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LETTER TO THE EDITOR

Force-induced unfolding of a homopolymer on a fractal lattice: exact results versus mean-field predictions

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Abstract

We study the force-induced unfolding of a homopolymer on the three-dimensional Sierpinski gasket. The polymer is subject to a contact energy between nearest-neighbour sites not consecutive along the chain and to a stretching force. The hierarchical nature of the lattice we consider allows for an exact treatment which yields the phase diagram and the critical behaviour. We show that for this model mean-field predictions are not correct; in particular, in the exact phase diagram there is *no* low-temperature re-entrance, and we find that the force-induced unfolding transition below the theta temperature is of second order.

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The recent development of single-molecule techniques has given experimentalists the opportunity to grab with suitable handles and mechanically manipulate, by means of optical tweezers [1] or cantilevers such as atomic force microscopes [2], proteins, molecular motors or DNA molecules. In this way it has become possible to measure or exert on these molecules forces in the piconewton range. In particular the effect of a stress on the giant molecule titin has been studied in [3–5], where it was found that a force-induced unfolding transition takes place between a compact native-like state and an extended state. The presence of strong hysteresis together with the rather abrupt jumps observed in the force versus elongation curves suggest that the unfolding is a first-order phase transition. On the theoretical side, many simple models have been proposed to make contact with these experiments (see e.g. [6–11] for the stretching of proteins and homopolymers, [12–15] for DNA unzipping and [16–18] for RNA unzipping). In particular, in [6, 7] the authors study the force-induced unfolding of a homopolymer and a heteropolymer in the mean-field approximation and find that in both cases the critical line

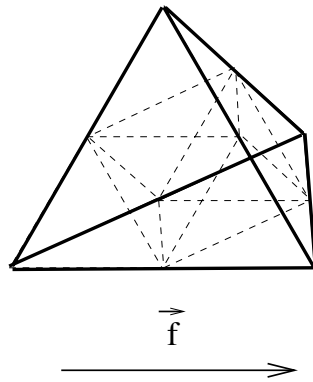


Figure 1. In this figure we show the 3DSG at the second stage of iteration construction. Four tetrahedra (dashed lines) at the first order of iteration are put together in order to form the tetrahedron which constitutes the 3DSG at the second iteration (bold lines). The stretching force \vec{f} acts along one of the edges of the 3DSG and is also shown in the figure.

separating the globule from the coil is re-entrant at low temperatures. This is analogous to what had been found for the phase boundary in the phase diagram valid for the DNA unzipping, where it has been proved exactly that in the presence of a pulling force mean field is correct [14].

When self-avoidance is incorporated in the models, exact results are rare and mean-field treatments become popular. In this work, we study exactly the force-induced unfolding of a self-avoiding walk (SAW) on a fractal lattice, the three-dimensional Sierpinski gasket (SG) [19,20]. This gasket has a fractal dimension $D_f = 2$, and this renders the system interesting from the theoretical point of view because we are below the upper critical dimension for theta collapse [21]. Mean-field theory would predict a re-entrance here because the Hamiltonian compact walks in this lattice have nonzero entropy as compared with the zero entropy of the completely stretched coil (the same argument as in [14]). However, the exact critical line that we find in the SG shows no re-entrance. Similarly, by comparing the free energies of the globule and that of the coil one would naively expect a first-order transition, whereas the exact calculation yields a second-order transition. Though we cannot conclude from this calculation that on Euclidean lattices the situation will also be analogous, we feel that this calculation should give a warning that the mean-field prediction need not be correct. The presence or absence of re-entrance on Euclidean lattices together with the nature of the transition is thus an intriguing question which deserves further work.

We consider a SAW on the three-dimensional Sierpinski gasket (3DSG) [19, 20], a hierarchical lattice with ramification number four and $D_f = 2$ (figure 1). We study the combined effect of a force \vec{f} which stretches the polymer along one edge of the SG (figure 1) together with a compacting self-attractive term, obtained by assigning a weight $\exp(\beta\epsilon)$ ($\epsilon > 0$) every time two non-consecutive sites of the SAW are nearest neighbours in the 3DSG. We call $\beta \equiv T^{-1}$ the inverse temperature. To describe the effect of the stretching force, we give each step of the walk an orientation and a weight $\exp(\beta f \Delta a)$, where $f \equiv |\vec{f}|$ is the modulus of \vec{f} and Δa is the projection of the oriented step along \vec{f} .

The calculation of the partition function and other thermodynamic quantities involves the evaluation of 25 generating functions (figure 2). 12 generating functions involve contributions of a SAW which enters at the n th-order SG at one vertex and goes out at one other vertex. 12 other generating functions arise when an (oriented) SAW starts from a vertex, goes out from another one and then re-enters the n th-order SG at a later stage. The last generating

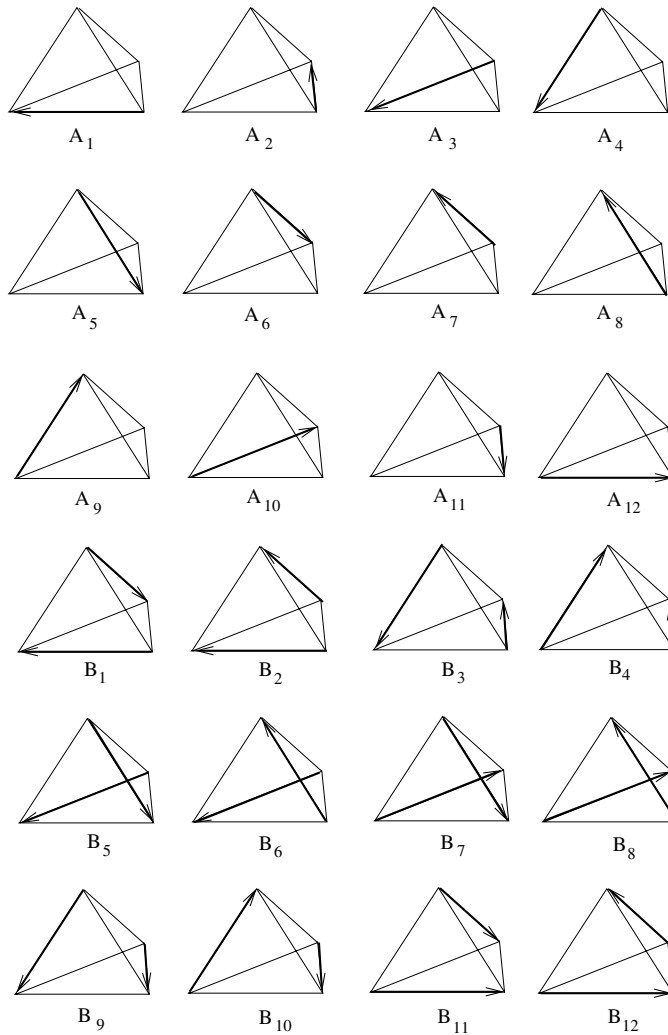


Figure 2. In this figure we show the generating functions at the first order together with their names given in the text.

function is the void. The one-leg generating functions are labelled $A_i, i = 1, \dots, 12$, and the two-leg contributions $B_i, i = 1, \dots, 12$. One can write recursion relations for the generating functions by exactly enumerating all walks in the SG on the computer: one has to sum up the contributions of SAWs at the n th-order SG in order to generate SAWs in the $(n + 1)$ th-order SG.

The initial conditions for the generating functions are

$$\begin{aligned}
 A_1 &= zy^{-1} & A_{2,3,4,8} &= zy^{-1/2} \\
 A_{5,9,10,11} &= zy^{1/2} & A_{6,7} &= z & A_{12} &= zy \\
 B_{1,2,3,6} &= z^2w^4y^{-1} & B_{4,5,8,9} &= z^2w^4 & B_{7,10,11,12} &= z^2w^4y
 \end{aligned}
 \tag{1}$$

where z is the SAW step fugacity, $y \equiv \exp(\beta f)$ and $w \equiv \exp(\beta \epsilon)$ is the weight responsible for the theta collapse in the absence of force.

Note that, as is apparent from the above equations, we have adopted the convention that interactions are restricted to sites within the first-order SG and moreover that after one SAW has touched one vertex in the SG it is obliged to exit from the SG at that order [20, 22, 23]. It has been proved that this approach is equivalent to the more general approach as regards universality of the phase transition [23].

When there is no pulling force the recursion relations simplify because

$$A_i \equiv A \quad B_i \equiv B \quad \forall i = 1, \dots, 12, \quad (2)$$

so one obtains [20]

$$A' = A^2 + 2A^3 + 2A^4 + 4A^3B + 6A^2B^2 \quad B' = A^4 + 4A^3B + 22B^4. \quad (3)$$

At non-zero \vec{f} , the equations retain the same structure but every B and every A has to be labelled by the appropriate number as found in the exact enumeration. To solve the model, we proceed as follows. First, we must find the fixed points of the recursion relations: in general, for every phase or critical point (line) there is a fixed point. Then, for every f and T fixed, we have to find the critical step fugacity, $z_c(\beta\epsilon, \beta f)$, such that the flux defined by the 25 recursion relations and initial conditions will bring the system to the fixed point corresponding to these values of f and T . This critical step fugacity $z_c(\beta\epsilon, \beta f)$ allows us to obtain a numerical expression for all the quantities we are interested in, namely, the free energy $F(\beta\epsilon, \beta f) \equiv \frac{1}{\beta} \log(z_c(\beta\epsilon, \beta f))$, the average elongation along the direction of the pulling force $\langle x \rangle(\beta\epsilon, \beta f)$ and the average number of contacts $\langle n \rangle(\beta\epsilon, \beta f)$, found by calculating the appropriate derivative of $F(\beta\epsilon, \beta f)$.

From the linearized recursion equations, it is possible to obtain the critical exponents of the phase transition. Every eigenvalue λ (there are at most as many such eigenvalues as there are recursion relations) of the linearized flux at given f and T defines two critical exponents, Y and ν , through

$$\lambda \equiv 2^Y \equiv 2^{\frac{1}{\nu}} \quad (4)$$

where $\nu \equiv \frac{1}{Y}$ is defined in terms of the average squared elongation $\langle x^2 \rangle$ as $\langle x^2 \rangle \sim N^{2\nu}$ [21] for large values of the number of steps in the SAW, N .

Performing this analysis for our model, we find six different fixed points. At zero force, we re-obtain the fixed points given in [20]. In particular, for $T < T_\theta \equiv \frac{2}{\log(3)}$, the theta collapse temperature in the absence of force, there is a zero-force compact fixed point for the recursion relations:

$$A_i = 0 \quad B_i = 22^{-1/3} \equiv B^* \quad \forall i = 1, \dots, 12. \quad (5)$$

For $T > T_\theta$, i.e. in the swollen phase, the fixed point that is approached is

$$A_i \simeq 0.4294 \dots \quad B_i \simeq 0.04998 \dots \quad \forall i = 1, \dots, 12. \quad (6)$$

Just at criticality at the theta temperature, $T = T_\theta$, the fixed point is

$$A_i = 1/3 \quad B_i = 1/3 \quad \forall i = 1, \dots, 12. \quad (7)$$

The corresponding critical indices ν (corresponding to the largest eigenvalues, λ_1 , in every one of the three regimes) are $1/2$, $0.5294 \dots$ and $0.7294 \dots$ respectively in the collapsed phase, at the theta point and in the swollen phase.

At $T < T_\theta$, there exists a critical line $f = f_c(T)$ separating a compact from an open phase. When $f < f_c(T)$ the recursion relations display another compact fixed point:

$$A_i = 0 \quad \forall i = 1, \dots, 12 \\ B_{4,5,8,9} = 22^{-1/3} \quad B_{1,2,3,6} = 0 \quad B_{7,10,11,12} = +\infty. \quad (8)$$

The divergence arises from the pulling force and one can be convinced that the two-leg generating functions are diverging (vanishing) for $L \rightarrow \infty$ (L is the system size, and one has $L = 2^{n-1}$ at the n th level of iteration in the construction of the 3DSG) as y^L (y^{-L}). Consequently, we can eliminate the divergences if for example we multiply the diverging functions for B_1 , and the vanishing ones for B_7 , and then take the square root of the result: if we do this all the two-leg generating functions converge to the fixed point $22^{-1/3}$ as in the zero-force compact phase. When the SAW is in the open phase ($f > f_c(T)$), the fixed point is

$$\begin{aligned} A_i &= 0 & \forall i = 1, \dots, 11 \\ A_{12} &= 1 \\ B_i &= 0 & \forall i = 1, \dots, 12. \end{aligned} \quad (9)$$

Finally, when the force is exactly tuned at the critical line, the fixed point which is approached is

$$\begin{aligned} A_i &= 0 & \forall i = 1, \dots, 11 \\ A_{12} &= \frac{1}{1 + 6 * 22^{-2/3}} \sim 0.5668 \equiv A^* \dots \\ B_{4,5,8,9} &= 22^{-1/3} & B_{1,2,3,6} = 0 & B_{7,10,11,12} = +\infty \end{aligned} \quad (10)$$

again the square root of the products of one diverging two-leg function multiplied by a vanishing two-leg function is $22^{-1/3}$. We shall see later that it is also possible to justify the value found numerically for the nonzero-force system. The exponent ν is equal to one-half for $f \leq f_c(T)$ and is unity in the open phase.

In practice, by taking advantage of the knowledge of the fixed points, one can devise a convenient way to calculate numerically the critical force as a function of temperature. Once the critical step fugacity, $z_c(\beta\epsilon, \beta f = 0)$, of the compact phase at a fixed temperature T is known one can further fix z to this value, and then tune f in order to pass from the compact fixed point to the critical line fixed point (within the precision allowed by the computer). In order to have a sufficient accuracy in these calculations, it proved necessary to use a computer with quadruple precision.

The phase diagram obtained numerically is shown in figure 3. Two remarks are in order. First, we notice that there is no re-entrance in the critical line, the slope at $T = 0$ being approximately -0.05 . This is at variance with the prediction possible on the basis of mean-field-like treatments (such as those done e.g. in [6, 7], see also below). Second, the behaviour of the critical line near T_θ is

$$f_c(T) \sim (T_\theta - T)^{a=0.87 \pm 0.01}, \quad (11)$$

in agreement with the prediction $a = \frac{\nu_\theta}{\phi} = 0.868$, where ν_θ is the critical exponent of the end-to-end distance at the theta temperature and ϕ is the theta transition crossover exponent [21] (see below for an argument leading to the behaviour in equation (11)).

We report in figure 4 the plot of $\langle x \rangle$ versus f at $T = 0.35$. This figure supports the hypothesis that the unfolding transition for the homopolymeric SAW on the 3DSG is of second order. This is in agreement with the argument based on the recursion relations given below. Our belief supported by the exact numerics is that the transition is of second order for any nonzero T and is of first order only at $T = 0$.

We now present some arguments to interpret our results (based on the renormalization group (RG) flux). Even though to write explicitly the equations and to cope numerically with them it was necessary to put the force in step by step, this is equivalent to evolving the $f = 0$ generating functions (equation (3)) and then putting in the dependence on \vec{f} at every iteration by

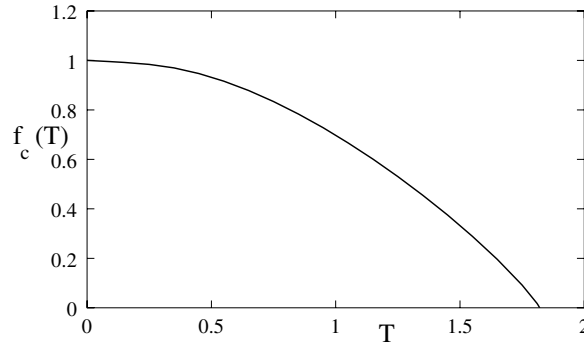


Figure 3. Plot of the phase diagram on the 3DSG found numerically. In this figure we have taken $\epsilon = 1/2$ to make the calculations.

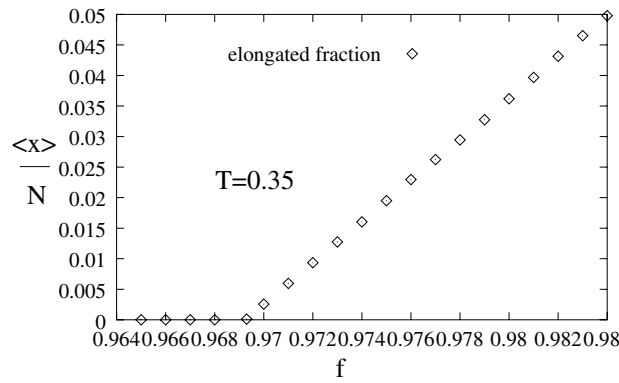


Figure 4. Plot of the average elongation scaled by N in the thermodynamic limit as a function of f for $T = 0.35$. The critical force found numerically, by imposing that the fixed point reached after iteration of the recursion is that of equation (10), is approximately 0.969... We have taken $\epsilon = 1/2$ in these calculations.

multiplying the generating functions by suitable powers of y . If we do this, we can exploit the symmetries of the problem, which mean that, before multiplying the generating functions by a y -dependent term, all one-leg and two-leg diagrams are separately equivalent. By noting the structure of the nonzero-force fixed points, one can argue that the one-leg generating functions must vanish in the compact phase as $A \sim C y_c^{-L}$, where $y_c \equiv \exp(\beta f_c(T))$ and C is a constant, for now undetermined. By matching the exponentials in equation (3), we obtain that the two equations, when $T \ll T_\theta$ ($T \rightarrow 0$), can be approximated by

$$A' = A^2 + 6A^2 B^2 \quad B' = 22B^4. \quad (12)$$

The flux corresponding to these RG equations is shown in figure 5. The non-trivial fixed point, (A^*, B^*) with both A^* and B^* non-zero, is obtained with $B^* = 22^{-1/3}$ and $A^* = \frac{1}{1+6(B^*)^2}$. Thus $A \sim C y_c^{-L}$ as $L \rightarrow \infty$, with $C = A^*$. When $T \rightarrow 0$, the fixed points can be approached very fast. This holds also in the full RG treatment (not simplified) since the terms that should evolve to zero have small initial values at low temperature. As a consequence, as $T \rightarrow 0$, the phase boundary of figure 3 is found by matching the initial conditions with the fixed-point values for A_{12} and any B . Thus the critical line is found by solving this system:

$$z_c = \exp(-2\beta\epsilon)(B^*)^{1/2} \quad z_c = \exp(-\beta f)A^* \quad (13)$$

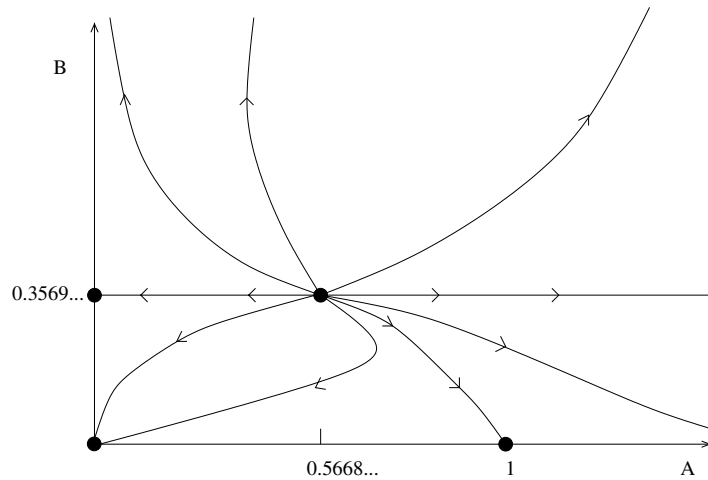


Figure 5. Plot of the flux lines resulting from the simplified recursion relations corresponding to equation (12).

where B^* and A^* are the nonzero fixed points of equation (12), corresponding to the critical force (such that $y^L A \sim 1$ for large L , see equation (10)). The critical line for $T \rightarrow 0$ is

$$f_c(T) \sim 2\epsilon + T \log \left(\frac{A^*}{(B^*)^{1/2}} \right) \sim 2\epsilon - 0.0525 \dots T, \tag{14}$$

so that $f_c(T)$ starts with negative slope as found numerically. For $f > f_c(T)$, the fixed point to be reached in the (A, B) plane of figure 5 is $(1, 0)$. We observe that for a small deviation from A^* the RG flux takes the SAW to the open fixed point by moving along the line $B(A)$, which we can find in the neighbourhood of (A^*, B^*) by requiring that it be a fixed line under the flux defined by the recursion equations. We require that $B(A) \sim B^* + c(\delta A)^\alpha$ in the neighbourhood of A^* . We thus need to solve the system

$$A' = [A^* + (\delta A)]^2 [1 + 6[B^* + c(\delta A)^\alpha]^2] \quad B(A') = 22[B^* + c(\delta A)^\alpha]^4 \tag{15}$$

in the unknown quantities c and α . We obtain $c = -1/12A^{*3}B^* \sim -1.2826 \dots$ and $\alpha = 2$, so the fixed line $B(A)$ smoothly approaches the fixed point at critical force. By inserting these values in the expression $B(A) \sim B^* + c(\delta A)^\alpha$ together with the ansatz

$$z_c(\beta f_c, \beta \epsilon) - z_c(\beta f, \beta \epsilon) \sim (f - f_c)^\gamma, \tag{16}$$

one obtains $\gamma = 2$, which implies $\langle x \rangle \sim (f - f_c)$ for $f \gtrsim f_c$ and the transition is of second order. This argument is strictly valid for low T . However it is unlikely that the order of the transition could change along the phase boundary and this is also confirmed by our numerics. The situation at the point $T = 0$ is somewhat special: the entropy vanishes and balancing the energetic terms gives a first-order transition.

One should notice the importance of the term $6A^2B^2$. Let us consider a mathematical simplified model in which the relevant equations are

$$A' = A^2 \quad B' = 22B^4 \tag{17}$$

in which the mixed term (physically due to stretched walks that still make an extensive number of contacts) is suppressed. This corresponds to balancing the free energy of a stretched coil with that of a compact globule. In this simplified treatment re-entrance is present, as can be

expected from naive estimates of the ground-state entropies of the stretched and compact state, and the transition is of first order.

Finally, we argue that the exponent a in equation (11) is given by $a = \frac{\nu_\theta}{\phi}$ as anticipated above. Near T_θ at zero force the free energy behaves as $F(T) \sim (T_\theta - T)^{2-\alpha=1/\phi}$. For $f \gtrsim 0$, on the other hand, at $T = T_\theta$, the free energy behaves as $F(f) \sim f^{1/\nu_\theta}$. Consequently, we obtain $a = \frac{\nu_\theta}{\phi}$ in equation (11). This is in agreement with the result found for $d = 3$ in [8], where the exponents both take their mean-field values (1/2), and also with the mean-field analysis in [6, 7], in which $\phi = 1$ and consequently $a = \nu$ (1/2 in the ideal case treated in [6, 7]).

In conclusion, we have presented an exact calculation of the phase diagram of a SAW in the presence of a compacting contact energy and a stretching force. We deem it is interesting because it can be analysed exactly. A mean-field-like treatment gives a re-entrant boundary and a first-order transition. Neither of these predictions is confirmed by the exact treatment, which gives a critical line with a zero-temperature negative slope and a second-order transition. This has been explained in a simple way by analysing a simplified version of the recursion relations, analogous to the real-space RG equations. Whether or not the critical line in the hypercubic lattice shows re-entrance is therefore not yet clear and appears to be an intriguing question. The 3DSG has $D_f = 2$ and so the most natural comparison is with the Monte Carlo simulations performed in [8], which indeed give a second-order transition, even though we cannot be sure that the order of the transition is the same in the two-dimensional real and fractal lattices. The behaviour of the critical force near the theta point has been found and a general argument, also valid for hypercubic lattices, has been given in agreement with the result we found here and also with the result found in $d = 3$ in [8].

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