{-1} b)}{2}\right). \end{aligned}$$

Computing

$$\left. \frac{\partial}{\partial b_k} \frac{\partial}{\partial b_l} \mathbb{E}(\exp(x, b)) \right|_{b=0} = \mathbb{E}(x_k x_l) = (h_0^{-1})_{kl}$$

we see that the matrix h_0 is just the inverse of the covariance function given by (1):

$$(h_0^{-1})_{kl} = \mathbb{E}(B^H(k) B^H(l)). \tag{2}$$

For the standard Brownian motion the well-known result is

$$H_0(x) = \frac{1}{2} \sum (x_k - x_{k-1})^2$$

i.e. an attractive quadratic interaction between nearest neighbors. For $N = 9$ we display the matrix elements

$$h_{4,k} = \begin{cases} 2 & \text{if } k = 5 \\ -1 & \text{if } k = 4, 6 \\ 0 & \text{otherwise} \end{cases}.$$

in Figure 1.

In the general case, a numerical inversion of the covariance matrix (2) can be done. For small H we find long range attraction corresponding to curlier polymers (Fig. 2), while for bigger H we observe a next-to-nearest neighbor repulsion (Fig. 3) which straightens them out.

3. The End-to-End Length

Central to the study of polymer conformations is the question of how their end-to-end distance R , with

$$R^2 = \mathbb{E}(|x_{N-1}|^2)$$

in our notation, scales with N as the number of monomers becomes large. In the ansatz

$$R \sim N^v,$$

v is the famous ‘‘Flory index’’ which was originally conjectured to depend on the dimension d as follows:

$$v = \frac{3}{d+2}. \tag{3}$$

Theoretical studies support this conjecture for $d = 1, 2$ while various less rigorous methods, from computer simulations to renormalization group theory, point to a slight deviation for $d = 3$, in agreement with experimental results:

Flory Theory Exp.

$d = 1 :$	1	1	
$d = 2 :$	0.75	0.75	0.79
$d = 3 :$	0.60	0.588	0.59
$d = 4 :$	0.5	0.5	

3.1. Extension to the fractional case

Recently Bornaes, Oliveira, and Streit⁵ have proposed a generalization of Flory’s conjecture to the fractional case with general Hurst index H :

$$v_H = \begin{cases} 1 & \text{if } d = 1 \text{ and } H > 1/2 \\ H & \text{if } dH > 2 \\ \frac{2H+2}{d+2} & \text{if otherwise.} \end{cases} \tag{4}$$

Here the first condition stems from the fact that the scaling exponent $v = 1$ is maximal, polymers will not grow faster than the number of monomers. The second condition reflects the fact that for $dH = 2$ fBm becomes self-intersection free,¹⁴ beyond that value the end-to-end-length will scale like for free fBm.

We mention in passing that there is also a proposition for a recursion formula, generalizing the one given by Kosmas and Freed¹¹ for the case of conventional Brownian motion.

3.2. Computer simulations - first results

As mentioned above, the non-Markovian nature of fBm produces considerable obstacles to the well established analytic methods for the determination of the Flory index when we try to generalize them to fBm. As it turns out,⁴ numerical simulations are quite manageable. We give here some preliminary results for the case $d = 1$, where the above-mentioned proposal would read

$$v_H = \frac{2H + 2}{3}$$

for $H \leq 1/2$ and $v_H = 1$ otherwise. Numerically the authors found

H	v_H	Simulation
0.10	0.73	0.772 ± 0.037
0.20	0.80	0.803 ± 0.012
0.35	0.90	0.917 ± 0.013

in preliminary computations; systematic and more detailed calculations are presently under way.⁴

For illustration we show characteristic examples of simulated (two-dimensional) conformations for $N = 30$, and Hurst indices $H = 0.1$, $H = 0.5$ and $H = 0.9$ in Figs. 4-6.

3.3. A remark on polymers in narrow tubes

Finally we add a short remark on polymers in “nano-tubes”. Following de Gennes,⁷ we consider tubes which are wider than the monomer size a , but much narrower than the polymer length Na .

$$a < D \ll Na.$$

Hence individual blobs of the polymer chain are restricted to a size $R \lesssim D$ and will contain

$$N_b \sim D^{1/v}$$

monomers. Dense packing of the blobs in the tube would imply a polymer length in the tube of

$$R_T \approx D \frac{N}{N_b} \sim ND^{1-1/v}.$$

For $v \approx v_H$ and $d = 3$ we would then have elongation with an inverse power of the tube diameter D , depending on the Hurst parameter H :

$$R_T \sim ND^{-\frac{3-2H}{2+2H}}.$$

In like style it is also not hard to extend de Gennes’ derivation of a non-linear Hooke’s law for the stretching of polymers.

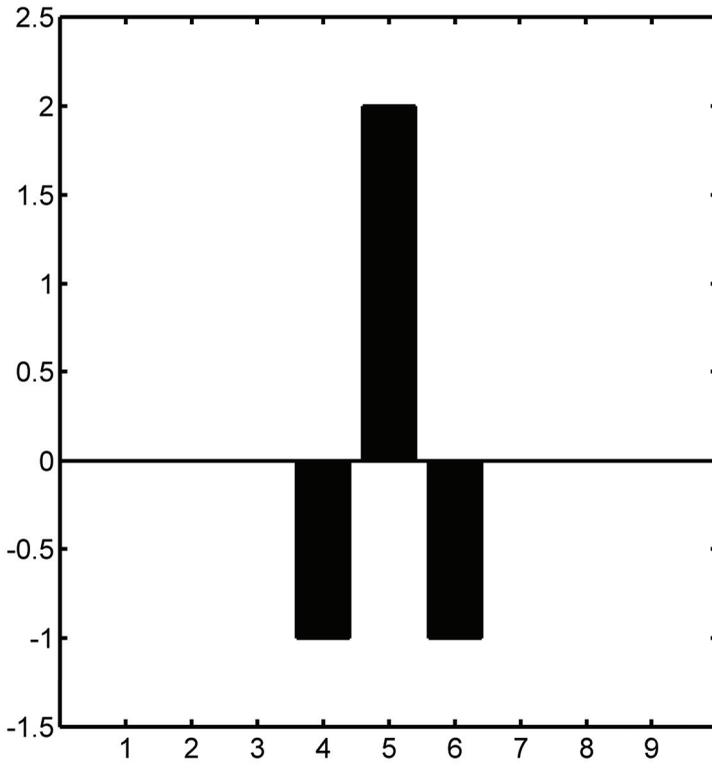


Figure 1. $H=0.5$

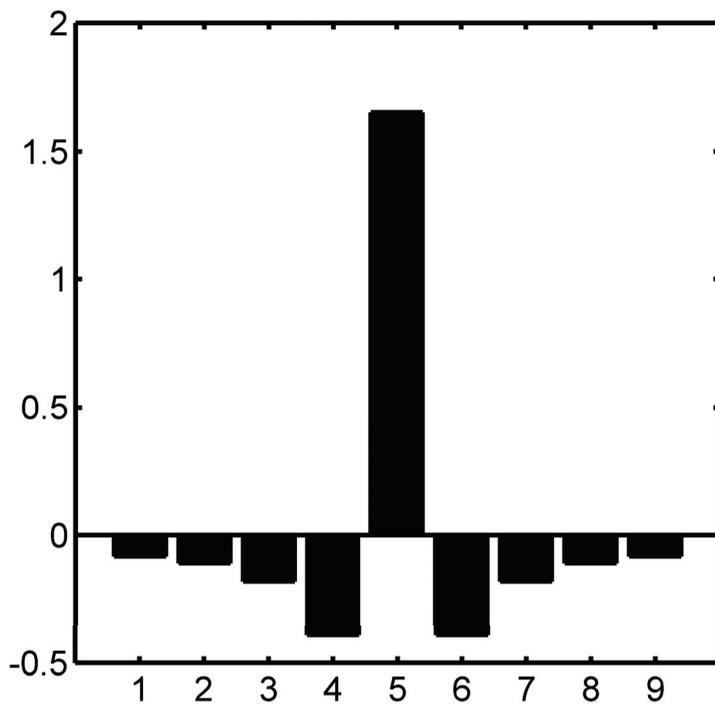


Figure 2. $H=0.1$

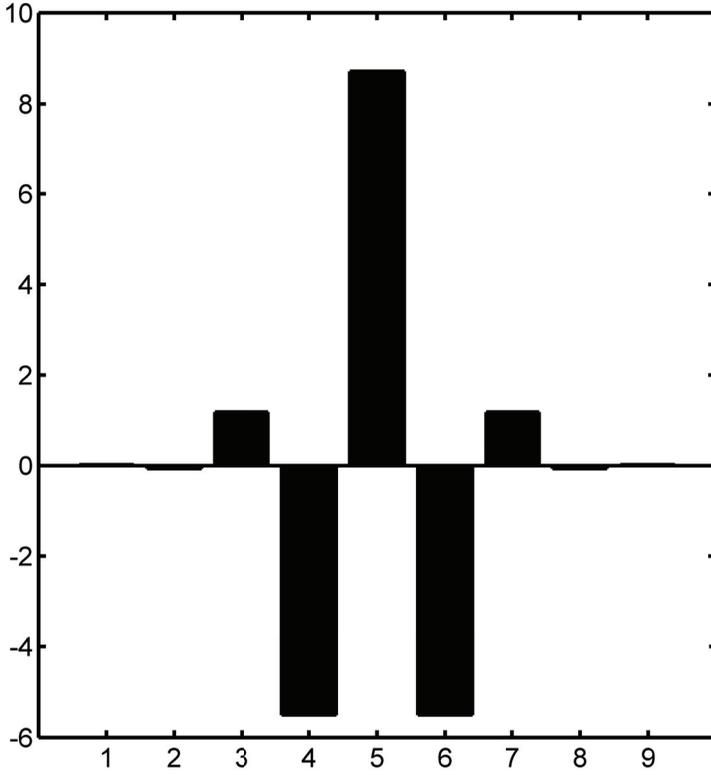


Figure 3. $H=0.9$

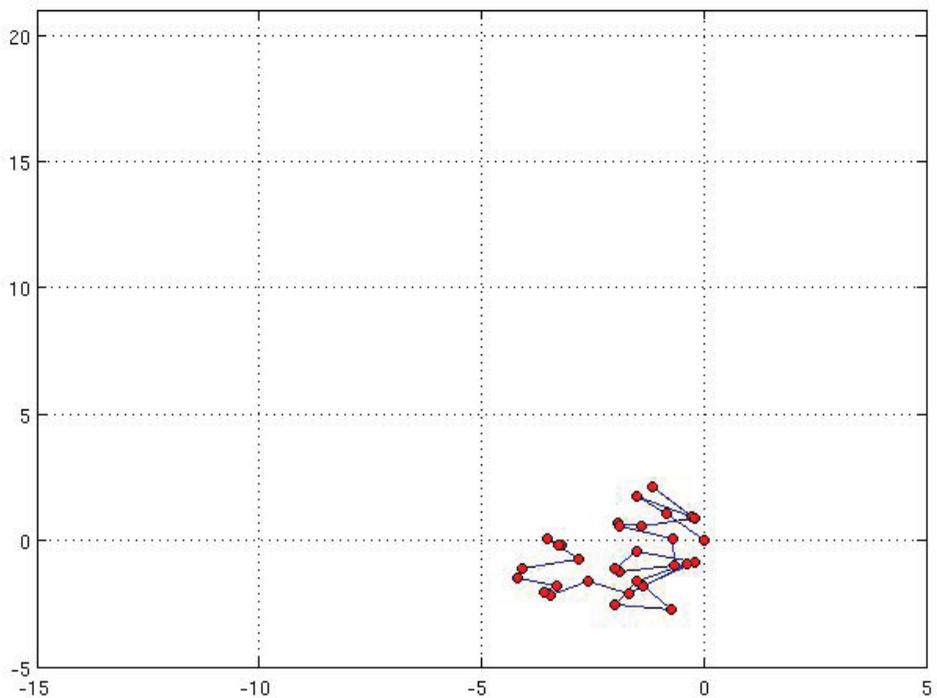


Figure 4. Self-repelling polymer: $H=0.1$

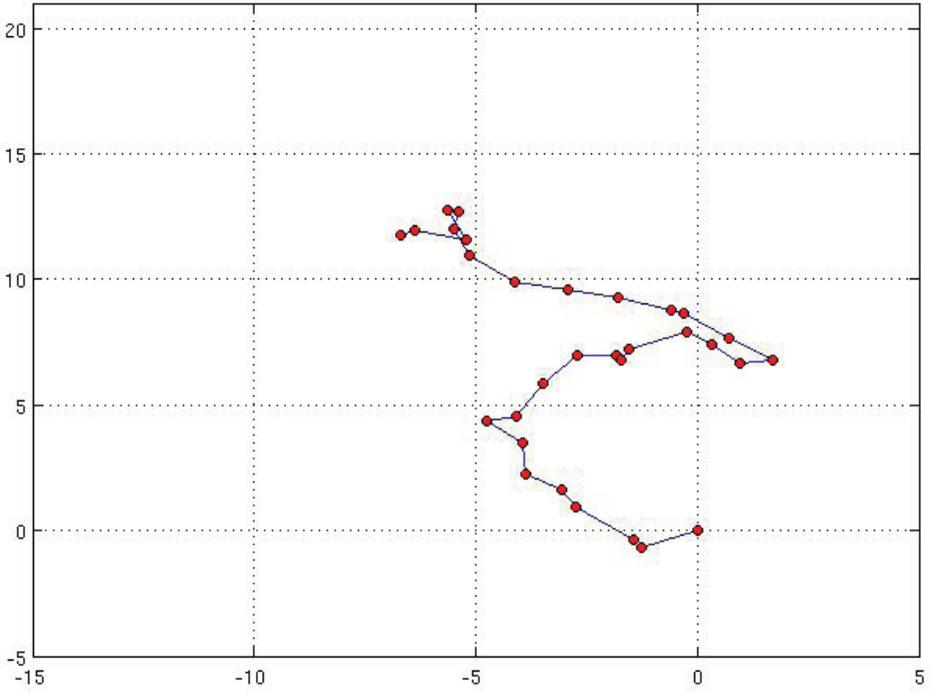
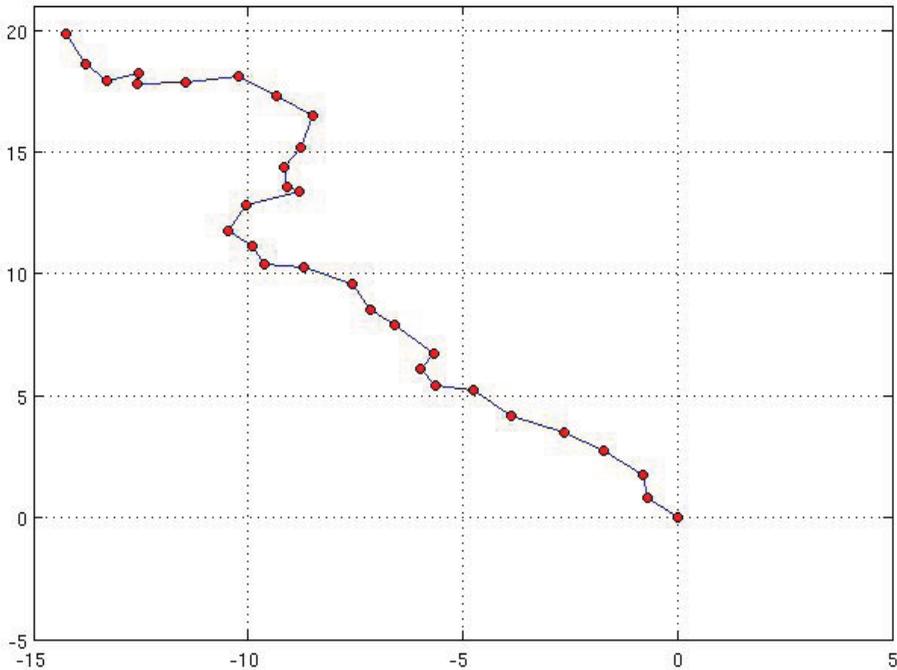


Figure 5. Self-repelling polymer: $H=0.5$

Figure 6. Self-repelling polymer: $H=0.9$

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References

1. G. Besold, H. Guo, M. J. Zuckermann: *Off-lattice Monte Carlo simulation of the discrete Edwards model*. J. Polymer Science B **38**, 1053–1068 (2000).
2. F. Biagini, Y. Hu, B. Øksendal, T. Zhang: *Stochastic Calculus for Fractional Brownian Motion and Applications*. Springer, Berlin, 2007.
3. P. Biswas, B. J. Cherayil: *Dynamics of Fractional Brownian Walks*. J. Phys. Chem. **99**, 816–821 (1995).
4. W. Bock et al.: *Computer Studies of Fractional Brownian Polymers*, in preparation.

5. J. Bornales, M. J. Oliveira, L. Streit: *Self-repelling fractional Brownian motion - a generalized Edwards model for chain polymers*. To appear in Proceedings of ICQBIC 2011. World Scientific, Singapore. <http://arxiv.org/abs/1106.3776>
6. S. F. Edwards: *The statistical mechanics of polymers with excluded volume*. Proc. Roy. Soc. 85, 613-624 (1965).
7. P. G. de Gennes: *Scaling Concepts in Polymer Physics*. Cornell Univ. Press, Ithaca, NY, (1979).
8. M. Grothaus, M. J. Oliveira, J.-L. Silva, L. Streit: *Self-avoiding fractional Brownian motion - The Edwards model*. J. Stat. Phys. 145, 1513–1523 (2011).
9. R. van der Hofstad, W. König: *A Survey of One-Dimensional Random Polymers*. J. Stat. Physics, **103**, 915-944 (2001).
10. Y. Hu and D. Nualart: *Renormalized self-intersection local time for fractional Brownian motion*. Ann. Probab., 33:948–983, 2005.
11. M. K. Kosmas, K. F. Freed: *On scaling theories of polymer solutions*. J. Chem. Phys. **69**, 3647-3659 (1978).
12. Y. Mishura: *Stochastic Calculus for Fractional Brownian Motion and Related Processes*. Springer LNM 1929 (2008).
13. A. Pelissetto, E. Vicari: *Critical phenomena and renormalization-group theory*. Phys. Reports **368**, 549–727 (2002).
14. M. Talagrand: *Multiple points of trajectories of multiparameter fractional Brownian motion*. Probab. Theory Related Fields **112**, 545–563 (1998).
15. S. R. S. Varadhan: Appendix to “*Euclidean Quantum Field Theory*” by K. Symanzik, in: R. Jost, ed., *Local Quantum Theory*, Academic Press, New York, p. 285 (1969).