Hierarchical Chain Model of Spider Capture Silk Elasticity

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Spider capture silk is a biomaterial with both high strength and high elasticity, but the structural design principle underlying these remarkable properties is still unknown. It was revealed recently by atomic force microscopy that an exponential force-extension relationship holds both for capture silk mesostructures and for intact capture silk fibers [N. Becker et al., Nat. Mater. 2, 278 (2003)]. In this Letter a simple hierarchical chain model was proposed to understand and reproduce this striking observation. In the hierarchical chain model, a polymer is composed of many structural motifs which organize into structural modules and supramodules in a hierarchical manner. Each module in this hierarchy has its own characteristic force. The repetitive patterns in the amino-acid sequence of the major flagelliform protein of spider capture silk is in support of this model.

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helices [4], or microcrystal structures [14]. The interactions among some of these motifs are much stronger than their interactions with other motifs; therefore, they form a structural module at the hierarchy level \( h_m - 1 \). These level-(\( h_m - 1 \)) modules are then merged into level-(\( h_m - 2 \)) modules through their mutual interactions. This merging process is continued, and finally, at the global scale, the whole spider silk string is regarded as a single module of the hierarchy level \( h = 0 \).

In nature, the structures of many biomaterials are, indeed, hierarchically organized. As a composite material, the chromosome is a mixture of DNA, histone, and other nonhistone structural proteins [15]. The DNA molecule first wraps onto histone proteins to form nucleosome particles, the basic units of chromosome. With the help of H1 histone, this linear sequence of nucleosomes are then coiled and folded to form the 30-nm chromatin fiber. With the help of other scaffold proteins, the chromatin fiber is then further coiled and folded at several levels to form the compact chromosome structure. As another example, the amino-acid sequence of a protein first forms basic structural modules of \( \alpha \) helix and \( \beta \) sheet, called secondary structures. By different ways of connections of these secondary modules, the protein constructs various tertiary topologies that are critical for its specific biological functions. In a higher level, these tertiary domains then form quaternary structures of protein complexes consisting of multiple chains [16]. Recent experimental and theoretical studies have shown that the force-induced unfolding of protein molecules is indeed processed in a hierarchical way; i.e., the tertiary structure precedes the secondary structures to be pulled over at increasing external forces [7,17].

Our hierarchical chain model may also serve as a framework to understand the mechanical property of these biomaterial systems.

Consider a polymer of contour length \( L_0 \). It is regarded as the module of hierarchy level \( h = 0 \) (the module \( M_0 \)). \( M_0 \) is composed of a tandem sequence of \( m_0 \) subunits \( M_1 \) of contour length \( L_1 = \frac{l_0}{m_0} \) (Fig. 1). Under the action of an external force field \( f \), the extension of \( M_0 \) is denoted as \( x_0(f) \). It was observed that water-induced protein mobility is a significant contribution to capture silk elasticity [18]. Therefore, we decompose \( x_0 \) into two parts: (i) the extension \( \Delta x_0 \) caused by the displacement and position rearrangement of these \( m_0 \) subunits, and (ii) the total extension \( m_0 x_1 \) caused by the inherent deformations of these \( m_0 \) subunits:

\[
x_0(f) = \Delta x_0(f) + m_0 x_1(f).
\]

Similarly, at the hierarchy level \( h = 1 \), each unit is itself composed of \( m_1 \) level-2 subunits \( M_2 \) of length \( L_2 = \frac{L_0}{m_0 m_1} \). Therefore, \( x_1(f) \) can be written as \( x_1(f) = \Delta x_1(f) + m_1 x_2(f) \), where \( \Delta x_1(f) \) is the contribution to the extension of a level-1 module due to the displacement and position rearrangement of its \( m_1 \) subunits, and \( x_2(f) \) denotes the extension because of the inherent deformation of a level-2 subunit \( M_2 \). As this structural hierarchy is continued, we arrive at the following expression concerning the total extension \( x(f) \):

\[
x(f) = \Delta x_0(f) + \sum_{h=0}^{m} m_0 m_1 \ldots m_h \Delta x_{h+1}(f).
\]

It is reasonable that the average extension \( \Delta x_h(f) \) of a \( M_h \) contributed by the reorientation or rearrangement of its level-(\( h + 1 \)) subunits is proportional to the relaxed contour length \( L_h \) of this module. To facilitate the following analytical calculation, let us assume \( \Delta x_h(f) \) has the following nonlinear form (we show that the final force-extension relationship is not sensitive to the specific assumption made here):

\[
\Delta x_h(f) = \begin{cases} 
\alpha L_{h} f / f_h, & f < f_h, \\
\alpha L_{h}, & f \geq f_h,
\end{cases}
\]

where \( \alpha \) is a dimensionless proportional constant; \( f_h \) is the characteristic force needed to displace and rearrange the positions of the \( m_h \) submodules contained in a \( M_h \) (during this process some sacrificial bonds are broken). Equation (4) is in agreement with the experimental observation [3] that, between adjacent rapture events, a capture silk responds to external stretching in a linear way. Denote \( \Delta E_h \) as the energy cost of breaking all the sacrificial bonds between a level-\( h \) module’s \( m_h \) subunits. From Eq. (4) we
know that $f_{h+1}/f_h = m_h \Delta E_{h+1}/\Delta E_h$. Consider a level $(h + 2)$ module $M_{h+2}^\alpha$: it is in $M_{h+1}^\alpha$ which in turn is in $M_h^\alpha$. $M_{h+2}^\alpha$ feels an internal energy $\epsilon$ due to its interaction with other subunits in $M_{h+1}^\alpha$, and it feels an external energy $\epsilon'$ due to its interaction with other subunits in $M_h^\alpha$ but not in $M_{h+1}^\alpha$. Based on Fig. 1, we know that $\Delta E_{h+1} = m_h \epsilon/2$ and $\Delta E_h = m_h m_{h+1} \epsilon'/2$. The hierarchical organization of the polymer requires that $\epsilon > \epsilon'$, so as to ensure that structural modules of shorter length scales are formed earlier. Based on these considerations, we arrive at the following self-similar scaling form:

$$f_{h+1} = (\epsilon/\epsilon') f_h = \beta f_h \quad (\beta = \epsilon/\epsilon' > 1). \quad (5)$$

The parameter $\beta$ characterizes the degree of coherence in the modular organization of the polymer: a large $\beta$ value means that a submodule has much stronger internal interactions compared with its external interactions.

From Eqs. (3) and (4) we find that when $f_{h-1} < f \leq f_h$

$$\frac{dx(f)}{df} = \sum_{h' \neq h} \frac{\alpha L_0}{f_{h'}} = \frac{\alpha \beta L_0}{\beta - 1} f^{-1}. \quad (6)$$

Equation (6) therefore recovers the experimental exponential force-extension relationship of Eq. (1) with

$$\ell = \frac{\alpha \beta}{\beta - 1} L_0. \quad (7)$$

The length constant $\ell$ is proportional to the relaxed contour length $L_0$ of the whole polymer, consistent with Ref. [3].

Figure 2 demonstrates the numerically calculated force-extension curve based on Eqs. (3)–(5). As a comparison, the experimental data [3] on intact spider capture silk is also shown. As $\beta \approx 2$ and the experimental exponential force range is roughly from $6 \times 10^{-5} N$ to $10^{-3} N$, it appears that 4–5 levels of hierarchy were probed.

The exponential relationship shown in the figure is insensitive to our particular assumption in Eq. (4), as long as the elastic response at each hierarchy level is nonlinear and bounded. As an example, the solid curves in Fig. 3 show the resulting force-extension relationship when Eq. (4) is replaced by

$$\Delta x_h(f) = \alpha L_h [1 - \exp(-f/f_h)]. \quad (8)$$

The same exponential behavior as in Fig. 2 is obtained. However, the hierarchical scaling form Eq. (5) is needed for the exponential force-extension correlations. For example, when Eq. (5) is replaced by a power law, $f_h \propto f_0 h^\gamma$, the response is not exponential (the dotted line in Fig. 3). We also noticed that, when in Eq. (5) the parameter $\beta$ is not a constant but fluctuates over some finite range of $\beta > 1$, the resulting force-extension curve is still exponential (Fig. 3, dashed lines).

In summary, we have developed a hierarchical chain model to understand the strength and elasticity of spider silks. Remarkably, this simple model was able to reproduce the peculiar exponential force-extension response of spider capture silk reported by Becker et al. [3]. The model can also be used as a framework to understand the elasticity of other spider silks and other biopolymers with hierarchically organized structures.

Becker et al. [3] have proposed an alternate and interesting idea to model the spider silk as a branched network model.
of interconnected springs. In their model, the system responds to external stretching by first unfolding the single spring at the root level, then the $m$ springs at the first branching level, then the $m^2$ springs at the second branching level, and so on. The hierarchical chain model developed here is different from the model of Becker et al. First, the molecule in the hierarchical chain model consists of a tandem sequence of structural modules of different length scales. Therefore, no assumption of branching structure is made in our model. Second, the response of the chain to external perturbations is in a hierarchical manner. If the external force is small, only those structural units of length scale comparable to the whole polymer length will be displaced and rearranged; structural units at short and moderate length scales will remain intact. As the external perturbation is elevated, additional structural units at shorter length scales are also deformed. Through such a hierarchical organization, a single polymer chain can respond to a great variety of external conditions; at the same time, it is able to keep its degree of structural integrity as high as possible. This hierarchical modular structure also indicates a broad spectrum of relaxation times. The modules at the shorter length scales will have much shorter relaxation times and will be refolded first when the external force decreases. This gap in relaxation times ensures that, after extension, the spider capture silk will return to its relaxed state gradually and slowly. This is a desirable feature for spider capture silk, because a too rapid contract following the insect’s impact would propel the victim away from the web.

The simple hierarchical chain model, while appealing, needs further experimental validation. This model seems to be supported by recent genetic sequencing efforts. By analyzing the cDNA sequence of the major protein of spider capture silk, the flagelliform protein, it was revealed that the amino-acid sequence of flagelliform has a hierarchy of modularity [19–21]. At the basic level, the flagelliform sequence is consisted of three repetitive modules (motifs): (i) the GPGGX motif (Gly-Pro-Gly-Gly-X, $X \epsilon \{\text{Ala, Ser, Tyr, Val}\}$); (ii) the GGX (Gly-Gly-X, $X \epsilon \{\text{Ala, Ser, The}\}$); (iii) the highly conserved spacer motif of length 28 amino acids. At the next level, an ensemble motif is formed, which is a tandem array of 43–63 GPGGX followed by 6–12 GGX, the spacer and another GGX [19]. At the even higher level, the ensemble motif then repeats itself about 14 times to form the flagelliform monomer. The variable residues $X$ are not randomly distributed along the protein sequence [19], which may encode important structural information. The structures of spider capture silks (and other spider silks) therefore have the potential to be hierarchically organized.

For spider capture silk, one important experiment will be to check the validity of Eq. (5) by single-molecule force spectroscopy. The characteristic forces $f_n$ may correspond to the forces at the saw-tooth rapture events observed by Hansma and coworkers [3]. Although the experimental curves of Ref. [3] is in agreement with Eq. (5), more systematic investigations are necessary to draw a solid conclusion.

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