

LETTER TO THE EDITOR

Fractal dimensionality of polymer chains

S Havlin and D Ben-Avraham

Department of Physics, Bar-Ilan University, Ramat-Gan, Israel

Received 5 January 1982

Abstract. We suggest that the concept of fractal dimensionality provides a useful characterisation of the configurational properties of a *single* polymer. From numerical studies of long polymers traced out by self-avoiding walks on a planar lattice, we find that the fractal dimensionality is well defined and has a constant value for most scales of length of the chain. It is shown that renormalisation group theory provides a theoretical basis for the concept of fractal dimensionality in polymers.

The statistical configurational properties of long polymer chains have been extensively studied both theoretically and experimentally (de Gennes 1979, Flory 1971). Extensive research has been done on quantities characterising a statistical ensemble of polymers (Domb 1969, McKenzie 1976, Wall *et al* 1963). However, no attempt has been made to characterise a *single configuration* of a single polymer. In the present work we treat the problem of describing the configurational shape of a *single* regular polymer. In particular, we seek a quantity which characterises a single configuration of a typical polymer in statistical equilibrium. Quantities such as the mean square end-to-end distance $\langle R_{N_0}^2 \rangle$ (N_0 being the number of monomers) or the mean radius of gyration (Domb and Hioe 1969, Lax and Gillis 1977, McCrackin *et al* 1973, Wall and Seitz 1979, Rapaport 1976) do not fulfil this requirement. For instance, one can think of a regular polymer chain for which bending about the middle does not change its general shape (i.e. it still is a regular polymer). However, such bending leads to a considerable change in $\langle R_{N_0}^2 \rangle$ and in its mean radius of gyration. In fact, it is known that even when $N_0 \rightarrow \infty$, the relative fluctuation in $\langle R_{N_0}^2 \rangle$ is of the order of unity (McKenzie and Moore 1971, Fisher 1966). We propose that a more useful way of characterising a single polymer is by specifying its fractal dimensionality, FD (Mandelbrot 1977, Stanley 1977, Stapleton *et al* 1980).

We find that the FD describes a single configuration of a single polymer. The FD of such a polymer is nearly equal to the average value of the entire ensemble of polymers.

In order to understand the concept of FD , consider a polymer traced out by a long self-avoiding walk. It can be viewed on different scales of length. The unit of length might range from a single step to the whole end-to-end length of the chain. In the lowest scale of length, we examine the walk from up close, so that we may distinguish different steps. As we move further away, we can no longer distinguish between individual steps; instead, small segments each containing several steps might appear as a single step and we thus see fewer details. In this way, we reach higher scales of length.

We now consider an infinite polymer chain. We choose a section of length a_0 and count the number b_0 of details we see in that section for a given magnification. Suppose that upon changing the magnification by a factor a_1/a_0 , we see b_1 details in the same section. Let

$$(b_1/b_0) = (a_1/a_0)^D. \quad (1)$$

If D is independent of the magnification factor a_1/a_0 for some range of scales, i.e. range of a_0 , the quantity D is called the fractal dimensionality of the polymer in this range. This definition is in accordance with the ideas developed by Mandelbrot (1977). The assumption that D is independent of a_0 expresses a self-similarity property of the polymer in different scales of length. We present evidence below for D 's independence of a_0 for a single polymer chain and thus propose that D is a useful parameter for characterising such polymers.

An equivalent way of defining the FD is as follows. Instead of magnifying the polymer, we inspect a longer section of length a_1 (keeping the same scale) and we count as before the number of details in both sections. If the polymer fulfils the self-similarity assumption, (1) still applies with the same value of D as before. For both definitions D represents how much the polymer is winding. If the polymer is a straight line, then clearly, $D = 1$, whereas for ideal random chains, D can be easily shown to equal 2.

It is useful to define the notion of a *local fractal dimensionality* (LFD) $D(a_0)$ according to the relation

$$b_1/b_0 = (a_1/a_0)^{D(a_0)}, \quad (a_1 - a_0)/a_0 \ll 1. \quad (2)$$

$D(a_0)$ differs from D of (1) in that it can be defined for any value of a_0 . (The word 'local' in LFD refers to the local scale of length.) By contrast, the fractal dimensionality D is defined, and coincides with $D(a_0)$, only when $D(a_0)$ does not depend on a_0 for a finite range of values of a_0 .

In the following we present numerical results for LFD and FD on polymers. We have studied self-avoiding walks on a two-dimensional square lattice generated by a Monte Carlo enrichment technique (Wall *et al* 1963). We produced 400 polymers of length $N_0 = 100$, 200 polymers with $N_0 = 200$, and 100 polymers with $N_0 = 400$. We choose the pair of parameters $s = 20$, $p = 11$ satisfying the equation $pe^{-\lambda s} = 1$ (λ is the usual attrition constant).

The LFD was measured in the following way. The mean square separation of the end points of a segment containing N links in a polymer consisting of N_0 links is defined by

$$\langle R_N^2 \rangle_{N_0} = \frac{1}{N_0 - N + 1} \sum_{i=1}^{N_0 - N + 1} \langle R_{i, i+N}^2 \rangle_{N_0} \quad (3)$$

where $\langle R_{i, i+N}^2 \rangle_{N_0}$ is the mean square separation between the i th and the $(i+N)$ th elements of the chain. The quantity $(\langle R_{N+1}^2 \rangle_{N_0} / \langle R_N^2 \rangle_{N_0})^{1/2}$ plays the role of a_1/a_0 in (2). Further, we expect that b_0 should be proportional to N and that b_1 should be proportional to $N + 1$. Thus, from (2), we obtain for the value of the LFD

$$D_{N_0}(N) = \ln\left(\frac{N+1}{N}\right) / \ln\left(\frac{\langle R_{N+1}^2 \rangle_{N_0}}{\langle R_N^2 \rangle_{N_0}}\right)^{1/2}. \quad (4)$$

The subscript N_0 emphasises the fact that we are considering finite polymers. It should

be noted that if $D_{N_0}(N) = D$ is a quantity independent of N , then (4) is equivalent to

$$[(\langle R_N^2 \rangle_{N_0})^{1/2}]^D = AN \quad (5)$$

where A is a constant of proportionality. If such is the case, then (5) may be used as a definition of D . Note that (5) serves as a definition of D only if it holds for a wide range of N . Thus in defining D we make use of many internal distances $\langle R_N^2 \rangle_{N_0}$.

In figure 1, we present a plot of $D_{N_0}(N)$ as a function of N/N_0 . The graph shows two different typical regions which correspond to different kinds of ranges of scales. The first range is the *main range* for which LFD is nearly constant. The other range at $N \sim N_0$ is the *end-to-end range* for which there is an abrupt increase in LFD. In fact, a third range is easily identified from the numerical data, the *geometrical range* which occurs near $N \approx 1$. In this range, LFD is slightly different from that of the main range.

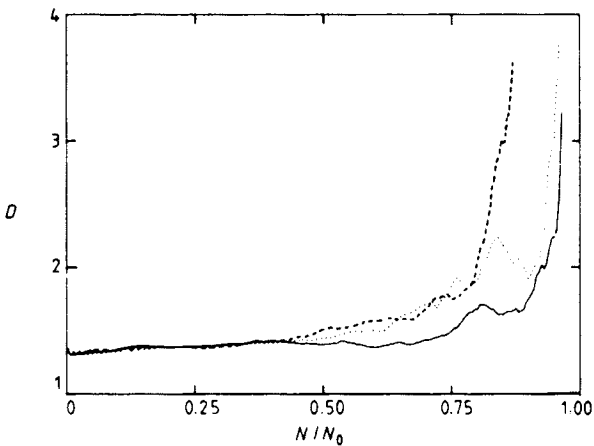


Figure 1. Plot of LFD $D_{N_0}(N)$ averaged over sets of polymers as a function of N/N_0 for different values of N_0 . The dotted, full and broken curves represent $N_0 = 100$, 200 and 400 respectively.

We suggest that the origin of the different behaviour of $D_{N_0}(N)$ in these three ranges is associated with edge effects. However, most of the scales of length of the polymers in the main range preserve in equilibrium a constant LFD. That is, they fulfil the self-similarity property suggested above.

The FD is measured according to equation (5) by plotting $\ln N$ as a function of $\ln(\langle R_N^2 \rangle_{N_0})^{1/2}$. The slope at each point on the resulting curve is the LFD and the part corresponding to the main range is a straight line. We calculate a best fit for this part and obtain $D = 1.36 \pm 0.04$. The value for A is found to be $A = 1.08 \pm 0.04$. It is interesting to note that the value obtained for $1/D$ as an *internal* exponent of the chain matches that of the usually measured (Domb 1969) end-to-end exponent ν a result which is by no means obvious. Indeed, the usual end-to-point exponent, ν , does not represent an *internal* self-similarity in contrast to FD.

Fractal dimensionality of a single chain. One of the main results of the present work is the usefulness of characterising a single polymer by its LFD. The same plot as we have prepared for a set of polymers is repeated for a single polymer chain (figure 2). It suggests that even a single long chain has a well defined FD, in the sense

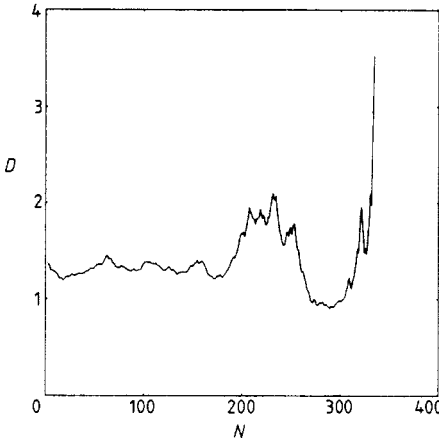


Figure 2. LFD of a single configuration of a polymer consisting of $N_0 = 400$ monomers.

that the value of FD measured for such a polymer is nearly equal to the average value of the set. Further evidence supporting this idea is presented in table 1 which shows that the deviation of FD from the average value of the set vanishes as $N_0 \rightarrow \infty$. Thus, in order to estimate D , it is enough to perform a measurement on a long *single*-polymer chain.

Table 1. The FD \bar{D} is averaged over the values of D in sets of polymers of length N_0 . The fluctuation $\Delta D = (D^2 - \bar{D}^2)^{1/2}$ vanishes as N_0 become infinite.

N_0	\bar{D}	ΔD
100	1.40	0.16
200	1.37	0.11
400	1.355	0.077

We now present the theoretical background for the FD. We base our treatment on the renormalisation group (RG) theory developed for polymers by de Gennes (1979), and we shall show that (5) follows from this theory.

It is well known that for an ideal random walk chain

$$\langle R_{N+1}^2 \rangle_{N_0} / \langle R_N^2 \rangle_{N_0} = (N + 1) / N \equiv g_N. \tag{6}$$

However, in self-avoiding chains, the excluded volume interaction swells the polymer. We describe this swelling by a factor $(1 + h)$ where h depends in general on g_N and on a dimensionless coupling constant u_N (see de Gennes 1979). That is

$$\langle R_{N+1}^2 \rangle_{N_0} = \langle R_N^2 \rangle_{N_0} g_N [1 + h(g_N, u_N)]. \tag{7}$$

The main idea of RG theory is to repeat this transformation many times, starting with $N \sim 1$ until $N \gg 1$. It is assumed that for large enough N , the coupling constant u_N reaches a finite limit u^* which is called the ‘fixed point’:

$$N_0 \gg N \gg 1, \quad u_n \rightarrow u^* = \text{constant}. \tag{8}$$

When the fixed point is reached, $h(g_N, u_N)$ no longer depends on u_N . Thus, instead of (7) one writes

$$\langle R_{N+1}^2 \rangle_{N_0} = \langle R_N^2 \rangle_{N_0} g_N [1 + h(g_N)], \quad N \gg 1. \quad (9)$$

From the semi-group property of the transformation, it follows that

$$1 + h\left(\prod_{i=j}^N g_i\right) = \prod_{i=j}^N [1 + h(g_i)]. \quad (10)$$

A general solution of (10) is

$$h(g_i) = g_i^{2\nu-1} - 1, \quad (11)$$

which, upon substituting in (9), yields

$$\langle R_{N+1}^2 \rangle_{N_0} / \langle R_N^2 \rangle_{N_0} = [(N+1)/N]^{2\nu}, \quad (12)$$

from which (5) follows if $\nu = 1/D$. Thus, we see that RG ideas lead to the concept of FD.

It should be noted that (12) holds only for $N \gg 1$ (i.e. not in the geometrical range), a result which is consistent with our numerical data. Moreover, when N is of the order of N_0 , another edge effect appears, that is, the effective coupling constant u_N tends to change again because of the decrease in the excluded volume interaction. Equation (12) is thus correct only in the main range, because only then $u_N \approx u^*$.

To summarise, we believe that the concept of fractal dimensionality provides a very useful description of the configurational properties of a single polymer. The LFD is a measure of how winding the polymer is for any scale of length (by contrast, the end-to-end distance is a property of the polymer for only one scale of length). In the range where the LFD is essentially constant, one can speak of FD of the polymer. Whenever the FD is defined it can be thought of as reflecting a self-similarity property of the polymer.

The usefulness of the FD concept lies in the fact that FD characterises and can be measured on a single polymer. The FD behaves like a macroscopic quantity in the sense that its uncertainty vanishes as the size of the system (N_0) increases. By contrast, the end-to-end distance behaves like a microscopic quantity because relative fluctuations remain finite even when $N_0 \rightarrow \infty$.

The authors wish to thank Professor C Domb, Professor M Luban, Professor B B Mandelbrot, Dr M Lax and Mrs C Brender for stimulating discussions and I Dayan, J Hashkes and S Simhon for carrying out the computer programming.

References

- Domb C 1969 *Adv. Chem. Phys.* **15** 229–59
 Domb C and Hioe F T 1969 *J. Chem. Phys.* **51** 1915, 1920–8
 Fisher M E 1966 *J. Chem. Phys.* **44** 616–22
 Flory P 1971 *Principles of Polymer Chemistry* (Ithaca, NY: Cornell University Press)
 de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
 Lax M and Gillis J 1977 *Macromolecules* **10** 3349
 McCrackin F L, Mazur J and Guttman M C 1973 *Macromolecules* **6** 859–71
 McKenzie D S 1976 *Phys. Rep.* **27** 37–88
 McKenzie D S and Moore M A 1971 *J. Phys. A: Gen. Phys.* **4** L82–6

- Mandelbrot B B 1977 *Fractals: Form, Chance and Dimension* (San Francisco: Freeman)
- Rapaport D C 1976 *J. Phys. A: Math. Gen.* **9** 1521-37
- Stanley H E 1977 *J. Phys. A: Math. Gen.* **10** L211-20
- Stapleton H J, Allen J P, Flynn C P, Stinson D G and Kurtz S R 1980, *Phys. Rev. Lett.* **45** 1456-9
- Wall F T, Windwer S and Gans P J 1963 *Meth. Comput. Phys.* **1** 217-43
- Wall F T and Seitz W A 1979 *J. Chem. Phys.* **70** 1860-3