Relaxation Dynamics of complex polymer networks

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Aim: To unveil how the dynamical features of the fractal cactus network are related to its geometry.

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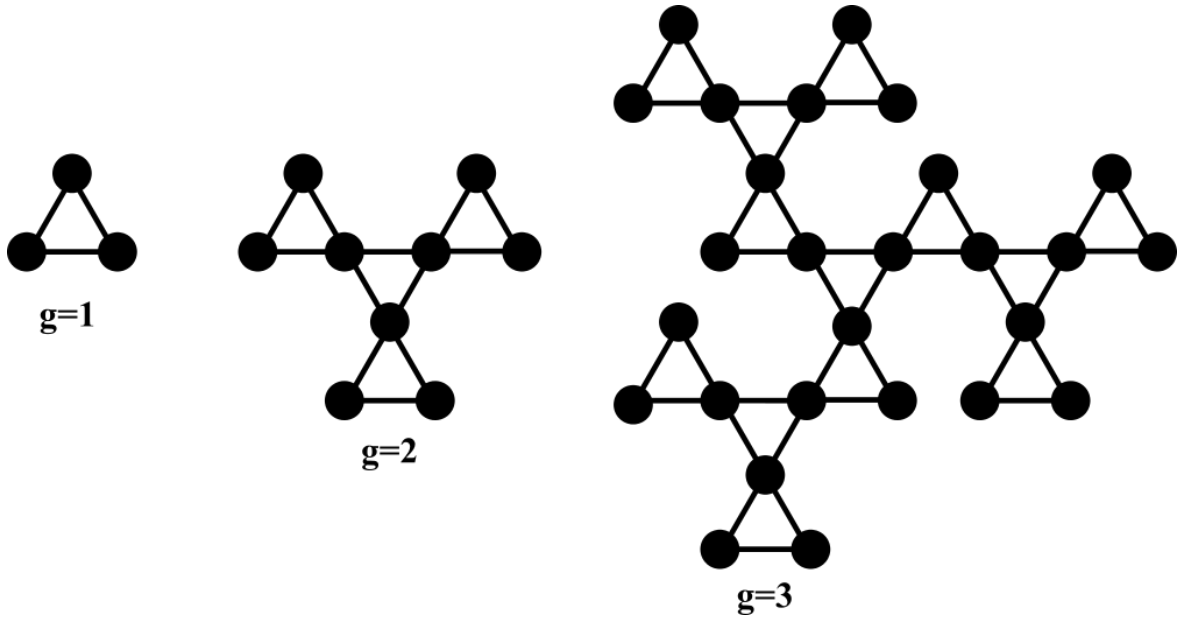
The construction procedure of the fractal cactus network



Fractal dimension $d_f = \frac{\ln 3}{\ln 2} = 1.58496 \ldots$

Spectral dimension $d_s = \frac{2 \ln 3}{\ln 6} = 1.22692 \ldots$

The first three generations of the fractal cactus have been experimentally synthesized.
These are the branched [4] triangulane and the branched [n] triangulanes (BTs).

Generalized Gaussian Structures (GGS) model

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- extension of the Rouse model to incorporate polymers with arbitrary topologies
- dynamical quantities can be determine based on the eigenvalues
- does not account for excluded volume effects and entanglement constraints

A GGS is modelled as a structure consisting of N beads (monomers) connected to each other by elastic (entropic) springs.

The conformation of a polymer is described by the set of position vectors $\{\boldsymbol{R}_n\}$, where $\boldsymbol{R}_n(t) = (X_n(t), Y_n(t), Z_n(t))$ is the position vector of the *n*th monomer at time *t*.

Dynamics of the polymer is described by the set of N linearly independent Langevin equations. For a particular monomer *i* it reads

$$\zeta \frac{\partial \boldsymbol{R}_i(t)}{\partial t} + K \sum_{j=1}^{N} \boldsymbol{A}\boldsymbol{R}_j(t) = \boldsymbol{f}_i(t) + \boldsymbol{F}_i(t)$$

where, $\zeta = 6\pi\rho a$ is the friction constant, $K = 3k_B T/l^2$ is the elasticity constant, f_i are random forces, and F_i denotes any external force that acts on a monomer

The topology of the polymer is accounted by the connectivity matrix $\mathbf{A} = (A_{ij})$

$$A_{ij} = \begin{cases} -1 \text{ if } i \text{ and } j \text{ are connected with a bond} \\ 0 \text{ otherwise} \end{cases}$$

A_{ii} equals the number of bonds emanating from the bead i

The system of the Langevin equations can be solved by diagonalizing the connectivity matrix

The average monomer displacement (stretching of the polymer under external force)

$$\ll Y(t) \gg = \frac{Ft}{N\zeta} + \frac{F}{\sigma N\zeta}\sum_{i=2}^{N}\frac{1-exp(-\sigma\lambda_i t)}{\lambda_i}$$

In the GGS model the mechanical relaxation moduli are given by

$$G'(\omega) = C/N\sum_{i=2}^{N}\frac{\omega^2}{\omega^2+(2\sigma\lambda_i)^2} \quad \text{(storage modulus)}$$

$$G''(\omega) = C/N\sum_{i=2}^{N}\frac{2\sigma\omega\lambda_i}{\omega^2+(2\sigma\lambda_i)^2} \quad \text{(loss modulus)}$$

The iterative method for determining the eigenvalues of the connectivity matrix

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- The calculation of the dynamical quantities is straightforward only for small structures where the numerical diagonalization is easy to perform.
- The topological details of the structure are revealed only in the intermediate time/frequency region which is bounded by large crossover domains.
- For small structures, the crossover domains blurred up the intermediate domain and no information can be extracted.
- For very large matrices the numerical diagonalizations are practically impossible to perform.
- To overcome the problem we developed an iterative procedure.

Fractal cactus network rescales under two specific real-space transformations

The result of the specific real-space transformations is the following relation

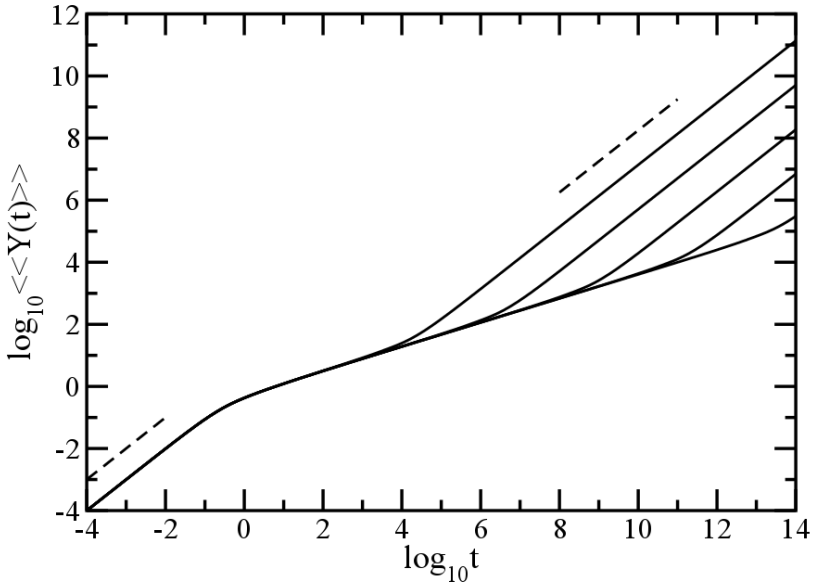
$$\lambda_{\pm}^{(g)} = \frac{6 \pm \sqrt{36 - 4 \cdot \lambda^{(g-1)}}}{2}$$

The degeneracy of the eigenvalues

$$\Delta_g = 1 + 3^{g-1}$$

Rouse dynamics: averaged monomer displacement

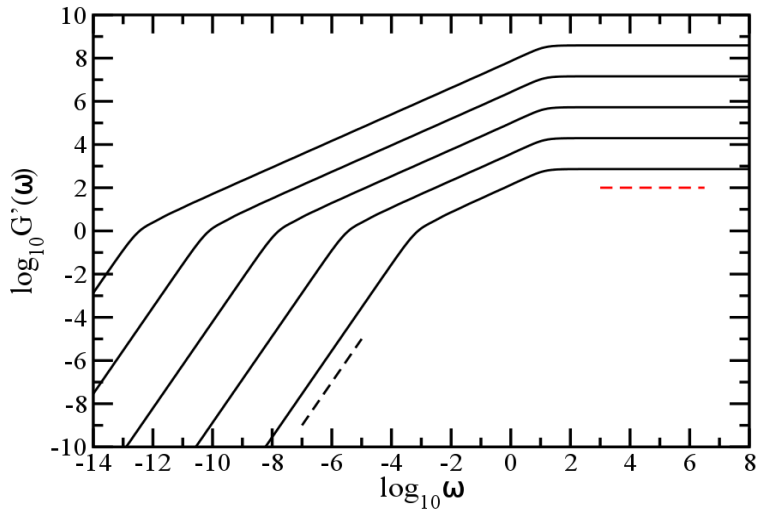
Fractal cactus networks with sizes ranging from $N = 3^6$ to $N = 3^{18}$ monomers.

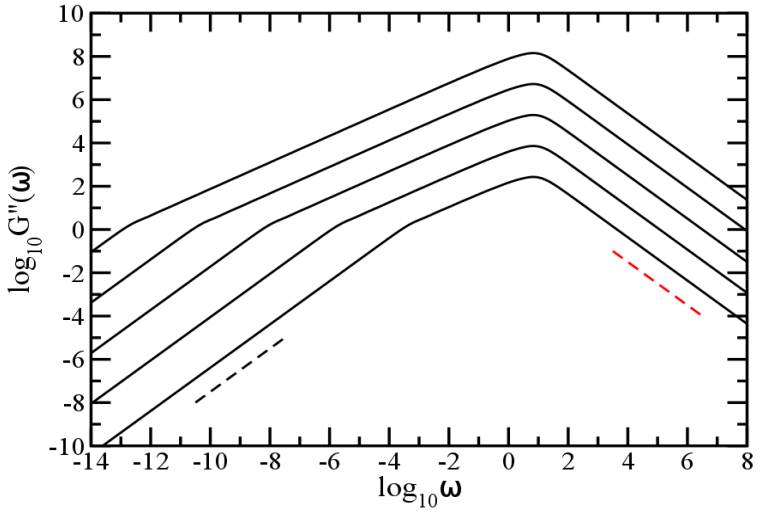


At very short times: $\ll Y(t) \gg \sim t$; only one monomer is moving
At very long times: $\ll Y(t) \gg \sim t/N$; the whole structure drifts
In the intermediate time domain: $\ll Y(t) \gg \sim t^{\gamma}$
For the largest fractal considered, the power-law exponent (slope of the curve) $\gamma = 0.389$
From the comparison with the theoretical value $\gamma_t = 1 - \frac{d_s}{2} = 0.38685$ results a **very good agreement**.

Rouse dynamics: mechanical relaxation moduli

Fractal cactus networks with sizes ranging from $N = 3^6$ to $N = 3^{18}$ monomers.





At very small frequencies: $G'(\omega) \sim \omega^2$ and $G''(\omega) \sim \omega$; represents mechanical response of the whole network
At very large frequencies: $G'(\omega) \sim \omega^0$ and $G''(\omega) \sim \omega^{-1}$; signifies single-monomer mechanical response
In the intermediate frequency domain: $G'(\omega) \sim \omega^{\alpha}$ and $G''(\omega) \sim \omega^{\beta}$
Going from $N = 3^6$ to $N = 3^{18}$ we have a change in the minimal slope from $\alpha = 0.662$ to $\alpha = 0.614$ and from $\beta = 0.575$ to $\beta = 0.605$.

From the comparison with the theoretical value $\frac{d_s}{2} = 0.61315$ results again a **very good agreement**.

We infer that the sole parameter of importance for the relaxation dynamics is the spectral dimension.

Summary and conclusions

- In this work we have analyzed the Rouse-type relaxation dynamics of a fractal cactus polymer network
- We have developed an iterative procedure for the determination of the whole eigenvalue spectrum of the connectivity matrix
- The general picture that emerges in the Rouse-type approach is that the dynamical quantities obey power law behavior and the sole fractal parameter of importance for the relaxation dynamics is the spectral dimension

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