

# Self-repelling fractional Brownian motion - a generalized Edwards model for chain polymers

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## Abstract

We present an extension of the Edwards model for conformations of individual chain molecules in solvents in terms of fractional Brownian motion, and discuss the excluded volume effect on the end-to-end length of such trajectories or molecules.

## 1 Introduction

Individual chain polymers in good solvents are typically modelled by trajectories of random walks, or - in the continuum limit - by Brownian paths. Such models by themselves however do not take into account that self-crossings of these paths should be suppressed, this "the excluded volume" effect will

make the trajectories less curly and more extended. Fractional Brownian paths have been suggested as a heuristic model for such swelling, or on the other hand for polymers in a collapsed state [2], but a more proper model would be based on self-avoiding random walks, or on a weight factor which penalizes self-crossings, such as in the continuum Edwards [3] [6] [20] [21] [22] [23] or the discrete Domb-Joyce [5] model.

The ensuing swelling of the molecular conformations is given by the Flory index [8] [9] which describes the scaling of the end-to-end distance as a function of the number of monomers. It has been extensively studied both in the (chemical) physics and the mathematics community. The physics literature is characterized by structural intuition and far-reaching predictions, the mathematical results are less far-reaching but provide the high reliability characteristic of the mathematical approach. Both are too vast to be quoted here, we refer for this to recent reviews [12] [18].

In the present paper, after a few words on fractional Brownian motion fBm, we shall see that one can extend to fBm the Edwards model of Brownian paths with exponentially suppressed self-intersections, a mathematical existence proof has been established recently [11]. In the third part of the paper we generalize some by now classical arguments from the physics literature to explore what the Flory index might be in the fBm case.

## 2 The fBm Edwards Model

### 2.1 Fractional Brownian Motion

Fractional Brownian motion on  $\mathbb{R}^d$ ,  $d \geq 1$ , with "Hurst parameter"  $H \in (0, 1)$  is a  $d$ -dimensional centered Gaussian process  $B^H = \{B^H(t) : t \geq 0\}$  with covariance function

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

For  $H = 1/2$  it is ordinary  $d$ -dimensional Brownian motion  $B$ . We refer to the recent monographs by Biagini et al. [1] and by Y. Mishura [16]; for self-intersection local times of fBm see Hu and Nualart [13].

## 2.2 The Edwards Model

Self-repelling Brownian paths for a time interval  $0 \leq t \leq l$  can be modelled via a "Gibbs factor" to suppress self-intersections:

$$G = \frac{1}{Z} \exp \left( -g \int_0^l ds \int_0^l dt \delta(B(s) - B(t)) \right).$$

Technically one defines this expression as a limit, using

$$\delta_\varepsilon(x) := \frac{1}{(2\pi\varepsilon)^{d/2}} e^{-\frac{|x|^2}{2\varepsilon}}, \quad \varepsilon > 0,$$

in particular

$$Z = \lim_{\varepsilon \rightarrow +0} \mathbb{E} \left( \exp \left( -g \int_0^l ds \int_0^l dt \delta_\varepsilon(B(s) - B(t)) \right) \right)$$

if this quantity is well defined; otherwise a renormalization is required, as, more generally, in Theorem 2.2 below.

Recently, generalizing an argument of Varadhan [20], this was extended in [11] to

$$G = \frac{1}{Z} \exp \left( -g \int_0^l ds \int_0^l dt \delta(B^H(s) - B^H(t)) \right),$$

as follows.

**Theorem 1** *The Edwards model is well defined for all  $H < 1/d$ , with*

$$G = \frac{1}{Z} \exp \left( -g \int_0^l ds \int_0^l dt \delta(B^H(s) - B^H(t)) \right).$$

**Theorem 2** *For  $H = 1/d$  and  $g$  sufficiently small*

$$G = \lim_{\varepsilon \searrow 0} \frac{1}{Z_\varepsilon} \exp \left( -g \int_0^l ds \int_0^l dt \delta_\varepsilon(B^H(s) - B^H(t)) \right),$$

with

$$Z_\varepsilon \equiv \mathbb{E} \left( \exp \left( -g \int_0^l ds \int_0^l dt \delta_\varepsilon(B^H(s) - B^H(t)) \right) \right)$$

is well-defined.

### 3 The Flory Index

When the number  $N$  of monomers of a polymer becomes large one expects its end-to-end length  $R$  to scale [10]

$$R(N) \sim N^v.$$

For (fractional) Brownian motion the root-mean-square length

$$R = \sqrt{\mathbb{E} (B^H(N)^2)}$$

is scaling with

$$v = H.$$

But the excluded volume effect makes the paths and polymers swell: the end-to-end length increases. For the Brownian motion case there is the famous Flory formula

$$v = v(d) = \frac{3}{d+2}$$

based originally on a mean field argument. Since its proposal by Flory [7] [9], numerous methods were invoked to put it on a more solid mathematical basis, a process which has up to now been fully successful in the case  $d = 1$  [12].

To obtain what may be considered as a first guess of a similar formula for fBm we shall return to the modest beginnings, generalizing Fisher's original argument [7] [8] (see e.g. the review given in McKenzie [15]) to the case at hand.

#### 3.1 The Fisher Argument

A partition function  $Z(R)$  for a freely jointed chain of  $N$  segments for which the end-to-end length has fixed modulus  $R$  is given by

$$Z(R) = aR^{d-1} \exp(-\frac{dR^2}{2N}),$$

and leads to a free energy

$$F_1 = -\ln Z \sim \frac{dR^2}{2N} - (d-1) \ln R.$$

Instead of such a chain a continuous model is that of a Brownian trajectory from time zero to time  $N$ , for which one computes

$$\mathbb{E} \left( \delta \left( B(N) - \vec{R} \right) \right) = (2\pi N)^{-d/2} \exp \left( -\frac{R^2}{2N} \right). \quad (1)$$

For the fBm case this formula generalizes to

$$\mathbb{E} \left( \delta \left( B^H(N) - \vec{R} \right) \right) = (2\pi N^{2H})^{-d/2} \exp \left( -\frac{R^2}{2N^{2H}} \right) \quad (2)$$

from which we see that  $N \rightarrow N^{2H}$ , and hence we should consider

$$Z(R) = a R^{d-1} \exp \left( -\frac{dR^2}{2N^{2H}} \right)$$

i.e.

$$F_1 = -\ln Z \sim \frac{dR^2}{2N^{2H}} - (d-1) \ln R.$$

For the repulsive excluded volume energy of fBm paths  $x$  with  $x(N) = \vec{R}$ ,

$$F_2 = -\ln \mathbb{E}_{x(N)=\vec{R}} \left( \exp \left( -g \int_0^N ds \int_0^N dt \delta(x(s) - x(t)) \right) \right)$$

dimensional considerations and mean field arguments [15] suggest

$$F_2 \sim \text{const.} \frac{N^2}{R^d}$$

Maximizing

$$F(N, R) = F_1(N, R) + F_2(N, R)$$

with regard to  $R$  leads to

$$0 = \frac{dR}{N^{2H}} - \frac{d-1}{R} - \text{const.} N^2 R^{-d-1}.$$

Assuming that the 2nd term is negligible one finds

$$R^{d+2} \sim N^{2H+2}$$

i.e.

$$R \sim N^{v_H}$$

with

$$v_H(d) = \frac{2H+2}{d+2}. \quad (3)$$

**Remark 3** *A polymer model with  $B(t^{2H})$  instead of  $B^H(t)$  would produce the same expression as in (2), hence also the same Flory index, but would not share the homogeneity implied by the stationary increments of  $B^H(\cdot)$ .*

### 3.2 The Critical Dimension

The derivation of  $v_H$  is evidently heuristic and needs validation. For this it is worth noting that for Brownian motion there is a critical dimension  $d_c = 4$  defined by the fact that for  $d \geq d_c$  there is no excluded volume effect, so that  $R$  scales like the unperturbed Brownian motion:

$$R \sim N^{1/2}$$

i.e.

$$v_{1/2}(4) = 1/2.$$

We can ask for which dimension, more generally, the fBm Flory index will show no excluded volume effect from self-crossings, i.e.

$$v_H(d_c) = H.$$

Inserting our ansatz (3) one finds

$$Hd_c = 2.$$

and indeed it is known (Theorem 1.1 of Talagrand [19]) that  $d$ -dimensional fBm has no double points iff

$$Hd \geq 2,$$

in other words, our  $v_H$  predicts  $d_c$  correctly.

**Remark 4** *As a consequence, any Flory formula should be considered only up to the critical dimension, i.e. as long as there are double points and an excluded volume effect. Similarly, any prediction of  $v_H > 1$  would be unphysical: the end-to-end distance cannot grow faster than the number  $N$  of monomers. In the case at hand this suggests for the one-dimensional case*

$$v_H(1) = \begin{cases} \frac{2H+2}{3} & \text{if } H \leq \frac{1}{2} \\ 1 & \text{if } H > \frac{1}{2} \end{cases}.$$

Note that for small  $H$  the scaling exponent as predicted would be strictly less than one while for the Brownian motion case

$$v_{1/2}(1) = 1$$

has been proven [12] [23]. The infimum

$$\lim_{H \rightarrow 0} v_H(1) = 2/3$$

happens to be the scaling exponent of the myopic random walk [12].

**Remark 5** In the attached figure 1 the two red lines correspond to  $v_H(d) = 1$  and to the critical dimension as a function of the Hurst index  $H$ , respectively. Above these the Flory index is unphysical. On the green lines  $v_H$  is validated. (The existence proof of the fBm Edwards model in [11] works below the dashed line.)

**Remark 6** For fixed dimension  $d$ , any extension  $F(H)$  of the Flory formula to general Hurst indices  $H$  will have to obey

$$F\left(\frac{1}{2}\right) = \frac{3}{d+2} \tag{4}$$

for the usual Brownian motion (Flory-Fisher), and

$$F\left(\frac{2}{d}\right) = \frac{2}{d} \tag{5}$$

at the critical point (Talagrand). Note that our ansatz (3)

$$F(H) = v_H(d) = \frac{2H+2}{d+2}$$

is just the unique linear interpolation between those two values.

### 3.3 A Recursion Formula

For  $H = 1/2$  Kosmas and Freed [14] derive a recursion formula

$$2 - \frac{1}{v(d)} = \frac{4-d}{3} \left( 2 - \frac{1}{v(1)} \right) \tag{((4.13))}$$

(Here and in the following we label formulas from - or analogous to those in - the paper [14] by their numbers in that article, in double brackets.)

The derivation of this formula is specific to the Brownian motion case and does not hold for general  $v_H$ . Hence in what follows we shall generalize their arguments which led to ((4.13)) to first obtain a valid recursion formula and then check whether it is satisfied by  $v_H$  as given in (3).

We begin by considering

$$Z(g, N) \equiv \mathbb{E} \left( \exp \left( -g \int_0^N ds \int_0^N dt \delta(B^H(s) - B^H(t)) \right) \right).$$

From the defining relation

$$\mathbb{E}(B^H(s)B^H(t)) = \frac{1}{2} \left( s^{2H} + t^{2H} - |s - t|^{2H} \right)$$

we see that for  $a > 0$  the processes  $\{B^H(t) : t > 0\}$  and  $\{a^{-H}B^H(at) : t > 0\}$  obey the same law. Making this substitution and a change of integration variables  $as = \sigma$ ,  $at = \tau$  we obtain

$$\begin{aligned} Z(g, N) &= \mathbb{E} \left( \exp \left( -ga^{Hd-2} \int_0^{aN} ds \int_0^{aN} dt \delta(B^H(s) - B^H(t)) \right) \right) \\ &= Z(a^{Hd-2}g, aN). \end{aligned} \quad ((2.14))$$

Likewise we find for the mean-square end-to-end distance

$$\langle R^2 \rangle \equiv \frac{1}{Z(g, N)} \mathbb{E} \left( (B^H(N))^2 \exp \left( -g \int_0^N ds \int_0^N dt \delta(B^H(s) - B^H(t)) \right) \right) \quad (6)$$

$$\langle R^2 \rangle = a^{-2H} \mathbb{E} \left( (B^H(aN))^2 \exp \left( -ga^{Hd-2} \int_0^{aN} ds \int_0^{aN} dt \delta(B^H(s) - B^H(t)) \right) \right)$$

$$= a^{-2H} f(a^{Hd-2}g, aN) \quad ((2.18))$$

$$= N^{2H} f(N^{2-Hd}g, 1). \quad ((2.19))$$

(Note the critical dimension  $Hd = 2$  where  $\langle R^2 \rangle^{1/2} \sim N^H$ .) For large  $N$  one expects a power law behavior for the unknown function  $f$ , i.e.

$$\langle R^2 \rangle \sim N^{2H} (N^{2-Hd}g)^x \quad ((2.22))$$



with an exponent  $x$  to be determined.

As a next step we restrict one coordinate of the positions,  $x_i(t) = B_i^H(t)$  to the interval  $[0, D]$  by inserting

$$1_{[0,D]}(B_i^H) = \begin{cases} 1 & \text{if } B_i^H(t) \in [0, D] \text{ for all } t \\ 0 & \text{otherwise} \end{cases}$$

into (6). One obtains

$$\begin{aligned} \langle R^2 \rangle_D &= \frac{1}{Z_D(g, N)} \mathbb{E} \left( 1_{[0,D]}(B_i^H) (B^H(N))^2 \exp \left( -g \int_0^N ds \int_0^N dt \delta(B^H(s) - B^H(t)) \right) \right) \\ &= \frac{a^{-2H}}{Z_D(g, N)} \mathbb{E} \left( 1_{[0,a^H D]}(B_i^H) (B^H(aN))^2 \exp \left( -a^{Hd-2} g \int_0^{aN} d\sigma \int_0^{aN} d\tau \delta(B^H(\sigma) - B^H(\tau)) \right) \right) \\ &= a^{-2H} F(a^H D, a^{Hd-2} g, aN) = N^{2H} F(N^{-H} D, N^{2-Hd} g, 1). \end{aligned} \quad ((4.3))$$

Now assume that asymptotically there is a dimensionless correction factor  $h$  for

$$\langle R^2 \rangle_D \approx \langle R^2 \rangle h \left( \frac{D}{\sqrt{\langle R^2 \rangle}} \right).$$

It should grow as  $D$  becomes small which suggests a power law behavior for the function  $h$ :

$$\langle R^2 \rangle_D \approx \langle R^2 \rangle \left( \frac{D}{\sqrt{\langle R^2 \rangle}} \right)^{-y} \quad ((4.5))$$

with  $y$  to be determined. As  $D$  approaches a minimal value  $D_0$  - approximately the extension of a monomer ("Kuhn length") - the polymer becomes effectively  $(d-1)$ -dimensional:

$$\langle R_{d-1}^2 \rangle \approx \langle R_d^2 \rangle_D \approx D_0^{-y} \langle R_d^2 \rangle^{1+\frac{y}{2}}. \quad ((4.6))$$

This provides a relation between the end-to-end length for dimensions  $d$  and  $d-1$ . To obtain from this a recursion relation, recall equation ((2.22)):

$$\langle R_d^2 \rangle \sim N^{2H+x(2-Hd)} g^x$$

and introduce instead of  $x$  the (unknown)

$$2v_H(d) \equiv 2H + x(2 - Hd)$$

so that

$$\langle R_d^2 \rangle = c_d N^{2v_H(d)} g^{\frac{2v_H(d)-2H}{2-Hd}} \quad ((4.8))$$

and

$$\langle R_{d-1}^2 \rangle = c_{d-1} N^{2v_H(d-1)} g^{\frac{2v_H(d-1)-2H}{2-H(d-1)}}. \quad ((4.9))$$

On the other hand from ((4.6)) we have

$$\langle R_{d-1}^2 \rangle \approx D_0^{-y} \langle R_d^2 \rangle^{1+\frac{y}{2}} = \text{const.} N^{2v_H(d)(1+\frac{y}{2})} g^{\frac{2v_H(d)-2H}{2-Hd}(1+\frac{y}{2})}. \quad (7)$$

Comparing exponents in these two expressions we find

$$\begin{aligned} v_H(d-1) &= v_H(d) \left(1 + \frac{y}{2}\right) \\ \frac{v_H(d-1) - H}{2 - H \cdot (d-1)} &= \frac{v_H(d) - H}{2 - Hd} \left(1 + \frac{y}{2}\right). \end{aligned}$$

The first of these equations gives

$$1 + \frac{y}{2} = \frac{v_H(d-1)}{v_H(d)},$$

with this the second one becomes

$$\frac{1}{v_H(d-1)} \frac{v_H(d-1) - H}{2 - H \cdot (d-1)} = \frac{1}{v_H(d)} \frac{v_H(d) - H}{2 - Hd}$$

i.e. this expression does not depend on the dimension  $d$  so that all the  $v_H(d)$  are given in terms of e.g.  $v_H(1)$  :

$$\begin{aligned} \frac{1}{v_H(d)} \frac{v_H(d) - H}{2 - Hd} &= \frac{1}{v_H(1)} \frac{v_H(1) - H}{2 - H}, \\ \implies v_H(d) &= \frac{(2 - H) v_H(1)}{(d-1) v_H(1) + 2 - dH}. \end{aligned} \quad (8)$$

**Proposition 7**

$$v_H(d) = \frac{2H + 2}{d + 2}$$

*satisfies this recursion equation, with*

$$\frac{1}{v_H(d)} \frac{v_H(d) - H}{2 - Hd} = \frac{1}{2H + 2}.$$

.

**Remark 8** *The standard Flory index (3) for  $H = 1/2$  obeys the recursion formula.*

**Remark 9** *The recursion formula (8) implies the correct critical behavior, i.e. any solution will obey  $v_H(d) = H$  for  $d = 2/H \equiv d_c$ , whatever the choice of  $v_H(1)$ . To see this explicitly, insert  $d = 2/H$  and find*

$$v_H\left(\frac{2}{H}\right) = \frac{(2-H)v_H(1)}{(2/H-1)v_H(1)+0} = H.$$

**Remark 10** *If  $v_H(1)$  turned out to be equal to one for all  $H$ , the recursion formula would suggest*

$$v_H(d) = \frac{2-H}{d+1-dH},$$

*an expression which then also produces the standard Flory formula for  $H = 1/2$ , as well as the critical dimension  $d = 2/H$ .*

## 4 Summary

The Edwards type model for self-repelling fBm now at hand will raise the question of how the end-to-end length of trajectories scales as a function of time (or "number of monomers"). The original Fisher argument, while criticized regarding its assumptions [17] [4], provides a simple heuristic "derivation" of the Flory formula which allows an extension to fBm. The obtained scaling law needs further verification; we note that it correctly predicts the critical dimension for which the excluded volume become negligible and obeys a recursion formula based on dimension reduction. The latter would provide a useful constraint on any alternate scaling laws.

\* \* \*

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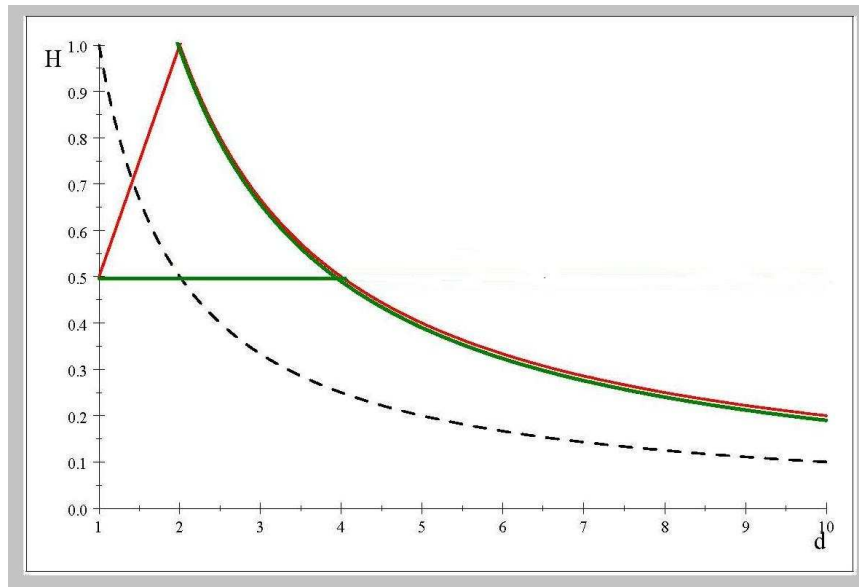


Figure 1: The domain of the Flory index