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https://royalsocietypublishing.org/doi/full/10.1098/rspa.2016.0060

PROCEEDINGS A

rspa.royalsocietypublishing.org

Research

Article submitted to journal

Subject Areas:
Review: rubber elasticity

Keywords:
Rubber elasticity, multiscale models, entropic elasticity

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Multiscale modelling of Rubber-Like Materials and Soft Tissues: *an appraisal*

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We survey, in a partial way, multiscale approaches for the modelling of rubber-like and soft tissues and compare them with classical macroscopic phenomenological models. Our aim is to show how it is possible to obtain practical mathematical models for the mechanical behaviour of these materials incorporating mesoscopic (network scale) information. Multiscale approaches are crucial for the theoretical comprehension and prediction of the complex mechanical response of these materials. Moreover, such models are fundamental in the perspective of the design, through manipulation at the micro and nano scales, of new polymeric and bio-inspired materials with exceptional macroscopic properties.

Dedicated to the memory of professor Michael Carroll (1936-2016).

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1. Introduction

The mechanical properties of rubber-like materials have been offering an outstanding challenge to the solid mechanics community for a long time. The mechanical behaviour of such materials is quite difficult to predict because rubber self-organizes into mesoscopic physical structures that play a prominent role in determining their complex, history dependent, and strongly nonlinear response.

In the first chapter of the celebrated book by Treloar [1] on the physics of rubber elasticity, we find an interesting implicit definition of a rubber-like material based on three simple requirements ([1] page 11):

1) The presence of long-chain molecules, with freely rotating links ;
2) Weak secondary forces between the molecules;
3) An interlocking of the molecules at a few places along their length to form a three-dimensional network.

The Treloar *cartoon* of the molecular structure of rubber represents a guideline to develop basic models of amorphous rubber-like materials and soft tissues. Indeed, Requirements 1) and 2) are the basic assumptions of the so-called entropic theory of elasticity, and Requirement 3) is equivalent to postulate the existence of a coherent solid network in which the molecules are linked together and do not move independently. We point out that these requirements are shared with several biological and bio-inspired materials. In the last decades theoretical developments in these fields have been strongly linked to the search of phenomenological macroscopic models, of multiscale material models, and to the techniques required to design new high-performance polymeric and bio-inspired materials [2–4].

Around 1930, *molecular* models were introduced to describe the mechanical behaviour of natural rubber, in order to deduce quantitative thermodynamical models based on the three requirements recalled above [5,6]. Around the same time the German engineer Heinrich Hencky was conducting some experiments on rubber belts furnished by the Goodyear Tire and Rubber Company to the Massachusetts Institute of Technology. He then proposed a phenomenological generalization of the classical linear theory of elasticity to cope with finite deformations *via* the introduction of the *Hencky strain measure* [7].

All these models have been unsuccessful for a general and proper treatment of the large deformation regime. Only with the celebrated Mooney paper in 1940 [8] and the following systematic investigations by Rivlin [9] do we encounter more actual phenomenological treatments of the mechanics of finite deformations of rubberlike materials. Truesdell and Noll's Handbuch ([10] page 118) recalls this period as follows.

> *We recall that at the beginning of the XIX century the knowledge of the classical theory of finite elasticity was based on "applied" papers often proposing "new" theories all either pointlessly special or wrong. Mainly only in Italy, due to the teaching and writing of Antonio Signorini, the correct approach to nonlinear elasticity was pursued, though little advanced.*

Later on, the advancements of the mechanical theory of rubber-like materials proceeded by following a twin-track approach, based on one hand, on the development of non Gaussian statistical or molecular theories and on the other hand, on the development of phenomenological constitutive models in continuum mechanics. Often the statistical method gave a deeper and more consistent insight into the molecular structure of rubber-like materials, whereas the continuum mechanics models were more successful in the representation of the macroscopic experimental behaviour. The dichotomy statistical *vs* continuum mechanics is exemplified by the necessity

of the so called C_2 *energy term*, pointing to the necessity of a synergic approach between the phenomenological and the statistical methods.

To summarize the related long lasting debate, we recall that the classical Gaussian approach of statistical mechanics for rubber allows us to deduce analytically the well known simple neo-Hookean model. This very special model, which was fundamental for its analytic simplicity in the understanding of many theoretical aspects of nonlinear elasticity theory, is satisfactory in the description of the macroscopic mechanical behaviour of rubber elasticity only under specific assumptions. Indeed, it was shown [11] that the neo-Hookean model is able to describe the experimental behaviour of rubber only for small and moderate shear deformations. On the contrary, the phenomenological Mooney-Rivlin constitutive theory, by complementing the neo-Hookean model with the so called C_2 term, delivers a simple solution to the above mentioned limits. As a result, while *Mooney theory does not provide a satisfactory and self-consistent basis for the representation of the properties of rubber in the most general state of strain* ([1] page 99), the confrontation of its predictions with the experimental data shows that this model is significantly more predictive than the neo-Hookean model.

This *scenario* opened a discussion on the reason for the *discordances* between the experimental behaviour and the statistical theory results (see [12] for an initial comment in this direction). Treloar [1] provides five possible reasons to understand the *molecular significance of the deviation from statistical theory* ([1] page 227)

1) non-Gaussian effects both for the chains and the network ;
2) internal energy effects;
3) chain entanglements;
4) irreversible effects;
5) non-random packing effects.

Today, many fundamental steps to solve these issues have been made and this crucial evolution has been at the root of a radical overhaul of the dichotomy recalled above. In particular, the application of nonlinear elasticity theory to the framework of biomechanics of soft tissues provided a new impetus for a synergetic approach between the statistical mechanics and the continuum mechanics theories. This synergy opened the path to a new generation of multiscale models [13–17] relating the macroscopic response to the material properties at lower scales. The complexity and the technological and scientific impact lead to a variety of new proposed multiscale approaches especially in the case of nanoscale elaborated materials (see *e.g.* [18] for a review related to nano composite polymers). In this fundamental evolution, we must not underestimate the crucial role of both experimental material mechanics and numerical analysis. The evolution in experimental expertise allows the comprehension of the behaviour at the network and single polymeric molecule scales (see *e.g.* [19], [17] and references therein). On the other hand numerical methods gave a strong impulse both for the analysis of the micro and nanoscale behaviour (e.g. Molecular Dynamics, Montecarlo and Brownian dynamics approaches [18]) and for the macroscopic strongly nonlinear differential evolutive problems (see *e.g* [23] and references therein).

The aim of this review is to provide an overview of this research activity. It is important to remark that we are not aiming at *any* completeness on the immense literature on the multi-scale modelling of rubber-like and soft materials (see for example [20–25]). Instead our discussion will be focused on the meso-macro scale passage, where the results have been shown to be efficient in the description of many phenomena, fundamental in technological applications, such as damage, residual stretches, healing, hysteresis. We are only considering some explicit examples showing the possibility of deriving three-dimensional macroscopic models starting from the material properties at lower scales. This possibility is fundamental not only to predict the mechanical behaviour of these materials, but also to design new rubberlike and bio-inspired materials based on the growing ability of manipulating them at the lowest scales. Fully multiscale approaches may

be imagined to be derived by a sequential multiscale passages, deducing the material properties at each scale by the properties of the previous lower scale (see again [18] for a review).

The plan of the paper is the following. The next section is devoted to recalling basic equations and some fundamental aspects of the theory of nonlinear elasticity related to the modelling of rubberlike materials (clearly this section is not an introduction to nonlinear elasticity and we assume that our readers are already familiar with this framework [10], [26]). In Section 3 we introduce the Gent model and other similar models and we explain how this simple model is related to the molecular character of the polymeric network. Section 4 is devoted to the *micro-macro* passage. Section 5 is a collection of some important results of the last few years. The last section is devoted to concluding remarks.

2. Basic Equations

Rubber-like materials are typically characterized by the ability of undergoing very large reversible deformation. As a consequence they are modeled (at least for a certain range of deformation, temperature and time scales) as hyperelastic materials. We now recall some basic results of the nonlinear theory of elasticity to fix the notation and give a rigorous and quantitative description of some of the previous comments.

Let us consider the deformation of a body Ω, $\Omega \ni \boldsymbol{X} \mapsto \boldsymbol{x} = \boldsymbol{x}(\boldsymbol{X})$ and let $\boldsymbol{F} = \mathrm{Grad}(\boldsymbol{x})$ be its gradient. Let then $\boldsymbol{B} = \boldsymbol{F}\boldsymbol{F}^T$ be the left Cauchy-Green deformation tensor and let

$$I_1 = \mathrm{tr}(\boldsymbol{B}), \quad I_2 = (I_1^2 - \mathrm{tr}(\boldsymbol{B}^2))/2, \quad I_3 = \det \boldsymbol{B}$$

be its principal invariants. If a material is hyperelastic and isotropic [11] we may introduce a strain-energy density function $W = W(I_1, I_2, I_3)$.

The usual moduli of the theory of linear elasticity, such as the tensile modulus or the bulk modulus, may be deduced in the limit of infinitesimal deformations. Because the modulus of bulk compression of rubber is quite high with respect to its tensile modulus, it is usual to treat rubber as incompressible. In this case only isochoric deformations are admissible, $I_3 = 1$, and $W = W(I_1, I_2)$ only.

In this setting the Cauchy stress tensor $\boldsymbol{T}$ is given by the representation formula

$$\boldsymbol{T} = -p\boldsymbol{I} + 2\frac{\partial W}{\partial I_1}\boldsymbol{B} - 2\frac{\partial W}{\partial I_2}\boldsymbol{B}^{-1}, \tag{2.1}$$

where p is the Lagrange multiplier associated with the constraint of incompressibility. Moreover, in the absence of body forces, the equilibrium equation is

$$\mathrm{div}\, \boldsymbol{T} = \boldsymbol{0}, \tag{2.2}$$

where div is the divergence operator with respect to $\boldsymbol{x}$.

The **basic problem** in this framework is the determination of the functional form of the energy density W. It is interesting, by analyzing the literature, to observe how scientists with different backgrounds face this problem from various angles and to show why a synergic contribution is crucial for a successful approach in this field. Typically, a mathematician is mainly interested in the understanding of the qualitative properties of the strain-energy functional to deduce the mathematical structure of the theory and the existence and regularity properties of the solutions. On the other hand, a material scientist could be interested only in having a mechanical model estimating and qualitatively describing the observed experimental phenomena. Finally, an engineer may be interested in simulations of mechanical devices and may be mainly focused on the possibility of quantitatively describing specific experimental data and of implementing numerically the model.

In this section we are not interested in analyzing the ability of a specific model to give a detailed description of the experimental data for a huge class of deformations. Instead we are interested in presenting the "building bricks" of the theories modelling the mechanical behaviour of rubberlike materials. A rational way to reach this goal is to analyze how different choices of the strain-energy

function W induce so called '*universal*' properties of their mechanical behaviour, to be compared with the experimental ones.

The most *representative* strain energy density function for the statistical theory of rubber-like materials is surely the neo-Hookean (single constant) model,

$$W = \frac{E}{6}(I_1 - 3), \tag{2.3}$$

where the small strain tensile modulus E can be related to molecular quantities (see *e.g.* [1]).

Observe that the neo-Hookean model belongs to a particular class of materials where the energy density depends on the first invariant only (*generalized neo-Hookean materials*), *i.e.* such that $W = W(I_1)$ only. On the other hand the Mooney-Rivlin material does not belong to this class, being described by the phenomenological constitutive equation

$$W = C_1(I_1 - 3) + C_2(I_2 - 3), \tag{2.4}$$

where C_1 and C_2 are two material constants whose mechanical meaning must be adjusted *a posteriori* to fit experimental data.

The strain energies (2.3) and (2.4) represent two particularly meaningful and simple prototypes of the various constitutive laws considered in the mechanical modelling of nonlinear incompressible elastic materials. Many other models have been proposed and a survey of these models can be found, for example, in Arruda and Boyce [14]. The variety, difference and number of the proposed models can be considered to give a measure of the uncertainty existing in the scientific literature about mechanical models for rubber-like materials.

(a) The C_2 term

The corresponding **first** question to address is the possibility of providing a rational approach to analyze the C_2 *vexata quaestio*. The mathematical problem is to test the *generalized neo-Hookean* hypothesis

$$W = W(I_1). \tag{2.5}$$

This is an important point because the molecular approach is usually associated with generalized neo-Hookean models. Rivlin and co-authors have proposed a detailed discussion about the C_2 term [27] (see also [28,29]), based on a comparison with experimental data. Here we present a theoretical systematic approach that identifies rationally the right experiments showing the *falsifiability* of the $\partial W/\partial I_2 = 0$ hypothesis. Specifically, Horgan and Saccomandi [30] and Wineman [31] have independently proposed to find out whether a strain-energy of the form $W = W(I_1)$ is a reasonable assumption by determining the existence of *universal relations*, *i.e.* equations that hold irrespective of the special form of W.

To illustrate explicitly this idea, let us consider the simple shear deformation

$$x = X + \kappa Y, \quad y = Y, \quad z = Z, \tag{2.6}$$

where κ is a constant measuring the *amount* of shear. This deformation is probably the simplest example of finite deformation we can imagine, and we recall, as noticed by Mooney in [8], that

> [...,] *if the sample is sheared by a shearing stress, or traction, Hooke's law is obeyed over a very wide range in deformation.*

Since as we now show, the proposed approach suggests that we find a discrepancy between simple shear data and a constitutive assumption of the form $W = W(I_1)$, then the root of this discrepancy can be considered *structural* because for simple shear, experimental data are easy to collect and compare with theoretical results.

In the case of (2.6) using (2.1) we obtain

$$T_{11} = -p + 2(1+\kappa^2)W_1 - 2W_2, \quad T_{12} = 2\kappa(W_1 + W_2), \quad T_{13} = T_{23} = 0,$$
$$T_{22} = -p + 2W_1 - 2(1+\kappa^2)W_2, \quad T_{33} = -p + 2W_1 - 2W_2,$$

where $W_i = \partial W(I_1, I_2)/\partial I_i, i = 1, 2$. By these equations we easily deduce the two trivial universal relations $T_{13} = T_{23} = 0$ and the celebrated Rivlin universal relation

$$T_{11} - T_{22} = \kappa T_{12}. \tag{2.7}$$

This last universal relation can be considered a measure of the nonlinearity of the material behaviour because in the linear theory of elasticity we have $T_{11} \equiv T_{22} = 0$.

Consider then a cubic specimen and assume that the faces normal to the $Z-$direction are traction free so that $T_{33} = 0$ and

$$p = 2W_1 - 2W_2.$$

We then deduce that

$$T_{11} = 2\kappa^2 W_1, \quad T_{12} = 2\kappa(W_1 + W_2), \quad T_{22} = -2\kappa^2 W_2, \quad T_{13} = T_{23} = T_{33} = 0.$$

Now we have three trivial universal relations $T_{13} = T_{23} = T_{33} = 0$, plus (2.7).

As a result, if we hypotize that $W = W(I_1)$ only, we obtain

$$T_{11} = 2\kappa^2 W_1, \quad T_{12} = 2\kappa W_1, \quad T_{22} = T_{13} = T_{23} = T_{33} = 0. \tag{2.8}$$

Hence we deduced the new trivial universal relation $T_{22} = 0$, peculiar to generalized neo-Hookean materials.

The experimental check of this new equation is quite simple. It is sufficient to drill a hole on the upper plate that we use to shear the material. Investigating wether the material stays flat ($T_{22} = 0$) or not ($T_{22} \neq 0$) in this hole (for example using digital image correlation) gives a quantitative measure of the falsifiability of the hypothesis $C_2 = 0$ [32].

We may then deduce that we need both invariants to derive a realistic constitutive equation. Observe that a similar argument may be used by considering the simple torsion experiment or the classical biaxial experiment. Of course, this simple example represents a prototype of the need for more general theories and for the contribution of modern continuum mechanics to extend the mechanical theories for rubberlike materials.

(b) Crucial points

The Mooney-Rivlin constitutive assumption (2.4) delivers a good model for an elastic material in simple shear, but it is not a satisfactory in other deformation classes. This statement is supported by the comparison of the prediction of the model with experimental data [1], but once again it is possible to give theoretical reasons that let us understand, in some sense *a priori*, the limits of such a model.

In this perspective, consider the following homogeneous deformation

$$x = \lambda^{-1/2}X + \kappa_1 Z, \quad y = \lambda^{-1/2}Y + \kappa_2 Z, \quad z = \lambda Z, \tag{2.9}$$

composed of a simple extension along the Z direction and two shears along the orthogonal axes. In the linear theory these three deformations are decoupled whereas they are coupled in nonlinear theory. In particular, with the Mooney-Rivlin model (2.4) the simple extension (described by the parameter λ) is coupled to the shear deformations (with amounts κ_1 and κ_2), but the two shear deformations are decoupled one from another. This represents a very special situation indicating some of the limits of the Mooney-Rivlin model.

A major advancement in nonlinear elasticity modelling of rubberlike materials, after the pioneer approaches recalled above, was made with by the introduction of the Ogden model (see [11], the reprint of the original paper in [33] and the recent [34]). As pointed out by Treloar ([1] page 235)

> *the utility of the Ogden formulation must be judged by its ability to represent the experimental data for rubber under all possible types of strain, preferably (though this is not a primary requirement) with the use of a relatively small number of terms.*

Indeed, the Ogden strain energy is one of the principal advances in the analysis of nonlinear elasticity: this model was the first form of the energy density that allowed the fitting of experimental data for a variety of deformation classes and a reasonable range of strains.

After the Ogden model, some important steps, in our opinion, represent further *breakthroughs* in the research field of nonlinear elasticity and constitutive modelling of rubber-like materials. These milestones are the Ball existence theorem in nonlinear elasticity [35], the Gent model [36], and the Ericksen extensions of nonlinear elasticity to non (rank-one) convex energies.

Ball's existence theorem [35] can be considered as a major advancement in the mathematical theory of nonlinear elasticity. Its assumptions can be also reframed in the framework of the so called Truesdell *Hauptproblem* [40], *i.e.* the problem of what requirements have to be imposed on the functional form of the strain-energy to ensure existence and well-posedness of the equations of nonlinear elasticity. In this respect we point out that this approach has been theoretically questioned by J.L. Ericksen in [39] as follows:

> *My view is that the domain of constitutive equations may include subdomains that are, in principle, inaccessible to the experimentalist... For solids, it is trickier to formulate physically appropriate stability criteria, and thus to classify similarly the different parts of the domain of constitutive functions... We do not evade the problem by discarding 'unreasonable' constitutive equations... There is a simple, classical example which serves to illustrate my views, as well as some of the subtleties which are to be expected: the equilibrium theory of the van der Waals fluid. Here, by commonly accepted stability calculations, we infer that part of the domain is not accessible to experiment, part is easily accessible, and part is accessible only if sufficient care is taken to minimize disturbances... I merely propose adoption of the mathematician's criterion: the weaker the hypothesis, the better the theorem. . . . Gradually, it has become clear that elasticity theory can predict effects that we do not commonly think of as being associated with the adjective 'elastic'. In such cases, we should, I think, let elasticity theory enter into free competition with other theories capable of describing the effect at hand . . .*

Based on these considerations, Ericksen extended Ball existence requirements, for example to non rank-one convex energy functions [38]. This kind of assumptions may also be deduced from a multiscale method, based on the Cauchy-Born hypothesis, for materials with a crystal microstructure [39]. This advance was fundamental to extend the mathematical framework of nonlinear elasticity to many material phenomena considered out of its range of applications. We refer for example to the pseudo and quasi-elastic behaviour [41,42], and damage and deformation localizations observed also in the case of rubber-like materials [43].

To be more explicit in the linear theory of elasticity, in order to ensure a mathematical and physical meaning, we require that the quadratic form energy density is *positive definite*. Ball's results bring *analogous* restrictions (such as polyconvexity) upon the strain energy in the nonlinear case. Here we do not focus on these important mathematical aspects of the constitutive theories of rubberlike materials, but we want to point out that they are often completely bypassed by the material science and engineering communities working in the field.

As we recalled above, in our opinion, another fundamental step in the modelling of rubberlike materials is represented by the simple idea of the Gent constitutive law, which described phenomenologically the results of the multiscale approach proposed by the Arruda and Boyce theory [37].

In that paper Arruda-Boyce [37] proposed a new multiscale theory based on the methodological procedure in the classical three-chains models of Flory and Rhener [44]. Their

paper lead to an important resurgence of interest in the non-Gaussian effects in the statistical mechanics derivation of the rubber-like models. The Arruda-Boyce model is based on:

1) the use of the inverse Langevin function[1] for the computation of the end-to-end distance for a single chain of the polymeric network ;
2) the eight chain network structure (see *e.g.* [13]) to perform the network average;
3) the *affine assumption* imposing the coincidence of the network chain stretches and macroscopic stretches.

The advantage of such a model is that it contains few constitutive parameters and that those parameters are directly connected to the microscopic properties of the material. However, we point out that the Arruda-Boyce model is a generalized neo-Hookean model, so that we may extend the previous criticisms to this model (see [47] for a detailed comparison of this model with experimental data). Moreover, due to the involvement of the inverse Langevin function, even the analysis of simple homogeneous deformations can be quite complicated. Despite these drawbacks it is important to point out that the Arruda-Boyce model has been the catalyst of a renewed interest in the entropic theory of elasticity and in the connections between the phenomenological and the molecular theories of elasticity. As a clear example of the following advancement in this field we may refer to the works by Göktepe and Miehe (see [23]). These authors, by extending the multi scale statistically based approach of Govindjee and Simo [45], and using a classical additive hypothesis for the energy density (see Flory and Erman [46]), deduced a multiscale constitutive law. Interestingly their theory takes care of non affinity effects and considers the anisotropic (Mullins type) damage effect due to the deformation driven network chains reorientation.

Another important point in the nonlinear theory of elasticity that we want to stress in this section is the determination of the constitutive parameters by fitting of the experimental data. We remark that this important step, often underestimated, may represent a crucial drawback of the models, and this problem is sheared by both the phenomenological and molecular approaches. Indeed, due to the amorphous character of rubber-like materials, molecular theories need the introduction of *ad hoc* phenomenological assumptions. Therefore some of the constitutive parameters in the framework of statistical mechanics cannot be obtained directly by *ab initio* considerations. As pointed out in [48] the major problem in fitting experiments is connected to the structure of the data we have to consider (i.e. a huge range of stretches involving mechanical quantities spread over significant differences of magnitude) and the necessity to deal with nonlinear methods. This situation introduces the possibility of non-uniqueness in the optimal set of parameters that may strongly vary in numerical fitting of very similar experimental data. This non-uniqueness can represent a limitation of the theory both in the perspective of a physical interpretation of these parameters and in the numerical applications. In particular, two distinct sets of parameters giving an equally good fitting in tension lead to completely different predictions for other deformations, see [48] for an example.

3. A molecular version of the Gent model

A fundamental advance in establishing the connection between continuum mechanics and statistical mechanics can be made based on the Gent model [36]. To have a detailed idea of the features of this model we refer to the two recent papers [49] and [50]. Here the aim is only to connect this model with the mesoscopic structure of material. In [17] this connection has been provided via the Arruda-Boyce model. Here we show that the Gent model is a *natural* three-dimensional version of a simple cartoon for a single chain entropic model.

We begin by assuming that entropic elasticity represents the right approach for the elasticity of a rubber-like material. In this framework the first step is to consider a model for the end-to-end distance of a macromolecule. We remember that the energy U of a single macromolecular chain

[1]The Langevin function is a special function defined as the inverse of $L(x) = \coth(x) - 1/x$

is given, under the entropic assumption, by $U = -TS$ where T is the absolute temperature and S is the entropy. The entropy is computed as $S = k_B \ln \Omega$ where k_B is the Boltzmann constant and Ω is the number of chain conformations realizing a given end-to-end vector $\boldsymbol{R}$. Therefore Ω is proportional to the probability distribution $p(\boldsymbol{R})$. Roughly speaking, as a chain is stretched, we change from a *more* probable state A to a lesser probable state B (*i.e.* $\Omega(A) > \Omega(B)$). In the extreme case of a chain stretched in a straight line $\Omega = 1$, so that $S = 0$ (limit extensibility state).

Several models have been proposed for an ideal chain. In particular the simple Gaussian assumption is successful in the low stretch regime [1]. On the other hand, if we are interested in the high *stretch* regime (when Ω approaches 1) we have to develop more complex and refined models. One such model is the *freely joint chain* (FJC) model, which involves the inverse Langevin function.

Schematically, to understand the FJC idealization of a single molecular chain, we introduce a molecular chain composed by a large number N of rigid rods, each of the same length l, hinged together see Fig.1. In this FJC scheme we do not incorporate the observation that the chain is not free in the space, but belongs to a polymeric network introducing several kinds of constraints (for example, the chains have to avoid each other and therefore the single rods composing the chain are not free to adopt any angle and any possible configurations). Instead we assume that they are confined to an ideal tube of diameter $D < l$.

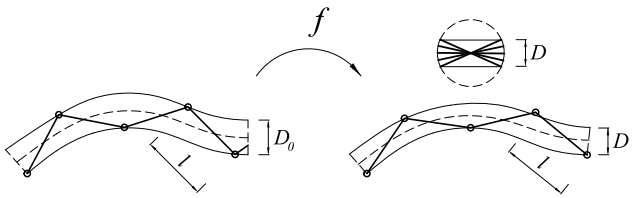

Figure 1. A cartoon of the 'FJC tube model' is obtained from this picture if we consider a straight tube. Then the projection of the rods composing the macromolecule on the axis of the cylinder is easy to obtain. On the other hand if we consider a curved tube, as is clearly the case in an entangled network, then the same projection depends on the curvature of the axis of the tube. In such a way we introduce additional parameters (the *persistence* length) and we obtain a different model [57].

The projection on the axis of the tube of the single chain is $\sqrt{l^2 - D^2}$ and because $L = Nl$ we find that in a simple one dimensional setting

$$R^2 = L^2 \left(1 - \frac{D^2}{l^2}\right). \tag{3.1}$$

On the other hand, it is well known that a rigid rod with a fixed point and free to have any orientation in the space can choose a number of configurations proportional to $4\pi l^2$, but if we confine it to a tube, then it is possible to choose only one set out of these orientations, proportional to D^2. Therefore, the entropy of a single rod can be computed (approximately) as $k_B \ln(D^2/l^2)$ for a single rigid rod and for the whole chain $S = Nk_B \ln(D^2/l^2)$. Thus, using (3.1), we have that the chain entropic energy is

$$G \approx -k_B T \frac{L^2}{l^2} \ln\left(1 - \frac{R^2}{L^2}\right). \tag{3.2}$$

An interesting feature of this formula is that in the limit (3.2) for $L \to \infty$ we obtain

$$G \approx -k_B \frac{T}{l^2} R^2,$$

i.e. the classical Gaussian approximation. On the other hand the force associated with (3.2) is

$$f \approx \frac{L^2}{l^2}\frac{k_B T R}{L^2 - R^2}, \tag{3.3}$$

an expression that blows up (as the energy (3.2)) when $R \to L$ *i.e.* as we approach the full chain extensibility. This is the characteristic *limiting chain effect*.

We point out that (3.2) is similar to the phenomenological energy density proposed by Gent in [36] for incompressible, isotropic, hyperelastic materials:

$$W = -\frac{E}{6} J_m \ln\left[1 - \frac{I_1 - 3}{J_m}\right]. \tag{3.4}$$

Here E is the small strain tensile modulus for incompressible materials, related to the infinitesimal shear modulus μ by the relation $\mu = E/3$. The parameter J_m gives a limit value of I_1 where the energy grows to infinity and represents a macroscopic counterpart of the chain contour length at the network scale, when the molecular chains reaches the fully stretched state. When $J_m \to \infty$ from (3.4) we recover the neo-Hookean model (2.3).

To understand more explicitly the analogy between the previous trivial single chain model and the Gent model, we recall a simple result by Kearsley [51] stating that the first invariant I_1 *is equal to three times the square of the stretch ratio of an infinitesimal line element averaged over all possible orientations*. This shows that J_m is a fair (and natural) measure of the average limit (contour) length of the chains composing the polymeric network. This is, moreover, the reason why we observe that when $J_m \to \infty$, (3.4) reduces to the (2.3) i.e. to an isotropic network of Gaussian chains. We may then deduce that the Gent model is a simple and direct generalization of the neo-Hookean strain energy density to take into account the non-Gaussian character of the macromolecular chains with finite contour length.

Another important mathematical aspect in the perspective of numerical applications is the choice of correct approximation of the different proposed constitutive functions. For example we observe that for a Gent material the generalized shear modulus is a rational function. This is in contrast to the majority of the models considered in phenomenological theories typically based on polynomial constitutive functions, coming from a truncated Taylor expansion. For rational functions it is standard to use *Padé approximants*, not only because they give a better approximation, but also because they take into account the presence of singularities [52], in contrast to polynomial approximations. In the framework of non-Gaussian models, singularities represent a crucial point for a correct material description, as they capture the so called entropic hardening, and induced deformation and damage localization phenomena observed experimentally. As another important example we remark that the inverse Langevin function cannot be expressed in terms of elementary functions and that this special function has a singularity when we approach the contour length of the macromolecular chain. Many authors have approximated (for example in the framework of finite element computations) this special function by using polynomials, but this is clearly a non correct approximation because it smoothes out the singularity. A rational (but very complex) approximation of the inverse Langevin function is introduced in the book by Treloar [1] and a Padé approximation was first introduced by Cohen in 1991 [53] (see also [54]). There the approximation proposed is at the sixth order in the stretch. Horgan and Saccomandi [17] realized that when you fix J_m (the maximum average contour length) and you search for a Padé approximation of the the eight-chain model proposed by Arruda and Boyce [37], then you obtain exactly the Gent model at lower order. In such a way it is possible also to give an a posteriori *molecular* interpretation of the Gent model which is exactly equivalent of the one proposed for the Arruda-Boyce model.

Having recalled the interesting physical interpretations of the Gent model, we point out that it belongs to the class of *generalized* neo-Hookean materials and thus it does not reproduce the experimental effects described in Section 2(b) in a satisfactory way. A natural question is therefore to understand if we are able to improve it by introducing the I_2 invariant and provide a

connection with the mesoscopic structure. To this end it is important to remember that Kearsley showed that the mean square change in area is related to I_2 [51].

Let us go back to the cartoon of the tube in Fig.1 to understand how it is possible to introduce the I_2 invariant in the modelling. If the cross-section area of the tube changes due to the macroscopic deformation $\boldsymbol{f}$, then it is possible to replicate our computations by introducing a multiplicative correction in the logarithmic term in (3.2). A similar idea has been introduced by Kroon [55] where the change of the microscopic tube dimensions has been shown to be proportional to the root mean square change of macroscopic area i.e. to an averaged term $\sqrt{I_2}/3$. Following this idea and using the properties of the natural logarithm, it is easy to deduce that the Gent model has to be modified as follows,

$$W = -C_1 J_m \ln\left[1 - \frac{I_1 - 3}{J_m}\right] + C_2 \ln\left(\frac{I_2}{3}\right). \tag{3.5}$$

Here C_1 and C_2 are two constants. Pucci and Saccomandi [56] proposed this model using a purely phenomenological methodology that allows a fitting of the data in uniaxial tension with a relative error kept under the 5% for the whole range of deformation.

Another way to improve the Gent model, but remaining in the generalized neo-Hookean class, is to use a more realistic model for the polymeric chain. In the framework of some bio-molecular materials it seems that a better model than the FJC chain of the macromolecular molecules is the Worm-Like Chain (WLC) model. Roughly speaking we obtain the WLC model by following the previous scheme now with the macromolecule no longer composed by hinged rods, but by hinged *beams*. Alternatively it is possible to deduce a WLC type energy by considering that the rods are rigid but the tube is curved like in Fig. 1. As a result, we find that the correlation among adjacent *monomers* is higher than in the FJC model and the singularity is quadratic in the stretch of the molecule. The phenomenological three-dimensional version of the WLC has been considered by various authors (see for example [57]) and we refer the readers to these papers for details.

What we want to propose here is, in the framework of the phenomenological theory of elasticity, a family of strain-energy functions defined as

$$W^{(m)}(I_1) = \frac{\mu}{3}\left[\frac{1}{2}(I_1 - 3) + \frac{J}{m\left(1 - \frac{I_1 - 3}{J}\right)^m} - \frac{J}{m}\right]. \tag{3.6}$$

where $m \geq 0$ is the exponent that controls the asymptotic behaviour of the model. Interestingly for $J \to \infty$ we obtain the classical neo-Hookean model. The generalized shear modulus associated with the family of strain-energy functions (3.6) is

$$Q^{(m)} = \frac{2\mu}{3}\left[\frac{1}{2} + \frac{1}{\left(1 - \frac{I_1 - 3}{J}\right)^{m+1}}\right]. \tag{3.7}$$

To study the behaviour of this model it is convenient to introduce the variable

$$\zeta = \frac{I_1 - 3}{J}$$

such that $\zeta \in [0, 1[$ and to reduce (3.7) to its dimensionless form i.e.

$$\frac{Q^{(m)}}{\mu} = \frac{2}{3}\left[\frac{1}{2} + \frac{1}{(1 - \zeta)^{m+1}}\right]. \tag{3.8}$$

Approaching $\zeta \to 1$ the asymptotic behaviour of (3.8) is

$$\frac{Q^{(m)}}{\mu} \approx -(-1)^m \frac{2}{3(\zeta - 1)^{m+1}}.$$

For $m = 1$ we recover the model proposed in [58] to mimic a network of WLC chains. In this case

$$\frac{Q^{(1)}}{\mu} \approx \frac{2}{3(\zeta - 1)^2}.$$

For $m = 0$ we obtain a model with the same asymptotic behaviour of the FJC model. Indeed, using some elementary calculus we find

$$W^{(0)} = \frac{\mu}{3}\left[\frac{1}{2}(I_1 - 3) - J\log\left(1 - \frac{I_1 - 3}{J}\right)\right], \quad Q^{(0)} = \frac{2\mu}{3}\left[\frac{1}{2} + \frac{1}{\left(1 - \frac{I_1 - 3}{\beta}\right)}\right]. \tag{3.9}$$

In this case

$$\frac{Q^{(0)}}{\mu} \approx -\frac{2}{3(\zeta - 1)}.$$

It is interesting to notice that the strain-energy function (3.9) is similar, but not identical to the Gent strain-energy (3.4).

These simple computations show the strength of the continuum mechanics perspective, which allows to model any kind of asymptotic behaviour when we approach the limiting chain behaviour via simple mathematical considerations. On the other hand it is clear that the chain confined in a tube gives a special status to the idea of Gent. The synergy between the two points of view is the key reason of the success of the modelling procedure that we sketched in this section. In the next section we explore an example of a more systematic and rigorous approach.

4. Multiscale and microstructure inspired continuum models

The possibility of material design down to the nano scale has made the request of new multiscale approaches a strongly appealing field of research (see *e.g.* [18] and references therein).

Here we refer to multiscale theories deducing macroscopic three-dimensional constitutive theories from a model for the single chain mechanical behaviour. A standard approach is to deduce the material behaviour of a real polymeric network by an "averaging procedure" that allows us to go from a single chain to a *bundle* of chains. This idea has been widely used for a long time and several possible methods are used to implement it (see for example the discussion in the book [1] or in [13]). The simplest method is based on the so-called "affine assumption". In this method we link the macroscopic deformation with the macromolecular network deformation via specific network cells (single chain, 4-chain tetrahedral structure, 8-chain cubic structure, 8-chain octahedral structures, etc.), oriented according the principal directions of the macroscopic deformation. More general assumptions considering "non affine" effects or full-network models can be considered.

In reality an actual description of a macromolecule *network* requires not only the choice of a mathematical average procedure, but the consideration of many other crucial effects. A network introduces enthalpic contributions due to chain-to-chain (or possibly chain-to-fillers) interactions and the associated complex phenomena of links breakage and re-crosslinking. This discussion is subtle because each link breakage not only induces by definition an enthalpic energy variation, but also, and more importantly, by varying the network conformation, it leads to a variation of the chains contour length and of the network natural configuration. The enthalpic contribution can be considered at the root of many crucial macroscopic effects such as damage, dissipation, anisotropy, residual stretches, deformation and damage localizations, which are all well known experimental phenomena in rubber and rubberlike materials. The theory is even richer if one considers the possibility of re-crosslinking effects (material healing) that is revealed macroscopically by internal hysteresis cycles. Another important effect is related to single chains models with variable material properties, when the single-chain is constituted by several material phases. For example, a soft (entropic) phase corresponding to a poorly entangled macromolecules plus a crystalline phase (typically in forms of β-sheets or α-helices).

Both the comprehension and the prediction of all these fundamental phenomena and the design of new polymeric and bioinspired materials will benefit, in our opinion, from a real synergic contribution of molecular and macroscopic continuum mechanics phenomenological theories. In this respect both the incredible progress in experiments and material manipulation at the macromolecular scale and the great advances in the extension of nonlinear theory of elasticity to phenomena often considered out of its range of application, are providing the necessary driving force.

To exemplify this possibility, we now describe some recent approaches starting from a microstructure inspired material constituted by a mixture of an elastic fraction and a breakable fraction. To describe the amorphous character of the network, constituted by chains of different length, we assume that the breakable fraction is constituted by chains that can undergo activation and breaking at different stretches. We then use a Griffith-like method to minimize the total (fracture plus entropic) energy.

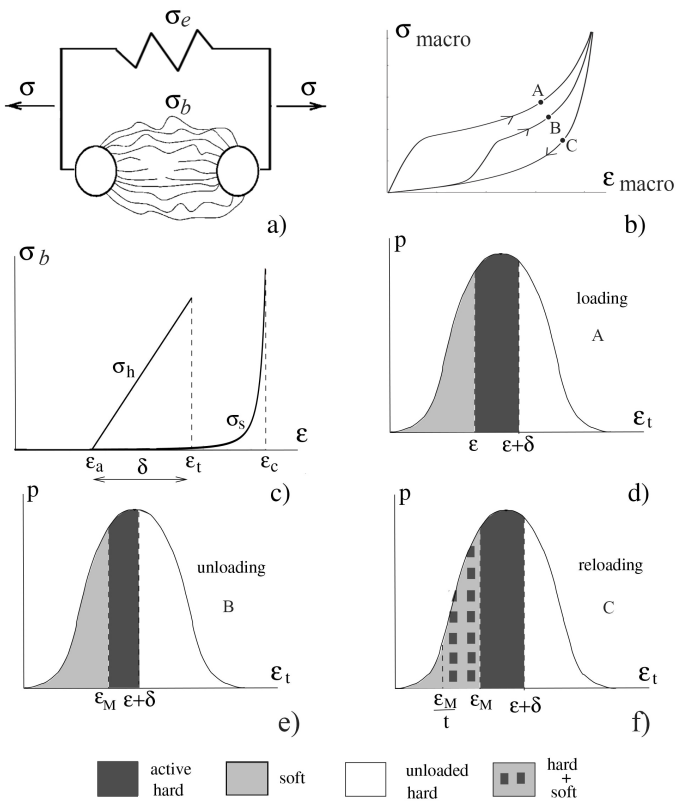

Figure 2. A cartoon of the basic model we propose where the network is composed by entropic non-gaussian chains and linear elastic springs.

In Fig.2$_a$ we have a cartoon of this idea. The material is composed by a hard and a soft phase (Fig.2$_c$). The soft phase is modeled using a Gent-like model (i.e. a model taking into account limiting chain extensibility). The hard phase is modeled by just considering a linear behaviour. Roughly speaking the soft phase represents the entropic energy of the network whereas the hard phase measures the presence of cross-links and the associated hentalpic contribution. To fix the ideas, imagine that the material is submitted to simple extension. If we increase the strain monotonically, at a certain activation threshold $\varepsilon = \epsilon_a$ a polymeric chain of the hard phase is

activated (see Fig.2$_c$) with a stress $\sigma_h = \sigma_h(\varepsilon)$. If the strain is increased further there exists another threshold $\varepsilon = \varepsilon_b := \epsilon_a + \delta$ where the cross-link is completely damaged and it stops to have a mechanical function, so that new monomers are available to the chain (soft phase with a new stress $\sigma_s = \sigma_s(\varepsilon)$. To model a real network we introduce a probability function depending on both ε_a and ε_b that can be deduced by simple cyclic experiments [16]. This is because the cross-links are not all activated and broken at the same value of ϵ_a. The presence of an initial elastic matrix of untangled chains is schematised in Fig.2$_a$ by a parallel spring. The possibility of a full breakage of the link may be simply introduced by assuming $\sigma_s = 0$, whereas the possibility of a hard-soft (folded-unfolded, helix-coil, etc.) transition is modeled by considering $\sigma = \sigma_s \neq 0$ after the link breakage. The possibility of re-crosslinking upon reloading, observed in many rubberlike and biological materials, can be also easily introduced in the model as represented in Fig.2$_f$ by assuming that the reverse (re-crosslinking) soft→hard transition can be observed upon unloading, as suggested by the experimental behaviour of many polymeric and biological materials. A possible association of the macroscopic hysteric behaviour (points A, B, C in Fig.2$_b$) to the microscale network evolution (Fig.2$_{d,e,f}$) is also schematically represented in the figure.

In the various stages of the deformation the material is composed by a variable amount of active hard and soft phases and the evolution of this mixture can model the strain-hardening phenomena, the stress-softening, the damage and the internal hysteresis of the material. This simple idea allows many degrees of freedom in the modelling of the mechanical behaviour of complex amorphous materials [16,43].

These ideas have been applied to deduce various three-dimensional models with the aim of discussing many mechanical phenomena of relevance for amorphous rubber-like materials. In [59] the Mullins effect in rubber-like solids is described using the notion of limiting chain extensibility associated with the Gent model. In relating this theory to the mechanisms of network alteration and to the pseudo-elasticity theory proposed in [60], it was possible to show the relationship of our basic idea with the Eckart theory of the evolution of the natural configurations as elaborated by Rajagopal and Wineman [61]. In [62] the role of healing was introduced to describe the internal hysteresis of rubberlike materials, and the model was shown to be successful: the experimental behaviour of rubber balloons with internal hysteresis damage has been successfully reproduced in [63]. On the same topic we point out the approach and the papers by Wineman and coworkers [64–67].

The above idea has been very promising also in the framework of the *mechanobiological* modelling of some biomaterials such as spider silk, see Ref. [68] where we modelled the soft phase using a simple Gent type energy of the Worm Like Chain form. Spider silks protein macromolecules have a hierarchical structure with a primary structure composed by an amino acid sequence of highly repetitive glycine and alanine blocks and a secondary structure level composed by short side chained alanine. Glycine is the main component of the amorphous matrix (the *soft phase*) and on other hand, nano-fibrils are found in the side chained crystalline domains in the form of β-sheets (the *hard phase*). A single spider can produce up to seven different types of silk for different uses and each spider and each type of silk has a set of mechanical properties optimised for their biological function. This is possible because the spider is able to control the mixture of the two hard and soft phases. By tuning this mixture it is possible to obtain very different mechanical behaviour as shown in Fig.3 (see [68]).

The second approach, applied to protein tissues [69], is a multiscale method that begins with a detailed description of the energetics at the scale of the single macromolecule (see the cartoon in Fig.4$_a$). When we consider the unfolding of giant proteins like titin (crucial for the passive elasticity of muscles), we have to account for a complete description of the force-length macromolecular behaviour that is characterized by a sawtooth stress plateau with each stress jump associated to the unfolding of a β-sheets domain [69] (see the Atomic Force Microscopy experiments of [19] reproduced in Fig.4$_c$). The unfolding of the β-sheets "dissipates" energy (as heat) and increases the free monomers available to the chain. In the cartoon of Fig.4$_a$ we imagine that the macromolecular chain is composed by rods and many bubbles (here modelled

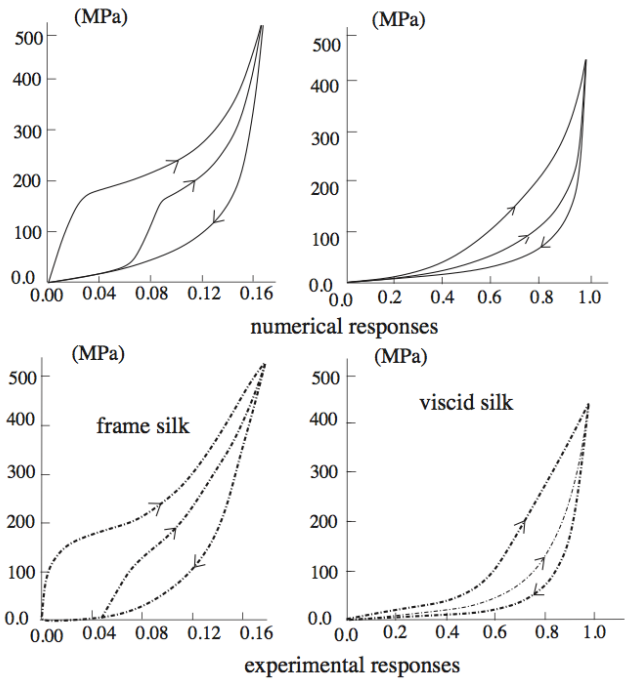

Figure 3. In the curves in the left column we have an ideal material composed by a mixture where the hard phase has a principal role. In the right column we have an ideal material where the soft phase plays the main role.

as rigid). Roughly speaking, when we pull the chain we open some bubbles, releasing monomers in the chain. This unfolding process is regulated by an energetic competition between the entropic energy decrease and the enthalpic energy associated with the folded-unfolded transition, modelled here through a classical Ising model. The contour length of the chain increases and the overall result of this structure is shown in Fig.4_b, where (see [69] for details) we schematise the energy we "dissipate", and Fig.4_c where we reproduce the experimental saw-tooth force evolution observed by AFM experiments of proteins macromolecules (see *e.g.* [19]). This peculiar plot originates from the discontinuous evolution of the contour length and changes of the entropic energy associated with the successive unfolding events.

The consistent thermodynamic continuum version of these approaches has then been obtained through two different change of scales [70]. First, since the macromolecules are typically characterised by a high number of crystal (hard) domains, we may consider [41] a discrete→continuum limit. We obtain a history dependent energy, depending on the fraction of unfolding domains, converging for the primary loading path to the convex hull of the energies represented in Fig.4_b. In this limit we obtain constant unfolding stress-plateaux of the force-length curve in Fig.4_c. Then, based on the choice of an appropriate cell structure [13] we deduce the macroscopic energy, with the elastic moduli directly related to the network scale properties of the material (contour length, Kuhn length, persistent length, number of chains, unfolding energy of the β sheets). When this limit is done carefully it is possible to introduce several effects, such as residual stress or growth effects, crucial for a realistic description of biological tissues. More specifically, in our model [70] we connected the macroscopic stretches to the chains elongations (the Cauchy-Born rule) based on the affine hypothesis [71] and an 8-chain network cell [13]. The predictability of the resulting model is described in Fig.$4_{d,e}$ for the cyclic loading of mouse skin reproduced by [72] and the shear behaviour of pig (passive) myocardium tissues reproduced by [73], respectively.

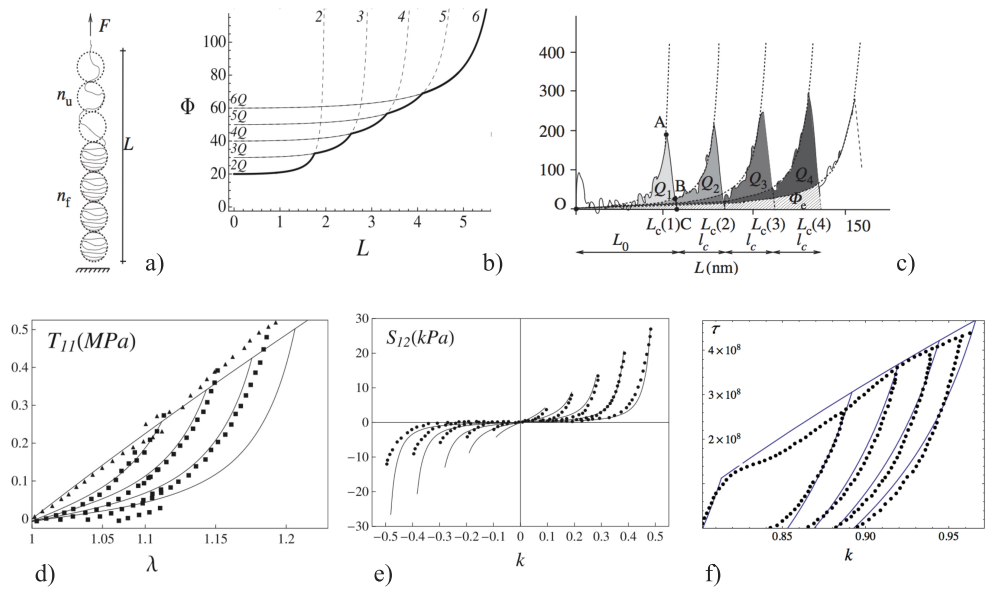

Figure 4. The sub-plot a) shows a cartoon of the macromolecule composed by rods and bubbles, i.e. structures that contain a reservoir of monomers and if opened change the contour length of the molecule. In b) we plot the total energy (Griffith like) minimisation method. Opening of a bubble has a twofold effect: it dissipate a certain amount of energy Q and it increases the contour length thus changing the elastic curve. Despite this complexity, the minimisation of the overall energy is possible. The corresponding sawtooth force [69] end-to-end length diagram is represented in c), reproducing the AFM experimental behaviour of the single macromolecule in [19]. In d) and e), based on an 8-chain cell scheme, we reproduce [70] the cyclic loading for mouse skin studied in [72] and the shear cycles of pig (passive) myocardium tissues reported in [73], respectively. In f), based on a 3-chain scheme, we reproduce the experimental behaviour of Senegalensis Nephila spider silks from [74].

The numerical extension of the model to the 3-chain approach has been exemplified in Fig.4_f where we reproduce the experimental behaviour of Senegalensis Nephila spider silks from [74]. The introduction of the 3-chain scheme lets us model the important anisotropic effect induced by the directional-dependent unfolding, due to the chain alignment along the most stretched directions.

Summarizing, by using a two-state scheme and a Griffith-like total energy minimization method, i.e. the minimization of the total (entropic plus unfolding) energy [69], we have been able to describe the unfolding of multi-domain macromolecules (proteins, silks, polysaccharides, nano-polymers) in a fully analytical framework. In doing so, we have been able to master the role of the different energetic components regulating the unfolding evolution. The explicit analytic deduction of the history-dependent, strongly nonlinear behaviour of the material has been presented in [70] where the damage, softening, growth, residual stretches have been analytically deduced, starting from the microscopic properties of the material. Roughly speaking we obtain a Gent-type constitutive law with a history-dependent limit threshold J_o and a variable natural configuration, based on the classical multiplicative decomposition of the deformation gradient in a growth and in an elastic component. The approach synthesized above shows the potentiality of deducing an actual continuum mechanics method, based on multi scale analyses, that can be used to explain many complex phenomena where the material alteration at the network scale of amorphous macromolecular materials is the driving force of some type of *phase transition* [75].

5. Concluding Remarks

We provided a synthetic (and incomplete) overview of how it is possible to introduce low scale effects in macroscopic modelling of polymeric modelling using both microstructure inspired or multiscale approaches. Our survey does not claim in any way to be a detailed review of the literature. Rather, it is an introduction to the modelling philosophy contained in [43] and [70]. In [43] we were able to prove that if at the mesoscale the polymeric network is constituted by distributions of elastic and breakable links with variable activation and fracture thresholds and we use a Griffith method, then we are able to describe the main experimental effects observed at the microstructure and macroscopic scale in disordered materials undergoing damage. Moreover, via this model we are able to generate non-convex macroscopic energies from micro-mechanics considerations. The thermodynamical consistency of the model, the three-dimensional extensions, and the possibility of deducing the corresponding macroscopic moduli, have been phenomenologically introduced in [16], based on a classical 'plasticity theory type' activation and breaking criterion, and explicitly deduced through a fully multiscale philosphy in [70]. Several successful applications of this idea have already been provided, but many other interesting applications are feasible.

ACKNOWLEDGEMENTS We are grateful for having shared with us their ideas and views about rubber mechanics to: M. F. Beatty, D. De Tommasi, M. Destrade, M. Hayes, C. Horgan, J. Murphy, R. Ogden, K. R. Rajagopal, I. Sgura. Our research is partially supported by GNFM of Italian Istituto Nazionale di Alta Matematica.

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