

Accepted Manuscript

MECHANICS OF MATERIALS WITH EMBEDDED UNSTABLE MOLECULES

Roberto Brighenti , Federico Artoni , Mattia Pancrazio Cosma

PII: S0020-7683(18)30475-X  
DOI: <https://doi.org/10.1016/j.ijsolstr.2018.11.022>  
Reference: SAS 10186



To appear in: *International Journal of Solids and Structures*

Please cite this article as: Roberto Brighenti , Federico Artoni , Mattia Pancrazio Cosma , MECHANICS OF MATERIALS WITH EMBEDDED UNSTABLE MOLECULES, *International Journal of Solids and Structures* (2018), doi: <https://doi.org/10.1016/j.ijsolstr.2018.11.022>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**Highlights**

- Probabilistic-based micromechanical modeling of polymers is considered
- Polymers with bi-stable molecules embedded in the chains network are studied
- Molecule conformation change switching is triggered by chemical or mechanical stimuli
- Mechanics of swelling is accounted for in the model
- A continuum model is obtained from the micromechanical approach

ACCEPTED MANUSCRIPT

Amended version of the manuscript ID: IJSS-D-18-00677\_R1

# MECHANICS OF MATERIALS WITH EMBEDDED UNSTABLE MOLECULES

*Roberto Brighenti*<sup>1\*</sup>, *Federico Artoni*<sup>1</sup>, *Mattia Pancrazio Cosma*<sup>1</sup>

<sup>1</sup> Department of Engineering & Architecture, University of Parma

Parco Area delle Scienze 181/A, 43124 Parma, ITALY

\*e-mail: brigh@unipr.it

---

## Abstract

Active structural systems and materials, typically used to develop sensors or actuators, are those capable of responding to external stimuli with some physical detectable reaction. The triggering stimuli can be of various nature, ranging from temperature, pH, light, mechanical stress, etc. In this context, responsive materials have the capability to react at the molecular level, showing some changes in their microstructure that can be detected and measured at the meso- or macro-scale level. This ability can be obtained in polymers and polymer-like materials through the introduction in their network of switchable molecules, characterized by two geometrically distinct stable states, where the switch from one to the other has can be seen as an instability phenomenon. In this research, we present a continuum mechanical model, developed starting from the micromechanics of the polymer network joined to molecules whose switching instability is induced by mechanical or chemical actions. The theoretical framework is presented by considering the general case of poly-disperse polymers and some final examples are given and discussed; the proposed model can be used as a tool for the development and design of smart responsive systems, applicable across a wide range of length scales.

---

**Keywords:** *mechanophores, polymers, responsive materials, bi-stable molecules, local instability.*

## Nomenclature

$A_n$	Avogadro's constant
$b$	Kuhn's length of a chain segment
$c_a$	Number of active chain per unit volume
$C_A, C_D$	Frequency factors
$C_s, \hat{C}_s$	Solvent's concentration in the reference state and solvent concentration triggering the conformation change of all the switchable molecules in the unit volume, respectively
$f_0, f$	Normalized distribution function of the polymer's chains end-to-end vector in the stress-free and in the current state, respectively
$\mathbf{F}, F_{ij}$	Deformation gradient tensor
$\mathbf{F}_m, \bar{\mathbf{F}}_m$	Deformation gradient tensor associated to the molecules switching mechanism and that of an equivalent material with switchable molecules uniformly oriented in any direction of the space
$t$	Time
$t'_m$	Threshold force required to change the conformation of a switchable molecule
$t_p$	Force acting on a polymeric chain
$h_r^{(N)}$	Fraction of the switched molecules connected to chains having end-to-end distance $r$ within the network $N$
$h^{(N)}$	Fraction of the switched molecules within the network with chains of length $N$
$\bar{h}$	Average fraction of the switched molecules among all the networks
$J$	Polymer volume change
$\bar{J}_m$	Volume change of a material with a random dispersion of switchable molecules
$J_{mix}$	Volume change of the material due to swelling
$k_A, k_D$	Activation and deactivation reaction rates of the switchable molecules, respectively
$k_B$	Boltzmann's constant
$\mathbf{L}, L_{ij}$	Material velocity gradient
$\mathcal{L}, \mathcal{L}^{-1}$	Langevin function and its inverse, respectively
$N$	Number of segments in a polymer chain belonging to a single network
$n_s$	Current number of solvent molecules available for one switchable molecule
$p$	Hydrostatic stress
$q(N)$	Probability distribution function of the number of Kuhn's segments in a polydisperse polymer
$\mathbf{r}$	End-to-end distance of a polymer chain

$\mathbf{P}_{net}$	First Piola stress tensor related to the mechanical deformation of the network
$\mathbf{P}_{mix}$	First Piola stress tensor induced by swelling of the network
$s$	Entropy of a single chain
$\mathbf{t}$	Force in a single chain
$T$	Absolute temperature
$V_s$	Volume of a mole of solvent
$W$	Potential energy
$\alpha$	Relative size of the switchable molecule
$\chi$	Flory-Huggins parameter governing the swelling phenomenon
$\Delta G_{A0}, \Delta G_{D0}$	Energies required for the forward and the backward switching, respectively
$\delta s_{sw}$	Size difference of the switchable molecule between the two stable states
$\varphi_0(\mathbf{r}), \varphi(\mathbf{r})$	Distribution function of the end-to-end vector in the stress-free and in the current state, respectively
$\varrho$	Total volume fraction of the switchable molecules contained in the polymer
$\varrho_r^{(N)} =$ $\varrho_{r,sw}^{(N)} + \varrho_{r,unsw}^{(N)}$	Volume fraction of the switchable molecules connected to the polymer's chains with length $r$ within the network with length $N$ ; switched and unswitched volume fractions within the single network, respectively
$\lambda_m$	Stretch of a switchable molecule from the unswitched to the switched state
$\lambda_p, \lambda'_p$	Stretch of a single polymer chain and its reduced value due to molecule switching
$\lambda$	Stretch of the single polymer chain
$\psi$	Deformation energy for a single chain
$\Psi_0, \Psi$	Network's deformation energy per unit volume in the stress-free and in the current configuration, respectively
$\Psi_{ext}$	Mechanical work per unit volume of the external forces
$\Psi_{mix}$	Deformation energy per unit volume due to swelling
$\Psi_{sw}$	Deformation energy per unit volume due to molecule switching
$\Pi$	Chemical potential
$\boldsymbol{\sigma}$	Cauchy stress
$\omega$	Deformation function

## 1. Introduction

In recent years, structural elements made of the so-called metamaterials – characterized by the presence in their structure of moving parts – have been studied and developed to obtain sensors or actuators. However, some dimensional limitations arise when such a technology is needed in small-scale applications, nowadays particularly required. In fact, microscale applications have known a wide diffusion in the last decades, and the development of smart responsive polymers, polymeric biomaterials, nano devices (capable, for instance, to transduce energy from one form to another) has received a huge research effort. The requirement of smaller and smaller systems for advanced nano- as well as for everyday-applications, has promoted the research in such a direction for the development of these devices and an interdisciplinary approach combining chemistry, physics, mechanics and technological aspects has emerged to be necessary to successfully and properly design the components' material, in order to make them suitable for specific applications [1-3]. The occurrence of an unstable mechanism arising in technological applications as well as in natural systems taking place in a very huge length and time scales, is often considered to be an undesirable phenomenon; however, if properly designed, instabilities in some circumstances can be exploited to get special materials having particular properties or behaviors [4-9].

Conformation change, physically belonging to the class of unstable phenomena, is known to occur in different situations: snapping transition can take place, for instance, in polymer films, leading to wrinkling and creasing of surfaces [10]. Some polymers present a folded microstructure whose unfolding can be considered as a switching mechanism [11], polymers designed to provide strength and flexibility have been developed through the insertion of unfolding cross-linker [12], while unfolding mechanisms as well as multistable states are often present in chemistry and biological systems – such as in immunoglobulin segments whose unfolding can be triggered by a mechanical force – and are responsible for the proper functions and intelligent responses shown by such systems [13-15].

In this framework, the so-called molecule switching represents a very promising mechanism to be harnessed to this aim; the above mentioned phenomenon exists in molecules or molecular systems characterized by two stable states (bi-stable molecules or isomers), in which the transition between the two states can be triggered and tuned through proper external stimuli such as chemical, temperature, light, electric and/or magnetic fields, mechanical stress, etc [16-20]. The two stable states are usually characterized by different geometrical, physical and, sometimes, chemical properties, and this can be exploited to get materials capable of a smart response; among the various property change that can be obtained through the switching mechanism, the geometric conformation difference between the two stable states can be readily exploited to get a molecular-level actuator, without any change in the chemistry of the material.

A geometrical switch, or conformation change, corresponds to a change in the spatial arrangement of the atoms within the molecule, without changing their connectivity; this entails that chemically the molecule remains the same, while its geometric size and shape can change significantly. For some molecules the existence of different conformational stable states – reachable through a so-called switching mechanism – with very large size difference between them, enables to get a macroscopic volume change when such a switching occurs in a collectively way, and can be exploited to develop actuating materials. Thanks to the conformation change taking place at the molecular level, the actuating response can be obtained for a portion of materials at any dimensional scale, enabling their use in a very wide range of dimensional scales useful in many advanced applications.

The distinct stable states of a switchable molecule correspond energetically to a local minimum of the Gibbs energy, and the change from one state to another requires to overcome an energy barrier. From this perspective, the switching mechanism can be considered as an instability phenomenon, whose occurrence is triggered by suitable external stimuli capable to provide the energy required to pass the above mentioned barrier.

In the present paper we develop a theoretical framework for the description of the mechanics of polymeric materials with embedded switchable molecules, whose conformation change can be triggered by external chemical or mechanical stimuli. The paper is organized as follows: in sect. 2 the switching of a bi-stable molecule is interpreted from a mechanical perspective, while in sect. 3 the mechanics of a polymer chain network is discussed from a statistical viewpoint and the arising stress state is related to the actual chains end-to-end distance distribution. Moreover, section 3 deals also with the description of the swelling phenomenon occurring in polymers prone to absorb a fluid, as typically occurs in pH-sensible polymers, whose pH change is typically driven by an absorbed fluid. In section 4 we consider the modelling of the molecule switching from an instability standpoint, while the mechanical behavior of polymers equipped with such molecules is illustrated in Section 5: starting from the developed micromechanical model, a continuum approach for the quantitative description of the mechanical response of active polymers whose switchable molecules can be activated by chemical and/or mechanical stimuli is formulated. Section 6 presents some numerical tests, dealing with the mechanical response of polymers equipped with switchable molecules; the influence of the main parameters involved in the considered phenomena, in term of deformation and stress state arising in the material, are discussed. The response of a strain reporting material tested experimentally in literature is also considered. Finally, section 7 drawn some conclusions and future perspectives.

## **2. Mechanics of bi-stable molecules**

The switching phenomenon in molecules has been experimentally observed (such as in azobenzene and spiropyran molecules, [21, 22]) and exploited to get specific functions out of a material subjected to specific stimuli [23, 24]. Typically, it is accompanied by a significant change of the geometric conformation of the positions of the constituting atoms which, when considered at the collective level, leads to a mesoscopic detectable deformation that appears, for instance, as a volume change of the material. This behavior is particularly effective when the switchable molecules are inserted as cross-

linkers in a highly deformable polymer network. The above mentioned macroscopic deformation can be harnessed to get specific functions, useful to actuating purposes, and is exploitable at any dimensional scale, thanks to the molecular nature of the involved bistable units.

Conformational change usually takes place as an instability phenomenon triggered by proper physical or chemical stimuli, so it can be quantitatively studied leveraging the theory of instability of mechanical systems [25, 26]. Materials with embedded bi-stable elements are characterized by a non-convex energy function; this character of the energy comes from the bi-stability property of the elements capable to assume different reversible but energetically equivalent arrangements.

Some molecules can reversibly shift between two or more stable states in response to environmental stimuli, such as pH change, light, temperature, electric field, mechanical actions, or in presence of a ligand [27]. A well-known molecule switching is the one associated to the change of color occurring, for example, in pH indicators; another example is the one of the colorless spiropyran molecules that are able to transform into a colored state, namely merocyanine, through a reversible reaction that can be induced, for instance, by light, temperature, metal ions or mechanical stress [28].

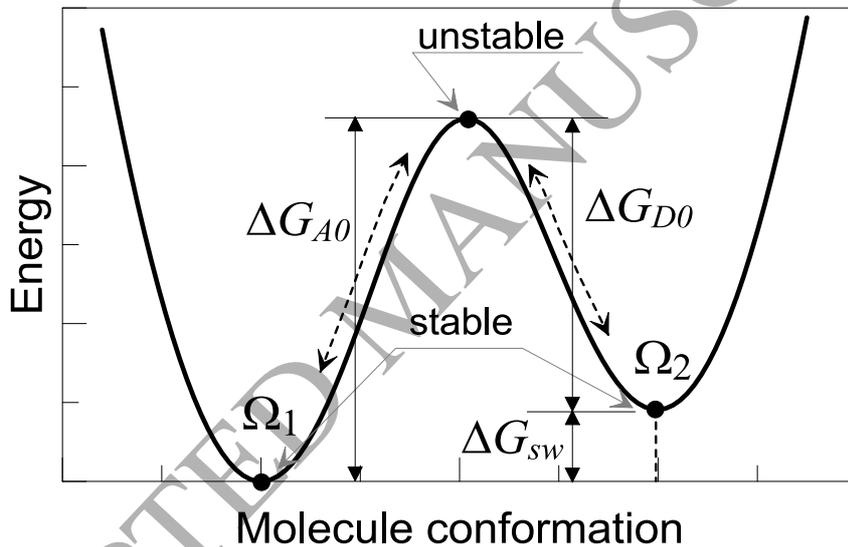
Synthetic molecular switches are relevant in nanotechnology where they can be used to develop molecular machines or responsive drug delivery systems; the comprehension of the mechanics of materials embedding switchable molecules is also important in biological systems, because many living functions are often based on such a switch between two different states [15].

We are here interested in molecule switching taking place between two geometrically distinct conformations of the bi-stable molecule; if the molecules are joined with others molecules (typically those of a polymeric network), their change in conformation reflects on the backbone hosting material and a macroscopic change can be also appreciated. From this viewpoint, a polymeric material with embedded switchable molecules can be assumed to have some of its cross-links to be replaced by bistable elements (molecules) whose effects influence the behavior of the polymer network itself.

From a mechanical viewpoint, the potential energy per unit volume of such a material can be expressed as:

$$W = \Psi(\mathbf{F}) + \sum_{act} \psi_{sw} - \Psi_{ext} \quad (1)$$

where  $\Psi(\mathbf{F})$  is the (convex) energy of the polymer backbone,  $\psi_{sw}$  is the Helmholtz energy associated with the conformation transition of the single switched molecule and  $\Psi_{ext}$  is the potential of the external actions. The summation in (1) is referred only to the activated molecules per unit volume, i.e. those that have switched from one stable state to the other one.



**Figure 1.** Energy vs conformation state of a bistable molecule. The two potential wells indicate the stable states  $\Omega_1$  and  $\Omega_2$  of the molecule, while the energy difference between them is  $\psi_{sw}$ .

The stable configurations of the molecule can be identified as those corresponding to the minimum of the energy vs the molecule's conformation (Fig. 1); the switching from the state  $\Omega_1$  to the state  $\Omega_2$  (forward switching) requires to overcome the energy barrier  $\Delta G_{A0}$ , while the change from the  $\Omega_2$  to the  $\Omega_1$  state (backward switching) requires the energy  $\Delta G_{D0}$ . The difference of the Gibbs energy between

the only two stable states is identified with  $\Delta G_{sw}$ . A detailed description of the mechanical modeling of switchable molecules through energetic consideration is provided in sect. 4.1.

### 3. Mechanics of a polymer chain network

In contrast to most crystalline-like materials, the mechanics of rubber-like ones (such as polymers, gels, etc. characterized by a microstructure made of an entangled network) is dominated by thermal fluctuations at the microscale; the elasticity of the material therefore depends on the entropy of the polymer chains. As it is well-known, the entropy  $s$  of a single chain can be easily related to the chain's stored energy  $\psi(r)$  as [29, 30]

$$\psi(r) = -T s(r) \quad (2)$$

where  $T$  is the absolute temperature of the material.

For deformation states not too close to the limit polymer's stretch – corresponding to the network chains nearly extended to their maximum elongation – the entropy function of the full network governs the response of the materials, so also the mechanical response of the polymer can be conveniently described through such a quantity, while for high deformation levels the internal energy cannot be neglected since it plays the main role.

Typically, the mechanics of long linear entangled chains is described by the classical rubber elasticity theory [31-34], according to which the distance between two subsequent joints in the polymer chain (end-to-end vector distance  $\mathbf{r}$ ) and its distribution within the network is the key factor to describe the deformation and the stress state of the polymer.

According to the freely-jointed chain model [35, 36], the polymer network is assumed to be composed of chains whose structure is made of  $N$  rigid segments of equal length  $b$ , connected at their extremities

and arranged according to the random-walk theory, while no correlation between the directions of segments' bond angles is assumed to exist.

Among the approaches developed to describe the mechanics of polymers, the ones based on the micromechanics of polymers' network are of great interest. In this context Ball et al. [37] developed a model based on the mechanics of the entangled chains composing the network, by accounting not only for their simple cross-linking – as typically assumed within the classical rubber elasticity theory – but also for their reciprocal interaction, leading to repulsive forces constituting a not negligible constraint in a real polymer where its chains cannot pass through each other.

Among the physics-based models, Beatty [38] showed that within the class of uniform non-Gaussian network models, the 4- and 8-chain ones share the property that all of their chains in a principal reference system are equally stretched and, therefore, they are described by the same constitutive equation obtained by Arruda and Boyce [39, 47]; moreover, he demonstrated that the 3-, 4-, and the 8-chain models may be derived from the Wu and van der Giessen full-network model [40] and obtained an average-stretch constitutive equation by approximating the Wu and van der Giessen equation derived for uniform networks.

In Miehe et al. [41] a micro-mechanically-based network model for rubbery polymers under large strains have been developed by representing the material microstructure through a micro-sphere, whose surface represents a continuous distribution of chain orientations in space; they adopted a non-affine micro-to-macro transition formulation based on a homogenization procedure of micro-variables evaluated on the above-cited micro-sphere of space orientations.

Puglisi and co-workers [42] proposed a general multiscale approach for three-dimensional networks (falling within the so-called Growth Mechanics framework), characterized by a strain-induced unfolding of the polymer chains, and derived a continuum model having a variable natural configuration, suitable to describe the mechanical response of biological tissues.

In [43] the Authors developed a model – based on few macromolecular parameters such as the chains' persistence and contour length – for the description of the mechanical behavior of protein materials, by also accounting for the damage and residual stretches, effects that typically play a non-negligible role in biological systems and on their functions. In [44] a model aimed at describing the non-linear response of rubbers in a wide range of stretches has been proposed; the successive stages of chains extension – starting from the small deformation regime (governed by the entropy decrease associated to the chains unfolding), up to the strain-hardening one and the sharp stiffening taking place when the chains extend towards their limit – have been considered and mathematically described.

In [45] a micromechanical model for describing the stress softening in isotropic rubbers (where the material is assumed to be constituted by a polymeric network reinforced with small rigid filler particles linked to both elastic and breakable polymer's chains), has been developed; the proposed approach enabled the simulation of the so-called Mullins effect arising in many rubberlike materials under cyclic loading. A general overview of the most diffused models (mathematical, phenomenological and physics-based) can be found in [46], where they are compared and critically discussed on the basis of their ability to reproduce experimental data, for a wide range of deformations under both uniaxial or biaxial stress states.

In the present paper we propose a statistical-based model, developed on the basis of the one presented in [47], properly extended to account for the polymer's chains relaxation induced by the switching mechanism of bi-stable molecules embedded in the material's network. In the following sections, the model is presented by firstly illustrating its statistical basis and the corresponding arising continuum model obtained from the micromechanics approach, where the swelling phenomenon and the mechanical effects induced by the bi-stable molecules are also taken into account.

### 3.1 Statistical description of a polymer network

From a statistical standpoint, the number of network's chains whose end-to-end vector is comprised between  $\mathbf{r}$  and  $\mathbf{r} + d\mathbf{r}$ , can be described by the distribution function  $\varphi(\mathbf{r})$ .

According to the standard statistical theory of rubber elasticity, in the polymer's natural (or reference) state such a distribution function can be expressed as:

$$\varphi_0(\mathbf{r}) = c_a \cdot f_0(\mathbf{r}) \quad (3)$$

where  $c_a$  is the number of active chains per unit volume (or chain concentration) and  $f_0(\mathbf{r})$  is, usually, assumed to be the standard Gaussian (normal distribution) function [29],

$$f_0(|\mathbf{r}|) = \left(\frac{3}{2\pi N b^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3|\mathbf{r}|^2}{2N b^2}\right),$$

characterized by mean value  $\mathbf{r} = \mathbf{0}$  and standard deviation  $\sqrt{N} b/3$ .

By noting that the end-to-end distance can be also expressed as  $r = |\mathbf{r}| = \lambda r_0$ , where  $r_0 = b\sqrt{N}$  and  $b, \lambda$  are the Kuhn length and the current stretch of the chain, respectively [29], the distribution function can be also rewritten more conveniently through the use of the deformation measure  $\lambda$  as:  $f_0(\lambda) = \left(\frac{3}{2\pi N b^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3\lambda^2}{2}\right)$ . In the above relations we assumed the affine deformation hypothesis, according to which the chains take the deformation of the continuum [48]; this assumption will be used throughout the manuscript. It has been demonstrated that the initial Gaussian distribution of the chain population  $f_0$  remains Gaussian also after the deformation if no chains are lost or gained during the deformation itself and if the chain kinetics (in the case of dynamic network) are independent, or weakly dependent on the chain's force [49].

It is worth mention that such a function is here assumed to describe only the active chains, i.e. those that are connected to the network in at least two points (dangling chains are considered to be inactive from the mechanics point of view) and that are collaborating to the load bearing mechanism of the material.

In the present paper we exclude any chain loss (failure) or chain gain (healing), so the probability of

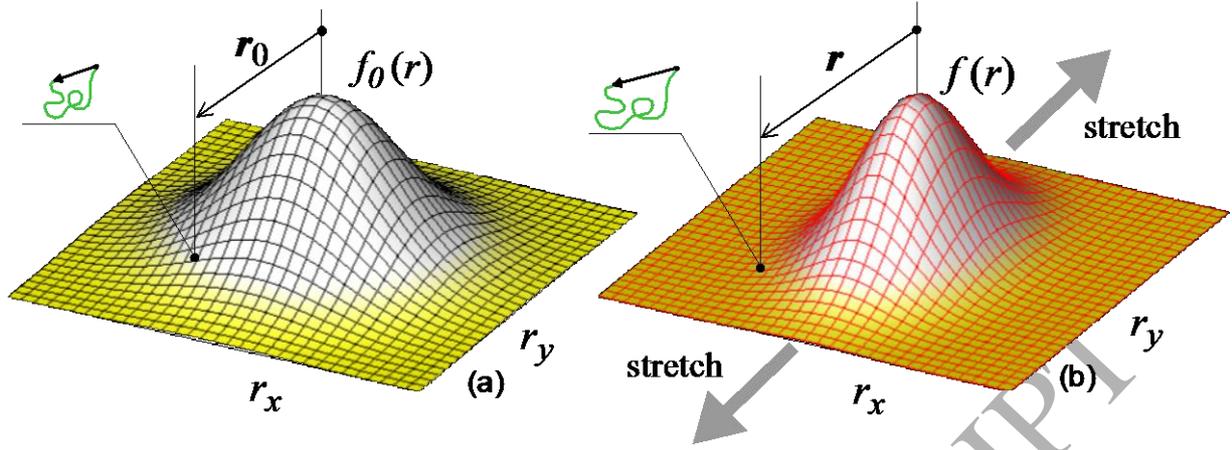
attached chains is always  $P_a = \langle f(\mathbf{r}, t) \rangle = 1$ , where  $\langle \blacksquare \rangle$  stands for  $\langle \blacksquare \rangle = \int_0^{2\pi} \int_0^\pi \left( \int_0^{Nb} \blacksquare r^2 dr \right) \sin \theta d\theta d\omega$  [39].

Assuming that the number of chains per unit volume  $c_a$  is large, the number of connected chains having a configuration between  $\mathbf{r}$  and  $\mathbf{r} + d\mathbf{r}$  within such a volume, can be expressed as

$$\varphi(\mathbf{r}, t) = c_a \cdot f(\mathbf{r}, t) \quad \text{with} \quad c_a = \langle \varphi \rangle \quad (4)$$

In general, according to the above discussion, the statistics of the chain arrangement requires to be described by the distribution function  $\varphi(\mathbf{r}) = \varphi(r, \theta, \omega)$  that provides the configuration of active chains (represented by the end-to-end distance  $r = |\mathbf{r}|$  and by its direction vector identified by the angles  $\theta$  and  $\omega$ ) throughout the configuration space. If the chains are randomly oriented in every direction of the 3D space (isotropic spatial distribution, typical of polymers in the stress-free state), the dependence upon the direction angles  $\theta, \omega$  can be neglected and the chain distribution is simply expressed through the function  $f_0(r)$ .

The elastic response of the polymer network to an applied deformation, entails the change of the above mentioned end-to-end vector distribution; the mechanical response of the material is thus fully described by the knowledge of the evolution of such a distribution function (Fig. 2). As stated above, the evolution of  $f(r, t)$  with the deformation must fulfil the conservation of the number of chains per unit volume if no chains are lost (chain failure),  $c_a = \text{const}$ . The deformation makes the distribution to change by inducing an elongating in the stretched direction and a narrowing in the transversal direction due to the isochoric nature of the deformation process; from a geometrical viewpoint, the chains conservation corresponds to that of the volume under the distribution function that must remain constant during the deformation process, i.e.  $\langle \varphi_0 \rangle = \langle \varphi \rangle = c_a \cdot \langle f_0(\mathbf{r}) \rangle = c_a$ .



**Figure 2.** (Color online) 2-D chain length distribution in the stress-free state,  $f_0(r)$  (a) and in a generic stretched state,  $f(r)$  (b).

Typically, the elastic energy stored in the single chain is made to depend on the actual end-to-end distance and so it is nonzero also in the reference state for all the chains for which  $\mathbf{r}_0 \neq \mathbf{0}$ , while it is zero only if  $\mathbf{r}_0 = \mathbf{0}$ ; according to the Langevin statistics of polymer network, valid also for chains under large deformations, the energy per single chain is given by [29]:

$$\psi = Nk_B T \cdot \left( \frac{\beta}{bN} r + \ln \frac{\beta}{\sinh \beta} \right), \quad \beta = \mathcal{L}^{-1} \left( \frac{r}{bN} \right) = \mathcal{L}^{-1} \left( \frac{\lambda}{\sqrt{N}} \right) \quad (5)$$

where  $k_B$  and  $T$  are the Boltzmann constant and the absolute temperature, respectively, while  $r = \lambda \cdot r_0$  and  $r_0$  are the end-to-end chain distance in the deformed and in the stress-free state, respectively, and  $\mathcal{L}(x)$  is the Langevin function defined as:  $\mathcal{L}(x) = \coth(x) - x^{-1}$  [29].

According to the above energy function, the force in the single chain is provided by:  $\mathbf{t}(N) = \partial\psi(\lambda, N)/\partial\mathbf{r}$ , where the dependence of  $\mathbf{t}$  on the chain length  $N$  has been emphasized,  $N$  being the number of Kuhn's segments.

It is worth noting that, for small deformations (i.e. for deformation levels far below the chain's limit stretch given by  $\lambda_{max} = \sqrt{N}$ , corresponding to a chain extension approaching its contour length  $Nb$ ),

the elastic energy stored in a single chain is typically expressed through a quadratic function of the end-to-end distance (Gaussian statistic), i.e.  $\psi = \frac{3k_B T}{2Nb^2} |\mathbf{r}|^2$ , while for chains undergoing large deformation the expression for  $\psi$  given by the Langevin statistics is more realistic.

The energy stored in the unit volume associated to the current stretched state of the polymer,  $\Psi$ , can thus be evaluated by integrating the energy of a single chain over the chains configuration space  $\Omega$ , spanning all the chains' lengths and orientations, i.e.:

$$\Psi = \int_{\Omega} \varphi(\mathbf{r}, t) \psi \, d\Omega = c_a \langle f(\mathbf{r}, t) \psi \rangle \quad (6)$$

As stated above, the mechanical energy corresponding to the undeformed network is nonzero, i.e.  $\Psi_0 = c_a \cdot \langle f_0 \psi \rangle > 0$  for  $\mathbf{F} = \mathbf{I}$  ( $\mathbf{F} = \partial \mathbf{x} / \partial \mathbf{X}$  is the deformation gradient tensor,  $\mathbf{x} = \omega(\mathbf{X})$  represents the deformed position of a point originally placed at  $\mathbf{X}$ , while  $\omega$  is the deformation function), while  $\langle f_0 \psi \rangle$ , evaluated through the initial distribution function  $f_0$ , corresponds to the lowest energy level, i.e. when all the chains are near rest. Thus, the potential energy per unit volume in the current (deformed) state must be evaluated as:

$$\Delta\Psi(t) = c_a \langle (f - f_0) \psi \rangle \quad (7)$$

that becomes identically zero in the undeformed state.

From the above equation, it is clear that the stored elastic energy is completely defined once the probability functions  $f, f_0$  and the current concentration of active chains are known. It's worth mention that this approach is valid as long as the network connectivity remains above the percolation threshold; indeed, as connection decreases and reaches the critical percolation value, a sudden drop in the network's mechanics takes place, as seen during the so-called reverse gelation phenomenon [50].

### 3.2 Stress state evaluation in a polymer network

We consider here the evolution of the distribution function  $\varphi(\mathbf{r}, t) = c_a f(\mathbf{r}, t)$  – representing the state of the network – induced by an applied deformation. Since the mechanical properties of a polymer network are related to its degree of cross-linking (here measured by  $c_a$ ) and to the statistical distribution of the chains end-to-end vectors, we must consider how they evolve and modify in time due to the applied deformation history. The Reynolds transport theorem can be used to express the variation within a given volume  $V$  of the current chain distribution. Since we assume that the total number of active chains does not change because of the deformation (no chains are lost or created) it reads [49]:

$$\frac{D}{Dt} \int_V c_a f(\mathbf{r}, t) dV = c_a \int_V \left[ \frac{\partial f(\mathbf{r}, t)}{\partial t} + \nabla f \cdot \dot{\mathbf{r}} + f(\nabla \cdot \dot{\mathbf{r}}) \right] dV = 0 \quad (8)$$

from which the time derivative of the function  $f(\mathbf{r}, t)$ ,  $\partial f(\mathbf{r}, t)/\partial t$ , can be localized at a given point of the chain space, identified by the end-to-end distance  $\mathbf{r}$ , as:

$$\frac{\partial f(\mathbf{r}, t)}{\partial t} = -\nabla f \cdot \dot{\mathbf{r}} - f(\nabla \cdot \dot{\mathbf{r}}) = -(\nabla f \otimes \mathbf{r}) : \mathbf{L} - f \mathbf{1} : \mathbf{L} = -(\nabla f \otimes \mathbf{r} + f \mathbf{1}) : \mathbf{L} \quad (9)$$

where the time derivative of  $\mathbf{r}$  has been written as  $\dot{\mathbf{r}} = \mathbf{L}\mathbf{r} = \dot{\mathbf{F}}\mathbf{F}^{-1}\mathbf{r} = \dot{\mathbf{F}}\mathbf{r}_0$ . We note that for an incompressible material  $\text{tr } \mathbf{L} = L_{ii} = \mathbf{1} : \mathbf{L} = 0$  ( $\mathbf{1}$  being the unit tensor) and so the second term in the above expression vanishes. From the observation of Eq. (9), it appears that the evolution of the distribution function  $f$  requires the evaluation of its material time derivative, so the function must be differentiable with respect to the chain space variables (components of the end-to-end vector) and to time.

Once the distribution function  $f(\mathbf{r}, t)$  is known at the current time instant  $t$ , the corresponding potential energy (7) – whose knowledge is sufficient to determine the stress state in the network – can be determined; the stress is expressed through the following deformation gradient derivative of the energy:

$$\mathbf{P}_{net}(t) = \frac{\partial \Delta \Psi(t)}{\partial \mathbf{F}} + p(t)J\mathbf{F}^{-T} = c_a \frac{\partial (\langle \psi(t) \rangle - \langle \psi \rangle_0)}{\partial \mathbf{F}} + p(t)J\mathbf{F}^{-T} \quad (10)$$

where  $\mathbf{P}_{net}$  is the nominal (i.e. evaluated in the reference configuration) first Piola stress tensor and  $p$  is the hydrostatic pressure, introduced as a Lagrange multiplier to enforce the incompressibility condition herein assumed for the polymer, being  $J = \det \mathbf{F}$ .

Let us now consider the term  $\partial (\langle \psi(t) \rangle - \langle \psi \rangle_0) / \partial \mathbf{F}$ ; it can be evaluated by considering that the distribution of chain lengths  $f(\mathbf{r}, t)$  is affected by the deformation, so

$$\mathbf{P}_{net}(t) = c_a \int_{\Omega} \frac{\partial [f(\mathbf{r}, t) - f_0(\mathbf{r})]}{\partial \mathbf{F}} \psi d\Omega + p(t)J\mathbf{F}^{-T} \quad (11)$$

The derivative of  $f(\mathbf{r}, t)$  with respect to  $\mathbf{F}$  required in (11), can be evaluated as [47]:

$$\frac{\partial f(\mathbf{r}, t)}{\partial \mathbf{F}} = \frac{\partial f(\mathbf{r}, t)}{\partial t} \frac{\partial t}{\partial \mathbf{F}} = \frac{\partial f(\mathbf{r}, t)}{\partial t} \dot{\mathbf{F}}^{-T} = - \left[ \mathbf{F}^{-1} \frac{\partial f(\mathbf{r}, t)}{\partial \mathbf{r}} \otimes \mathbf{r} + f(\mathbf{r}, t) \mathbf{F}^{-1} \right]^T \quad (12)$$

Finally, the nominal (first Piola) and the corresponding true (Cauchy) stress tensors become:

$$\mathbf{P}_{net}(t) = c_a \frac{\partial \langle \psi(t) \rangle}{\partial \mathbf{F}} + p\mathbf{F}^{-T} = \int_{\Omega} \frac{\partial f(\mathbf{r}, t)}{\partial \mathbf{F}} \psi d\Omega + p(t)\mathbf{F}^{-T} \quad (13)$$

$$\boldsymbol{\sigma}(t) = c_a J^{-1} \frac{\partial \langle \psi \rangle}{\partial \mathbf{F}} \mathbf{F}^T + p(t) = c_a \int_{\Omega} - \left[ \frac{\partial f(\mathbf{r}, t)}{\partial \mathbf{r}} \otimes \mathbf{r} + f(\mathbf{r}, t) \mathbf{1} \right] \psi d\Omega + p(t) \mathbf{1} \quad (14)$$

where it has been assumed that  $J = 1$  in order to fulfill the incompressibility constraint.

On the other hand, the Cauchy stress tensor  $\boldsymbol{\sigma}$  can be evaluated more simply as follows; let us consider the time derivative of the energy of the system in a given state:

$$\frac{\partial \Psi}{\partial t} = c_a \int_{\Omega} \dot{f}(\mathbf{r}, t) \psi(t) d\Omega = \left[ c_a \int_{\Omega} (-\nabla f(\mathbf{r}, t) \otimes \mathbf{r}) \psi(t) d\Omega \right] : \mathbf{L} \quad (15)$$

where  $\dot{f}$  has been expressed through (9). By using the divergence theorem and assuming the boundary terms to vanish, we have

$$\frac{\partial \Psi}{\partial \mathbf{t}} = \left[ c_a \int_{\Omega} f(\mathbf{r}, t) [\nabla \psi(\mathbf{t}) \otimes \mathbf{r}] d\Omega \right] : \mathbf{L} = \left[ c_a \int_{\Omega} f(\mathbf{r}, t) \mathbf{t} \otimes \mathbf{r} d\Omega \right] : \mathbf{L} \quad (16)$$

In the above expression the term  $\nabla \psi = d\psi/dr = \mathbf{t}$  represents the force in the chain [32]. Now, by considering that the stress state can be obtained through Eqs (10), (14), and adopting the chain rule, we finally obtain the Cauchy stress tensor:

$$\begin{aligned} \boldsymbol{\sigma}(\mathbf{t}) &= J^{-1} \mathbf{P}_{net} \mathbf{F}^T = J^{-1} \left( \frac{\partial \Delta \Psi}{\partial \mathbf{t}} \frac{\partial \mathbf{t}}{\partial \mathbf{F}} \right) \mathbf{F}^T = c_a \int_{\Omega} [f(\mathbf{r}, t) - f_0(\mathbf{r}, t)] \mathbf{t}(\mathbf{r}, t) \otimes \mathbf{r} d\Omega + p(t) \mathbf{1} = \\ &= \int_{\Omega} [\varphi(\mathbf{r}, t) - \varphi_0(\mathbf{r}, t)] \mathbf{t}(\mathbf{r}, t) \otimes \mathbf{r} d\Omega + p(t) \mathbf{1} \end{aligned} \quad (17)$$

where the hydrostatic stress tensor accounts for the incompressibility constraint. By adopting the Langevin model, suitable for both moderate or large deformations, the chain force  $\mathbf{t}$  in (17) results to be explicitly related to its stretch as follows:

$$\mathbf{t}(\mathbf{r}, t) = \frac{\partial \psi(\mathbf{t})}{\partial \mathbf{r}} = \frac{1}{b\sqrt{n}} \frac{\partial \psi}{\partial \lambda} = \frac{\mathbf{r}}{|\mathbf{r}|} \cdot \frac{k_B T}{b} \cdot \mathcal{L}^{-1} \left( \frac{\lambda}{\sqrt{N}} \right) \quad (18)$$

where the term  $\mathbf{r}/|\mathbf{r}|$  identifies the unit vector in the direction of the force  $\mathbf{t}$ . The expression (17) for the true stress is more suitable for our purpose of evaluating the effect of the switchable molecules, since it is very easy to account for the chain force relaxation induced by the molecule switching once the value of the corresponding relaxed deformation is known.

### 3.3 Mechanics of polymer swelling

Since we consider switchable molecules sensible to chemical actions, such as pH change, the presence of a solvent phase that permeates the polymer network has to be assumed. The fluid uptake by a polymer (namely a gel) is a well-known phenomenon and is herein recalled in term of its mechanical aspects; it will be subsequently taken into account in all the following formulation.

Polymers are usually incompressible, so when they are prone to swelling in presence of a solvent, their volume change is due only to the fluid absorption. The mechanics of the polymer swelling process can be described in term of the total energy of the system that is now written as

$$\Psi_t(\mathbf{F}, C_s) = \Psi(\mathbf{F}) + \Psi_{mix}(C_s) + \Psi_{ext} + p(J - 1 - v_s C_s) \quad (19)$$

where  $\Psi$  is the standard elastic energy,  $\Psi_{ext}$  is the energy associated to stress state induced by the external actions, and the last term enforces the material's volume change to be equal to the volume of the fluid entered into the network; the deformation gradient tensor must obey now the new constraint equation  $\det \mathbf{F} = J = J_{mix} = (1 + v_s C_s)$ . According to the above volumetric change, the deformation gradient tensor can be assumed to be multiplicatively decomposed as  $\mathbf{F} = \mathbf{F}_e \cdot J_{mix}^{-1/3} \mathbf{1}$ ,  $\mathbf{F}_e$  being the purely mechanics external stretch applied to the material and  $J_{mix}^{-1/3} \mathbf{1}$  the hydrostatic deformation gradient tensor associated to the fluid absorption, also called growth tensor in the literature [51, 52].

Finally,  $\Psi_{mix}(C_s)$  is the energy associated with the polymer-solvent mixing, depending of the actual solvent concentration  $C_s$  in the polymer. It is expressed as [53]:

$$\Psi_{mix} = -\frac{k_B T}{V_s} \cdot \left[ (J - 1) \ln \left( 1 + \frac{1}{J} \right) - \frac{\chi}{J} \right] = -\frac{k_B T}{V_s} \cdot \left[ V_s C_s \ln \left( 1 + \frac{1}{V_s C_s} \right) - \frac{\chi}{1 + V_s C_s} \right] \quad (20)$$

$V_s, C_s$  being the volume of a mole of solvent and the concentration of solvent entered in the unit volume of polymer in the reference state and  $\chi$  is the Flory-Huggins parameter, respectively. The pressure  $p$  in (19) is the osmotic pressure exerted by the fluid on the network, considered here as a Langrange multiplier enabling to fulfill the volumetric constraint  $J = J_{mix}$ .

Following the classic Flory-Rehner theory [31], the free energy of the coupled system made of polymer and solvent is the sum of the network's free energy  $\Psi$  and of the potential energy of the solid-fluid solution,  $\Psi_{mix}$ . The chemical potential  $\Pi$ , which is responsible of the motion of the solvent molecules, can be obtained as  $\Pi = \partial \Psi_{mix} / \partial C_s$ .

The equilibrium equations and the solvent balance can be readily obtained as Euler equations by the energy derivation w.r.t. the two field variables. The condition  $\partial \Psi_t / \partial \mathbf{F} = 0$  leads to the equilibrium

equation in the reference configuration; correspondingly, in the current configuration it reads  $\boldsymbol{\sigma} - p\mathbf{1} = \boldsymbol{\sigma}_{ext}$ , where  $\boldsymbol{\sigma}$  is the true stress tensor computed according to eq. (17) and  $\boldsymbol{\sigma}_{ext}$  is the external true stress.

In order to obtain the evolution of the solvent concentration, a constitutive relation between the chemical potential and the solvent flux is required; a possible choice is provided by theory developed by Hong et al. [53], that relates the solvent flux to the gradient of the chemical potential through a nonlinear mobility tensor. However, the application of such a theory is not trivial when a single material point is considered. Instead, in this paper we adopt the theory proposed by Tanaka [54], where the energy dissipation due to the fluid-polymer friction is introduced. The loss of energy can be written using a dissipation function as  $R = \frac{1}{2}\zeta\dot{C}_s$ , where  $\zeta$  can be interpreted as a friction coefficient. The theory has been proposed under the assumption of small deformation, so the friction coefficient is considered to be a material property. The solvent balance is obtained from [55]

$$\frac{\partial \Psi_t}{\partial C_s} = \frac{\partial R}{\partial \dot{C}_s} \rightarrow \Pi + v_s p = \zeta \dot{C}_s \quad (21)$$

physically, this relation means that the balance between the chemical potential and the osmotic pressure determines the time evolution of the solvent concentration in the material point.

#### 4. Instability approach to molecule switching

In order to derive the concept of stability within a continuous solid at the local level, let us consider the dynamic linear momentum balance in presence of inertia actions and viscous effects; in the reference configuration it reads:

$$P_{ij,j} + \rho_0 b_i - \eta \frac{D\omega}{Dt} - \rho_0 \frac{D^2\omega}{Dt^2} = 0 \quad (22)$$

$\rho_0, \eta$  being the mass density in the undeformed configuration and the coefficient of viscous damping, respectively. The stability condition can be studied by perturbing the above dynamic equilibrium

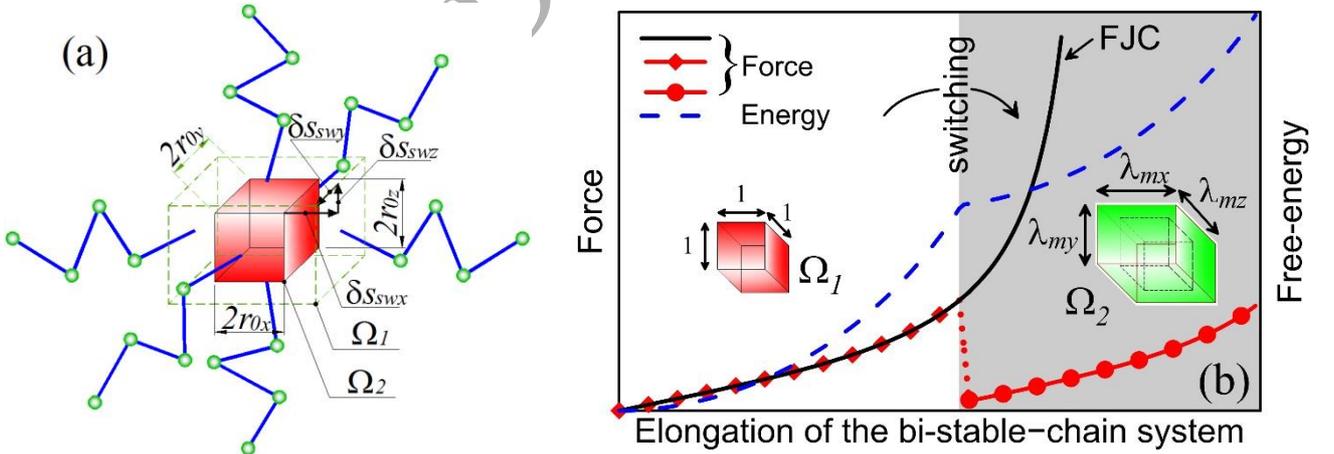
equations through the variation in a small time interval,  $\dot{\omega}$ , of the deformation function  $\omega$ , evaluated by assuming that the perturbation leaves the applied forces and the network distribution unchanged (i.e.  $\dot{f} = 0$ ); the perturbation of (22) is  $\dot{P}_{ij,j} - \eta \frac{D\dot{\omega}}{Dt} - \rho_0 \frac{D^2\dot{\omega}}{Dt^2} = 0$ , while the corresponding variation of the Piola stress becomes:

$$\dot{P}_{ij} = \frac{\partial^2 \Delta \Psi}{\partial F_{ij} \partial F_{hk}} \frac{\partial F_{hk}}{\partial t} \quad (23)$$

By referring to the current configuration, the variation of the true stress tensor (17) can be expressed as:

$$\dot{\sigma}_{ij}(t) = \dot{P}_{ih}(t) F_{jh} = c_a \langle (f - f_0) \dot{t}_i \cdot r_j \rangle \quad (24)$$

where the rate of the chain's force is defined as  $\dot{t} = \frac{\partial \psi}{\partial r} = \frac{1}{b\sqrt{n}} \frac{\partial \psi}{\partial \lambda} = \frac{r}{|r|} \cdot \frac{k_B T}{b} \cdot \mathcal{L}^{-1} \left( \frac{\lambda}{\sqrt{N}} \right)$ ; in our case it is due to the molecule switching, responsible for the localization of the deformation, corresponding to a jump in the velocity gradient field [56].



**Figure 3.** (Color online) Scheme of the switching of the molecule attached to polymer chains (a); bistable molecule-chain force vs elongation and corresponding free energy of the system (b).

In Fig. 3a the geometrical transformation of the molecule during switching is schematically illustrated; the molecule is assumed to expand along the three Cartesian coordinate axes by increasing its initial size from  $(2r_{0x} \times 2r_{0y} \times 2r_{0z})$  to  $[2(r_{0x} + \delta s_{swx}) \times 2(r_{0y} + \delta s_{swy}) \times 2(r_{0z} + \delta s_{swz})]$ ; the corresponding force-elongation and the free energy-elongation graphs are shown in Fig. 3b, where the two stable configurations of the molecule have been indicated. In Fig. 3b the bistable molecule-chain force vs elongation and the corresponding free energy are shown; the molecule switching entails a snap-through-like response, while the energy function  $\psi$  appears to be non-convex. This corresponds to the so-called material or pointwise instability criterion; from the macroscopic viewpoint (global stability), the stability must be assessed through the so-called quasiconvex envelope of  $\psi$ . However, this discussion is beyond the scope of the present study since we are not interested in the global stability of the polymeric material and will be not considered here; interested readers can refer to specialized literature for further information [57].

#### 4.1 Mechanisms inducing molecule switching

In the case of a polymer characterized by a single network having chains of equal length  $N$  with embedded switchable molecules, the change of energy per unit volume of such a material  $\Delta\Psi_M$  can be expressed as:

$$\Delta\Psi_M = \langle \Delta\varphi[(1 - \varrho)\psi - h(\mathbf{F}, C_s) \varrho \psi_{sw}] \rangle \quad (25)$$

where  $\varrho^{(N)} = \langle \varrho_r^{(N)} \rangle$  is the volume fraction of the switchable molecules contained in the material ( $\varrho_r^{(N)}$  being the volume fraction, for the network  $N$ , of molecules attached to chains of length  $r$ );  $h^{(N)}(\mathbf{F}, C_s)$  indicates the fraction of switched molecules among the total volume fraction  $\varrho^{(N)}$  present in the considered network, for a given deformation gradient tensor  $\mathbf{F}$  and solvent concentration  $C_s$ . Since the switched or unswitched state of the molecule depends on the force acting on it (or equivalently to the force acting on the chain to which the molecule is attached), and since, for a given  $N$ , such a force for

a given  $\mathbf{F}$  depends on the chain end-to-end distance  $r$ , the fraction of switched molecules within the network can be evaluated as:

$$h^{(N)}(\mathbf{F}, C_s) = \langle h_r^{(N)}(\mathbf{F}, C_s) \cdot f \rangle \quad (26)$$

where  $h_r^{(N)}$  represents the fraction of molecules transformed into their new conformation, joined to the chains with end-to-end distance  $r$ , among those belonging to the network  $N$  in turn.

Since the equilibrium between the switched (*sw*) - unswitched (*unsw*) states has a kinetic nature, the volume fraction of switched molecules, connected to the chains with a given chain length  $r$  ( $q_{r,sw}$ ), must obey the well-known balance reaction law, analytically described through the standard kinetic equation [58, 59]:

$$\frac{dq_{r,sw}^{(N)}}{dt} = k_A \cdot q_{r,unsw}^{(N)} - k_D \cdot q_{r,sw}^{(N)} \quad (27)$$

where  $q_r^{(N)} = q_{r,sw}^{(N)} + q_{r,unsw}^{(N)}$  is the volume fraction of the switchable molecules connected to the polymer's chains with end-to-end distance  $r$ , within the network with length  $N$ ,  $q_{r,unsw}^{(N)} = (1 - h_r^{(N)})q_r^{(N)}$  is the volume fraction of the unswitched molecules and  $k_A, k_D$  are the activation and deactivation reaction rates of the molecules, respectively.

Since the volume fraction of switched molecules can be written as  $q_{r,sw}^{(N)}(\mathbf{F}, C_s) = h_r^{(N)}(\mathbf{F}, C_s) \cdot q_r^{(N)}$ , the above relation can be also expressed as:

$$\frac{dh_r^{(N)}}{dt} = k_A - (k_A + k_D) \cdot h_r^{(N)} \quad (28)$$

The function  $h_r^{(N)}(\mathbf{F}, C_s)$  provides the time evolution of the corresponding fraction of activated molecules joined to chains of length  $r$ , with respect to all the switchable molecules contained in the reference volume. The reaction rates  $k_A, k_D$  in (28) are related to the energy barrier between the two

stable states ( $\Omega_1$  and  $\Omega_2$ , Fig. 1), and are affected by the force acting on the molecule. Typically, the reactions rates are expressed through the Arrhenius equation; for a force-free chain the reaction rates  $k_{A0}, k_{D0}$  are given by:

$$k_{A0} = C_A \cdot \exp\left(-\frac{\Delta G_{A0}}{k_B T}\right), \quad k_{D0} = C_D \cdot \exp\left(-\frac{\Delta G_{D0}}{k_B T}\right) \quad (29)$$

where  $C_A, C_D$  are the so-called frequency factors [15], and  $\Delta G_{A0}$  and  $\Delta G_{D0}$  are the energies required to move from the unswitched to the switched state and vice versa, respectively. The effect of a mechanical force acting on the polymer chain must be accounted for in (29) since the switching transformation (typically consisting in a molecule expansion) is favored by the presence of a mechanical stress and by the presence of some chemical species; their influence can be quantified through a proper reduction (increase) of  $\Delta G_{A0}$  ( $\Delta G_{D0}$ ) expressed as:

$$\Delta G_A = \Delta G_{A0} - t_p \cdot \delta s_{sw} - \Delta G_{A0} \cdot \frac{C_s}{\hat{C}_s}, \quad \Delta G_D = \Delta G_{D0} + t_p \cdot \delta s_{sw} + \Delta G_{D0} \cdot \frac{C_s}{\hat{C}_s} \quad (30)$$

where  $t_p$  is the force in the polymer chain connected to the switchable molecule, and  $\delta s_{sw}$  represents the size variation (displacement) of the molecule from the unswitched to the switched state.

Analogously, the presence of a solvent triggering the forward switching mechanism and hindering the backward one, can be quantified through the actual solvent concentration  $C_s$  and the solvent concentration capable of switching all the molecules present in the unit volume of the material,  $\hat{C}_s$ . It is worth noting that, since the volume change in the polymer is due only to the swelling phenomenon, the solvent concentration can be expressed as:  $C_s = \frac{J_{mix} - 1}{v_s}$  (see sect. 3.3).

By substituting (30) in (29), the amended energy barriers become:

$$k_A = k_{A0} \cdot \exp\left(\frac{t_p \cdot \delta s_m}{k_B \cdot T}\right) \cdot \exp\left(\frac{\Delta G_{A0}}{k_B \cdot T} \cdot \frac{C_s}{\hat{C}_s}\right), \quad k_D = k_{D0} \cdot \exp\left(-\frac{t_p \cdot \delta s_m}{k_B T}\right) \cdot \exp\left(-\frac{\Delta G_{D0}}{k_B T} \cdot \frac{C_s}{\hat{C}_s}\right) \quad (31)$$

The above expressions represent the more general case in which the switching mechanism is favored also by the presence of a chemical action (such as in the case of pH-sensible switching molecules), so the energy barriers (30) must be further corrected by accounting for such an effect [59].

By keeping constant the force applied to the polymer chain and the solvent concentration, the reaction rates  $k_A, k_D$  are constant, and the solution of Eq. (28) becomes:

$$h_r^{(N)}(t) = \frac{k_A}{k_A + k_D} [1 - e^{-(k_A+k_D)t}] \quad (32)$$

while the corresponding solution in the steady state ( $t \rightarrow \infty$ ) is  $h_{r(\infty)}^{(N)} = \lim_{t \rightarrow \infty} h_r^{(N)}(t) = k_A/(k_A + k_D)$ .

The presence of the solvent within the network, implies that the mechanism of fluid uptake (swelling) has occurred in the material; such a phenomenon must be also considered from the mechanical view point since it induces an additional stress state in the material. This aspect has been considered in sect. 3.3 and will be further extended in sect. 5 where the continuum approach to the problem is developed.

#### 4.2 Polymer chain deformation in presence of a switchable molecule

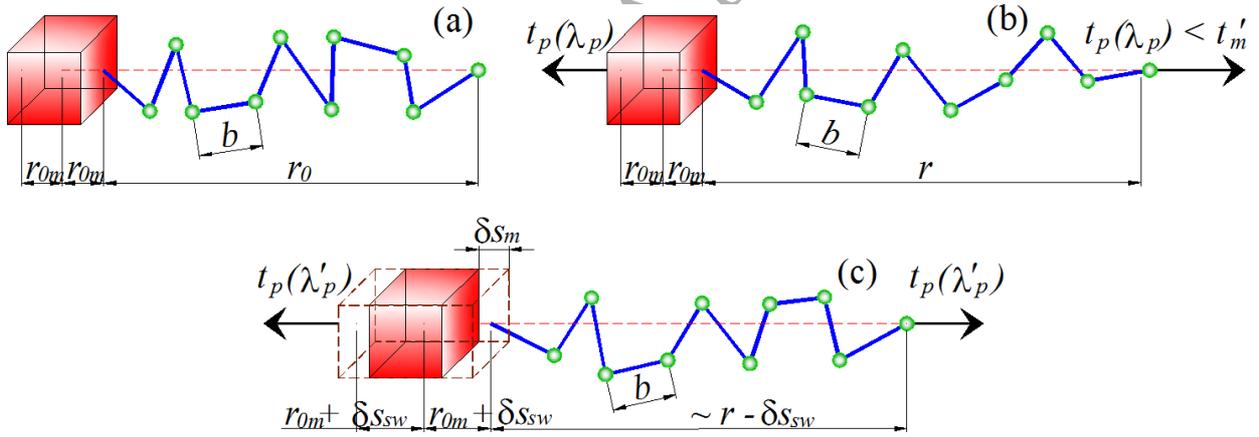
The molecule switching herein considered corresponds to an unstable phenomenon taking place when the energy barrier existing between the two stable states is overcome; the required energy can be provided, beyond the presence of a sufficiently high thermal fluctuations in the material's microstructure, by mechanical or chemical stimuli. Such a switching mechanism entails a variation of the end-to-end distance of the chain containing the unstable molecule, so the chain force changes abruptly because of the chain relaxation. Let us consider a single polymeric chain joined with a switchable molecule: under an external force the chain elongates starting from its initial end-to-end distance  $r_0 = |\mathbf{r}_0|$  to the current value  $r = |\mathbf{r}|$  so the stretch is equal to  $\lambda_p = r/r_0$ .

According to the random walk theory, the average end-to-end distance of a chain made of  $N$  Kuhn's segments of length  $b$  each is  $r_0 = b\sqrt{N}$ . Before the instability occurs, the polymer chain's stretch is given by  $\lambda_p$ , while after switching the chain's stretch reduces to:

$$\lambda'_p = \lambda_p - \frac{r_{0m}}{r_0}(\lambda_m - 1) = \lambda_p - (\lambda_m - 1)\alpha \quad (33)$$

being  $\alpha = r_{0m}/r_0$  the initial molecule to chain length ratio ( $r_{0m}$  being the initial molecule size), while  $\lambda_m = 1 + \frac{\delta s_m}{r_{0m}}$  is the stretch of the molecule itself after the unstable switching has occurred.

By assuming that the switchable molecule in its initial conformation ( $\lambda_m = 1$ ) has a small size compared to the end-to-end distance of the polymer chain,  $r_{0m} \ll r_0$  (i.e.  $\alpha \cong 0$ ), the chain's stretch corresponds to that without any attached molecule, i.e.  $\lambda'_p \cong \lambda_p$ .



**Figure 4.** (Color online) Scheme of the switchable molecule jointed with a polymeric chain. Stress-free state (a), loaded state before instability (b) and chain's relaxed state after switching (c).

We make use of the affine deformation hypothesis, according to which the chains take the deformation of the continuum where they are immersed in [60]; by assuming the material to be deformed according to the macroscopic right Cauchy–Green deformation tensor expressed as  $\mathbf{C} = \mathbf{U}^2 = \Lambda_i^2 \mathbf{e}_i \otimes \mathbf{e}_i$ ,

( $i = 1, 2, 3$ ,  $\Lambda_i$  being the three principal stretches along the Cartesian co-ordinate axes), the stretch in the chains is given by  $\lambda = \lambda_p = \frac{|F r_0|}{|r_0|}$ .

If the polymer is poly-dispersed, i.e. if it is made of different networks (each one characterized by chains with a given number of Kuhn's segments  $N$ ), whose statistical distribution is given by the probability function  $q(N)$ , the force arising in the chain belonging to the  $i$ -th network characterized by chains with  $N_i$  segments, is given by:

$$|\mathbf{t}(N_i)| = \frac{k_B T}{b} \cdot \mathcal{L}^{-1} \left( \frac{\lambda}{\sqrt{N_i}} \right) \quad (34)$$

and the average force in the polymer network is given by:

$$\bar{t} = \int_{N_{min}}^{+\infty} |\mathbf{t}(N)| q(N) dN, \quad \text{with} \quad \int_{N_{min}}^{+\infty} q(N) dN = 1 \quad (35)$$

The effective stretch in the generic chain connected to a switchable molecule is given by

$$\lambda'_p(N) = \lambda_p(N) - (\lambda_m - 1) \alpha \mathcal{H}(\lambda, r, n_s) \quad (36)$$

where the step function  $\mathcal{H}(\lambda, r, n_s)$ , accounting for the unswitched ( $\mathcal{H} = 0$ ) or switched ( $\mathcal{H} = 1$ ) state of the molecule, is defined as:

$$\mathcal{H}(\lambda, r, n_s) = H(t_p) + H(n_s) - H(t_p) \cdot H(n_s) \quad (37)$$

$$H(t_p) = \begin{cases} 0 & \text{if } t_p < t'_m \\ 1 & \text{if } t_p \geq t'_m \end{cases}, \quad H(n_s) = \begin{cases} 0 & \text{if } n_s < S_r \\ 1 & \text{if } n_s \geq S_r \end{cases}$$

where  $t_p(N) = |\mathbf{t}(N)|$  indicates the force arising in the chain with  $N$  segments under the stretch  $\lambda$ .

In the above expression  $H(t_p)$  is the Heaviside function defined according to the threshold force  $t'_m$  required to switch the molecule, and  $H(n_s)$  is the Heaviside function defined on the basis of the current number  $n_s$  of solvent molecules available for one switchable molecule, and on the

stoichiometric ratio  $S_r$  (number of solvent moles necessary to induce the switching of one molecule). The last step function  $H(n_s)$  becomes equal to 1.0 if the actual  $n_s$  is greater than  $S_r$ .

## 5. Polymers with embedded switchable molecules: a continuum model

Moving up to the continuum scale, the kinematic effect of the molecules switching (here assumed to be kinematically an expansion phenomenon) can be quantified through the corresponding quantity at the nanoscale. Let us assume that the switchable molecules pass from their initial to the switched state by expanding along the molecule's principal directions (defining the local orthogonal reference system 1, 2, 3), according to the stretches  $\lambda_{m1}, \lambda_{m2}, \lambda_{m3}$ . The volumetric expansion ratio of the single molecule is given by:

$$J_m = \det \mathbf{F}_m = \lambda_{m1} \lambda_{m2} \lambda_{m3} \quad (38)$$

where  $\mathbf{F}_m$  is the deformation gradient tensor of a material made only of uniformly oriented switchable molecules. On the other hand, in a real polymer the switchable molecules are randomly dispersed throughout the network, and so it is reasonable to adopt a uniform probability distribution for their orientation in the 3D space. The deformation gradient tensor of a continuum material made only of randomly oriented switchable molecules, can be simply obtained through the integral over all the possible orientations within the solid angle:

$$\bar{\mathbf{F}}_m = \frac{1}{S} \int_S \mathbf{A} \cdot \mathbf{F}_m \cdot \mathbf{A}^T dS = \frac{\lambda_{m1} + \lambda_{m2} + \lambda_{m3}}{3} \mathbf{1} = \lambda_m \mathbf{1} \quad (39)$$

where  $S$  is the surface of the sphere with unit radius, and  $\mathbf{A}$  is the three-dimensional rotation operator. Due to the molecules switching, the material undergoes a hydrostatic-like stretch whose amount is given by  $\lambda_m = (\lambda_{m1} + \lambda_{m2} + \lambda_{m3})/3$ ; the corresponding volume expansion ratio is given by:

$$\bar{J}_m = \det \bar{\mathbf{F}}_m = \lambda_m^3 = \left( \frac{\lambda_{m1} + \lambda_{m2} + \lambda_{m3}}{3} \right)^3 > 1 \quad (40)$$

while, the reduced stretch  $\lambda'_p$  in the polymer chain (see eq. (33)) becomes:

$$\lambda'_p = \lambda_p - (\lambda_m - 1)\alpha \quad (41)$$

Similarly to what made at the nanoscale in the previous sections, the mechanical continuum model of a polymer containing switchable molecules can be developed by adopting an energetic approach. In the following we assume that: *i*) the polymer's network is made of chains linked together only through switchable molecules, *ii*) the polymer is incompressible in the dry state (i.e. the mechanical stresses cannot induce any volume change), *iii*) an applied deformation changes the volume fraction of the fluid uptaken by the material, and *iv*) the molecule switching induces a volumetric deformation of the polymer without influencing the swelling mechanism.

The variation of the mechanical energy per unit volume of the polymer, evaluated from the initial stress-free and unswollen state to the current one,  $\Delta\Psi_m$ , can be written by adding up the contribution coming from the deformation induced by mechanical actions,  $\Delta\Psi$ , the contribution to the switching mechanism of the switchable molecules,  $\Psi_{sw}$ , and the contribution produced by the polymer fluid uptake,  $\Psi_{mix}$  (swollen state). For sake of generality, it is here assumed that the polymer is composed by several networks (i.e. by chains with different numbers of Kuhn's segments  $N$ , whose distribution in the material is described by the probability function  $q(N)$ ), and so Eq. (25) takes the form:

$$\begin{aligned} \Delta\Psi_M &= \int_{N_{min}}^{+\infty} q(N) \langle \Delta\varphi[(1 - \varrho)\psi - h(\mathbf{F}, C_s) \varrho \psi_{sw}] \rangle dN + (1 - \varrho)\Psi_{mix} = \\ &= (1 - \varrho)(\overline{\Delta\Psi} + \Psi_{mix}) - [\bar{h}(\mathbf{F}, C_s) \varrho] \Psi_{sw} \end{aligned} \quad (42)$$

where the integral over all the networks have been explicitly indicated.

In the above relation the purely mechanical and the swelling energy are both assumed to be related to the material volume fraction  $1 - \varrho$  of the polymer, i.e. the polymer's volume fraction made of switchable molecules is assumed to be not involved in these two deformation mechanisms. In (42)  $\varrho_{sw} = \bar{h} \cdot \varrho$  is the effective volume fraction of the switched molecules among all the networks and chain end-to-end distances, while  $\bar{h}(\mathbf{F}, C_s)$ ,  $\overline{\Delta\Psi}$  are:

$$\bar{h}(\mathbf{F}, C_s) = \int_{N_{min}}^{+\infty} h^{(N)}(\mathbf{F}, C_s) q(N) dN = \int_{N_{min}}^{+\infty} q(N) \langle h_r^{(N)}(\mathbf{F}, C_s) \cdot f \rangle dN \quad (43a)$$

$$\overline{\Delta\Psi} = \int_{N_{min}}^{+\infty} q(N) \langle \Delta\varphi \psi \rangle dN \quad (43b)$$

i.e.  $\bar{h}$  is the average fraction of molecules switched in their expanded state, among the total volume fraction  $\varrho$ , and  $\overline{\Delta\Psi}$  the energy variation of all the networks. Finally, the functions  $h_r^{(N)}(\mathbf{F}, C_s)$  in (43a) comes from the solution of the differential equation (28).

Since it is reasonable to assume that during the polymerization of the material, the probability that one switchable molecule is attached to a specific chain of length  $r$  is independent by such a length, the volume fraction related to a single network  $\varrho^{(N)}$  can be expressed as  $\varrho^{(N)} = \langle \varrho_r^{(N)} \cdot f \rangle$ , while the total volume fraction is  $\varrho = \int_{N_{min}}^{+\infty} \varrho^{(N)} q(N) dN$ .

The variation of the purely mechanical energy of the network,  $\Delta\Psi$ , is given by Eq. (7) where  $J \cong 1$  is the polymer volume change due to external mechanical actions, evaluated by neglecting both the expansion of the switchable molecules and swelling; the corresponding stress state is given by Eq. (17). The deformation energy associated to the swelling can be written by assuming that the polymer's volume change due to the molecule switching does not influence significantly the swelling phenomenon; the overall volumetric fraction is thus related to the current material's volume fraction  $\varrho_m$  (including both the polymer and the switchable molecules) according to the relation

$$\varrho_m = \frac{\varrho J_{sw} + (1 - \varrho)}{\varrho J_{sw} + (1 - \varrho) J_{mix}} \quad (44)$$

while  $\varrho_m + \varrho_s = 1$ ,  $\varrho_s = C_s v_s$  being the solvent volume fraction.

Finally, the energy decrease per unit volume of material made of switchable molecules due to the switching phenomenon, is given by [61]:

$$\Psi_{sw}(\mathbf{F}, C_s) = -\frac{A_n}{V_m} (f'_m \delta s_{sw}) \cong -\frac{A_n}{V_m} w \quad (45)$$

where  $A_n$  is the Avogadro number,  $V_m$  is the volume one mole of switchable molecules, and  $w = t'_m \delta s_m$  is the energy release per single molecule, evaluated by assuming that during the switching mechanism the force in the connected chain remains nearly constant and equal to the threshold switching force,  $t'_m$ .

Since the energy released per unit volume due to the switching mechanism,  $\Psi_{sw}$ , is provided by the surrounding stretched network and, eventually, by the chemical agent, the final energy stored in the material (42) reduces; in fact, by assuming that the switching mechanism corresponds to a geometrical expansion of the molecules, the network stress state  $\mathbf{P}_{net}$  relaxes to  $\mathbf{P}'_{net}$ :

$$\begin{aligned} \mathbf{P}'_{net} &= \frac{\partial[(1 - \varrho)\Delta\Psi + \bar{h}(\mathbf{F}, C_s) \varrho \Psi_{sw}]}{\partial \mathbf{F}} = \\ &= \left\{ c_a \int_{N_{min}}^{+\infty} q(N) \int_{\Omega} [f(\mathbf{r}) - f_0(\mathbf{r})] \left[ (h_r^{(N)} \varrho^{(N)}) \mathbf{t}' + (1 - h_r^{(N)} \varrho^{(N)}) \mathbf{t} \right] \otimes \mathbf{r} d\Omega dN \right\} \mathbf{F}^{-T} \\ &\quad + pJ\mathbf{F}^{-T} \end{aligned} \quad (46)$$

with a corresponding decrease of the stored energy, while  $\mathbf{t}' = \mathbf{t}'(N, r) = \frac{r}{|r|} \cdot \frac{k_B T}{b} \cdot \mathcal{L}^{-1}\left(\frac{\lambda'_p}{\sqrt{N}}\right)$  is the relaxed force in the chain obtained by using the reduced stretch  $\lambda'_p$  given by eq. (41).

From the above equation, it can be recognized that the relaxation of the stress tensor induced by the molecules switching,  $\mathbf{P}_{net} - \mathbf{P}'_{net}$ , can be written as:

$$\begin{aligned} \mathbf{P}_{net} - \mathbf{P}'_{net} &= \frac{\partial [\bar{h}(\mathbf{F}, C_s) \varrho \Psi_{sw}]}{\partial \mathbf{F}} = \\ &= \left\{ c_a \int_{N_{min}}^{+\infty} q(N) \int_{\Omega} [f(\mathbf{r}) - f_0(\mathbf{r})] (h_r^{(N)} \varrho^{(N)}) (\mathbf{t} - \mathbf{t}') \otimes \mathbf{r} d\Omega dN \right\} \mathbf{F}^{-T} \end{aligned} \quad (47)$$

Finally, the equilibrium equations and the Neumann boundary conditions, written in the reference state,  $\Omega_0$ , are given by:

$$\begin{aligned} \text{Div}(\mathbf{P}'_{net} + \mathbf{P}_{mix} + \mathbf{P}_{sw}) + \mathbf{B} &= \mathbf{0} \text{ in } \Omega_0 \\ (\mathbf{P}'_{net} + \mathbf{P}_{mix} + \mathbf{P}_{sw}) \cdot \mathbf{N} &= \mathbf{T}_{ext} \text{ on } \partial\Omega_0 \end{aligned} \quad (48)$$

where  $\mathbf{B}$ ,  $\mathbf{T}_{ext}$  are the vector of the volume and traction forces, respectively, and  $\mathbf{N}$  is the normal to the undeformed boundary of the solid.

## 6. Simulations

The above developed theoretical model is now used to simulate some problems involving the mechanical macroscopic response of polymers containing switchable molecules under the action of external mechanical stress or of a chemical agent contained in a solvent.

The examples are carried out by solving the governing equations referred to a single point of the material, assumed to be representative of the volume of polymer under study. In particular, *i*) we use the evolution law (Eq. (9)) to update the chain distribution function  $f(\mathbf{r})$  starting from the initial reference one  $f_0(\mathbf{r})$  of the polymer, and by using the given applied velocity deformation gradient  $\mathbf{L}$ ; *ii*) once the current  $f(\mathbf{r})$  is known, the stress state can be evaluated through the use of Eq. (17), where the hydrostatic stress  $p$  is determined from the boundary conditions of the problem in turn. Once  $p$  is

known, *iii*) the solvent concentration  $C_s$  in the point under study is obtained by using the evolution Eq. (21) and its initial value  $C_s(t = 0)$ . For each network and every chain end-to-end vector  $\mathbf{r}$ , *iv*) the force  $\mathbf{t}(\mathbf{r}, t)$  in the chain is determined by using Eq. (18) and, *v*) after updating (through Eq. (29)) the coefficients of the Arrhenius Eq. (28), *vi*) the fraction  $h_r^{(N)}$  of switched molecules is updated. The above described procedure is repeated through the time steps until the whole deformation history has been completed.

Three parametric studies are firstly reported and discussed in order to underline the role played by the different mechano-chemical involved parameters and, finally, an experimental test reported in the literature, related to the response of a PMMA sample added with spiropyran mechanophores under mechanical actions, is simulated and the obtained results compared.

The material's parameters, assumed to be the same for all the presented examples except when differently specified, are the following: polymer's shear modulus  $\mu = 2$  MPa, absolute temperature  $T = 300$  K, Flory-Huggins parameter  $\chi = 0.4$  (the assumed Flory's parameter corresponds to a good polymer-solvent affinity), conformational change characterized by a size variation of the switchable molecule of  $\delta s_{sw} = 10b$  occurring with the same amount along the three Cartesian coordinate axes (so  $\lambda'_p(N) = \lambda_p - \alpha \left(1 + \frac{\delta s_m}{r_{0m}} - 1\right) = \lambda_p(N) - \frac{\delta s_m}{b\sqrt{N}}$ ), solvent molar volume  $v_s = 5$  dm<sup>3</sup>/mol, stoichiometric ratio  $S_r = 10$ , swelling's friction coefficient  $\zeta = 10^{-19}$  Jm<sup>3</sup>s/mol, energy barrier for switching activation  $\Delta G_A = 5 \cdot 10^{-25}$  J, and deactivation  $\Delta G_D = 10^{-20}$  J, activation and deactivation frequencies  $C_A = 10^{-10}$  and  $C_D = 10^{-5}$  Hz, respectively.

## 6.1 Polymer with switchable molecules under a monotonic mechanical action

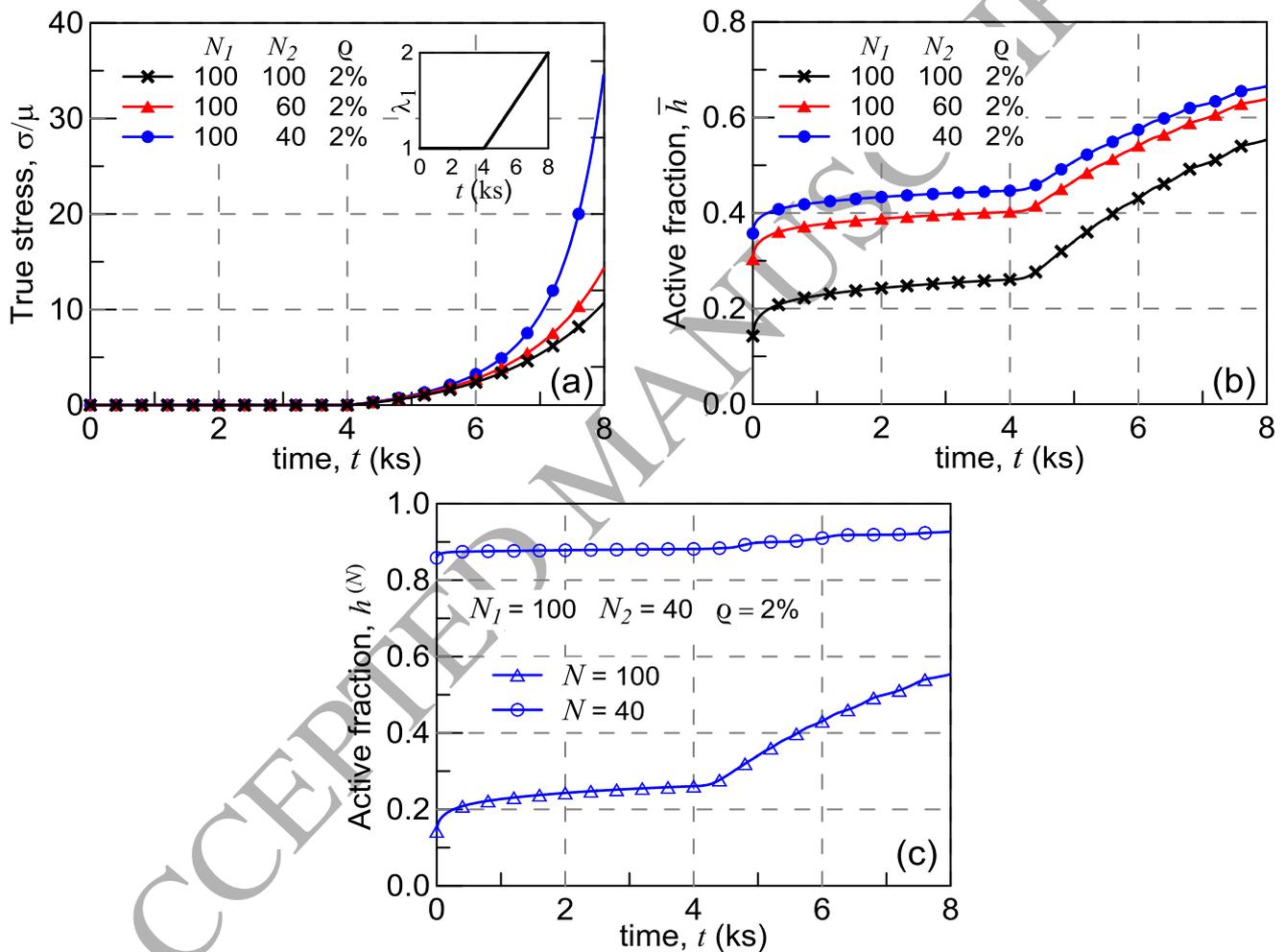
In the first example, the polymer containing switchable molecules is under the action of a linearly increasing external mechanical uniaxial stretch (ranging from  $\lambda = 1$  to  $\lambda = 2$  in 4 ks, applied after an

initial unstretched period of 4 ks adopted here to reach the steady state (kinetic equilibrium of the switching mechanism), without any chemical agent capable of inducing the molecules expansion. The volume fraction of the switchable molecules in the dry state of the polymer is assumed to be equal to  $\varrho = 2\%$ .

The polymer is assumed to be made of a double network (where the first one, characterized by molecules with  $N_1$  Kuhn's segments, contribute to the 70%, and the second one, characterized by molecules with  $N_2$  Kuhn's segments, contribute to the 30% of the total volume of material); a fixed value  $N_1 = 100$  is adopted, while the second network has been assumed to have three different possible lengths,  $N_2 = 100, 60, 40$ . This allows us to study the effect of the molecule switching mechanism taking place in polydisperse polymers. The dimensionless true stress-stretch curves  $(\sigma/\mu - \lambda)$  are illustrated in Fig. 5a; it can be noted that the stress arising in the polymer with the shorter (second) network is, as expected, the highest one. A zero stress practically arises during the time interval 0-4 ks because the molecule expansion occurring in such a period comes simply from the kinetic switching equilibrium and no significant network deformation takes place. In Fig. 5b the evolution of the scalar quantity  $\bar{h}$  is illustrated: again, during the first time period 0-4 ks, the increase of the average fraction of switched molecules is due only to the evolution of the kinetic equilibrium law, while during the application of the stretch, the function  $\bar{h}$  increases significantly because of the tensile forces arising in the network's chains. It's worth noting that the polymer with the shortest (second) network, presents the highest values of  $\bar{h}$ , thanks to the higher forces induced in such a case for the same amount of stretch; in this latter case the mechanical stimuli is thus more effective in inducing the molecule switching. In Fig. 5c the fraction of switched molecules within the single networks vs time is illustrated: again, the case of the shortest network ( $N_2 = 40$ ) displays the highest value of the function  $h^{(N)}$ , thanks to the higher values of the chain forces.

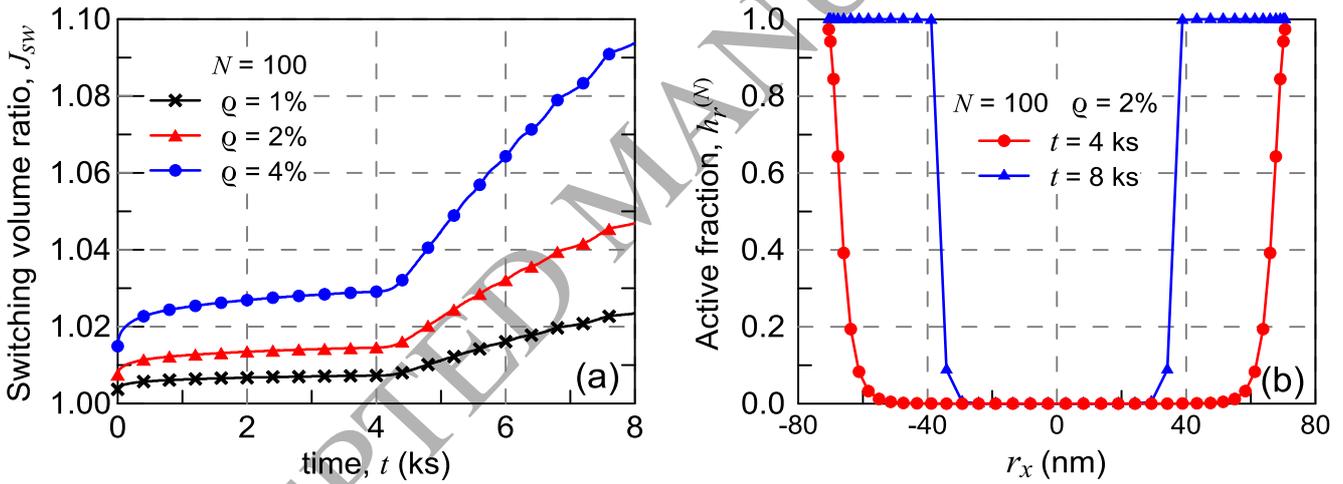
In Fig. 6a the volume change due to the molecule switching,  $J_{sw}$ , is illustrated for the particular case  $N_1 = N_2 = 100$  by varying the volume fraction of the embedded molecules, i.e. by assuming the three

values  $\varrho = 1, 2, 4\%$ ; it appears that such a fraction plays a crucial role in the overall volume expansion of the polymer that is assumed, as recalled above, to be mechanically incompressible if considered alone, i.e. without solvent absorption. It's worth noting that the polymer's chains are always stretched (also if the applied external stretch is zero) because, according to the rubber elasticity theory, the chains are unstretched only if  $|\mathbf{r}| = 0$ ; thus, the polymer in its initial configuration has all its chains tensioned, except the ones with a zero end-to-end distance.



**Figure 5.** (Color online). Dimensionless stress evolution in time for the three different polymers considered (a). Mean fraction of expanded molecules vs time for the three different polymers considered (b). Fraction of expanded molecules related to each network,  $h^{(N_1)}$  and  $h^{(N_2)}$  vs time (c).

Finally, in Fig. 6b the distribution of the function  $h_r^{(N)}$  vs the  $x$ -component of the end-to-end distance  $r$  (see also Fig. 2) is represented for the case  $N_1 = N_2 = 100$ ; initially ( $0 \leq t \leq 4$  ks), the fraction of switched molecules is greater for large values of  $r_x$ , being the most elongated chains the most stretched ones; the effect of the tensile force on the chains reduces the activation energy and increases the deactivation one according to Eq. (30), leading to greater values of  $h_r^{(N)}$  for such a chain configuration. After the application of the stretch ( $t > 4$  ks), the chains present a greater end-to-end distance with respect to the state before stretching and so the function  $h_r^{(N)}$  assumes a narrower distribution (compare the blue line with the red one in Fig. 6b), with high values taking place also in the region close to the origin.



**Figure 6.** (Color online). Volume expansion vs time for the polymer with  $N_1 = N_2 = 100$ , and three different contents of switchable molecules,  $q = 1, 2, 3\%$  (a). Function  $h_r^{(N)}$  vs the  $x$ -component of the end-to-end distance  $r$  at two different time instants for the polymer with  $N_1 = N_2 = 100$  (b).

From the above discussion it can be appreciated that the proposed model captures the main physical aspects involved in a stretched polymer with embedded switchable molecules sensible to mechanical stimuli.

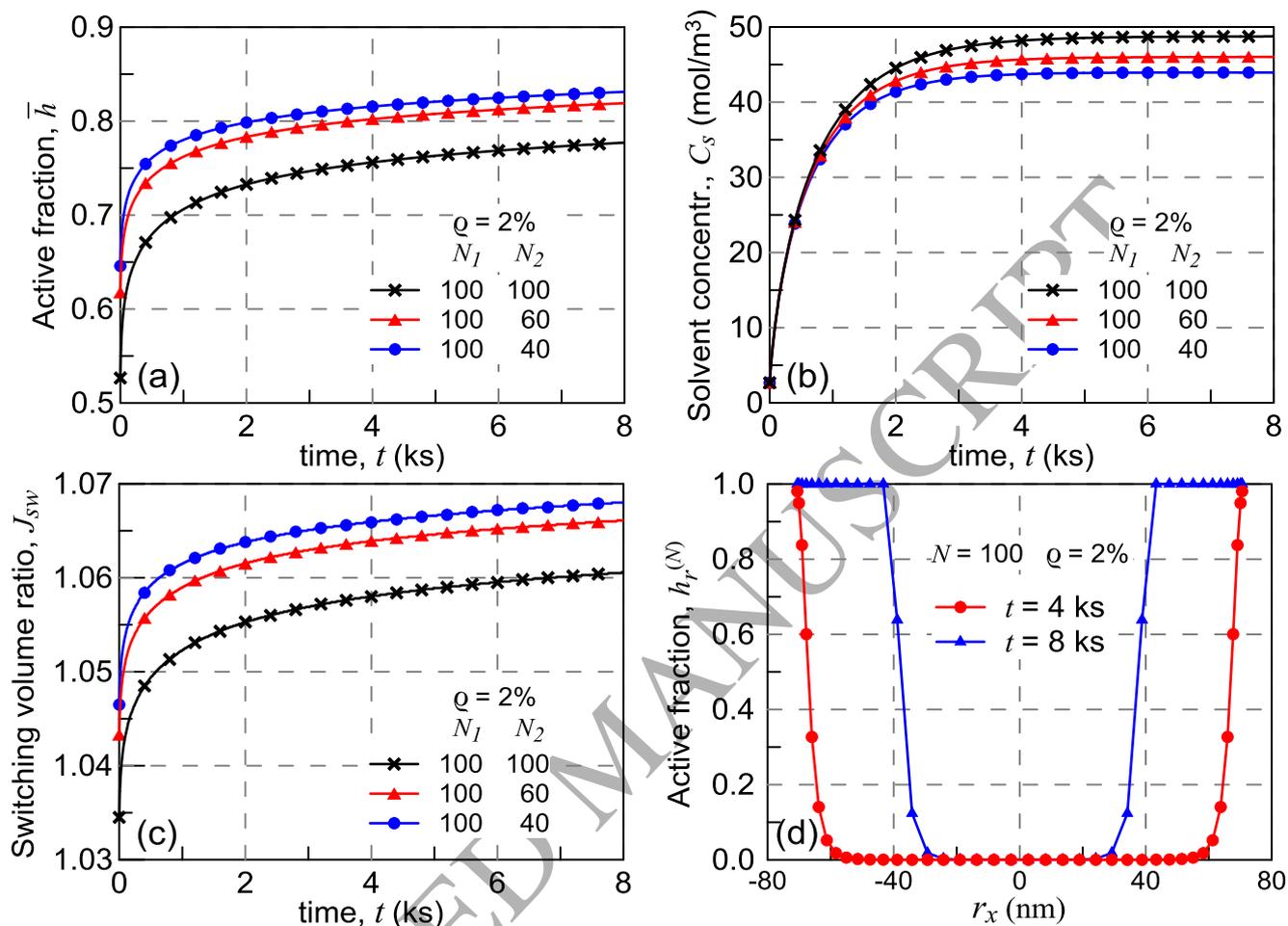
## 6.2 Polymer with switchable molecules in presence of a solvent

In the present example, the polymer containing a volume fraction  $\varrho = 2\%$  of switchable molecules is exposed to a chemical agent; consequently, the swelling occurs over time, and the molecules switch as soon as they enter in contact with the solvent. The polymer is assumed to be made of a double network (where the first one, characterized by molecules with  $N_1$  Kuhn's segments, contribute to the 70%, and the second one, characterized by molecules with  $N_2$  Kuhn's segments, contribute to the 30% of the total volume of material): a fixed  $N_1 = 100$  is assumed, while the second network assumes three values of the chains' length,  $N_2 = 100, 60, 40$ .

The average fraction of switched molecules *vs* time is shown in Fig. 7a for the three polymers considered; as expected, the more stiff is the polymer ( $N_1 = 100, N_2 = 40$ ) the more stretched it is during the swelling process and so the molecules switching is favored, as witnessed by the highest values of  $\bar{h}$ . In Fig. 7b the solvent concentration  $C_s$  *vs* time is represented; it appears that the most compliant polymer ( $N_1 = N_2 = 100$ ) allows the solvent to enter more easily into the material and so the fluid concentration is higher. In Fig. 7c, that shows a trend similar to that of Fig. 7a, the volume expansion caused only by the molecules switching  $J_{sw}$  is illustrated; as stated above, the volume change induced by the molecules switching is more effective in the most stretched network, i.e. for  $N_1 = 100, N_2 = 40$ . Fig. 7d represents the function  $h_r^{(N)}$  *vs* the  $x$ -component of the end-to-end distance  $r$  (see Fig. 2) for the case  $N_1 = N_2 = N = 100$ ; the fraction of switched molecules is initially greater for large values of  $r_x$ , being the most elongated chains also the most stretched ones. After the swelling had occurred, the shape of the function  $h_r^{(N)}$  becomes narrower because of the stretch induced by the solvent absorption expansion.

The present example can be considered to be a little bit tricky because the volume expansion occurs due to the interplay of two different mechanisms: the swelling and the molecules switching; thus, it is difficult to distinguish the contribution coming from each of them. However, the model allows to

account for all the main mechanical aspects involved in a polymer with chemically-sensible switchable molecules during solvent absorption.

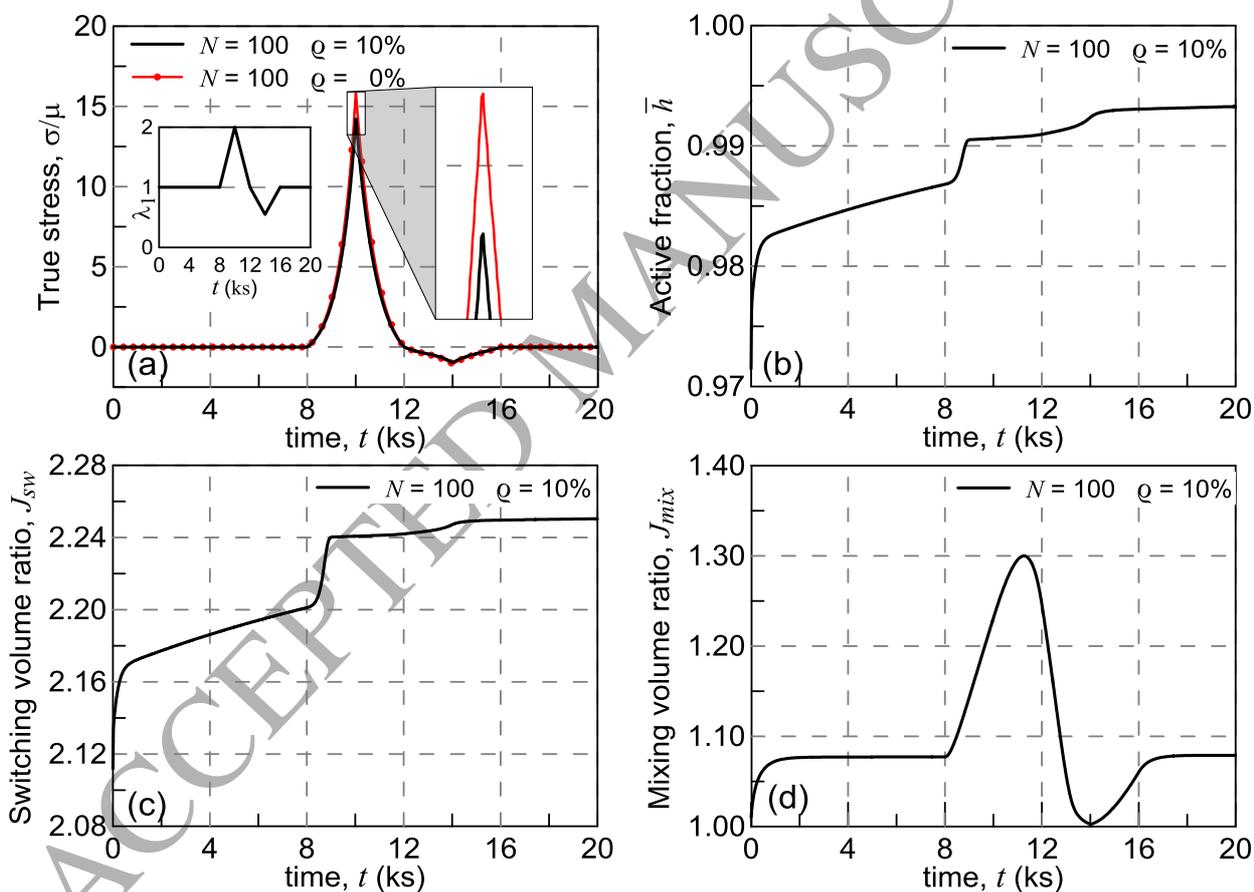


**Figure 7.** (Color online). Mean fraction of expanded molecules vs time for the three different polymers considered (a). Solvent concentration  $C_s$  vs time for the three polymers (b) Volume change of the polymer due only to the chemically-switched molecules (c). Function  $h(N, r_x)$  vs the  $x$ -component of the end-to-end distance  $r$  at two different time instants for the polymer with  $N = N_1 = N_2 = 100$  (d).

### 6.3 Polymer with switchable molecules under a cyclic mechanical stress in presence of a solvent

The present case involves a single network polymer (with  $N_1 = N_2 = 100$ ), enriched with switchable molecules under a prescribed load history, whose stretch vs time trend is shown in the insert of Fig. 8a; the presence of a solvent phase is also assumed. The material is characterized by the Flory-Huggins

parameter  $\chi = 1.8$  (the assumed Flory's parameter corresponds to a low polymer-solvent affinity), molecules' conformational change with a size variation  $\delta s_{sw} = 50b$ , switchable molecule contents  $\varrho = 0\%$  and  $10\%$ , solvent molar volume  $v_s = 5 \text{ dm}^3/\text{mol}$ , swelling's friction coefficient  $\zeta = 10^{-19} \text{ Jm}^3/\text{s}/\text{mol}$ . Initially, in order to reach the steady state for the swelling and the switching mechanism, the polymer is kept in a stress free state and is allowed to swell freely for 8ks; then, a tensile cycle is applied by stretching the material linearly in time up to  $\lambda = 2$  (in 2 ks) and then back to  $\lambda = 1$  (in the subsequent 2 ks). After that, a smaller compressive cycle is applied by reaching the stretch  $\lambda = 0.6$  in 2 ks and then back to  $\lambda = 1$  in 2 ks.



**Figure 8.** Plot of the dimensionless stress vs time during the deformation cycles (a); average fraction of switched molecules vs time (b). Volume deformation due to molecule switching only (c) and swelling volume change (d).

During the first time interval ( $0 \text{ s} \leq t \leq 8 \text{ ks}$ ) the material undergoes unconstrained swelling, reaching a volume expansion of about 8%, while the molecules switching contributes to expand the material of about 220% in the same time period (Fig. 8c, d); the stress remains practically zero during the free swelling phase. When the stretch cycles are applied, a stress increase can be observed during tensile stretching ( $1 \leq \lambda \leq 2$ ) as well as a further volumetric expansion due to the increase of the number of switched molecules (see Fig. 8b for  $\bar{h}$ ) and an increase of the swelling expansion promoted by the further fluid uptake favored by the applied stretch. It can be noticed that the stress value in the polymer is higher in the case without switching molecules ( $\varrho = 0\%$ ) because no stress relaxation in the chains takes place in absence of molecules undergoing conformational change (see detail in Fig. 8a). During unloading, the fraction of switched molecules does not change significantly because the switching mechanism is sensible only to a tensile force, being the compression not allowed to occur in the polymer chains. The same comments can be done for the volume change induced by molecules switching.

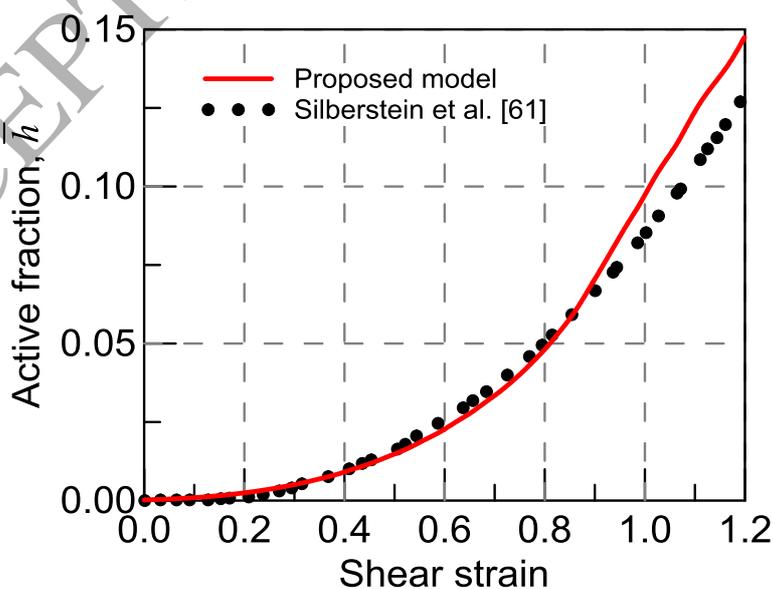
#### 6.4 Polymer enriched with a spiropyran mechanophores

Finally, the proposed model is used herein to simulate the experimental outcomes reported in Silberstein et al. [61]; a PMMA sample added with a small volume fraction of spiropyran mechanophores is mechanically stretched by applying an increasing torsion load, while the main experimental outcome is the activation level of the mechanophores. The mechanophore can be considered as a switchable molecule, because it is characterized by two distinct states, called spiropyran and merocyanine, separated by an energy barrier. The merocyanine form is easily detectable because it is fluorescent and so it can be easily quantified in the sample; in our simulations we associate the activation level to the average fraction  $\bar{h}$  of switched molecules.

The material considered in [48] is characterized by the following properties: shear modulus  $\mu = 7.4 \cdot 10^8$  Pa, the average Gibbs energy for activation and deactivation,  $\Delta G_{A0} = 8 \cdot 10^{-20}$  J/molecule,  $\Delta G_{D0} = 2.5 \cdot 10^{-19}$  J/molecule, respectively. The load is monotonically increased at constant rate; the test is performed at room temperature and no solvent is present. From the experimental results in [48], the activation phenomenon appears to be barely influenced by the applied strain rate.

In order to fit the mechanical response of the material with the experimental data, the polymer is assumed to be made of a single network characterized by  $N = 2000$ . The length difference between the spiropyran -merocyanine states is small compared to the chain length, and it is assumed to be  $\delta_{sw} = 5b$ . Finally, the activation and deactivation rates are assumed to be  $k_A = 10^{-22}$  and  $k_D = 10^{-5}$  Hz, respectively; it is worth noting that the assumed rate values are related to the adopted experimental time scale.

In figure 9 the evolution of the active fraction vs the applied monotonic stretch value is shown; the experimental data obtained by Silberstein et al. [61] are also reported for comparison. The results from simulations and experiments appear to be in a satisfactory agreement, especially for shear strain values lower than about 0.9.



**Figure 9.** Plot of the active fraction of a spiropyran mechanophore during a monotonic mechanical test. Experimental data taken from Silberstein [61] compared with the proposed model.

The present model, developed for the simulation of polymers with embedded switchable molecules sensible to mechanical and/or chemical stimuli, can thus be suitably applied to simulate the response of self-diagnostic (or strain-sensitive) materials being based on the same underneath physics.

## 7. Conclusions

Active materials, that can be exploited to operate as sensors or actuators, are capable to physically respond with a macroscopically detectable change to external stimuli of various nature. Polymeric materials – containing molecules capable of abruptly change their conformation (change in shape and/or size) – jointed to their network, are quite attracting in modern advanced applications because they can be used to develop active components at any dimensional scale. In this context, the conformational change of molecules can be seen as an unstable phenomenon that can be properly harnessed to get a smart response or sensing functionalities of materials operating in particular environmental conditions.

In the present study we have developed a micromechanical model for polymers containing switchable molecules whose conformation change between two stable and distinct states, has been considered as an instability phenomenon. The change in conformation has been assumed to be induced by both mechanical or chemical actions, according to a kinetic equilibrium law. Since the chemical stimuli entails the presence of a solvent in the material's network, the mechanics of swelling has also been accounted for in the model. The full theoretical micromechanical framework, developed for a general polydisperse polymer, has been presented and its continuum counterpart has been illustrated. Finally, some examples related to the response of polymers with embedded switchable molecules under mechanical and/or chemical stimuli, and the response of a strain-sensing material reported in literature

have been illustrated and critically discussed. The developed theory provides a simple and physically-based tool to quantitatively study and design smart responsive, active materials; furthermore, the capability to deal with polymers constituted by different networks, paves the way to the design of polymers whose macroscopic smart response – triggered by mechanical and/or chemical stimuli – can be tailored according to the desired functionality.

### **Declaration of Conflicting Interests**

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

### **Funding**

The author(s) received no financial support for the research, authorship, and/or publication of this article.

### **References**

- [1] D. Liu, E. Cheng, Z. Yang, DNA-based switchable devices and materials. *NPG Asia Materials*, 3.12 (2011), 109–114.
- [2] H. Li. Kinetics of smart hydrogels responding to electric field: a transient deformation analysis. *International Journal of Solids and Structures*, 46(6), (2009), 1326–1333.
- [3] A.D. Drozdov, J. deClaville Christiansen, C.G. Sanporean. Inhomogeneous swelling of pH-responsive gels. *International Journal of Solids and Structures*, 87, (2016), 11–25.
- [4] A. Passian, T. Thundat, Materials science: The abilities of instabilities. *Nature*, 487.7408 (2012), 440–441.
- [5] J. J. Kaufman, G. Tao, S. Shabahang, E. H. Banaei, D. S. Deng, X. Liang, S. G. Johnson, Y. Fink, A. F. Abouraddy, Structured spheres generated by an in-fibre fluid instability. *Nature*,

487.7408 (2012), 463–467.

- [6] D. M. Kochmann, K. Bertoldi, Exploiting microstructural instabilities in solids and structures: from metamaterials to structural transitions. *App. Mech. Rev.*, 69.5 (2017), 050801.
- [7] P. Wang, F. Casadei, S. Shan, J. C. Weaver, K. Bertoldi, Harnessing buckling to design tunable locally resonant acoustic metamaterials. *Physical review letters*, 113.1 (2014), 014301.
- [8] M. Pezulla, S. A. Shillig, P. Nardinocchi, D. P. Holmes, Morphing of geometric composites via residual swelling. *Soft Matter*, 11.29 (2015), 5812–5820.
- [9] I. Benichou, S. Givli, Structures undergoing discrete phase transformation. *Journal of the Mechanics and Physics of Solids*, 61.1 (2013), 94–113.
- [10] D. Chen, J. Yoon, D. Chandra, A. I. Crosby, R. C. Hayward, Stimuli-responsive buckling mechanics of polymer films. *Journal of Polymer Science Part B: Polymer Physics*, 52.22 (2014), 1441–1461.
- [11] S. Cocco, J. F. Marko, R. Monasson, A. Sarkar, J. Yan, Force-extension behavior of folding polymers. *The European Physical Journal E*, 10.3 (2003), 249–263.
- [12] A. M. Kushner, V. Gabuchian, E. G. Johnson, Z. Guan, Biomimetic design of reversibly unfolding cross-linker to enhance mechanical properties of 3D network polymers. *Journal of the American Chemical Society*, 129.46 (2007), 14110–14111.
- [13] P. E. Marszalek, H. Lu, H. Li, M. Carrion-Vazquez, A. F. Oberhauser, K. Schulten, J. M. Fernandez, Mechanical unfolding intermediates in titin modules. *Nature*, 402.6757 (1999), 100–103.
- [14] M. Rief, M. Gautel, F. Oesterhelt, J. M. Fernandez, H. E. Gaub, Reversible unfolding of individual titin immunoglobulin domains by AFM. *Science*, 276.5315 (1997), 1109–1112.
- [15] C. Bustamante, Y. R. Chemla, N. R. Forde, D. Izhaky, Mechanical processes in biochemistry. *Annual review of biochemistry*, 73.1 (2004). 705–748.
- [16] M. D. Manrique-Juarez, S. Rat, L. Salmon, G. Molnár, C. M. Quintero, L. Nicu, H. J. Shepherd,

- A. Bousseksou, Switchable molecule-based materials for micro-and nanoscale actuating applications: Achievements and prospects. *Coordination Chemistry Reviews*, 308 (2016), 395–408.
- [17] A. Natansohn, P. Rochon, Photoinduced motions in azo-containing polymers. *Chemical reviews*, 102.11 (2002), 4139–4176.
- [18] T. Kim, L. Zhu, R. O. Al-Kaysi, C. J. Bardeen, Organic photomechanical materials. *ChemPhysChem*, 15.3 (2014), 400–414.
- [19] A. Priimagi, C. J. Barrett, A. Shishido, Recent twists in photoactuation and photoalignment control. *Journal of Materials Chemistry C*, 2.35 (2014), 7155–7162.
- [20] R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. Bastiaansen, D. J. Broer, B. L. Feringa, Molecular machines: nanomotor rotates microscale objects. *Nature*, 440.7081 (2006), 163.
- [21] B. C. Bunker, B. I. Kim, J. E. Houston, R. Rosario, A. A. Garcia, M. Hayes, D. Gust, S. T. Picraux, Direct observation of photo switching in tethered spiropyrans using the interfacial force microscope. *Nano Letters*, 3.12 (2003), 1723–1727.
- [22] W. R. Browne, B. L. Feringa, Light switching of molecules on surfaces. *Annual review of physical chemistry*, 60 (2009), 407-428.
- [23] T. Kim, L. Zhu, R. O. Al Kaysi, C. J. Bardeen, Organic photomechanical materials. *Chem Phys Chem*, 15.3 (2014), 400–414.
- [24] S. L. Gilat, S. H. Kawai, J. M. Lehn, Light-triggered molecular devices: Photochemical switching of optical and electrochemical properties in molecular wire type diarylethene species. *Chemistry-a European Journal*, 1.5 (1995), 275–284.
- [25] G. Puglisi, L. Truskinovsky, Mechanics of a discrete chain with bi-stable elements. *Journal of the Mechanics and Physics of Solids*, 48.1 (2000), 1–27.
- [26] B. Haghpanah, L. Salari-Sharif, P. Pourrajab, J. Hopkins, L. Valdevit, Multistable Shape-

- Reconfigurable Architected Materials. *Advanced Materials*, 28.36 (2016), 7915–7920.
- [27] R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, A chemically and electrochemically switchable molecular shuttle. *Nature*, 369.6476 (1994), 133–137.
- [28] R. Klajn, Spiropyran-based dynamic materials. *Chemical Society Reviews*, 43.1 (2014), 148–184.
- [29] L. R. G. Treloar, The elasticity of a network of long-chain molecules.— III. *Transactions of the Faraday Society*, 42 (1946), 83–94.
- [30] O. K. Vorov, D. R. Livesay, D. J. Jacobs, Conformational entropy of an ideal cross-linking polymer chain. *Entropy*, 10.3 (2008), 285–308.
- [31] P. J. Flory, *Principles of polymer chemistry*. Cornell University Press, 1953.
- [32] P. J. Flory, *Statistical mechanics of chain molecules*. Wiley-Interscience, New York, 1969.
- [33] M. Gordon, *The Physics of Rubber Elasticity*. LRG Treloar, Clarendon Press, Oxford, 1975.
- [34] P. J. Flory, J. Rehner Jr, Statistical mechanics of cross-linked polymer networks I. Rubberlike elasticity. *The Journal of Chemical Physics*, 11.11 (1943), 512–520.
- [35] P. E. Rouse Jr, A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *The Journal of Chemical Physics*, 21.7 (1953), 1272–1280.
- [36] R. A. Orwoll, W. H. Stockmayer, Stochastic models for chain dynamics. *Advances in Chemical Physics: Stochastic Processes in Chemical Physics*, 15 (2007), 305–324.
- [37] R. C. Ball, M. Doi, S. F. Edwards, M. Warner, Elasticity of entangled networks. *Polymer*, 22(8) (1981), 1010–1018.
- [38] M. F. Beatty, An average-stretch full-network model for rubber elasticity. *Journal of Elasticity*, 70(1-3) (2003), 65–86.
- [39] E.M. Arruda and M.C. Boyce, A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials. *J. Mech. Phys. Solids* 41 (1993) 389–412.

- [40] P.D. Wu and E. van der Giessen, On improved network models for rubber elasticity and their application to orientation hardening in glassy polymers. *J. Mech. Phys. Solids* 41 (1993) 427–456.
- [41] C. Miehe, S. Göktepe, F. Lulei, A micro-macro approach to rubber-like materials—part I: the non-affine micro-sphere model of rubber elasticity. *Journal of the Mechanics and Physics of Solids*, 52(11) (2004), 2617–2660.
- [42] D. De Tommasi, G. Puglisi, G. Saccomandi, Multiscale mechanics of macromolecular materials with unfolding domains. *Journal of the Mechanics and Physics of Solids*, 78 (2015), 154–172.
- [43] G. Puglisi, D. De Tommasi, M. F. Pantano, N. M. Pugno, G. Saccomandi, Micromechanical model for protein materials: From macromolecules to macroscopic fibers. *Physical Review E*, 96(4) (2017), 042407.
- [44] M. Destrade, G. Saccomandi, I. Sgura, Methodical fitting for mathematical models of rubber-like materials. *Proc. R. Soc. A*, 473(2198) (2017), 20160811.
- [45] D. De Tommasi, G. Puglisi, G. Saccomandi, A micromechanics-based model for the Mullins effect. *Journal of Rheology*, 50(4) (2006), 495–512.
- [46] G. Marckmann, E. Verron, Comparison of hyperelastic models for rubber-like materials. *Rubber chemistry and technology*, 79(5) (2006), 835–858.
- [47] R. Brighenti, F. Artoni, F. J. Vernerey, M. Torelli, A. Pedrini, I. Domenichelli, E. Dalcanale, Mechanics of responsive polymers via conformationally switchable molecules. *Journal of the Mechanics and Physics of Solids*, 113 (2018), 65–81.
- [48] W. Kuhn, F. Grün, Beziehungen zwischen elastischen Konstanten und Dehnungsdoppelbrechung hochelastischer Stoffe. *Colloid & Polymer Science*, 101.3 (1942), 248–271.
- [49] F. J. Vernerey, R. Long, R. Brighenti, A Statistically-Based Continuum Theory for Polymers with Transient Networks. *Journal of the Mechanics and Physics of Solids*, 107 (2017), 1–20.
- [50] P. W. Kasteleyn, C. M. Fortuin, Phase transitions in lattice systems with random local properties.

Journal of the Physical Society of Japan Supplement, 26 (1969), 11.

- [51] D. De Tommasi, G. Puglisi, G. Saccomandi, Multiscale mechanics of macromolecular materials with unfolding domains. *Journal of the Mechanics and Physics of Solids*, 78 (2015), 154–172.
- [52] A. DiCarlo, S. Quiligotti, Growth and balance. *Mechanics Research Communications*, 29(6) (2002), 449–456.
- [53] W. Hong, X. Zhao, J. Zhou, Z. Suo, A theory of coupled diffusion and large deformation in polymeric gels. *Journal of the Mechanics and Physics of Solids*, 56.5 (2008), 1779–1793.
- [54] T. Tanaka, D. J. Fillmore, Kinetics of swelling of gels. *The Journal of Chemical Physics*, 70.3 (1979), 1214–1218.
- [55] M. Doi, Gel dynamics. *Journal of the Physical Society of Japan*, 78.5 (2009), 052001-052001.
- [56] G. L. Sewell, Stability, equilibrium and metastability in statistical mechanics. *Physics Reports*, 57.5 (1980), 307–342.
- [57] A. Raoult, Quasiconvex envelopes in nonlinear elasticity. In *Poly-, Quasi-and Rank-One Convexity in Applied Mechanics*, 17-51, Springer, Vienna, 2010.
- [58] P. Hänggi, P. Talkner, M. Borkovec, Reaction-rate theory: fifty years after Kramers. *Reviews of modern physics*, 62.2 (1990), 251–341.
- [59] H. A. Kramers, Brownian motion in a field of force and the diffusion model of chemical reactions. *Physica*, 7.4 (1940), 284–304.
- [60] M. Boyce, E. Arruda, Constitutive models of rubber elasticity: a review, *Rubber Chem. Tech.*, 73.3 (2000), 504–523.
- [61] M. N. Silberstein, K. Min, L. D. Cremer, C. M. Degen, T. J. Martinez, N. R. Aluru, S. R. White, N. R. Sottos, Modeling mechanophore activation within a crosslinked glassy matrix. *Journal of Applied Physics*, 114.2 (2013), 023504.