Self-Avoiding Random Paths
and Macromolecules

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INTRODUCTION

Let us think about a New York tourist wandering aimlessly through the grid of Manhattan streets and avenues.

The *Stubborn Tourist* will go straight ahead all day and so the distance R from his hotel will be proportional to the time T he has been walking:

$$R \sim T.$$

The *Aimless Tourist* on the other hand will change directions randomly at each street crossing, so he will not get very far, in fact his average distance <R> from the hotel after long walks will grow much more slowly in time. The mathematics of random walks tells us that

$$< R > \sim T^{1/2}.$$

The *Discriminate Tourist* also changes directions randomly, but always avoiding those street crossings where she had been before.

For all we know her average distance from the hotel will grow in time as follows:
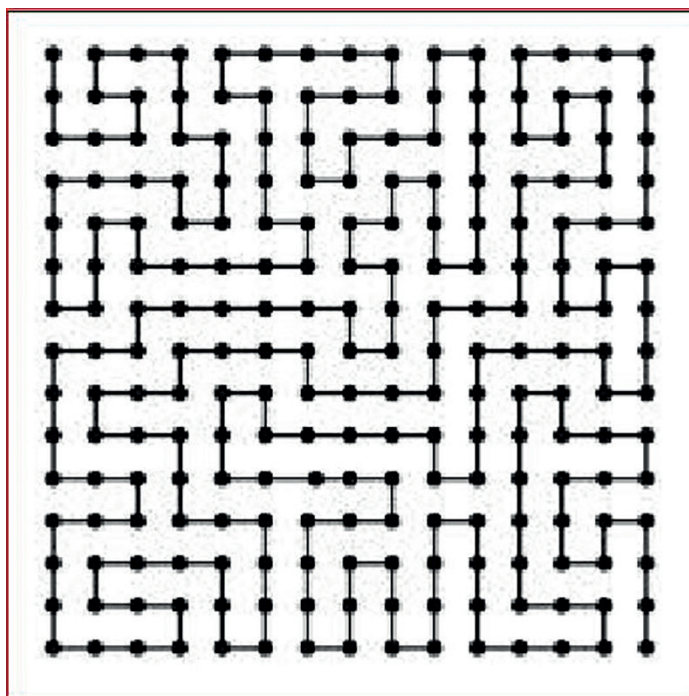
$$< R > \sim T^{3/4}.$$

If you can prove this, you may expect a Nobel Prize or a Fields medal, depending on whether you come from a physics or mathematics department.

SELF-AVOIDING RANDOM WALKS

Now we are talking of these "self-avoiding random walks". Here[2] is a special one that touches every street crossing or "grid point":

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[2] From https://en.wikipedia.org/wiki/Self-avoiding_walk

No doubt a pretty tough task to do, see e.g. Madras, Slade (1996).

In the 1950s, Paul Flory (Chemistry Nobel Prize 1974) was interested in chain polymers, in particular in their shape when they are floating in a good solvent.
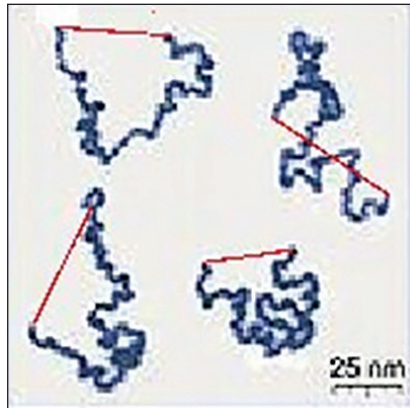
By now, with atomic force microscopes, we can have a look at them.[3]

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[3] *https://en.wikipedia.org/wiki/Polymer*
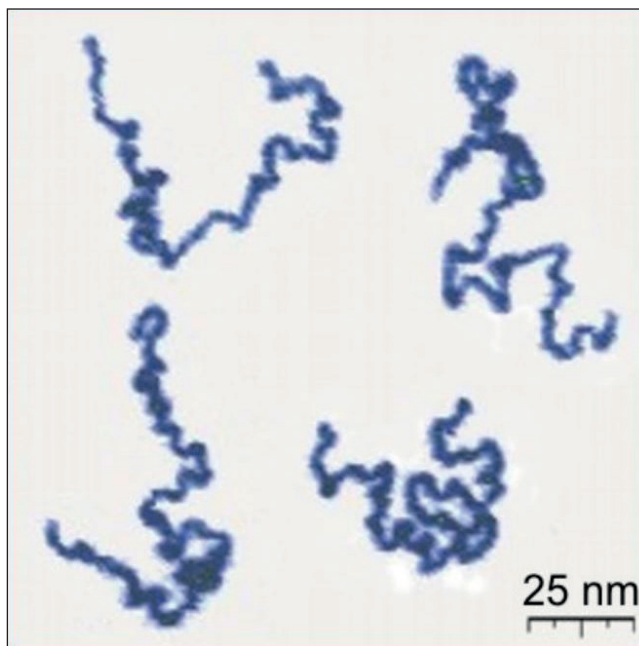
Actually these are almost 2d conformations, of poly (2-vinylpyridine) molecules in water, clinging to a surface (Roiter, 2005).

A characteristic quantity of such conformations is their "end-to-end length" R,

In particular one wants to know how it grows when the number N of constituent monomers becomes large.

For a freely floating polymer (in 3 dimensions) Flory predicted

$$< R >\sim N^v$$

with

$$v = 3\,/5$$

and later M. Fisher extended this to other dimensions d with the formula

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

SCALING: THE CONTINUUM LIMIT

Let us have another look at the aimless walker and his position R_N after N turns on some large quadratic grid. Now imagine you shrink the grid length by a factor ε. The path will get more wiggly, but also shorter. To compensate that, we let him make more turns. If we set

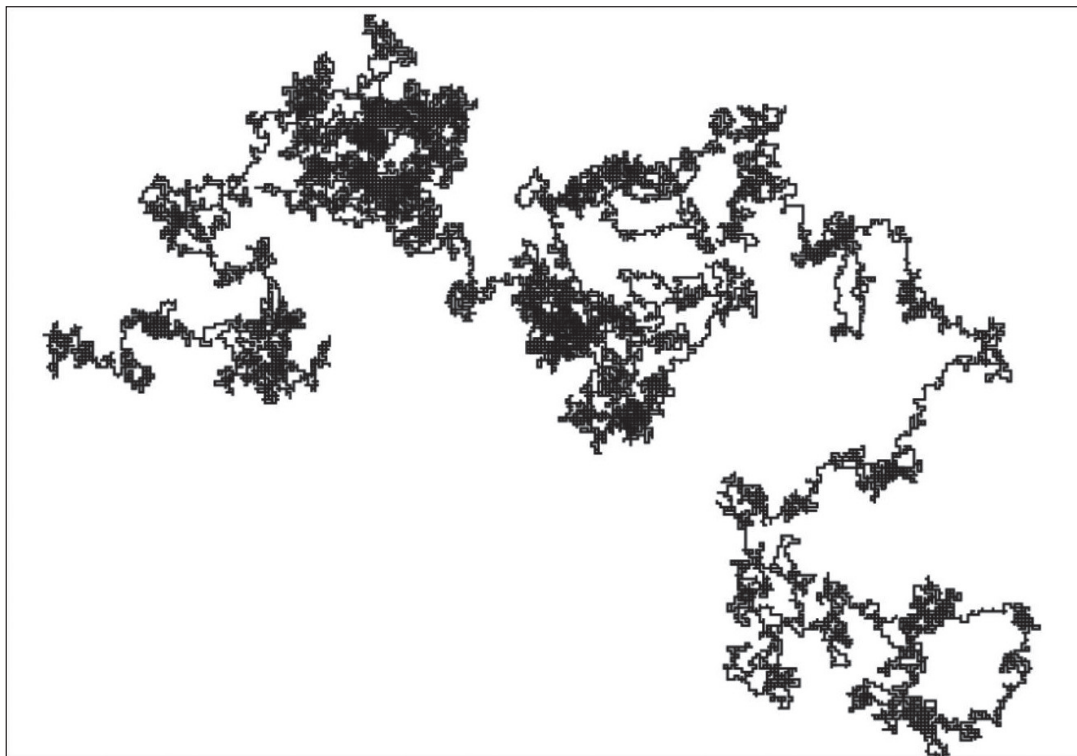$$R_\varepsilon(N) = \varepsilon R(\varepsilon^{-2}N)$$

then it is easy to see that the mean square length of the new path is equal to N as before:

$$< R_\varepsilon(N)>^2 = \varepsilon^2 < R(\varepsilon^{-2}N)>^2 = N$$

Now consider the limit ε→0:

$$B(t) = \lim_{\varepsilon \to 0} R(\varepsilon^{-2}t)$$

The paths get VERY wiggly in this limit – they change direction at every instant

In fact they are a mathematical model for Brownian motion, the "Wiener process" in mathematical terminology.

These paths are continuous lines without derivatives, in physical terms they describe motion without a proper velocity. Prompted by Einstein's famous paper, Perrin observed of the "Brownian motion" of dust specks under the microscope:

> "..,the particle tracks are so convoluted that the observed track is always infinitely simpler and shorter than the real one. In particular velocity in a short time interval does not converge to a well-defined limit; rather it keeps growing and changes direction in a crazy manner… Also, in no point can one fit a tangent, thus observing in nature objects previously imagined only by mathematicians, and up to now considered to be just mathematical curiosities…"[4]

These Brownian trails are actually fractals. While lines and "nice" curves have dimension one, the Brownian paths have fractal dimension D=2.

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[4] My translation from J. Perrin (1913).

From our construction we see that Brownian motion is scale invariant in the following sense

$$B(nt) \sim n^{1/2} B(t),$$

I.e. its scaling index is v=1/2.
This is a special case of the formula

$$v = 1/D$$

connecting fractal dimension D and scaling index v for scale invariant paths in general.

For the outer contours surrounding a Brownian trail in the plane, Mandelbrot[5] predicted the dimension D=4/3.

Note that these contours are by definition self-avoiding. Assuming that they are scale invariant the above formula would produce

$$v = 1/D = 3/4$$

in accordance with Flory's prediction (for much more on this see Lawler, Schramm, Werner).

Mathematically the random process B(t)

1. conventually starts at zero:

$$B\{0\} = 0,$$

2. is Gaussian as a consequence of the Central Limit Theorem

3. has mean zero:

$$< B(t)> = 0,$$

4. has increments of the form

$$<(B(t) - B(s))^2 > = t - s \ \ for \ \ t > s$$

From this it is easy to show that

$$<(B(t) - B(s)) B(\sigma)> = 0 \ \ for \ \ t > s \geq \sigma$$

meaning that the increment B(t)-B(s) from time s to time t is uncorrelated with the position B(σ) at earlier time σ. Like our walkers, this process moves on without memory of the past.

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[5] It is enjoyable to hear Mandelbrot himself about this observation in a TED lecture on Youtube: "Benoit Mandelbrot: Fractals and the art of roughness"

In introductory treatises of polymer physics Brownian motion trails are often used to describe polymer conformations, but then quickly abandoned: they have MANY self-crossings – realistic models must suppress these.

We can do this as follows. Consider the so-called self -intersection local time

$$L = \int dt_1 \int dt_2 \, \delta(B(t_2) - B(t_1)).$$

δ is the Dirac delta function, positive when $B(t_2)=B(t_1)$, and zero otherwise so L gets positive contributions whenever the path returns at some time t_2 where it was at time t_1. Hence a weight function

$$(1/Z)exp(-gL)$$

will not eliminate self-crossings completely but will suppress them exponentially.

This basically is the famous Edwards Model for "weakly self-avoiding Brownian motion". An analogous model can be constructed for weakly self-avoiding walks on a lattice (Domb-Joyce model).

The great advantage is that one does not have to struggle with the complicated question of strictly self-avoiding paths, while on the other hand universality arguments from physics make it plausible that the scaling behavior of paths will be the same in both cases.

Informally, the overall probability density for the random paths is then

$$\varrho \sim exp(-H)$$

with

$$H = \ H_1 + H_2 = \ \tfrac{1}{2}\int dt(\dot{B}(t))^2 + \ g\int dt_1 \int dt_2 \, \delta(B(t_2) - B(t_1))$$

and so paths with a small H will be most probable. To minimize H we will take a very crude approach.

The 1st term has the physical dimension of $(Length)^2/Time$, the second has $(Time)^2/(Length)^d$. Now look at the sum:

$$f(R) = R^2/T + \ T^2/R^d$$

And lo and behold: the minimum of this function is at

$$R \sim T^v \ \ with \ \ v = \ 3/(d+2)$$

suggesting that the weakly self-avoiding paths scale just like Flory and Fisher predicted for the chain polymers.

A CLOSER LOOK AT THE INTERSECTION LOCAL TIME

Mathematically the local time L is a rather singular object because of the Dirac delta. One needs to replaces it by a nice function δ_ε and study the limit:

$$L_\varepsilon = \int d^2t \, \delta_\varepsilon(B(t_2) - B(t_1)) \rightarrow \int d^2t \, \delta(B(t_2) - B(t_1)) = L.$$

as ε goes to zero.

This works fine for d=1. For d=2 however, the expectation of the local time becomes divergent in the limit:

$$\lim_{\varepsilon \to 0} < L_\varepsilon > = \infty,$$

but when subtracted, the "centered" limit

$$L_\varepsilon - < L_\varepsilon > \rightarrow L_c$$

is finite and gives rise to a well-defined Edwards model (Varadhan, 1970). For d=3 more complicated renormalizations are required.

HOW GOOD IS FLORY'S PREDICTION?

Let us now inspect Flory's formula $R \sim T^v$ with $v = 3/(d+2)$. For $d = 1$ the prediction v=1 is obvious: in one dimension the self-avoiding walker can only move forward, so distance R will be proportional to travel time T.

The first and last case are more or less obvious: in one dimension the self-avoiding walker can only move forward, so distance R will be proportional to travel time T. In four dimensions it is known that Brownian motion has no double points, so self-crossings do not happen and we have the $R \sim T^{1/2}$ of ordinary Brownian motion. So what is known about the other cases?

For d=2,3 there have been extensive computer simulations of long self-avoiding random paths on lattices. For $d = 2$ Li, Madras, Sokal (1995) found

$$v = 0.74967 \pm 0.0001$$

to be compared with Flory's v=0.75.

For $d = 3$ enumerations of self-avoiding walks gave

$$v = 0.5876 \pm 0.0006$$

which definitely does not agree with Flory's v=0.60.

Predictions from Physics – Theory and Experiment

For d = 2 Nienhuis (1982), based on arguments from quantum field theory (provided by de Gennes, physics Nobel prize 1991) and on the assumption that there exists a conformal invariant scaling limit, argued that indeed v = 3/4. (There are experiments, e.g. on DNA in fluid films, which give v≈0.79.)

For d=3 field theoretic renormalization group calculations give v = 0.588... in accord with the lattice simulations above. Experimental measurements on polymers in good solvents produce v ≈ 0.586.

Mathematical Results

For d=1 there is something to prove for weakly self-avoiding paths, they can go back, if only with a low probability, but R. v. d. Hofstad, F. den Hollander, W. Koenig (1997) have indeed proven v = 1.

For d=2 G. F. Lawler, O. Schramm, W. Werner (Fields Medal) have proven in 2004 that if a conformally invariant scaling limit exists, it is a so-called Schramm-Loewner evolution $SLE_{8/3}$.

For d = 5 Hara and Slade (1992) showed that the self-avoiding random walk is asymptotically Brownian and thus obeys $<R>\sim T^{1/2}$.

The borderline case d = 4 is actually more subtle, with an expected logarithmic correction to $<R>\sim T^{1/2}$. Nothing is rigorously proven for d=3.

PATHS WITH A MEMORY

Fractional Brownian motion

Recall our definition of Brownian motion via its increments

$$<(B\ (t) - B(s))^2 > =\ t - s\ \ for\ \ t > s$$

from which we concluded that those paths have no memory, or in polymer language, there is no long--range interaction along the chain.

To describe the latter we now change the rules:

$$<(B^H\ (t) - B^H(s))^2 > =\ (t-s)^{2H}\ \ for\ \ t > s,$$

introducing thus a new class of processes $B^H(t)$, called "fractional Brownian motion" where the "Hurst parameter" H may take values between zero and one, usual Brownian motion corresponding to H=½.

A closer look reveals that, for t>s> σ $<(B^H(t)-B^H(s))\ B^H(σ)>$ is negative for H < ½, zero for H = ½, and positive for H > ½.

This implies that for large H the trajectories tend to advance, while for small H they are curlier than those of Brownian motion. In this way we can study curled up or persistent paths through the choice of H.

Existence, Scaling

(Weakly) self-avoiding fractional paths are presently being studied in a joint project between groups in Kaiserslautern, Lisbon, Iligan, Madeira and Bielefeld. A first step in this direction was a mathematical one and produced the following theorem (M. Grothaus *et al.*, 2011)

THEOREM: "For the regime Hd ≤ 1 and sufficiently small g>0

$$exp(-gL_c) \in L_1(d\mu(B^H))$$

Hence, suitably normalized by a constant Z, the function

$$\rho(B^H) = (1/Z)exp(-gL_c(B^H))$$

is a well-defined probability density, suppressing self-intersections of fractional Brownian motion.

The Scaling Index

Using the heuristic dimensional argument as above, Bornales *et al.* (2013) predicted the scaling index to be

$$v = (2H + 2)/(d + 2)$$

and computer simulations were started by Bock *et al.*, first for d=1. Recall that in the Brownian case the trajectories become straight in d=1.

But for small Hurst index the trajectories tend to be curlier, and the above heuristic formula would predict

$$v = (2/3)(H + 1) \ \ for \ \ H \leq 1/2.$$

Here is what we found in simulations (Bock *et al.* 2015), with the straight line representing the prediction:
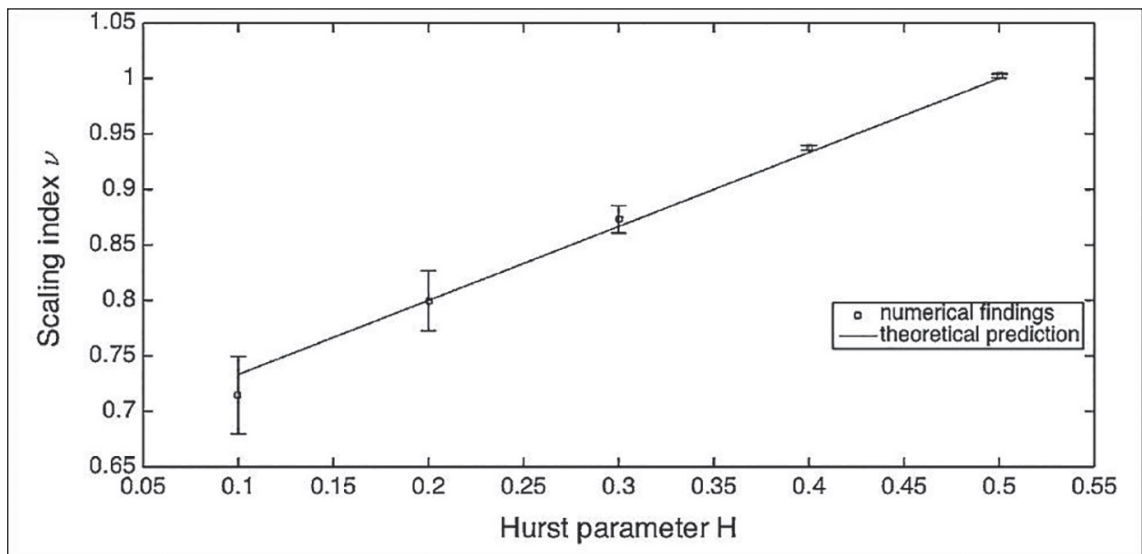
OUTLOOK

The Kaiserslautern-Lisbon-Iligan-Madeira-Bielefeld collaboration is now further looking at self--avoiding fractional Brownian motion regarding in particular

- more detail for the d=1 case, the so-called radius of gyration (Bock, Cabahug, Streit in preparation),
- improved, faster simulation algorithms, in particular for d>1,
- more on mathematical questions: "stochastic quantization" formulas for the fractional self-avoiding trails (Bock *et al.*, 2017, 2018),
- periodic and branching trajectories (Bock, Bornales, Streit, in preparation),
- extension to a larger class of random processes (Silva, Streit, 2018).

(Comunicação apresentada à Classe de Ciências
na sessão de 15 de março de 2018)

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