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Supercontraction of spider silks as a humidity-driven phase transition

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Abstract. Spider silks have been intensively studied among natural materials for their extreme mechanical properties such as very high strength, ultimate strain, and toughness. Another striking phenomenon characterizing spider silk, known as supercontraction, is a substantial contraction, up to a half of the initial length, occurring when an unconstrained silk thread is exposed to a wet environment. We propose a multiscale model that deduces the hygro-dependent macroscopic behaviour of the spider silks starting from the nano and micro-structure properties of the material. In particular, we describe the influence of humidity at the macromolecular scale by considering the moisture effects disrupting hydrogen-bonds and enabling the decrease of the natural (zero force) end-to-end chains length due to entropic effects. The main novelty of our theoretical approach is a description in the field of solid-solid phase transitions, with the system undergoing a transition driven by humidity from an unfolded, hard dry to a folded, soft wet configuration. Based on a statistical mechanical approach, we are able to describe the temperature dependence of the supercontraction effects and its cooperative properties quantitatively predicting the observed experimental behaviour.

Introduction

Spider silk is the most studied natural material for his extreme mechanical properties, in particular the strength and the toughness overcoming also many high-performance man-made materials. Moreover, in the framework of biomimetics, spider silks are considered as the basis of a new class of high-performance fibers [1,2]. However, the behavior of the spider silk is very sensitive to external environmental conditions. More in detail, a Relative Humidity (RH) above a certain critical threshold, may give rise to an abrupt variation of material properties and a significant reduction in the fiber length, known as *supercontraction* and discovered by Work in 1977 [3]. This contraction is due the influence of the hydration water molecules at the macromolecular scale that disrupt Hydrogen-bonds, thus enabling the decrease of the natural end-to-end chain length due to entropic effects [4–6].

The observation of a stress reaching values of tens of MPa in experiments at fixed length is very interesting also in the perspective of humidity driven actuators and sensors [7–9]. The silk properties change is localized in a small range of RH (few points percent) and this is related to the transition from a stiff state to a rubbery state undergoing entropic coiling [10,11] with important analogies with the glass transition typically induced by temperature in polymers. As in the case of other solids undergoing phase transitions, such as shape memory nanowires, where one observes a switch from the austenitic to the martensitic phase or in protein materials undergoing unfolding from a stiff to a softer configurations [12], the evolution of the system is regulated by the transition strategy among different phase configurations as the external fields are modified [13]. In this perspective, starting from the pioneering work of Müller and Villaggio [13], extended to include the fundamental thermal effects based on a Statistical Mechanics approach, lattices of elements with non-convex energies and intrinsic discrete length-scale have been used to mimic many biological systems, such as the misfolding and refolding in proteins [14,15], the DNA denaturation and replication [16,17], the attachment and detachment of tau proteins in the neuronal axon, usually associated to neurodegenerative diseases [18,19], and in the study of focal adhesions [20,21].

Here we extend this approach to study the experimentally observed transition in spider silks, describing the mechanical properties of the soft and hard phases of the silks at the molecular length scale. Specifically, we extend the model proposed in [12,22] to account for the effect of the relative humidity inducing the supercontraction, here modelled as a phase transition. This effect is due to an internal change of the natural configuration of the hard phase, and it can be described, following the classical Landau approach to phase transition, by introducing a RH-dependent transition energy as show in FIG. 1. The behavior of the silks is also highly affected by temperature effects (see Refs. [11,23]). Thus, in this paper we introduce thermal fields in the framework of equilibrium Statistical Mechanics, that has been proved to be an effective tool for describing thermal effects in multistable systems [24–27]. We deduce an analytic approach quantitatively describing the humidity and temperature effects in the supercontraction phenomenon. Such analytic results are in our opinion fundamental also in the spirit of biomimetics.

Model

Following the theoretical model developed in [22], we analyse a discrete chain with N two-state elements (see Fig. 1), each described by a bistable potential energy having two wells characterized by different elastic constants k (unfolded state) and αk (folded state), where $0 < \alpha < 1$. Moreover, the two states have their equilibrium lengths equal to l and χl with $0 < \chi < 1$.
Following an Ising type approach the overall energy assumes the compact form

$$\Phi = \sum_{i=1}^{N} \left\{ Q(S_i) + \frac{K(S_i)}{2} \left[\left(\lambda_i - \lambda_0(S_i) \right) l \right]^2 \right\} - J \sum_{i=1}^{N-1} S_i S_{i+1} \tag{1}$$

where the internal variables $S_i = \pm 1$ identify the phase (energy wells) of each spring. Here, λ_i is the stretch of the i-th spring and $\lambda_0(-1) = 1, \lambda_0(+1) = \chi,$ are the natural configurations. The parameter $J > 0$ penalizes energy interfaces. It is useful to take into account the nondimensional energy φ

$$\varphi = \frac{\Phi}{J} = \sum_{i=1}^{N} \left\{ \tilde{Q}(S_i) + \frac{\tilde{K}(S_i)}{2} \left[\left(\lambda_i - \lambda_0(S_i) \right) \right]^2 \right\} - \sum_{i=1}^{N-1} S_i S_{i+1} \tag{2}$$

where $\tilde{Q}(S_i) = Q(S_i)/J$ and $\tilde{K}(S_i) = K(S_i)l^2/J$, $\tilde{k} = kl^2/J$ and $\tilde{K}(-1) = \tilde{k}$ and $\tilde{K}(+1) = \alpha\tilde{k}$. The main novelty of the proposed approach is the microstructure-inspired assumption of Q depending on the relative humidity as

$$\tilde{Q}(RH) = \frac{1}{\mathrm{J\,h(RH)}} \tag{3}$$

where we included the dependence on the relative humidity in the quantity h(RH); this dependence will be specialized in the following to adapt the results of the model to the experimental results.

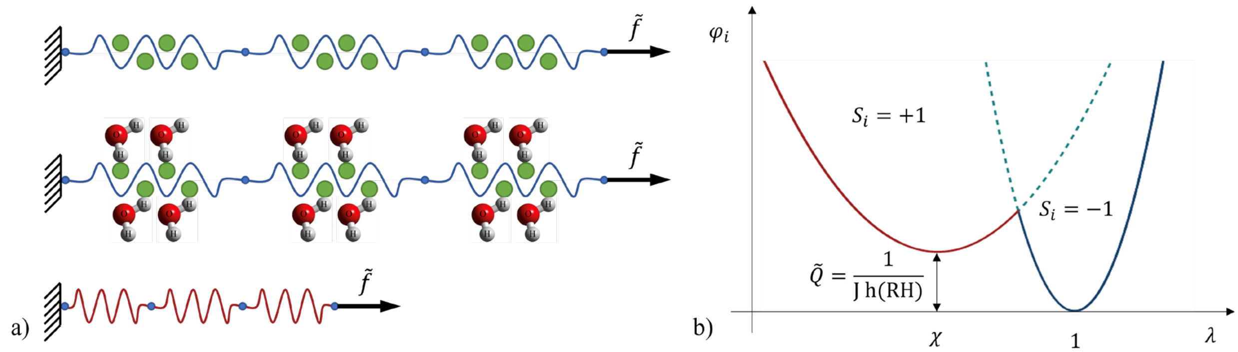

Figure 1: a) Scheme of a chain with three elements. Top: the chain is in the unfolded configuration ($\boldsymbol{S_i = -1}$) with the green circles representing the H-bonds naturally present in the silk; middle: the hydration water molecules link and disrupt the H-bonds; bottom: final folded (supercontracted) configuration ($\boldsymbol{S_i = +1}$). b) Scheme of the energy wells of a single element.

To introduce temperature effects in the framework of the equilibrium Statistical Mechanics, we consider the canonical partition function also including the fixed force acting on the last element of the chain (the so-called Gibbs ensemble):

$$Z_G(\tilde{f}) = l^N \sum_{\{S_i\}} \int_{\mathbb{R}^N} e^{-\tilde{\beta}(\varphi - \tilde{f}\sum_{i=1}^N \lambda_i)} d\lambda_1 \dots \lambda_{N.} \tag{4}$$

Here, the non-dimensional force is defined as $\tilde{f} = f\, l/J$ and

$$\tilde{\beta} = \beta\, J = \frac{J}{k_B T}. \tag{5}$$

The sums over $\{S_i\}$ must be considered extended to the values $+1$ and -1 for each spin variable ($i = 1, \dots, N$).

By definition, the Gibbs free energy is

$$\mathcal{G} = -\frac{1}{\tilde{\beta}} \ln Z_G(\tilde{f}). \tag{6}$$

Thus, in order to evaluate the unrestrained supercontraction phenomenon, we compute the expectation value of the average deformation of the chain for $\tilde{f} = 0$, as

$$N\bar{\lambda} = \langle \sum_{i=1}^N \lambda_i \rangle = -\frac{d\mathcal{G}}{d\tilde{f}}\Big|_{\tilde{f}=0}. \tag{7}$$

A direct evaluation of this quantity, (see [22] for detailed calculations) gives

$$\bar{\lambda} = \frac{1}{2}\left[\left(1 + \frac{c_- - c_+}{\sqrt{\Delta}}\right) + \chi\left(1 - \frac{c_- - c_+}{\sqrt{\Delta}}\right)\right], \tag{8}$$

where $c_- = c(-1)$ and $c_+ = c(+1)$ with

$$c(s_i) = \sqrt{\frac{2\pi}{\tilde{\beta}\tilde{k}(s_i)}}\, e^{-\tilde{\beta}\,\tilde{Q}(s_i)}, \Delta = (c_+ - c_-)^2 + 4\,c_+\,c_-\,e^{-4\tilde{\beta}}. \tag{9}$$

Experimental comparison

The effectiveness of the model in reproducing the experimental behavior of the phase transition occurring in spider silks, i.e. the supercontraction, is verified by quantitatively comparing the values of the silk thread stretch as a function of the external humidity at different temperatures. In Fig. 2 we represent by markers the experiments performed on *Argiope trifasciata* spider silk fibers [23], that exhibits a relevant contraction, reaching less than half of its length in dry conditions. The curves obtained by Eq. (7) are accurate in predicting the main physical phenomena observed during the phase transition at variable RH and temperature. We assumed $\mathrm{h}(RH) = \gamma\sqrt{\frac{RH}{100}}$ obtaining $\tilde{Q}(RH) = \frac{1}{\delta\sqrt{RH/100}}$, with $\delta = J\,\gamma$. We use the experimental data at the reference temperature ($T_r = 20°C$) to fit the parameters of the model δ and $\tilde{\beta}_r$, whereas from Eq. (4) we can compute the values $\tilde{\beta} = \tilde{\beta}_r\, T_r/T$ for other temperatures. We remark that for the main parameters of the model we employed the values measured during the experiments in [23], i.e. $\chi = 0.46$ corresponding to the stretch of the fiber at the saturation of the RH and $\alpha = 0.005$ corresponding to the ratio of the stiffness of the silk in the full supercontracted (soft, folded) state and pristine (hard, unfolded) state.

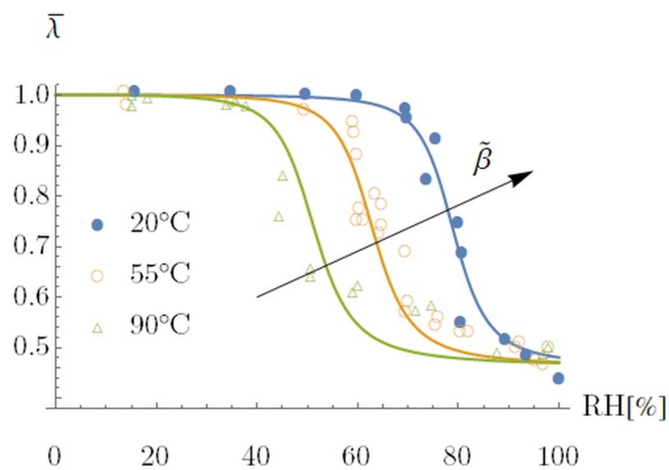

Figure 2: Comparison of the model with experiments [23]. Values of the parameters : $\boldsymbol{\alpha = 0.005}$; $\boldsymbol{\chi = 0.46, \tilde{\beta}_r = 1.4, \delta = 0.59}$.

Thus, based on minimal assumptions on the microscopic structure, we can describe a solid-solid phase transition, with the system undergoing an unfolded-folded (hard→soft) transition driven by the humidity. Based on an equilibrium statistical mechanical approach, we can deduce analytically the temperature dependence of the supercontraction effect and its cooperative properties, quantitatively predicting the observed experimental behavior.

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