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LETTER TO THE EDITOR

A Levy flight approach to diffusion on a SAW with cross-links

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Abstract. We reconsider the problem of diffusion on a self-avoiding walk with local bridges. Levy flight arguments are presented to estimate the spectral dimension, based on known results on the statistics of loops in a SAW. Agreement with ESR experiments on proteins and with numerical simulations is found to be satisfactory.

It is well known that different physical properties of a fractal structure are characterised by different dimensions which, in general, do not coincide with the *fractal dimension* d_f. A celebrated example is the *spectral dimension* d_s [1], which describes the low-frequency phonon density of states ($\rho(\omega) \underset{\omega \to 0}{\sim} \omega^{d_s - 1}$), or equivalently the asymptotic behaviour of a random walker moving on the fractal structure, which obeys the diffusion law: $R^2 \sim t^{d_s/d_f}$. For percolation clusters, d_s is close to $\frac{4}{3}$ in any dimension [1] and is thus different from d_f. For a linear structure such as a polymer, it is obvious that $d_s = 1$. Indeed, a random walk on the structure obeys $s^2 \sim t$, where s is the arc length of the walker; $d_s = 1$ then follows from $R \sim s^{1/d_f}$. More generally, a value of d_s different from 1 (d_f being unchanged) would mean that diffusion along the polymer is anomalous and follows $s^2 \sim t^{d_s}$.

Electron-spin-lattice relaxation experiments on some proteins allow us to estimate d_s for these structures through the temperature dependence of the relaxation rate†. The interesting and surprising result of Stapleton *et al* [3] is that $d_s = 1.65 \pm 0.04$ for several different proteins (including myoglobin and ferricytochrome c), which is very close to their (x-ray) *measured* fractal dimension $d_f \simeq \frac{5}{3}$. This value of d_f is that expected for a usual three-dimensional self-avoiding walk (SAW)‡ (see, for example, [4]). However, d_s appears to be somewhat larger than 1, which corresponds to *hyperdiffusion* and precludes a simple interpretation as a usual random walk along a SAW. As discussed in [5], hyperdiffusion generally arises either from strong correlations or from a broad distribution of elementary step lengths (Levy flight). The aim of this letter is to suggest that a natural origin for the latter mechanism exists in this problem and to present a simple estimation of the resulting value of d_s.

Indeed, as first proposed in [6], a possible way out of $d_s = 1$ is to take into account the possibility for the walker to take shortcuts whenever two non-consecutive monomers of the SAW are nearest neighbours in space (see figure 1). These shortcuts do exist for

† We deal in this letter with the diffusion problem, i.e. *scalar* excitations. It could well be that, for proteins, the vectorial character of the excitations has some importance, as discussed in [2].

‡ This result is, by itself, rather unexpected owing to the complex nature of protein chemistry.

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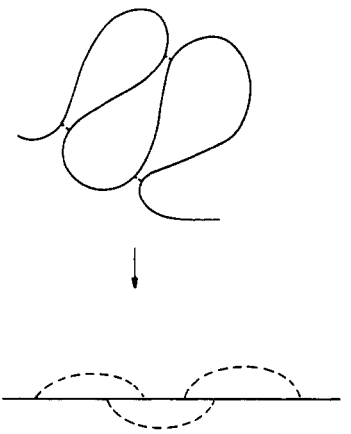

Figure 1. Unfolding a self-avoiding walk with local bridges generates long-range (Levy-like) steps.

the phonon problem, since cross-links (e.g. hydrogen or disulphide bonds, etc) play the role of additional 'massless springs'. Those springs rigidify the structure and thus deplete the low-frequency (long-wavelength) density of states. It was argued in [6] that, if there is a sufficiently large fraction of these shortcuts, the walker will eventually see the underlying Euclidean space rather than the structure itself and would thus diffuse according to $R^2 \sim t$, thus leading to $d_s = d_f$. This proposal has been widely discussed in the two-dimensional case. Real space renormalisation group techniques [7, 8] and Monte Carlo simulations [7, 9–11] have been used to investigate the diffusion law. The results show quite a large scatter, ranging from $d_s < 1$ ($d_s = 0.96$ in [7]) to $d_s > 1$ ($d_s = 1.04$ in [11]) or $d_s = 1$ (in [10]). However, all are quite far from the fractal dimension $d_f = \frac{4}{3}$ of a 2D SAW, thus invalidating the argument of [6], suggesting that $d_s = d_f$ for a SAW with local bridges.

We propose to use a Levy flight argument, to which we now turn, in order to evaluate d_s for this problem. A jump of the walker across a local bridge amounts to a step of length l when measured along the chain, where l is the size of the loop joining the two monomers (see figure 1). The probability distribution of the loop sizes is a known quantity of polymer physics: its asymptotic behaviour is characterised† by the contact exponents introduced by des Cloizeaux [12]. For a loop well inside the chain, one has, for large l,

$$P(l) \sim l^{-\nu(d+\theta_2)} \tag{1}$$

where θ_2 is known exactly from conformal invariance in two dimensions [13] and up to order ε^2 in an $\varepsilon = 4 - d$ expansion [12]. The asymptotic behaviour of $P(l)$ is thus

$$P(l) \sim A_d l^{-\mu} \begin{cases} \mu = 2.18 & \text{in } d = 3 \\ \mu = \frac{43}{16} & \text{in } d = 2. \end{cases} \tag{2}$$

Two comments are now in order.

† Note that $P(l)$ is not exactly the quantity considered in [12]. However, as the number of loops is proportional to the number of monomers, the two quantities have the same asymptotic behaviour.

(i) $\int lP(l)\,dl$ converges, thus leading to a finite fraction of contact points, as noted in [12]. However, this does not imply (as claimed in [14]) that loops are irrelevant to diffusion, since

(ii) $\int l^2P(l)\,dl$ diverges, which is precisely the condition under which normal diffusion breaks down. Indeed, suppose, as a first approximation to the real diffusion process, that on each monomer the walker can choose the size l of its jump according to the probability distribution $P(l)$. Then, for $P(l)\sim l^{-\mu}$ with $2<\mu<3$, this 'uncorrelated Levy flight model' leads to a diffusion law [15]†: $s^2\sim t^{d_s}$ with $d_s=2/(\mu-1)>1$. However, this is only a first approximation, since the configuration of the polymer is in fact *quenched*: on each monomer, the length of the possible jump is fixed once for all. To take this effect of *spatial correlations* into account, one can refine the preceding argument in a self-consistent way, in the spirit of [5]. A diffusion law of the form $s^2\sim t^{d_s}$ means that each link is crossed $t^{1-d_s/2}$ times and that $t^{d_s/2}$ different links are probed; each link thus contributes to a typical displacement $(t^{1-d_s/2})l_i$ and thus

$$s\sim(t^{1-d_s/2})^{1/2}\sum_{i=1}^{t^{d_s/2}} l_i. \tag{3}$$

If the l_i are distributed according to $P(l)\sim l^{-\mu}$, then

$$\sum_{i=1}^{M} l_i\sim M^{1/(\mu-1)} \tag{4}$$

and self-consistency thus requires $d_s=1-d_s/2+d_s/(\mu-1)$, leading to

$$d_s=2(\mu-1)/(3\mu-5). \tag{5}$$

The values of d_s obtained for two- and three-dimensional SAW according to our two approximation schemes ('uncorrelated' and 'correlated' Levy flights) are summarised in table 1, together with the experimental value for proteins [3] and the most recent numerical one for 2D SAW [11]. The good agreement appears to us as a convincing clue that the Levy flight mechanism described here does capture the essential physical features of the problem.

Let us conclude with a few remarks.

(*a*) Note that the enhanced diffusion law *along* the SAW truly enhances the diffusion in the underlying Euclidean space (and thus modifies the phonon spectrum according to $\rho(\omega)\sim\omega^{d_s-1}$), despite the local character of the bridges. Indeed, for large enough

Table 1. Values of d_s for SAW with local bridges, according to the two Levy flight arguments described in the text.

μ ($=\nu(d+\theta_2)$)	d_s, uncorrelated Levy flight	d_s, correlated Levy flight	d_s, experimental	
$d=2$	$\frac{43}{16}$	$\frac{32}{27}\simeq 1.19$	$\frac{54}{49}\simeq 1.10$	1.04 (numerical [11])
$d=3$	2.18 (order ε^2)	1.69	1.53	1.65 ± 0.04 (proteins [3])

† In $d>4$, one has $\nu=\frac{1}{2}$, $\theta_2=0$, and thus $\mu=2$. Nevertheless, diffusion becomes normal ($d_s=1$), since the number of contact points is no longer thermodynamical ($A_d=0$) and the Levy flight effect thus disappears.

time (many local bridges visited), s is also large, and thus the relation $\overline{R^2} \sim (\overline{s^2})^{1/d_f} \sim t^{d_s/d_f}$ is valid.

(*b*) The fact that local bridges can generate a Levy-like behaviour was already noticed in [7], but surprisingly the resulting effect was argued to be a slowing down of diffusion ($d_s < 1$) rather than an enhancement. An exactly solvable example where Levy-like bridges can be shown to enhance diffusion is the Koch curve studied in [16] (note, however, that the step sizes in this example are hierarchically distributed). Note furthermore that $d_s > 1$ means that the end-to-end resistance of the structure grows like N^{δ} with an exponent $\delta = 2/d_s - 1 < 1$.

(*c*) If our mechanism is the correct one, it means that the statistics of long loops is crucial, and thus that small-cell real space RG or Monte Carlo simulations on too small chains would fail to produce the correct d_s value. As a consequence, we suggest that any convincing numerical study of d_s should be accompanied by a check that, not only d_f, but also the loop statistics of the generated SAW are in agreement with known results. In this respect, it is interesting to note that, if one takes for μ the numerical determination of [17]: $\mu = 2.95 \pm 0.2$ in 2D (obtained by enumeration), one finds from (5) $d_s \simeq 1.01$, which is quite close to the Monte Carlo values quoted above. The problem of convergence of μ and d_s towards their asymptotic values is obviously quite hard.

(*d*) We have implicitly assumed throughout this letter that the fraction f of monomers belonging to no loops is zero in $d = 2$ and $d = 3$, otherwise one would necessarily obtain $d_s = 1$ in the asymptotic limit. This point is, to our knowledge, not definitely settled [18]. According to [19], it remains finite at first order in $\varepsilon = 4 - d$. However, even if this was to be true for $d = 2$ and 3, the density of states would have the following form: $\rho(\omega) \sim f + (1-f)\omega^{d_s - 1}$, thereby defining a crossover frequency

$$\omega_c = \left(\frac{f}{1-f}\right)^{1/(d_s-1)}$$

to be compared with the minimal frequency of the experiment ($1/R^2 \sim 1/N^{2\nu}$, or $k_B T$). It seems to us that the number N_c thus defined would be so large that the diffusion regime relevant to experiments would still be the one studied in this letter, namely the large loop contribution.

(*e*) We have not mentioned another experiment [20] on a protein (ferridoxin) whose fractal dimension appears to be close to $\frac{4}{3}$, which is the fractal dimension of a 2D SAW. Nevertheless, it is not clear to us whether the whole statistics of loops has a 2D nature. On the contrary, we feel that the 3D nature of the structure could generate an intermediate statistics for $P(l)$, and thus a value of d_s intermediate between 1.10 and 1.53. The experimental value is 1.34 ± 0.05.

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References

[1] Alexander S and Orbach R 1982 *J. Physique Lett.* **43** L625
Rammal R and Toulouse G 1983 *J. Physique Lett.* **44** L13
[2] Herrmann H J 1986 *Phys. Rev. Lett.* **56** 2432

[3] Stapleton H J, Allen J P, Flynn C P, Stinson D G and Kurtz S R 1980 *Phys. Rev. Lett.* **45** 1456
[4] de Gennes P G 1985 *Scaling Concepts in Polymer Physics* (Cornell: Cornell University Press)
[5] Bouchaud J P, Georges A and Le Doussal P 1988 *J. Physique* submitted
[6] Helman J S, Coniglio A and Tsallis C 1984 *Phys. Rev. Lett.* **53** 1195
[7] Chowdhury D and Chakrabarti B K 1985 *J. Phys. A: Math. Gen.* **18** L377
[8] Christou A and Stinchcombe R B 1986 *J. Phys. A: Ma.h. Gen.* **19** L357
[9] Yang Y S, Liu Y and Lam P M 1985 *Z. Phys.* B **59** 445
[10] Stella A L, Dekeyser R and Maritan A 1986 *Fractals in Physics* ed L Pietronero and L Tosatti (Amsterdam: Elsevier)
[11] Manna S S and Roy A K 1987 *Phys. Rev.* A **35** 4023
[12] des Cloizeaux J 1980 *J. Physique* **41** 223
[13] Duplantier B 1987 *Phys. Rev.* B **35** 5290
[14] Cates M E 1985 *Phys. Rev. Lett.* **54** 1733
[15] Mandelbrot B B 1982 *The Fractal Geometry of Nature* (San Francisco: Freeman)
[16] Maritan A and Stella A 1986 *Phys. Rev.* B **34** 456
[17] Redner S 1980 *J. Phys. A: Math. Gen.* **13** 3525
[18] Duplantier B and des Cloizeaux J private communication
[19] Ball R C and Cates M E 1984 *J. Phys. A: Math. Gen.* **17** L531
[20] Allen J P, Colvin J T, Stinson D G, Flynn C P and Stapleton H J 1982 *Biophys. J.* **38** 299