A thermodynamic analysis of the spider silk and the importance of complexity

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Abstract

The spider silk is one of the most interesting bio-materials investigated in the last years. One of the main reasons that brought scientists to study this organized system is its high level of resistance if compared to other artificial materials characterized by higher density. Subsequently, researchers discovered that the spider silk is a complex system formed by different kinds of proteins, organized (or disorganized) to guarantee the required resistance, which is function of the final application and of the environmental conditions. Some spider species are able to make different silks, up to twelve, having a composition that seems to be function of the final use (i.e. dragline web, capture web, etc). The aim of this paper is to analyze the properties of the spider silk by means of a thermodynamic approach, taking advantage of the well-known theories applied to polymers, and to try to underline and develop some intriguing considerations. Moreover, this study can be taken as an example to introduce and discuss the importance of the concept of optionality and of the anti-fragile systems proposed by N. N. Thaleb in his book “Antifragile: Things that gain from disorder”.

1 General Introduction

The present work can be divided in three sections. In the first one, a general description of the silk using the olog approach[1] is proposed. This part is useful to schematize the possible behaviour of the spider silk. In the second section, the
hierarchical nature of the spider silk is investigated through a thermodynamic approach. The right side of Figure 2.1 shows two examples of the spider web, while in the left side of the picture a scheme of the hierarchical spider silk structure is depicted. It was the starting point to build up the description proposed. Finally,

![Figure 1: On the left, a spider web; on the right, a schematic picture of the spider silk structure.](image)

in the third section, it has been discussed how the interpretation proposed can be taken as an example to explain the importance of the antifragile theory of N. N. Thaleb[2], where the antifragility should not be interpreted only as a toughness anymore. From another point of view, the interpretation proposed suggests that the nature follows the ideas of complexity and optionality: maybe the most important keys to survive. The olog approach was considered necessary to create an initial and general scheme of the structure of the spider silk (see Figure 2), putting in evidence important aspects necessary to build up the proposed interpretation. In order to approach the problem from a thermodynamic point of view, the starting point taken into the account was the equation of free energy proposed by Helmholtz (2.1):

$$dA = -TdS + \mu dN + \sigma d\epsilon$$  \hspace{1cm} (1)

The equation (2.1) collects all the terms that describe “where” the energy is stored in a system. The free energy (F) represents the work that the system is able to do on the environment or, from another point of view, the energy that the system can provide when it is stressed by an external force. In order to use the equation of the free energy, it was necessary to identify all possible actors that play a role in the “energy storage”. Referring to the general scheme of the internal structure of the spider silk (see Figure 1) and starting from the internal structure deeply studied in literature at the level of protein composition [4,5], different responses can occur at the microscopic level when a spider web is stressed. Upon the occurrence of an external stress, the following phenomena were considered at the microscopic level:
the crystalline part of the silk, formed by $\beta$-sheets based proteins, becomes oriented on the force direction, thus reaching an internal order (i.e. the rectangles represented in Figures 1 and 3).

- the amorphous phase, that links the $\beta$-sheets structures, is stretched and the hydrogen bonds (H-H) between these glycine chains are broken. At the same time, the distance between the $\beta$-sheets increases and the system starts to work as a spring.

- the same behaviour of the $\beta$-sheets occurs at the amorphous bonds level, i.e. the long chains of glycine are stretched.

After the third step, and before to reach the rupture, the system may offer a final resistance (proportional to the Young’s modulus $E_{\text{silk}}$ of the entire system). Anyway, in this study this behaviour was evaluated negligible and therefore was not considered. After these considerations, it is possible to re-write the equation (2.1) as follows:

$$A = -T(S_\vartheta + S_M + S_m) + \mu \Theta + \sigma \epsilon$$

(2)

The last term on the right side was neglected, and the three entropic terms were differently approached. The first entropic term, $S_{\text{beta}}$, refers to the $\beta$-sheets orientation and was considered as a first response of the material. Having the possibility to re-organize its internal structure, the spider silks re-arranges itself in order to exhibit the maximum level of resistance. It passes from a disordered phase to an ordered one. From a theoretical point of view, part of the internal energy stored is thus employed to change its configuration or, from another point of view, it is initially stored into the disordered configuration (i.e. the spiders exploit the disorder). Looking for a representation of this behaviour, the literature provided an exhaustive scheme of the spider silk response (see Figure 3)\cite{6,7}. In particular, the phenomenon of $\beta$-sheets orientation is well depicted passing from panels g to h, before and after the stretching.
2 Thermodynamic Formulation

The entropic term due to the initial disorder can be written using the Boltzmann’s relation (3.1):

\[ S_\vartheta = -k_B \ln W \]  \hspace{1cm} (3)

where \( k_B \) is the Boltzmann’s constant and \( W \) is the configuration assumed by the system. The possible mobility of the \( \beta \)-sheets in a plane was considered to describe the configuration of the system. If a \( \beta \)-sheet is not oriented in the stress direction, it rotates up to reach the longitudinal direction. In other words, the energy stored as disposition with respect to the longitudinal direction is utilized at this level. In light of this aspect, the configuration entropy was used considering the possibility to have many small systems able to rotate and having initial directions in the range \([-\pi/2, \pi/2]\); where 0 degrees is the condition when the \( \beta \)-sheets are aligned. Therefore, a \( \beta \)-sheet can assume two positions per rotation having the same energy quantity. Re-writing the equation (3.1), it is possible to assess that:

\[ W(\vartheta) = \sum_i p_i \ln p_i = \sum_i n_i e^{\frac{E_i}{k_B T}} \ln \left( n_i e^{\frac{E_i}{k_B T}} \right) \]  \hspace{1cm} (4)

where \( n_i \) is the number of the states and \( E_i \) is the energy stored. Taking into the account that the energy is a force per displacement, it is possible to consider a total rotation of the \( \beta \)-sheets when an external stress is applied. In particular:

\[ E_i = F_i \vartheta d = A l_\text{R} F_{\text{ext}} \cos(\pi/2 - \vartheta) \vartheta d \]  \hspace{1cm} (5)
where \( Al_{\%} \) is the percentage of the entire volume composed by Alanine, which is the main component of \( \beta \)-sheet structures, \( F_{ext} \) is the external force exerted and \( d \) is the entire length of the piece of web analyzed. By substituting the equation (3.3) in the equation (3.2), it is possible to obtain the equations (3.4):

\[
W(\vartheta) = \sum_i p_i \ln p_i = \sum_i n_i \underbrace{\frac{\frac{Al_{\%} F_{ext} \cos(\pi/2 - \vartheta)}{k_B T}}{\ln(n_i) \frac{\frac{Al_{\%} F_{ext} \cos(\pi/2 - \vartheta)}{k_B T}}{\ln(n_i) \frac{Al_{\%} F_{ext} \cos(\pi/2 - \vartheta)}{k_B T}}}}_{(6)}
\]

or (3.5),

\[
S_\vartheta = -k_B \ln W(\vartheta) \tag{7}
\]

The other two entropic terms were obtained starting from a thermodynamic model [8−11] commonly used to describe the behaviour of polymers. The idea was to employ the theory separately, describing the silk at two levels and building up two different entropic terms. Indeed, observing the model proposed for the spider silk, it can be intuitively noticed that before the breakage of all the H-H bonds, and immediately after the alignment of the \( \beta \)-sheets, the silk starts to be stretched and its internal rigid components are subjected to a sort of deformation that augments the distance between them. A general scheme used to describe this theoretical behaviour is depicted in Fig. 3.1. At this level no breakage of bonds occurs, and

![Figure 4: Macrostructure where the \( \beta \)-sheets are linked one to each other (A). The structure, simplified with nodes and bonds, undergoes a relaxation when an external stress is applied (B)](image)

the entropy varies because of the changes in the organization of the structure. The entropic term describes the passage from an higher level of disorder to a lower one, with the occurrence of a transformation. The second and third entropic terms were built up starting from the same theory explained above but applied to a lower scale, where the H-H bonds in the amorphous phase are broken and another step of relaxation occurs. Referring to the Fig. 3.1, it is possible to put in evidence different aspects. The scheme of the structure (i.e. nodes and bonds) are composed by bonds with the same length, \( b \), that link not contiguous species. In particular, the end-to-end distance is:

\[
R_E = \sum_{i=1}^{N} \bar{r}_i \tag{8}
\]
\[ \langle R_E^2 \rangle = Nb^2 \] (9)

This result follows from the ones obtained by Khun on the rubber \[ ^8 \].

Passing to a lower level, the third entropic term was analyzed with a similar approach, the freely joined chains theory (FJC)\[ ^{12} \], which was considered much more significant to describe the system. Carrying out the calculus, it is possible to extrapolate two potentials related to the “macro” and “micro” applications of the theory.

\[ TS_M = k_B T \ln p(M) = k_B T H(M) = \frac{3}{2} k_B T b \sqrt{N A l \%} \] (10)

\[ TS_M = k_B T \ln p(m) = k_B T h(m) = \frac{3}{2} k_B T b^2 \sqrt{N} \] (11)

In the first relation, an important role is played by the \( A l \% \) term, which is the percentage of the volume able to perform this macro-behaviour. Indeed, the entropic term \( SM \) was built with the aim to describe the macroscopic behaviour performed by the \( \beta \)-sheets components. Once all the entropic terms reported in equation (2.2) have been thoroughly discussed, the attention can be now focused on the term \( \mu \Phi \), which describes the energy stored in the H-H bonds between the proteins. The number of these bonds should not be fixed. Indeed, as the silk reology is strictly related to the RH level of the environment and as by nature the silk has an hydrophobic behaviour, it is possible that exposing a smaller surface to a higher humidity level the contraction of the structure could bring to the formation of a higher number of H-H bonds. Referring to the literature and on the experiments performed\[ ^{13,14} \], the resistance of the spider silk is strictly dependent on the relative humidity of the air. Intuitively, in conditions of high relative humidity (RH) the intrinsic hydrophobic nature of the silk leads to a contraction of the web and thus to a higher storage of energy. More specifically, in presence of water, even if from one side the silk is able to increase, at time 0, the quantity of energy stored, on the other hand there is a higher possibility for the proteins to restore H-H bonds with water molecules. This theory is supported by the fact that when the humidity is higher than a certain limit, the Young’s module decreases and the resilience response of the silk increases. Referring to this interpretation, the energy stored and in particular the number of bonds are strictly related to the RH level:

\[ \mu \propto RH \text{ or } \mu(RH) \] (12)

It is impossible to know exactly the location and the number of the bonds present in each structure. For this reason, the approach chosen is also for this case probabilistic. It is possible to define the number of bonds \( \mu \) as follows, in function of the RH value:

\[ \mu(RH) = \frac{1}{\sqrt{2\pi \sigma^2(RH)}} e^{-\frac{\mu^2}{2\sigma^2(RH)}} \] (13)

The number of bonds at different RH conditions should be determined through experimental tests. The choice to employ this kind of distribution came out from
the experimental evidences reported by Vehoff and co-workers[5]. Once to have explicated all the terms, the equation (2.2) can be re-written as follows:

\[ A = -k_B T \ln \left\{ \sum_i n_i e^{-\frac{A \log F_{ext}(\pi/2-\vartheta_i) \vartheta_i d}{kB}} \ln \left( n_i e^{-\frac{A \log F_{ext}(\pi/2-\vartheta_i) \vartheta_i d}{kB}} \right) \right\} + \frac{3}{2} k_B T b \sqrt{AlgN} + 3 \frac{k_B T}{b^2} \sqrt{N} + \Theta \left( \frac{1}{\sqrt{2\pi\sigma^2(RH)}} e^{-\frac{\mu^2}{2\sigma^2(RH)}} \right) \]  

(14)

From this equation, it is finally possible to extrapolate the value of the force:

\[ F = \frac{dA}{dx} \]  

(15)

Experimental tests and comparison with other results taken from the literature will be conducted in order to calculate the value of equation 3.11.

3 Conclusion

This study deals with the simple description of a natural material such as the spider silk. The main goal of the present work is to start from the natural complexity of the spider silk to put in evidence a general formulation of its mechanical behaviour, useful to design new materials with the same operating principle[15]. From another point of view, this study wants to pose some considerations on how the complexity in collaborative systems is one of the prerogative to survive. This aspect is at the base of the anti-fragile theory and of its peculiar optionality characteristic. The optionality of the spider silk could be considered as an interesting example and supports the theory of N. N. Thaleb. One of the most fascinating aspects of the present study on the spider silk lies within its particular nature. Indeed, it seems that spiders had well understood how to exploit natural principles such as entropy and strength of collaborating systems[16]. When a spider makes a web, it has not the possibility to forecast all the different conditions in which the web will operate. The lack of this possibility makes the spider to develop a strategy for building up a versatile material, able to store energy at different scales, that interact each other, and to resist at different conditions. A social example can be extrapolated from this consideration: a social multicultural community such as the one in a small company in the R&D department able to face unpredictable events. For this reason, the spider silk can be considered as an anti-fragile material and a good example of social anti-fragile communities or behaviours. It is not so tough to resist to a specific external stress, but it is tough enough to learn from the environment, rearranging itself in function of the humidity and becoming able to resist at different external stresses. This last capacity comes from the possibility of the silk to adapt its structure: from a certain point of view, the silk learns and reorganizes its components once the environmental conditions taught to it in which conditions it is going to operate. The social communities should operate
following an equivalent approach. Even if we are comparing a thinking being with an inanimate material, one more time the nature is teaching us how the forecast is much less important if we learn to be prepared to face all possible conditions. On the other hand, this is a prerogative of the wise people.

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