Relaxation Dynamics of a Crumpled Globule

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Abstract — The relaxation dynamics of elastic networks of crumpled (fractal) globules obtained by computer simulation of the collapse of a polymer chain in different modes is studied. It is shown that, in their dynamic properties, folded globules are similar to proteins, molecular machines.

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1. INTRODUCTION

It is known that the non-phantom nature of polymer chains gives rise to two types of interactions: bulk interactions, which disappear for infinitely thin chains and topological interactions, operative even for zero-thickness chains. At sufficiently high temperatures (in “good solvent”), a polymer molecule has a strongly fluctuating coiled structure without a definite thermodynamic state. At temperatures below a certain critical value of \( \theta \) (on “poor solvent”), a polymer molecule composed of \( N \) units links of length \( l \) collapses into a weakly fluctuating globular structure of size \( R \sim N^{1/3} \). The classical works [1, 2] devoted to studying the coil-globule transition without topological interactions demonstrated that the conformation of the chain in the globular phase is similar to a Brownian random walk trajectory. However, when the topological factors are taken into account, because of the additional repulsion between folds, the chain folding may turn out to be different [3]. In particular, for unentangled conformatons at temperatures below \( \theta \)-point, there may exist some critical length \( g^* \) depending on the temperature and bulk interactions, such that chain fragments larger than \( g^* \) collapse. For not too short chains, these \( g^* \)-unit segments act as new “monomeric blocks” (or first-level folds). A chain segment containing several successive folds-blocks may collapse “in its own volume,” forming second-level folds; then, second-level folds form third-level fold, etc. (Fig. 1a). The process of hierarchical folding of the entire chain is complete when all the \( g^* \)-unit segments of the chain will occur inside a single common fold. A specific feature of such a crumpled (also called “fractal”) globule is that, if the entanglement of folds at all levels is forbidden, the hierarchical structure of the folds is not disrupted, being thermodynamically equilibrium.

2. ULTRAMETRIC DESCRIPTION OF THE FOLDED CONFORMATION

The state of a chain unit in the folded conformation can be conveniently characterized by a set of indices, which defines in which first-level fold (which is located in a particular second-level fold, which, in turn, is located in a particular third-level fold, etc.) a given unit is situated. These sets of indices can be compared to pathways in a treelike graph (Cayley tree) with ramification index \( p \), leading from the root to its “leaves” (knots at the tree border). The set of “leaves” specifies the space of states for the chain units in the folded conformation, with each path leading from the top of the tree to a particular leaf uniquely describing the hierarchy of folds for the corresponding units of the chain; each sub-tree represents a fold of definite scale (Fig. 1b). The ramification index \( p \) of the Cayley tree specifies the number of folds enclosed into a higher-level fold of the hierarchy.

Note that, in the description of the folded conformation in terms of the treelike graph, the conformation of the chain is determined not by the location of the chain units in the space, but by the enclosures of the folds in which the chain units are located. For any two units \( i \) and \( j \), there is always one and only one minimum fold of level \( \gamma \) within which units \( i \) and \( j \) are situated in different folds of level \( \gamma - 1 \). The “conformational distance” between units \( i \) and \( j \) in this description is the scale of the smallest fold comprising both units or, equivalently, the scale of the largest fold comprising only one unit. For a self-similar hierarchy of
folds (regularly ramified Cayley tree), the scale of any fold is determined only by the hierarchy level γ to which it belongs. Accordingly, the level γ(i, j) to which the smallest fold common for units i and j belongs defines the distance between units i and j. This distance is ultrametric, i.e., obeys the strong triangle inequality. Note that, for a regularly ramified tree, the scale of a fold of level γ (number of “leaves” of the tree, i.e., chain units in the fold) is γ. The conformational distance between of hierarchy γ(i, j) can also be conveniently defined as γ(i, j). In this case, the distance between two units is simply equal to the scale of the smallest fold common to them.

Thus, a polymer chain in a predetermined folded conformation can be thought of as a chain of units located at certain points of the ultrametric space. If a folded conformation has a probability measure, the conformation can be described as a path of a random (model) process in the ultrametric space, i.e., chain units in the fold) is γ. The conformational distance between of hierarchy γ(i, j) can also be conveniently defined as γ(i, j). In this case, the distance between two units is simply equal to the scale of the smallest fold common to them.

Consider the issue of stability of the folded globule. Introduce an additional repulsion between chain units in the globular phase, depending on the ultrametric (conformational) distance and temperature:

\[
\frac{d\varphi(i, s)}{ds} = \sum_{j \neq i} w(j) \varphi(j, s) - \sum_{j \neq i} w(i) \varphi(j, s) + \frac{T - \theta}{\theta} \sum_{i \neq j} w(i) \varphi(j, s).
\] (2)

Using p-adic Fourier transform makes it easy to calculate the eigenvalues of the operator in the right side of Eq. (2):

\[
\lambda_\gamma(T) = -p^{-\alpha \gamma} + T - \theta \left( -p^{-\alpha \gamma} + \frac{1}{p-\alpha-1} p^{-\alpha} \right).
\] (3)

The solution to the equation \(\lambda_\gamma(T) = 0\) determines the hierarchy of critical temperatures, \(T_1 < T_2 < T_3 < \ldots < T_{\text{max}}\), at which the folds lose stability. At \(T \leq \theta\), all (nonzero) eigenvalues \(\lambda_\gamma(T)\) are negative and all folds are stable. Folds are sequentially destroyed above the \(\theta\)-point: when the minimum critical temperature \(T_1\) is reached, the biggest fold begins to disintegrate, while the folds of lower levels from a largest fold remain sta-