



Full length article

Swelling-driven mechanics of partially cross-linked polymer gels: Steady state solutions

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ABSTRACT

The study aims to investigate how the mechanics of swelling of a polymer gel is affected by the presence of free-chains due to a partial cross-linking process. The analysis is focused on the equilibrium solution of the mechano-diffusion problem under different *as-prepared* states, corresponding to different polymer network fractions before diffusion starts. The limit situations of perfectly cross-linked polymer gel and solution of polymeric chains are recovered by the model.

1. Introduction

Polymer gels are elastic materials swollen by a fluid. The elastic properties are inherited from the cross-linked network, together with the resistance to dissolution, and the swelling properties are related to the migration of the solvent through the network and to gel's ability to absorb fluids coming from the hydrophilic functional groups attached to the polymer skeleton (Doi, 2013). Swelling of polymer gels is a classical problem in polymer science and is typically based on a binary point of view: a polymer gel consists of polymer (elastic) network and liquid (Chester & Anand, 2010; Doi, 2009; Hong, Zhao, Zhou, & Suo, 2008; Lucantonio, Nardinocchi, & Teresi, 2013). Actually, some fraction of the polymer can be left unattached to the network by the cross-linking procedure or can get detached by the cross-linking process (Nandi & Winter, 2005). In these cases, the polymer gel includes also not cross-linked polymer macromolecules (chains), denoted as free-chains.

There are a few relevant reasons which motivated our study. Firstly, the fraction of loose chains may be large and affect the swelling-driven mechanics of the polymer gel (Nandi & Winter, 2005). Secondly, free-chains can be released into the liquid bath, where the polymer gel is embedded, changing the chemical properties of the bath itself and, as a secondary effect, affecting the swelling of the gel (Bernheim-Groswasser, Livne, Nardinocchi, Recrosi, & Teresi, 2024). Thirdly, the presence of free-chains in a polymer gel is at the basis of the so-called residual swelling, which is driven by the concentration gradient of free chains across the gel (Pezzulla, Shillig, Nardinocchi, & Holmes, 2015; Wang, Das, Joshi, Shaikkea, & V.S., 2024). Finally, the consideration of an increase in the free-chains, due to breaking mechanisms of the chemical bonds between the polymeric chains induced by aging or chemical agents, may be relevant in the swelling-driven mechanics of polymer gels (Wang, Akbulatov, Chen, et al., 2022; White, 2006). This latter is strongly affected by the stiffness of the polymer network, which depends on the cross-linking density, which on its turn, depends on the effective chemical bonds density. Actually, we leave this issue for future studies; however, the proposed modeling allows for an easy integration of a change in free-chains content, which would correspond to a decrease in the cross-linking density of the polymer network.

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We consider a polymer gel that is ternary in nature and consists of network polymer, free-chains and liquid. As typical in mechano-diffusion theories, it is viewed as a homogenized continuous body, denoted as *partially cross-linked polymer gel* (Chester & Anand, 2010; Hong et al., 2008; Lucantonio et al., 2013), which the liquid and the free-chains can diffuse through. This approach, definitely similar to the one of poromechanics (Coussy, 2004), adopts a non-symmetric point of view in the description of the different continua which constitute the polymer gel. In particular the total stress acting on the overall polymer gel is preferred to the partial stresses, typical of the theory of mixtures, to account for the balance of linear momentum. This also allows to circumvent the hurdle of the specification of traction boundary conditions on the different components, see among others (Massoudi, 2008; Rajagopal & Tao, 1995; Sciarra, Dell'Isola, & Hutter, 2001) and references therein.

The free-chains content is a characteristic of the *as-prepared* state of the polymer gel and is identified through the *polymer network fraction*. To make easier the future consideration of a polymer network fraction which changes in time due to cross-links breaking, we introduce a reference configuration, defined through a *cleaning free-chains out process*, which consists of the sole cross-linked polymer gel. The possible release of free-chains in the liquid bath and the analysis of its effects on the swelling-driven mechanics of the polymer gel make mandatory to include the liquid bath in the study. So, differently from what is usually done in mechano-diffusion theories, we study the system of polymer gel and liquid bath. So, the variables of the theory describe the state of both the body and the bath. They include the gel displacement and the liquid and free-chains concentration in the body, the number of liquid and free-chains moles in the bath.

The balance laws of the theory come out from basic principles (principle of null virtual working and masses conservation) and the thermodynamics of the body and bath system are characterized starting from the largely studied thermodynamics of the polymer gel, based on the Flory–Rehner model. As usually done in Flory–Rehner models, we also assume as natural state of the theory the reference configuration of the body, which consists only of the dry polymer network. The body and bath system is assumed to be a closed system by enforcing a few relations, which link the state variables of the theory and are viewed in the model as internal constraints.

We focus on the study of the equilibrium states of the body and bath system under free conditions and under uniaxial traction. The solutions of both problems come from a system of a (small) number of algebraic equations, which are highly nonlinear due to the nonlinear constitutive equations of the theory and so numerically solved. The results of the theory are shown for different values of the initial content of free-chains in the polymer gel. The two limit situations, that is, the solution of polymeric chains and the perfectly cross-linked polymer gel, are included in the model (see Table 1).

2. Background

Stress-diffusion theories deal with swelling-driven mechanical deformations in polymer gels, which are assumed to be perfectly cross-linked. Typically, the liquid-polymer mixture is treated as a single continuum body, allowing for mass flux of the liquid, whose reference configuration is a three-dimensional region \mathcal{P}_d of the Euclidean space \mathcal{E} , representing the polymer network. The state of the polymer gel \mathcal{P}_d is described by the displacement \mathbf{u}_d from \mathcal{P}_d and the liquid molar concentration c_s per unit current volume. The displacement \mathbf{u}_d is a vector field that assigns to each material point $X \in \mathcal{P}_d$ and time $\tau \in \mathcal{T}$ a place $x \in \mathcal{E}$:

$$x = X + \mathbf{u}_d(X, \tau) = f_d(X, \tau) \in \mathcal{E}, \quad (2.1)$$

with the map f_d describing the motion of the body (Gurtin, Fried, & Anand, 2010).

The region of space $\mathcal{P}_\tau = f_d(\mathcal{P}_d, \tau)$ occupied by the body at τ represents the actual configuration of \mathcal{P}_d at time τ ; \mathbf{m} and \mathbf{n} are the unit normal fields to the boundary $\partial\mathcal{P}_d$ of \mathcal{P}_d and $\partial\mathcal{P}_\tau$ of \mathcal{P}_τ , respectively. Given a motion, each $f_d(\cdot, \tau)$ is a deformation of \mathcal{P}_d , with the deformation gradient $\mathbf{F}_d(X, \tau) = \nabla f_d(X, \tau) = \mathbf{I} + \nabla \mathbf{u}_d(X, \tau)$ at X as a linear map from the translation space \mathcal{V} of \mathcal{E} to \mathcal{V} ; the corresponding Jacobian determinant and adjugate are denoted with $J_d = \det \mathbf{F}_d$ and $\mathbf{F}_d^* = J_d \mathbf{F}_d^{-T}$.

Any regions $D \subset \mathcal{P}_d$ is convected in $D_\tau = f_d(D, \tau)$ by the motion f_d for all τ . We write $\mathbf{v}(x, \tau)$ for the spatial velocity field of the body, such that, $\mathbf{v}(x, \tau) = \mathbf{v}(f_d(X, \tau), \tau) = \mathbf{v}_m(X, \tau) = \dot{\mathbf{u}}_d(X, \tau)$, where the pedix m is used to identify the material representation of the spatial field \mathbf{v}^1 . We also write dv and $\mathbf{n} da$ for the current volume and facet (oriented area) elements corresponding to the reference volume and facet elements dV_d and $\mathbf{m} dA_d$; it holds:

$$dv(x, \tau) = dv(f_d(X, \tau), \tau) = J_d(X, \tau) dV_d(X) \quad \text{and} \quad (dv(x, \tau))^\circ = \text{div} \mathbf{v}(x, \tau) dv(x, \tau), \quad (2.2)$$

where we denoted with $(\cdot)^\circ$ the total time derivative (see Appendix). Finally, we remember that $da = |\mathbf{F}_d^* \mathbf{m}| dA_d$ and $\mathbf{n} = \mathbf{F}_d^* \mathbf{m} / |\mathbf{F}_d^* \mathbf{m}|$.

The liquid concentration c_s is a spatial field defined on the current configuration that assigns to each place x and time τ the number of liquid moles, reckoned per unit volume of the current configuration, in such a way that the liquid volume in the volume element dv is $dv_l = \Omega c_s dv < dv$ with Ω [m³/mol] the liquid (solvent) molar volume.

The balance of forces and the law for liquid conservation are formulated in material and spatial terms, respectively, in a global form, and the localized material equations which must hold in \mathcal{P}_d are derived.

¹ In the following, the change of description relating a reference field a_m on $\mathcal{P}_d \times \mathcal{T}$ to the corresponding spatial field a_s on $\mathcal{P}_\tau \times \mathcal{T}$, both fields conveying the same physical information, will be frequently tackled; thus, it is worth adopting a compact notation, by introducing the map $a_s \circ f$ defined by

$$a_s \circ f : (X, \tau) \mapsto a_s(f(X, \tau), \tau) = a_m(X, \tau), \quad \text{or, in short} \quad a_s \circ f = a_m. \quad (2.2)$$

. See Gurtin et al. (2010) for further details.

Table 1
List of main symbols and their nomenclature.

Symbols	Nomenclature
τ	physical time
$\mathcal{P}_d, \mathcal{P}_\tau$	reference, actual (at τ) configurations of the polymer body respectively
\mathcal{P}_0	initial (at $\tau = 0$) or <i>as-prepared</i> configuration of the polymer body
\mathcal{P}_e	the actual configuration of the polymer body that is homogeneous and at equilibrium
X, x	position vectors of a material point in $\mathcal{P}_d, \mathcal{P}_\tau$ configurations respectively
f_d, f_0, f	maps of the deformation from the configurations $\mathcal{P}_d, \mathcal{P}_d, \mathcal{P}_0$ to $\mathcal{P}_\tau, \mathcal{P}_0, \mathcal{P}$ respectively
\mathbf{u}_d	displacement field of the configuration \mathcal{P}_τ with respect to \mathcal{P}_d
$\mathbf{F}_d, \mathbf{F}_0, \mathbf{F}$	gradients of the deformation maps f_d, f_0, f respectively
J_d, J_0	Jacobian determinants of the deformation maps f_d, f_0 respectively
$\lambda_d, \lambda_0, \lambda$	principal stretch ratios in the case of homogeneous isotropic deformations $\mathbf{F}_d, \mathbf{F}_0, \mathbf{F}$ respectively
\mathbf{S}_d, \mathbf{T}	reference Piola–Kirchhoff, actual Cauchy stress fields respectively
dA_d, da	infinitesimal oriented areas associated to $\mathcal{P}_d, \mathcal{P}_\tau$ respectively
\mathbf{m}, \mathbf{n}	unit normals associated to dA_d, da respectively
dV_d, dv	infinitesimal volume elements associated to $\mathcal{P}_d, \mathcal{P}_\tau$ respectively
dv_n, dv_l, dv_f	volumes of network, liquid solvent, free-chains respectively within dv
V_d, V_0	total reference (dry), initial volumes respectively of the polymer body
v_l, v_f	total actual volumes of liquid solvent, free-chains respectively within the polymer body
V_l, V_f	total initial volumes of liquid solvent, free-chains respectively within the polymer body
c_d, c_s	actual molar concentrations of liquid solvent with respect to $\mathcal{P}_d, \mathcal{P}_\tau$ respectively
g_d, g_s	actual molar concentrations of free-chains with respect to $\mathcal{P}_d, \mathcal{P}_\tau$ respectively
g_{d0}	initial molar concentration of free-chains with respect to \mathcal{P}_d
ϕ_0, ϕ	initial, actual gel fractions of the polymer body respectively
h_d, h_s	instantaneous solvent flux across dA_d, da respectively
j_d, j_s	instantaneous free-chain flux across dA_d, da respectively
μ_c, μ_c^b	chemical potentials of the solvent in the polymer body, the bath respectively
μ_g, μ_g^b	chemical potentials of the free-chains in the polymer body, the bath respectively
μ_c^o, μ_g^o	chemical potentials of the pure solvent, the pure free-chains respectively
N_c, N_g	total current number of moles of the solvent, the free-chains respectively in the bath
N_{c0}, N_{g0}	total initial number of moles of the solvent, the free-chains respectively in the bath
V_n, v_b	initial, actual volumes of the bath respectively
Ω, Λ	molar volumes of the solvent, the free-chains respectively
G_d	shear modulus of the dry network
χ	Flory parameter describing the enthalpic interaction between solvent and polymer network

2.1. Balance of forces and liquid mass

In mechanics, the work is the chief integral quantity, and balance equations are naturally expressed in integral form in terms of working. The working is a continuous, linear, and real-valued functional on the space of test velocities $\tilde{\mathbf{u}}$ and is split additively into the elementary internal working $d\mathcal{W}^i(\tilde{\mathbf{u}})$ and external working $d\mathcal{W}^e(\tilde{\mathbf{u}})$:

$$d\mathcal{W}^i(\tilde{\mathbf{u}}) = \mathbf{S}_d \cdot \nabla \tilde{\mathbf{u}} dV_d \quad \text{and} \quad d\mathcal{W}^e(\tilde{\mathbf{u}}) = \mathbf{s} \cdot \tilde{\mathbf{u}} dA_d, \quad (2.4)$$

where the reference stress \mathbf{S}_d and the reference traction vector \mathbf{s} have been introduced and vanishing bulk forces have been considered. The request that $\mathcal{W}^i(\tilde{\mathbf{u}})$ and $\mathcal{W}^e(\tilde{\mathbf{u}})$ be equal for any test velocities $\tilde{\mathbf{u}}$, delivers the local form of the balance equation of forces and corresponding natural boundary conditions (BCs)

$$\operatorname{div} \mathbf{S}_d = \mathbf{0} \quad \text{in } \mathcal{P}_d \quad \& \quad \mathbf{S}_d \mathbf{m} = \mathbf{s} \quad \text{on } \partial \mathcal{P}_d, \quad (2.5)$$

where \mathbf{s} is controlled on the boundary $\partial \mathcal{P}_d$ of the body. The indifference of the inner working with respect to change of frames delivers the further condition: $\mathbf{S}_d \mathbf{F}_d^T \in \mathbb{S}\text{ym}$. When evaluated on velocity fields, the internal working delivers the elementary mechanical power

$$d\mathcal{W}_m = \mathbf{S}_d \cdot \dot{\mathbf{F}}_d dV_d. \quad (2.6)$$

The diffusion equation for the liquid is formulated through a liquid mass conservation law assuming that changes in the concentration c_s of the solvent in any elementary volume dv are most generally brought about by diffusion across its boundary da if any internal sources are absent. Introducing the rate q_s of solvent transported into the elementary volume dv across its boundary da by the solvent flux \mathbf{h}_s , the conservation law takes the form

$$(c_s dv)^\circ = q_s da \quad \text{with} \quad q_s = -\mathbf{h}_s \cdot \mathbf{n}. \quad (2.7)$$

Eq. (2.7) delivers the local spatial balance law; we have

$$(c_s dv)^\circ = c_s^\circ dv + c_s dv^\circ = (c_s^\circ + c_s \operatorname{div} \mathbf{v}) dv, \quad (2.8)$$

and

$$-\mathbf{h}_s \cdot \mathbf{n} da = -\operatorname{div} \mathbf{h}_s dv, \quad (2.9)$$

that is,

$$\dot{c}_s + \operatorname{div} (c_s \mathbf{v}) = -\operatorname{div} \mathbf{h}_s \quad \text{in } \mathcal{P}_\tau \times \mathcal{T}. \quad (2.10)$$

Eq. (2.10) can be rewritten as

$$\dot{c}_s + \operatorname{div} (c_s (\mathbf{v} + \frac{\mathbf{h}_s}{c_s})) = 0 \quad \text{with} \quad \mathbf{v} + \frac{\mathbf{h}_s}{c_s} = \mathbf{v}_l, \quad (2.11)$$

where \mathbf{v}_l is the liquid velocity. The same Eq. (2.7), after appropriate pull-back, delivers the local material balance law:

$$(c_s dv)^\circ = \overline{c_m} J_d dV_d = \dot{c}_d dV_d \quad \text{and} \quad -\mathbf{h}_s \cdot \mathbf{n} da = -J_d \mathbf{F}_d^{-1} \mathbf{h}_m \cdot \mathbf{m} dA_d = -\mathbf{h}_d \cdot \mathbf{m} dA_d, \quad (2.12)$$

that is,

$$\dot{c}_d = -\operatorname{div} \mathbf{h}_d \quad \text{in } \mathcal{P}_d \times \mathcal{T} \quad \text{with} \quad q_m = -\mathbf{h}_d \cdot \mathbf{m}, \quad (2.13)$$

where $\mathbf{h}_m = \mathbf{h}_s \circ f$ is the solvent material flux. Specification of q_m on the boundary $\partial \mathcal{P}_d$ gives the Neumann BC, such that a positive boundary source q_m corresponds to a flux entering the body. If Dirichlet-type BCs are prescribed on $\partial \mathcal{P}_d$, we would have,

$$\mathbf{u} = \bar{\mathbf{u}} \quad \text{and} \quad c_d = \bar{c}_d \quad \text{on} \quad \partial \mathcal{P}_d \times \mathcal{T}. \quad (2.14)$$

Finally, the system requires the initial conditions on the state variable of the problem \mathbf{u} and c_d .

We can also define the chemical power by introducing the chemical potential μ_c of the liquid in the gel to represent energy flow due to liquid transport:

$$d\mathcal{W}_c = -\mu_c \mathbf{h}_d \cdot \mathbf{m} dA = -\operatorname{div} (\mu_c \mathbf{h}_d) dV_d = (\mu_c \dot{c}_d - \mathbf{h}_d \cdot \nabla \mu_c) dV_d. \quad (2.15)$$

2.2. Thermodynamics

The constitutive equation for the stress \mathbf{S}_d measured with respect to the dry configuration \mathcal{P}_d , from now on denoted as dry-reference stress, and for the chemical potential μ_c are derived from the classical Flory–Rehner (FR) thermodynamics. It is based on a free energy ψ per unit dry volume which depends on the deformation gradient \mathbf{F}_d from the dry configuration of the polymer gel through an elastic component ψ_e , and on the molar solvent concentration c_d per unit dry volume through a polymer–solvent mixing energy ψ_m : $\psi = \psi_e + \psi_m$. The natural state corresponding to the FR free energy is obtained for $\mathbf{F}_d = \mathbf{I}$ and $c_d = 0$, that is, it corresponds to the reference dry configuration.

Further a local constraint prescribing that changes in volume of the gel body are exclusively due to solvent absorption or release is imposed,

$$J_d = \det \mathbf{F}_d = \hat{J}(c_d) = 1 + \Omega c_d. \quad (2.16)$$

It means that the current volume element dv of the polymer gel is given by the network volume element dV_d plus the amount of liquid $dv_l = \Omega c_d dV_d$ in that volume element: $dv = dV_d + \Omega c_d dV_d = \hat{J}(c_d) dV_d$. Including this constraint, the definition of a restricted Flory–Rehner free energy density reads,

$$\psi_r(\mathbf{F}_d, c_d, p) = \psi_e(\mathbf{F}_d) + \psi_m(c_d) - p(J_d - \hat{J}(c_d)), \quad (2.17)$$

where the pressure p (assumed positive when compressive) represents the reaction which maintains the local constraint.

The constitutive relations for the stress \mathbf{S}_d and the chemical potential μ_c come from thermodynamic development, following the so-called Coleman–Noll procedure (Coleman & Noll, 1963), imposing at thermodynamic equilibrium the equivalence between the rate of change of total free energy and the expended mechanical (2.6) and chemical (2.15) power. As a consequence, the following thermodynamically consistent constitutive equations follow:

$$\mathbf{S}_d = \hat{\mathbf{S}}_d(\mathbf{F}_d) - p \mathbf{F}_d^* \quad \text{and} \quad \mu_c = \hat{\mu}_c(c_d) + p \Omega, \quad (2.18)$$

with

$$\hat{\mathbf{S}}_d(\mathbf{F}_d) = \frac{\partial \psi_e}{\partial \mathbf{F}_d} \quad \text{and} \quad \hat{\mu}_c(c_d) = \frac{\partial \psi_m}{\partial c_d}. \quad (2.19)$$

We intend to follow the FR thermodynamic model by choosing the reference dry state \mathcal{P}_d as the natural state, which corresponds to choosing $\psi_e(\mathbf{I}) = 0$ and $\psi_m(0) = 0$. So, we write the neo-Hookean elastic energy ψ_e :

$$\psi_e(\mathbf{F}_d) = \frac{G_d}{2} (\mathbf{F}_d \cdot \mathbf{F}_d - 3), \quad (2.20)$$

G_d being the shear modulus of the dry network, which is strictly related to the dimension of the polymer gel and strongly affects his swelling state. We also write the polymer–solvent mixing energy as:

$$\psi_m(c_d) = \mu_c^o c_d + \frac{RT}{\Omega} h(c_d), \quad (2.21)$$

with μ_c^o the chemical potential of the pure liquid and

$$h(c_d) = \Omega c_d \ln \frac{\Omega c_d}{1 + \Omega c_d} + \chi \frac{\Omega c_d}{1 + \Omega c_d}, \quad [h] = 1. \quad (2.22)$$

Therein, R ($[R] = J/(Kmol)$), T ($[T] = K$), and χ are the universal gas constant, the absolute temperature, and the Flory parameter describing the enthalpic interaction between the solvent and the polymer network, respectively.² It holds that for $c_d \rightarrow 0$, $\psi_m(c_d) \rightarrow 0$.

From (2.19)₁ and (2.20), the constitutive equation $\hat{S}_d(\mathbf{F}_d)$ for the dry-reference stress is derived; from (2.19)₂, (2.21), and (2.22) the constitutive equation $\hat{\mu}_c(c_d)$ for the chemical potential is derived. This latter can also be rewritten as function of J_d by exploiting the local constraint (2.16); with a slight abuse of notation, we write $\hat{\mu}_c(c_d) = \hat{\mu}_c(J_d)$:

$$\hat{\mu}_c(J_d) = \mu_c^o + RT \left(\ln \frac{J_d - 1}{J_d} + \frac{1}{J_d} + \frac{\chi}{J_d^2} \right). \quad (2.23)$$

2.3. Free-swelling of polymer gels

The free-swelling problem is posed as a boundary value problem (BVP) with null boundary loads and under the influence of the control parameter μ_e , defined as the chemical potential of the bath which surrounds the body,

$$\mathbf{S}_d \mathbf{m} = \mathbf{0} \quad \text{and} \quad \mu_c = \mu_e \quad \text{on} \quad \partial \mathcal{P}_d. \quad (2.24)$$

It is worth noting that the BC on the chemical potential is an implicit way to require that the Dirichlet BC (2.14)₂ is satisfied, as solvent concentration \bar{c}_d at the boundary cannot be controlled explicitly. Specifically, we should write

$$c_d = \bar{c}_d \quad \text{with} \quad \mu_c = \hat{\mu}_c(\bar{c}_d) + p\Omega = \mu_e \quad \text{on} \quad \partial \mathcal{P}_d. \quad (2.25)$$

Shortly, we write $\mu_c = \hat{\mu}_c(c_d) + p\Omega = \mu_e$, that is, Eq. (2.24)₂.

In the special case of homogeneous and isotropic free-swelling, the solution as $\tau \rightarrow \infty$ describes a homogeneous equilibrium state \mathcal{P}_e of the gel body. Such a solution is typically written in terms of the free-swelling degree, $J_d^{1/3}$, which is controlled by the value μ_e of the chemical potential of the bath. The governing equations of this state can be written as,

$$\mathbf{S}_d = \mathbf{0} \quad \text{and} \quad \mu_c = \mu_e \quad \text{in} \quad \mathcal{P}_d. \quad (2.26)$$

Assuming an isotropic deformation $\mathbf{F}_d = J_d^{1/3} \mathbf{1}$ and using the constitutive Eqs. (2.18)₁ and (2.19)₁, the condition above of zero stress yields the pressure p at \mathcal{P}_e :

$$G_d \mathbf{F}_d - p \mathbf{F}_d^* = \mathbf{0} \quad \Rightarrow \quad p = G_d J_d^{-1/3}. \quad (2.27)$$

Substituting this expression for p in the constitutive relation (2.18)₂ for the chemical potential yields a non-linear equation relating μ_e and J_d :

$$\hat{\mu}_c(J_d) + G_d J_d^{-1/3} \Omega = \mu_e. \quad (2.28)$$

For $\mu_e \rightarrow -\infty$, corresponding to polymer being surrounded by air, $J_d \rightarrow 1$ and Eq. (2.28) describes the equilibrium reference dry state \mathcal{P}_d of the network (Fig. 1, left panel). For $\mu_e = \mu_c^o$, that is for a bath consisting of pure liquid, Eq. (2.28) describes the equilibrium swollen state \mathcal{P}_e (Fig. 1, right panel). The intermediate state (Fig. 1, middle panel) corresponds to the initial time, before diffusion starts. Then, the equation $\mathbf{S}_d = \mathbf{0}$ and $J_d = 1$ delivers the trivial solution $J_d = 1$.

Remark. The amount of swelling J_d is controlled by the chemical potential μ_e of the bath and is completely independent on the initial dry volume. At the equilibrium state \mathcal{P}_e , the volume of the liquid uptaken by the gel is

$$v_l = \Omega c_d V_d = (J_d - 1) V_d, \quad (2.29)$$

that is, the liquid volume v_l depends linearly on the original dry volume V_d of the body. Moreover, the size of liquid bath does not appear in the equations above. The underlying assumption is that we are dealing with free swelling of a body in an infinite bath and the amount v_l of liquid is always available, whichever is the value of J_d we obtain from Eq. (2.28).³

² Within Flory thermodynamics, the enthalpic interactions between the solvent and the polymer network are completely summed up in the parameter χ , which measures the affinity between polymer and liquid and affects gel swelling at equilibrium. An interesting study on the role of χ in determining multiple solution of the free-swelling steady problem in perfectly cross-linked gels has been presented in Duda, Souza, and Fried (2010).

³ For instance, for $G_d = 4.0E04$ Pa, $\Omega = 9.92E-05$ m³ mol⁻¹ and $\chi = 0.2$, at $T = 373.15$ K we get $J_d = 27.1$. Given a dry volume of $V_d = 1E-06$ m³, we get $v_l = 2.61E-05$ m³.

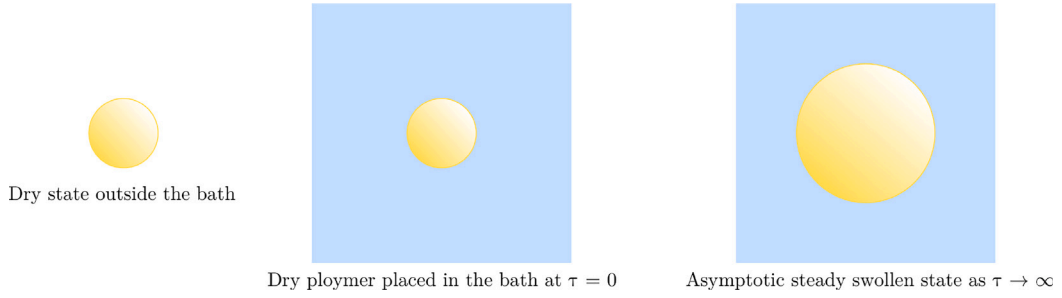


Fig. 1. The dry network \mathcal{P}_d (left); the initial state \mathcal{P}_0 of the gel in the bath, before diffusion starts (center); the homogeneously swollen and stress-free state \mathcal{P}_e (right).

2.4. Swelling of polymer gels: the body and bath system

The same problem may be viewed from a different perspective, which as well sets the stage for analysis of the free-swelling of partially cross-linked polymer gels. Apart from the domain of the gel body itself, we now include in the above model the domain of the bath while assuming that they are both contained in a fixed box.

It is important to remark a few aspects of the problem:

1. including the bath in the system means giving up the control of the chemical potential μ_e of the bath;
2. we are concerned with only one incompressible species in the bath, i.e. the liquid; hence, there is no need to introduce a concentration variable in the bath to aid its description (this is not the case in the gel body because there are two species, the polymer network and the liquid);
3. we assume that homogeneity is maintained within the bath due to lack of concentration gradients and further we are not concerned with the flow due to pressure gradients within the bath as only steady state solutions are indeed considered.

Here, \mathcal{P}_0 denotes the initial state of the gel body, before diffusion starts at time $\tau = 0$ and V_b the initial bath volume (see Fig. 1, middle panel). The variables describing the gel body state are the displacement \mathbf{u}_d and the liquid concentration c_d , previously introduced. Assuming that the external boundary of the fixed box is impermeable, at any time $\tau \in \mathcal{I}$, the current bath volume $v_b(\tau)$ is known once the current liquid volume v_l in the gel has been evaluated:

$$v_b(\tau) = V_b - \int_{\mathcal{P}_d} \Omega c_d dV_d = V_b - \int_{\mathcal{P}_d} (J_d - 1) dV_d, \quad (2.30)$$

where the local constraint (2.16) has also been used.

Remark. We could also evaluate $v_b(\tau)$ by solving an extra mass balance equation for the liquid within the bath domain under the assumption of continuity of the liquid across the shared boundary between the bath and the gel body, as we shall do for partially cross-linked bodies. In that case, we would write,

$$\frac{\dot{v}_b}{\Omega} = \int_{\partial\mathcal{P}_d} q_i da \quad \text{with} \quad q_i = -\mathbf{h}_i \cdot (-\mathbf{n}), \quad (2.31)$$

where q_i is the rate of solvent transported across an elementary surface of the shared boundary and \mathbf{h}_i the corresponding surface flux. Note that the external boundary of the bath does not contribute to such a supply due to its impermeable nature. Starting from (2.31), the continuity of the liquid across the shared boundary, $q_i = -q_s$, the local balance of liquid moles in the gel body (2.13) and the local constraint (2.16) combine to give

$$\dot{v}_b = - \int_{\mathcal{P}_d} \dot{J}_d dV_d, \quad (2.32)$$

to be solved with the initial condition $v_b(0) = V_b$.⁴

2.4.1. Thermodynamics of the body–bath system

Thermodynamics must be formulated including not only the restricted FR free energy (2.17) of the gel body, but also the free energy contribution of the bath. So, a new restricted total free energy Ψ is introduced which includes the free energy density per

⁴ It is worth noting that to guarantee that $v_b(\tau) \gg 0$, an unilateral constraint on J_d or on c_d should be incorporated in the formulation. However, the current study is not concerned with such a limiting case. It is assumed that while V_b is finite, it is sufficiently large so as to ensure the presence of the bath all along the boundary $\partial\mathcal{P}_d$ for all times $\tau \in \mathcal{T}$.

unit initial bath volume of the liquid in the bath:⁵

$$\psi_b(v_b) = \mu_c^o \frac{v_b}{\Omega} \frac{1}{V_b}. \quad (2.33)$$

Thus, the restricted total free energy Ψ takes the form

$$\Psi = \int_{\mathcal{P}_d} \psi_r(\mathbf{F}_d, c_d, p) dV_d + \psi_b(v_b) V_b. \quad (2.34)$$

At thermodynamic equilibrium, the time derivative of the free energy of the system, must be equal to the expended mechanical and chemical power in the system. As far as the time derivative of Ψ is concerned, we get

$$\dot{\Psi} = \int_{\mathcal{P}_d} \left(\left(\frac{\partial \psi_e}{\partial \mathbf{F}_d} - p \mathbf{F}_d^* \right) \cdot \dot{\mathbf{F}}_d + \left(\frac{\partial \psi_m}{\partial c_d} + \Omega p \right) \dot{c}_d - (J_d - \hat{J}(c_d)) \dot{p} \right) dV_d + \frac{\partial \psi_b}{\partial v_b} V_b \dot{v}_b. \quad (2.35)$$

On the other hand, while the elementary mechanical power $d\mathcal{W}_m = \mathbf{S}_d \cdot \dot{\mathbf{F}}_d dV_d$ maintains its usual form, the chemical power must also take into account the bath contribution which is expressed by introducing the chemical potential μ_c^b of the liquid in the bath besides that of the liquid in the gel body, as,

$$\mathcal{W}_c = - \int_{\partial \mathcal{P}_d} \mu_c \mathbf{h}_d \cdot \mathbf{n} dA_d - \int_{\partial \mathcal{P}_\tau} \mu_c^b \mathbf{h}_i \cdot (-\mathbf{n}) da = \int_{\mathcal{P}_d} (\mu_c \dot{c}_d - \nabla \mu_c \cdot \mathbf{h}_d) dV_d + \mu_c^b \frac{\dot{v}_b}{\Omega},$$

where the divergence theorem in combination with the local liquid molar balance (2.13) in the gel body and the global liquid molar balance (2.31) in the bath have been employed. At thermodynamic equilibrium,

$$\mathcal{W}_m + \mathcal{W}_c = \dot{\Psi} \quad (2.36)$$

Following the same steps previously shown, the constitutive equations for the reference-dry stress \mathbf{S}_d , the chemical potential μ_c of the liquid in the gel and the chemical potential μ_c^b of the liquid in the bath are identified:

$$\mathbf{S}_d = \frac{\partial \psi_e}{\partial \mathbf{F}_d} - p \mathbf{F}_d^*, \quad \mu_c = \frac{\partial \psi_m}{\partial c_d} + \Omega p, \quad \mu_c^b = \mu_c^o. \quad (2.37)$$

As discussed earlier, the homogeneous equilibrium state under isotropic free-swelling of the gel body is characterized by zero stress and an isotropic deformation $\mathbf{F}_d = \lambda \mathbf{I}$. Moreover, the chemical equilibrium on $\partial \mathcal{P}_d$ between liquid in the body and in the bath, that is, $\mu_c = \mu_c^b$ delivers the same Eq. (2.28) already discussed.

Finally, (2.30) implies that the change in the volume of the liquid bath corresponds to the change of the body volume, that is,

$$v_b - V_b = -(J_d - 1) V_d \geq 0. \quad (2.38)$$

It means that the initial volume bath must be such to guarantee that the inequality (2.38) holds.

3. Partially cross-linked polymer gels

For partially cross-linked polymer gels, the stress-diffusion theory must include consideration of the free-chains. The liquid-polymer mixture is still treated as a single continuum body, which allows for mass flux of the liquid and of the free-chains. The theory is based on the balance equations governing the diffusion of the liquid and the free-chains, and the forces acting on the gel body. Further the dissipation inequality prescribes the thermodynamic restrictions on constitutive recipes appropriate for partially cross-linked polymeric gels.

3.1. State variables and balance laws for the polymer gel

We assume that the domain of definition of all the state variables of the polymer gel is a reference configuration \mathcal{P}_d , corresponding to the dry polymer network, before exposure to solvent and without any free-chains. This choice is driven by the idea to extend the current model to include the consideration of a polymer network fraction which changes in time due to cross-links breaking; in this case, a reference configuration which corresponds to the initial polymer network fraction (before cross-links breakage) may be more convenient.

In order to describe the state of such a polymer, we retain the state variables introduced earlier, that is, displacement of the body \mathbf{u}_d (a material field) and liquid molar concentration c_s (a spatial field), and further introduce the spatial field g_s as the free-chain molar concentration per unit current volume. Consequently, the free-chains volume in any given volume element dv is $dv_f = \Lambda g_s dv < dv$ with Λ [m³/mol] the polymer molar volume.

With this, the volume element dv consists of liquid volume dv_l , free-chains volume dv_f and network volume dv_n ; this latter cannot change in any configuration, that is, $dv_n = dV_d$:

$$dv = dv_l + dv_f + dv_n = \Omega c_s dv + \Lambda g_s dv + dV_d. \quad (3.39)$$

⁵ Note that $\frac{v_b}{\Omega}$ is the number of liquid moles in the bath and the derivative of ψ_b with respect to the number of moles is indeed μ_c^o .

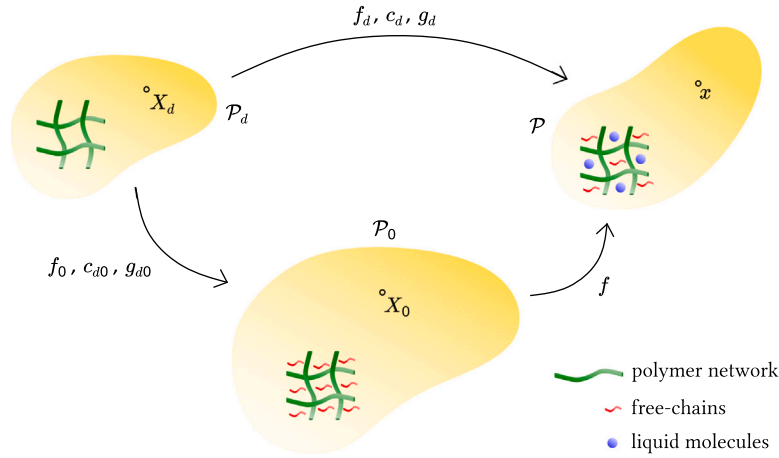


Fig. 2. Different states of the polymer gel and their relationships: the dry state \mathcal{P}_d only consists of polymer network, the *as-prepared* state \mathcal{P}_0 before swelling starts consists of polymer network and free-chains, the current state \mathcal{P} consists of polymer network, free-chains and liquid.

The initial configuration \mathcal{P}_0 of the polymer, before any diffusion starts, consists of network and free-chains. We denote it the *as-prepared* state and write

$$V_0 = V_d + V_f, \tag{3.40}$$

where V_f is the volume of free-chains present in V_0 and V_d is the volume of the dry configuration \mathcal{P}_d . We write $g_d = J_d g_m$ for the free-chains concentration per unit dry volume of the polymer network, where $g_m(X, t) = g_s(f_d(X, t), t)$ is the material representation of the spatial field g_s and

$$dv = \Omega c_d dV_d + \Lambda g_d dV_d + dV_d. \tag{3.41}$$

As $dv = J_d dV_d$, it holds

$$J_d = 1 + \Omega c_d + \Lambda g_d = \hat{J}_d(c_d, g_d), \tag{3.42}$$

which corresponds to a local constraint that is similar to (2.16) of the perfectly cross-linked case.

At the initial state, $c_d = 0$ and the concentration g_{d0} of the free-chains is assumed to be known. So, we evaluate the volume V_d of the polymeric dry network as

$$V_d = \phi_0 V_0 \quad \text{with} \quad \phi_0 = \frac{1}{J_0} \quad \text{and} \quad J_0 = 1 + \Lambda g_{d0}. \tag{3.43}$$

It corresponds to say that the operation of *cleaning free-chains out* is described through a homogeneous deformation f_0^{-1} of gradient $\mathbf{F}_0^{-1} = (1 + \Lambda g_{d0})^{-1/3} \mathbf{I}$ from \mathcal{P}_0 to \mathcal{P}_d , which is assumed to be known (see Fig. 2).

So, ϕ_0 characterizes the polymer at its initial *as-prepared* state. A perfectly cross-linked polymer corresponds to $\phi_0 = 1$, that is, $V_0 = V_d$. On the other side, a polymer solution, that is, the set of long-chain polymers before the cross-linking process, corresponds to $\phi_0 \rightarrow 0$; in this case, $V_0 \rightarrow V_f$ and $V_d \rightarrow 0$. We call ϕ_0 the *initial network fraction*; it can take values in the range $(0, 1]$.

Within the present study, ϕ_0 is a design parameter which can be controlled in the polymerization phase. It affects the polymer network component of the *as-prepared* state, whose volume V_d changes with ϕ_0 .

In addition to the local liquid molar balance (2.13) in the gel body and the balance (2.5) of force, we need to introduce the free-chain molar balance, written as,

$$\dot{g}_d = -\text{div} \mathbf{j}_d \quad \text{in} \quad \mathcal{P}_d \times \mathcal{T}, \tag{3.44}$$

where \mathbf{j}_d is the flux of the free-chains across any elementary surface within the reference configuration of the body and it could be specified as a Neumann BC. One can show that, this flux can be decomposed additively into two contributions, which allow us to describe the two physical mechanisms of transport: (1) transport due to diffusion of free-chains within the gel body, corresponding to a contribution $\hat{\mathbf{j}}_d$, and (2) transport due to the advection of the free-chains along with the liquid, corresponding to a contribution $(g_d/c_d)\mathbf{h}_d$. As a consequence, Eq. (3.44) admits the alternative representation

$$\dot{g}_d = -\text{div} \hat{\mathbf{j}}_d - \text{div} \left(\frac{g_d}{c_d} \mathbf{h}_d \right) \quad \text{in} \quad \mathcal{P}_d \times \mathcal{T}. \tag{3.45}$$

The Dirichlet BCs associated to the molar balances can be specified implicitly, as explained earlier, and are for the liquid and the free-chains, respectively,

$$\mu_c = \mu_c^b \quad \text{and} \quad \mu_g = \mu_g^b \quad \text{on} \quad \partial \mathcal{P}_d, \tag{3.46}$$

where μ_g^b is introduced as the chemical potential of the free-chains in the bath. It is to be noted that in the case of perfectly cross-linked polymer swelling in a pure liquid bath, the right-hand side of the Dirichlet BC (2.24)₂ involved a constant, that was the chemical potential $\mu_e = \mu_e^o$ of the bath. For partially cross-linked polymer gels, the bath cannot be considered as a pure liquid owing to the possible presence of free-chains released from the gel body. Thus, the right-hand sides of the Dirichlet BC (3.46) involve μ_c^b and μ_g^b , which are functions of the bath composition, as we will see in the following. Finally, we assume that at the initial time the free-chains concentration in the body is g_{d0} .

3.2. State variables and balance laws for the bath

We adopt a global view of the bath by introducing the total number N_c of liquid moles and N_b of free-chain moles, as the state variables of the bath. Such a choice implies that we are not concerned with the local flow within the bath and consequently there is no need to introduce the local molar concentrations. Within this framework, the liquid molar balance within the domain \mathcal{B}_τ occupied by the bath is written as

$$\dot{N}_c = \int_{\partial\mathcal{B}_\tau^i} q_i da + \int_{\partial\mathcal{B}_\tau^e} q_e da_e = - \int_{\partial\mathcal{B}_\tau^i} \mathbf{h}_i \cdot (-\mathbf{n}) da - \int_{\partial\mathcal{B}_\tau^e} \mathbf{h}_e \cdot \mathbf{n}_e da_e, \quad (3.47)$$

where the pedix e identifies quantities associated to the external boundary $\partial\mathcal{B}_\tau^e$ of the bath, $\partial\mathcal{B}_\tau^i = \partial\mathcal{P}_\tau$ and $\partial\mathcal{B}_\tau = \partial\mathcal{B}_\tau^i \cup \partial\mathcal{B}_\tau^e$. We transform the integral on $\partial\mathcal{B}_\tau^i$ into an integral on the current boundary $\partial\mathcal{P}_\tau$ of the polymer by employing the continuity of the liquid across the shared boundary, that is, we set $q_i da = -q_s da$. Moreover, we assume that $\partial\mathcal{B}_\tau^e$ is an impermeable boundary and set $q_e da_e = 0$.⁶ With this, Eq. (3.47) reduces to

$$\dot{N}_c = \int_{\partial\mathcal{P}_d} \mathbf{h}_d \cdot \mathbf{m} dA_d. \quad (3.48)$$

This is an ODE in time, coupled to the mechanical and fluid problems of the polymer. It needs to be solved along with an initial condition; we assume that at time $\tau = 0$ the bath consists of pure solvent with a given number of moles, N_{c0} , implying a known initial volume $V_b = \Omega N_{c0}$ of the bath.

Following a similar derivation, the free-chain molar balance within the domain \mathcal{B}_τ is written as,

$$\dot{N}_g = \int_{\partial\mathcal{P}_d} \mathbf{j}_d \cdot \mathbf{m} dA_d, \quad (3.49)$$

with an initial condition $N_{g0} = 0$ corresponding to the pure solvent bath.

We introduce two global constraints requiring that the total volume of the liquid and of the free-chains at any time τ within the system must be equal to the corresponding volumes at the initial time:

$$\Omega N_c + \int_{\mathcal{P}_d} \Omega c_d dV_d = V_b, \quad \Lambda N_g + \int_{\mathcal{P}_d} \Lambda g_d dV_d = \int_{\mathcal{P}_d} \Lambda g_{d0} dV_d, \quad (3.50)$$

owing to the impermeability of the external boundary of the bath. These equations play the same role as Eq. (2.30) when no free-chains flow through the body.

It is worth noting that, differently from what happens when the bath consists of liquid only, now the two variables N_c and N_g affect the chemical equilibrium of the body and, consequently, Eqs. (3.50) need to be considered as internal constraints.

3.3. Thermodynamics of the body and bath system: partially cross-linked polymer gels

We introduce a reduced total free energy Ψ , that includes, in addition to the reduced FR free energy of the gel body:

- (a) the Flory–Huggins (FH) free energy density $\psi_b(N_c, N_g)$ of the bath, viewed as a mixture of liquid and free-chains;
- (b) the two global constraints (3.50) through the introduction of Lagrange multipliers π_c and π_g respectively.

The FR free energy of the gel body is represented as a generalization of the FR free energy which holds for perfectly cross-linked polymer gels. As we shall see in the following, it includes the elastic energy density associated to the polymer network and the mixing free energy corresponding to both the liquid molecules and the free-chains. Thus, the total free energy reads

$$\begin{aligned} \Psi = & \int_{\mathcal{P}_d} (\psi_F(\mathbf{F}_d, c_d, g_d) - p(J_d - \hat{J}_d(c_d, g_d))) dV_d + \psi_b(N_c, N_g) V_b \\ & - \pi_c (\Omega N_c + \int_{\mathcal{P}_d} \Omega c_d dV_d - V_b) - \pi_g (\Lambda N_g + \int_{\mathcal{P}_d} \Lambda (g_d - g_{d0}) dV_d). \end{aligned} \quad (3.51)$$

It is worth noting that the free energy $\psi_F(\mathbf{F}_d, c_d, g_d)$ is a FR-like free energy density of partially cross-linked polymers defined up to a constant corresponding to the value it takes on the *as-prepared* state and $\psi_F(\mathbf{I}, 0, 0) = 0$, that is, the reference configuration is a natural configuration for the body.

⁶ We infer that the right-hand-side of (3.47) would possibly be a known quantity if the flux on $\partial\mathcal{B}_\tau^e$ is specified.

Following the same procedure as is Section 2.4.1, we study the thermodynamic equilibrium by equating the time derivative of the free energy of the system and the expended power in the system. The time derivative of Ψ now reads,

$$\begin{aligned} \dot{\Psi} = & \int_{\mathcal{P}_d} \left(\left(\frac{\partial \psi_F}{\partial \mathbf{F}_d} - p \mathbf{F}_d^* \right) \cdot \dot{\mathbf{F}}_d + \left(\frac{\partial \psi_F}{\partial c_d} + \Omega(p - \pi_c) \right) \dot{c}_d \right) dV_d \\ & + \int_{\mathcal{P}_d} \left(\left(\frac{\partial \psi_F}{\partial g_d} + \Lambda(p - \pi_g) \right) \dot{g}_d - (J_d - \hat{J}_d(c_d, g_d)) \dot{p} \right) dV_d \\ & + \left(\frac{\partial \psi_b}{\partial N_c} V_b - \Omega \pi_c \right) \dot{N}_c + \left(\frac{\partial \psi_b}{\partial N_g} V_b - \Lambda \pi_g \right) \dot{N}_g \\ & - (\Omega N_c + \int_{\mathcal{P}_d} \Omega c_d dV_d - V_b) \dot{x}_c - (\Lambda N_g + \int_{\mathcal{P}_d} \Lambda (g_d - g_{d0}) dV_d) \dot{x}_g. \end{aligned} \quad (3.52)$$

The mechanical power still retains its usual form, that is, $d\mathcal{W}_m = \mathbf{S} \cdot \dot{\mathbf{F}}_d dV_d$. On the other hand, the chemical power must now take into account the contributions of both the liquid and the free-chains in the entire body–bath system. The chemical power thus reads,

$$\begin{aligned} \mathcal{W}_c = & - \int_{\mathcal{P}_d} (\mu_c \mathbf{h}_d \cdot \mathbf{m} + \mu_g \mathbf{j}_d \cdot \mathbf{m}) dA_d - \int_{\mathcal{P}_r} (\mu_c^b \mathbf{h}_i \cdot (-\mathbf{n}) da + \mu_g^b \mathbf{j}_i \cdot (-\mathbf{n})) da \\ = & \int_{\mathcal{P}_d} (\mu_c \dot{c}_d - \nabla \mu_c \cdot \mathbf{h}_d + \mu_g \dot{g}_d - \nabla \mu_g \cdot \mathbf{j}_d) dV_d + \mu_c^b \dot{N}_c + \mu_g^b \dot{N}_g, \end{aligned} \quad (3.53)$$

where the divergence theorem in combination with the local molar balances (2.13) and (3.44) in the gel body, global molar balances in the bath of the liquid (3.48) and of the free-chains (3.49), were employed. Consequently, at thermodynamic equilibrium the following state equations hold,

$$\begin{aligned} S_d = \frac{\partial \psi_F}{\partial \mathbf{F}_d} - p \mathbf{F}_d^*, \quad \mu_c = \frac{\partial \psi_F}{\partial c_d} + \Omega(p - \pi_c), \quad \mu_g = \frac{\partial \psi_F}{\partial g_d} + \Lambda(p - \pi_g), \\ \mu_c^b = \frac{\partial \psi_b}{\partial N_c} V_b - \Omega \pi_c, \quad \mu_g^b = \frac{\partial \psi_b}{\partial N_g} V_b - \Lambda \pi_g. \end{aligned} \quad (3.54)$$

3.3.1. Free energy density of a partially cross-linked polymer gel

As noted in Section 2.2, the classical FR theory for swelling polymers is based on a linear superposition of the elastic and mixing free energies, resulting in a free energy density of the gel body. Such superposition is as well assumed to be applicable to partially cross-linked polymer gels with some modifications, as was done in Douglas and McKenna (1993) and Nandi and Winter (2005). Only the cross-linked polymer chains are assumed to contribute to the network's elasticity. However, it is also assumed that the elastic free energy density ψ_e of the gel body is affected by the free-chains only due to their presence/absence.

In what follows, ϕ represents the local gel fraction of the polymer that is the ratio, within any given volume element, of the cross-linked network volume dV_d to the current total polymer volume $dV_d + dv_f$. Dividing the numerator and denominator of this ratio by dV_d , one can obtain the following expression for the local gel fraction,

$$\phi(g_d) = \frac{1}{1 + \Lambda g_d}; \quad (3.55)$$

it holds $\phi(g_{d0}) = \phi_0$. Note that the gel fraction is a function of the molar concentration of the free-chains and as $g_d \rightarrow 0$, $\phi(g_d) \rightarrow 1$.

Another property of interest concerning the polymer gel is the impact of the presence of the free chains on its cross-link density ν , which is the ratio of the density ρ_n of the bulk polymer and the average molecular weight M_c of the strands between the cross-links. It is a measure of the quality of cross-linking within the network and is related to the initial concentration of the free-chains after the cross-linking process according to the expression,

$$\nu = \frac{\rho_n}{M_c} \phi_0. \quad (3.56)$$

To take into account that the contribution to the elastic free energy density is only due to network chain connectivity, we assume that

$$G_d = \kappa k_B T \nu = \kappa k_B T \frac{\rho_n}{M_c} \phi_0. \quad (3.57)$$

In the equation above, $\kappa \leq 1$ is a parameter determined by experimental fitting and it accounts for the various inhomogeneities and dangling chains that represent network imperfections, and k_B is the Boltzmann constant. Note that as $g_{d0} \rightarrow 0$, $\phi_0 \rightarrow 1$ and G_d tends to the classical elastic modulus of a perfectly cross-linked polymer introduced in Section 2.2.

The polymer-solvent mixing free energy is assumed to be an extension of the classical expression introduced in (2.21) to the context of a partially cross-linked polymer (Nandi & Winter, 2005). It is written as,

$$\psi_m(c_d, g_d) = \mu_c^o c_d + \frac{RT}{\Omega} h(c_d, g_d) + \mu_g^o g_d + \frac{RT}{\Lambda} j(c_d, g_d), \quad (3.58)$$

with the functions $h(c_d, g_d)$ and $j(c_d, g_d)$ defined as

$$\begin{aligned} h(c_d, g_d) = \Omega c_d \ln \left(\frac{\Omega c_d}{1 + \Omega c_d + \Lambda g_d} \right) + \chi \Omega c_d \left(\frac{1 + \Lambda g_d}{1 + \Omega c_d + \Lambda g_d} \right), \\ j(c_d, g_d) = \Lambda g_d \ln \left(\frac{\Lambda g_d}{1 + \Omega c_d + \Lambda g_d} \right). \end{aligned} \quad (3.59)$$

Note that we have considered the enthalpic interaction parameter χ to be same for the interactions of the liquid with either the network or the free-chains, as the latter have the same nature as that of the polymeric network.

Finally, we can define the FR like free energy density ψ_F of partially cross-linked polymers employing a linear superposition of elastic and mixing free energies:

$$\psi_F(\mathbf{F}_d, c_d, g_d) = \psi_e(\mathbf{F}_d) + \psi_m(c_d, g_d), \quad (3.60)$$

with the elastic energy $\psi_e(\mathbf{F}_d)$ given by Eq. (2.20). Using the new free-energy density in the Eqs. (3.54), the Coleman–Noll procedure allows to identify the admissible constitutive relations for the reference stress \mathbf{S}_d , the chemical potential μ_c of the liquid in the gel and the chemical potential μ_g of the free-chains in the gel as

$$\mathbf{S}_d(\mathbf{F}_d, p) = G_d \mathbf{F}_d - p \mathbf{F}_d^*, \quad (3.61)$$

$$\begin{aligned} \mu_c(c_d, g_d, p, \pi_c) = & \mu_c^0 + RT \ln \left(\frac{\Omega c_d}{1 + \Omega c_d + \Lambda g_d} \right) + RT \left(\frac{1 - (\Omega - \Lambda) g_d}{1 + \Omega c_d + \Lambda g_d} \right) \\ & + RT \chi \left(\frac{1 + \Lambda g_d}{1 + \Omega c_d + \Lambda g_d} \right)^2 + \Omega(p - \pi_c), \end{aligned} \quad (3.62)$$

$$\begin{aligned} \mu_g(c_d, g_d, p, \pi_g) = & \mu_g^0 + RT \ln \left(\frac{\Lambda g_d}{1 + \Omega c_d + \Lambda g_d} \right) + RT \left(\frac{1 + (\Omega - \Lambda) c_d}{1 + \Omega c_d + \Lambda g_d} \right) \\ & + RT \chi \left(\frac{\Omega \Lambda c_d^2}{(1 + \Omega c_d + \Lambda g_d)^2} \right) + \Lambda(p - \pi_g). \end{aligned} \quad (3.63)$$

3.3.2. Free energy of a biphasic bath

The expression for the change in the total free energy of the bath viewed as a Flory–Huggins solution composed of the liquid as the solvent and the free-chains as the solute is

$$\begin{aligned} \Psi_b(N_c, N_g) = & \psi_b(N_c, N_g) V_b \\ = & \mu_c^0 N_c + RT N_c \ln v_c + \mu_g^0 N_g + RT N_g \ln v_g + RT \chi N_c v_g, \end{aligned} \quad (3.64)$$

where the volume fractions of the liquid v_c and of the free-chains v_g are introduced and defined as

$$v_c(N_c, N_g) = \frac{\Omega N_c}{\Omega N_c + \Lambda N_g}, \quad v_g(N_c, N_g) = \frac{\Lambda N_g}{\Omega N_c + \Lambda N_g}. \quad (3.65)$$

Consequently, the constitutive equations for the chemical potential of the liquid μ_c^b and of the free chains μ_g^b in the bath can be derived by using Eqs. (3.54). As noted earlier, the reference dry configuration \mathcal{P}_d of the polymer body is its natural state. At the initial time, we have $\psi_F(\mathbf{F}_0, 0, g_{d0}) = \psi_{F0} \neq 0$ in the body and $\Psi_b(N_{c0}, 0) = \Psi_{b0} \neq 0$ in the bath.

4. Free-swelling of a partially cross-linked polymer: homogeneous steady-states

A free-swelling state corresponds to zero tractions on the boundary of the gel body. A distinguished free swelling state is the homogeneous equilibrium state corresponding to an isotropic deformation $\mathbf{F}_d = \lambda_d \mathbf{I}$ of the gel body. Due to the homogeneous nature of the body, the balance of forces implies a zero stress within the gel body: $\mathbf{S}_d = 0$. With this, (3.54)₁ yield

$$\boxed{\frac{\partial \psi_F}{\partial \mathbf{F}_d} - p \lambda_d^2 \mathbf{I} = \mathbf{0}}, \quad (4.66)$$

which holds true everywhere within \mathcal{P}_d . The chemical equilibrium at the shared boundary between the bath and the body requires that $\mu_c = \mu_c^b$ and $\mu_g = \mu_g^b$. By using the state Eqs. (3.54) for the chemical potentials, the two conditions can be written as

$$\boxed{\frac{\partial \psi_F}{\partial c_d} - \frac{\partial \psi_b}{\partial N_c} V_b + \Omega p = 0} \quad \text{and} \quad \boxed{\frac{\partial \psi_F}{\partial g_d} - \frac{\partial \psi_b}{\partial N_g} V_b + \Lambda p = 0}. \quad (4.67)$$

As $\mathbf{F}_d = \lambda_d \mathbf{I}$, the local volumetric constraint is written as

$$\boxed{\lambda_d^3 - 1 - \Omega c_d - \Lambda g_d = 0}, \quad (4.68)$$

and the global constraints (3.50) remains the same:

$$\boxed{\Omega N_c + \Omega c_d V_d = V_b}, \quad \boxed{\Lambda N_g + \Lambda g_d V_d = \Lambda g_{d0} V_d}. \quad (4.69)$$

Eqs. (4.66)–(4.69) are a system of 6 algebraic equations to be solved to get the 6 scalar unknowns, which characterize the homogeneous isotropic free-swelling problem: $(\lambda_d, c_d, g_d, N_c, N_g, p)$.

Table 2

Material properties of the gel body and the bath.

Ω [m ³ mol ⁻¹]	Λ [m ³ mol ⁻¹]	χ [-]	R [J mol ⁻¹ K ⁻¹]	T [K]	κ [-]	k_B [J K ⁻¹]	ρ_n [kg m ⁻³]	M_c [kg mol ⁻¹]
9.92E-05	3.29E-05	0.2	8.3145	373.15	1.0	1.38E-23	7.12E02	7.3E03

Once known the free-swelling deformation λ_d from \mathcal{P}_d , the deformation $\lambda = \lambda_d/\lambda_0$, with $\lambda_0 = (1 + \Lambda g_{d0})^{-1/3}$ from the initial state can be calculated. Employing the particular expressions for $\psi_F(\mathbf{F}_d, c_d, g_d)$ and $\psi_b(N_c, N_g)$ defined earlier, the previous system of 6 algebraic equations can be reduced as follows:

$$\begin{aligned}
G_d \lambda_d \mathbf{I} - p \lambda_d^2 \mathbf{I} &= 0, \\
\ln \left(\frac{\Omega c_d}{1 + \Omega c_d + \Lambda g_d} \right) + \left(\frac{1 - (\Omega - \Lambda) g_d}{1 + \Omega c_d + \Lambda g_d} \right) \\
+ \chi \left(\frac{1 + \Lambda g_d}{1 + \Omega c_d + \Lambda g_d} \right)^2 - \ln v_c - \left(1 - \frac{\Omega}{\Lambda} \right) v_g - \chi v_g^2 + \frac{\Omega}{RT} p &= 0, \\
\ln \left(\frac{\Lambda g_d}{1 + \Omega c_d + \Lambda g_d} \right) + \left(\frac{1 + (\Omega - \Lambda) c_d}{1 + \Omega c_d + \Lambda g_d} \right) \\
+ \chi \left(\frac{\Omega \Lambda c_d^2}{(1 + \Omega c_d + \Lambda g_d)^2} \right) - \ln v_g - \left(1 - \frac{\Lambda}{\Omega} \right) v_c - \chi \frac{\Lambda}{\Omega} v_c^2 + \frac{\Lambda}{RT} p &= 0, \\
\lambda_d^3 - 1 - \Omega c_d - \Lambda g_d &= 0, \\
\Omega N_c + \Omega c_d V_d - V_b &= 0, \\
\Lambda N_g + \Lambda (g_d - g_{d0}) V_d &= 0.
\end{aligned} \tag{4.70}$$

It is worth noting that the initial configuration \mathcal{P}_0 of the gel body before diffusion starts is an equilibrium configuration that can be obtained as the solution of the above system of equations corresponding to the boundary conditions describing an empty bath, that is, $N_c = 0$ and $N_g = 0$, that is, neglecting the chemical equilibrium Eqs. (4.70)_{2,3} and assuming $c_d = 0$ and $g_d = g_{d0}$. On the other side, the reference configuration \mathcal{P}_d of the gel body is an equilibrium configuration that can be obtained as the solution of the Eqs. (4.70)_{1,4} with $\lambda_d = 1$ and the pressure $p = G_d$.

The new equilibrium and swollen configuration \mathcal{P}_e of the gel body can be obtained as solution of the system of 6 algebraic equations, and its characteristics are discussed in the following study.

4.1. Results and discussion

The study aims to highlight how the free-chains which are in the gel body at its initial state impact on the swelling properties of the gel. We do it by assuming that the *as-prepared* state of the body is known, that is, the initial volume V_0 before swelling starts and the initial polymer network fraction ϕ_0 are known. Specifically, we fix V_0 and view ϕ_0 as a parameter in the study. As $\phi_0 = (1 + \Lambda g_{d0})^{-1}$, the parametric study is equivalently based on the parameter g_{d0} , that is, the initial homogeneous concentration of the free-chains in the gel.⁷ We also assume that the initial volume of the liquid bath V_b is known and fixed.

It is worth noting that the reference volume of the dry network scales with the parameter ϕ_0 as $V_d = \phi_0 V_0$, so affecting the concentration measures per unit reference volume of both the liquid and the free-chain components c_d and g_d in the gel body, respectively.

We fix $V_0 = 2.5\text{E}-07$ m³ and $V_b = 1\text{E}-03$ m³ as initial volumes of the gel and of the pure liquid bath, and list the numerical values for all the material parameters involved in the study in Table 2.

Liquid and free-chains concentration in the gel body. As first, we know that fixing the initial volume V_0 means that as ϕ_0 decreases the free-chains component increases, and the shear modulus decreases as $G_d \simeq \text{cost} \cdot \phi_0$ (see Eq. (3.57)). So, the standard mechano-diffusion theory for perfectly cross-linked polymers with lower and lower shear modulus would suggest that for ϕ_0 decreasing the amount of the liquid volume v_l uptaken by the body at the equilibrium increases.

The blue starred curve in the left panel of Fig. 3 confirms our expectations. At $\phi_0 = 1$, we get $v_l \simeq 30V_d$, that is, as for $\phi_0 = 1$ $V_d = V_0$, $v_l \simeq 30V_0$. However, for $\phi_0 \ll 1$, the initial volume V_0 is kept fixed whereas the initial polymer network V_d decreases with ϕ_0 (see Eq. (3.43)).

⁷ Let us remember here that $\phi_0 = 1$ means zero free-chains component and $\phi_0 = 0$ means zero polymer network component in the initial volume.

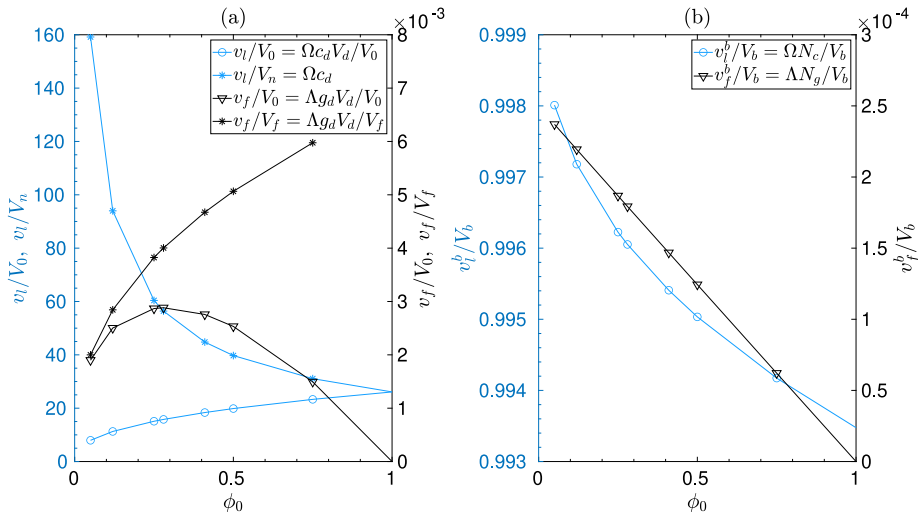


Fig. 3. $v_l/V_0, v_l/V_d, v_f/V_0, v_f/V_d$ steady-state homogeneous solutions of the system of Eqs. (4.70), for various initial gel fractions ϕ_0 employing a constant shear modulus $G_d = \phi_0(4E04)$ Pa.

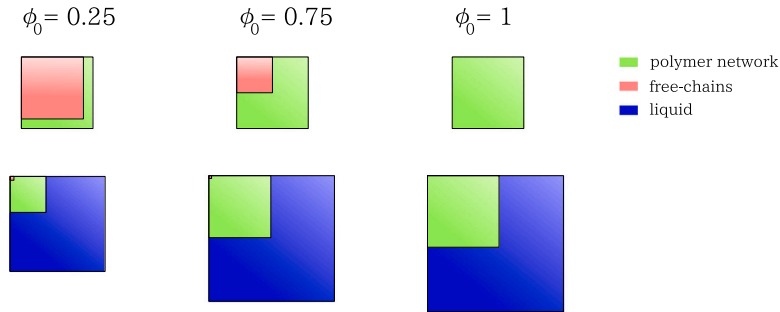


Fig. 4. Compositional representation of the swelling mechanism from the *as-prepared* state (top row) to the swollen steady state (bottom row) of the gel body. The volumes used are from the results in Fig. 3 for $\phi_0 = 0.25, 0.75, 1$. The volume of liquid uptaken v_l is scaled-down in all cases by 10 for clarity.

To correctly estimate the result for different $\phi_0 \ll 1$, we should compare the uptaken liquid volume v_l with respect to the same amount of polymer network, that is, v_l/V_d . Indeed, the blue starred curve confirms our expectations: increasing the amount of free chains, that is, decreasing ϕ_0 , the ratio v_l/V_d grows. Fig. 3, left panel, shows as the amount of liquid volume uptaken by the body is about 60 times the polymer network volume for $\phi_0 = 0.25$, 30 times the polymer network volume for $\phi_0 = 0.75$ and 25 times the polymer network volume for $\phi_0 = 1$. The misleading aspect of the blue circled curve is that it describes the ratio v_l/V_0 between the uptaken liquid volume and the initial volume, whose polymer network component is smaller and smaller as ϕ_0 is smaller and smaller. In these cases, the ratio v_l/V_0 described by the blue circled curve does not deliver a significant measure of the uptaken liquid. A schematic of the compositions of the various components is shown in Fig. 4 to aid the above interpretation. Likewise, the black starred curve shows the ratio between the volume v_f of free-chains in the body at equilibrium and its initial value V_f . For ϕ_0 decreasing, that is V_f decreasing, the final volume of free chains is lower and lower.

Liquid and free-chains concentration in the bath. The right panel of Fig. 3 shows the situation from the side of the bath. Firstly, if we do not have free-chains in the body at the initial state ($\phi_0 = 1$), we cannot have them at the final state as the bath at the initial state consists only of liquid (black triangled curve). On the other hand, if we have more free-chains at \mathcal{P}_0 , we also find more free-chains in the bath at the final state.

Secondly, the liquid in the bath changes with ϕ_0 , coherently with the change of the liquid volume in the body. To see it, it is convenient to compare the blue circled curve v_l^b/V_b in the right panel with the blue circled curve v_l/V_0 in the left panel. Indeed, in this case, we are comparing the two key quantities v_l and v_l^b , which are conveniently represented with respect to fixed, even if different, volumes, which do not change with ϕ_0 .

Swelling deformation and free-chains concentration. Fig. 5 (left panel) shows the change in the final values of the two key state variables of the problem, which are c_d and g_d , due to changes in ϕ_0 . We represented the liquid concentration density per unit initial volume, that is, c_d/J_0 as it is a fixed volume for different ϕ_0 . Considering c_d/J_0 means considering the number of moles per unit of *as prepared* volume V_0 . The blue circled curve shows that, as already shown by the blue circled curve in Fig. 3, to ϕ_0 decreasing it

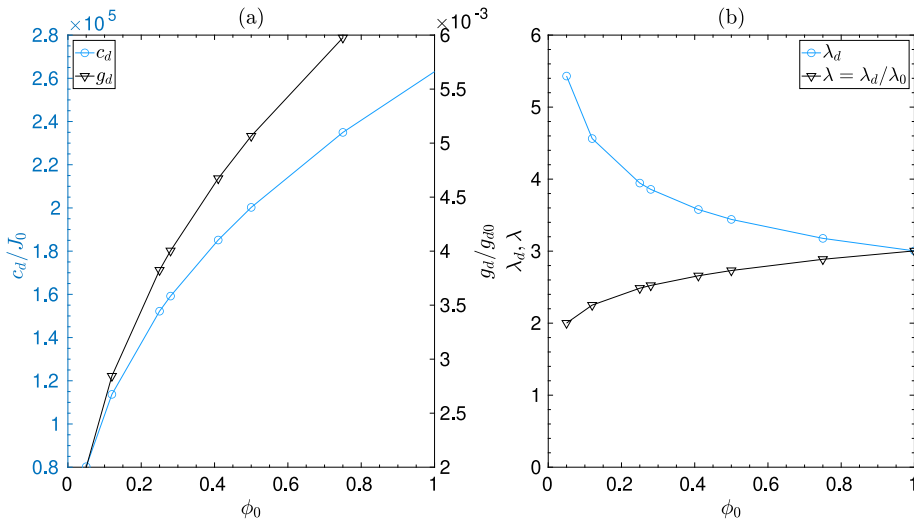


Fig. 5. c_d/J_0 , g_d/g_{d0} , λ_d , λ solutions of the steady-state homogeneous solutions of equations (4.70), for various initial gel fractions ϕ_0 employing a constant shear modulus $G_d = \phi_0(4E04)$ Pa.

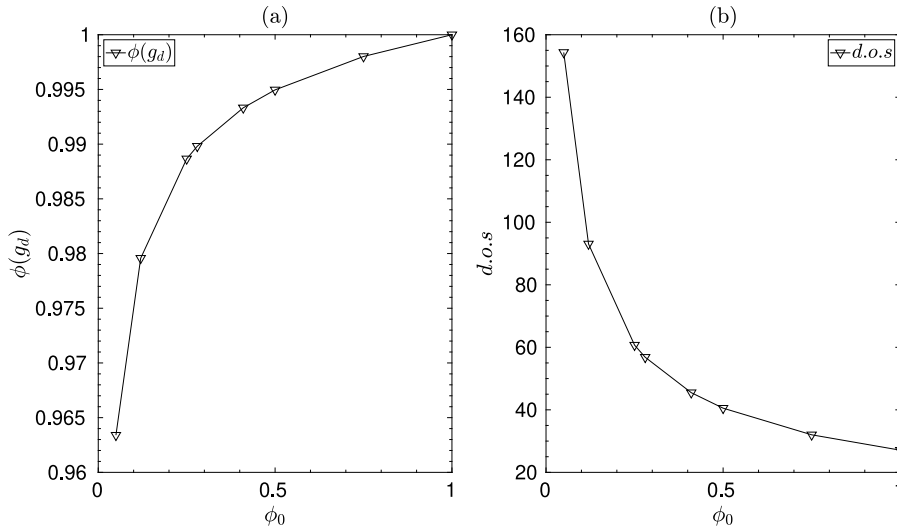


Fig. 6. $\phi(g_d)$ and $d.o.s$. steady-state homogeneous solutions of the system of Eqs. (4.70), for various initial gel fractions ϕ_0 employing a constant shear modulus $G_d = \phi_0(4E04)$ Pa.

corresponds a decreasing concentration field. On the other side, the black triangled curve shows that the ratio between the amount of free-chains at the final state and at the initial state decreases with the decrease in the initial network fraction.

Fig. 5 (right panel) puts in contrast the swelling deformation from the reference and from the initial state. For $\phi_0 = 1$, the two state coincide, that is, $\lambda_0 = 1$ and $\lambda_d = \lambda$. For $\phi_0 \ll 1$, the swelling deformation from the reference dry state grows when the initial polymer network decreases.

Polymer network fraction and degree of swelling. Finally, Fig. 6 (left panel) shows the polymer fraction $\phi(g_d)$, that is, the ratio within any given volume element, of the cross-linked network volume dV_d to the current total polymer volume $dV_d + dv_f$ as given by Eq. (3.55). The same figure (right panel) shows the $d.o.s$. quantity, defined as *degree of swelling* in Nandi and Winter (2005). Specifically, it is defined as

$$d.o.s. = \frac{1 + \Omega c_d + \Lambda g_d}{1 + \Lambda g_d}, \tag{4.71}$$

and aims to roughly estimate the amount of change in volume due to the liquid (indeed, for $c_d = 0$, $d.o.s. = 1$). The black triangled curve in the left panel shows that the polymer network fraction is always smaller than the initial network fraction ϕ_0 , for any value

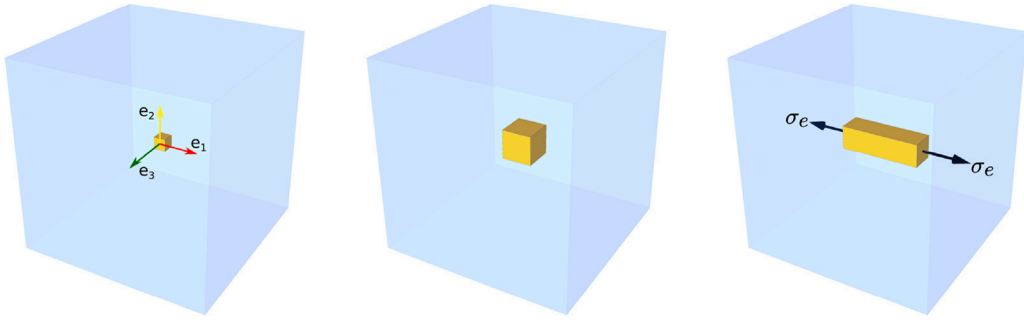


Fig. 7. Schematics depicting the various stages of response of the parallelepiped gel (in yellow) within the bath (light blue) for the case $\phi_0 = 0.25$: (a) The initial state \mathcal{P}_0 , (b) the equilibrium swollen state \mathcal{P}_e with zero imposed uni-axial load, (c) \mathcal{P}_e with positive imposed uni-axial load of $\sigma_e = 10$ kPa.

of ϕ_0 . So, free-chains are released in the bath. The black triangled curve in the right panel shows that the *d.o.s.* is much more important for decreasing initial polymer fraction, as already discussed above.

5. Partially cross-linked gels under step traction: homogeneous steady-states

We consider a parallelepiped-like gel whose edges are aligned along the directions of an orthonormal basis $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ of the three-dimensional vector space \mathcal{V} (see Fig. 7). The equilibrium swollen state \mathcal{P}_e of the gel that we aim to characterize is determined by the amount g_{d0} of the free-chains in the initial state \mathcal{P}_0 and by a traction σ_e applied on the end faces of the parallelepiped in the direction of its long axis \mathbf{e}_1 . We assume that the parallelepiped at its initial state has a volume $V_0 = 2.5\text{E-}07 \text{ m}^3$ and $V_f = \Lambda g_{d0} V_d = (1 - \phi_0) V_0$ is the initial content of free-chains that is expected to affect the traction test. The initial volume of the bath is $V_b = 1\text{E-}03 \text{ m}^3$. The imposed uni-axial load is assumed to induce a homogeneous and transversely isotropic deformation, which we represent as:

$$\mathbf{F} = \lambda_1 \mathbf{e}_1 \otimes \mathbf{e}_1 + \lambda_T \check{\mathbf{I}}, \quad \check{\mathbf{I}} = \mathbf{I} - \mathbf{e}_1 \otimes \mathbf{e}_1, \tag{5.72}$$

from the initial state \mathcal{P}_0 ; hence, $\mathbf{F}_d = \lambda_0 \lambda_1 \mathbf{e}_1 \otimes \mathbf{e}_1 + \lambda_0 \lambda_T \check{\mathbf{I}}$, where λ_1 and λ_T are introduced as the principal stretches along the longitudinal and transverse directions respectively. The stress shares a similar structure as that of the deformation. The Cauchy stress $\mathbf{T} = \sigma_1 \mathbf{e}_1 \otimes \mathbf{e}_1 + \sigma_T \check{\mathbf{I}}$, can be derived by an appropriate push-forward from the constitutive equation for the reference Piola–Kirchhoff stress (3.61) as

$$\mathbf{T} = \frac{1}{J_d} \mathbf{S}_d \mathbf{F}_d^T = \frac{1}{J_d} (G_d \mathbf{F}_d - p \mathbf{F}_d^* \mathbf{F}_d^T), \tag{5.73}$$

that is,

$$\sigma_1 = \frac{G_d}{\lambda_T^2 \lambda_0} \lambda_1 - p \quad \text{and} \quad \sigma_T = \frac{G_d}{\lambda_1 \lambda_0} - p. \tag{5.74}$$

It is to be noted that starting from the initial state \mathcal{P}_0 , both the diffusion process across the body–bath boundary and the deformation due to the imposed uni-axial traction are assumed to start simultaneously. The instantaneous (fast) response of the gel to such a traction would be a pure mechanical deformation assuming that the diffusion process has a much higher characteristic time compared to the mechanical response. The slow response, on the other hand, is described by a system of equations which are slightly different from the earlier case of free-swelling Section 4 with respect to the mechanical part. Indeed, instead of the condition $\mathbf{T}\mathbf{n} = \mathbf{0}$ on $\partial\mathcal{P}_t$, the stress traction on the boundary now has to satisfy the conditions

$$\mathbf{T}\mathbf{n} = \begin{cases} \sigma_e \mathbf{n} & \text{for } \mathbf{n} = \pm \mathbf{e}_1 \\ \mathbf{0} & \text{for } \mathbf{n} = \pm \mathbf{e}_2, \pm \mathbf{e}_3 \end{cases} \quad \text{on } \partial\mathcal{P}_t.$$

In what follows, we are interested in this slow response of the gel. The corresponding mechanical equilibrium under the prescribed external traction implies a homogeneous stress state within the gel body given by

$$\sigma_1 = \sigma_e \quad \text{and} \quad \sigma_T = 0 \quad \text{in } \mathcal{P}_t. \tag{5.75}$$

By using the Eqs. (5.74), we have:

$$\boxed{\frac{G_d}{\lambda_T^2 \lambda_0} \lambda_1 - p = \sigma_e \quad \text{and} \quad \frac{G_d}{\lambda_1 \lambda_0} - p = 0.} \tag{5.76}$$

Moreover, since $\mathbf{F}_d = \lambda_0 \mathbf{F}$ and Eq. (5.72) holds, the local volumetric constraint can be rewritten as

$$\boxed{J_0 (\lambda_1 \lambda_T^2) - 1 - \Omega c_d - \Lambda g_d = 0.} \tag{5.77}$$

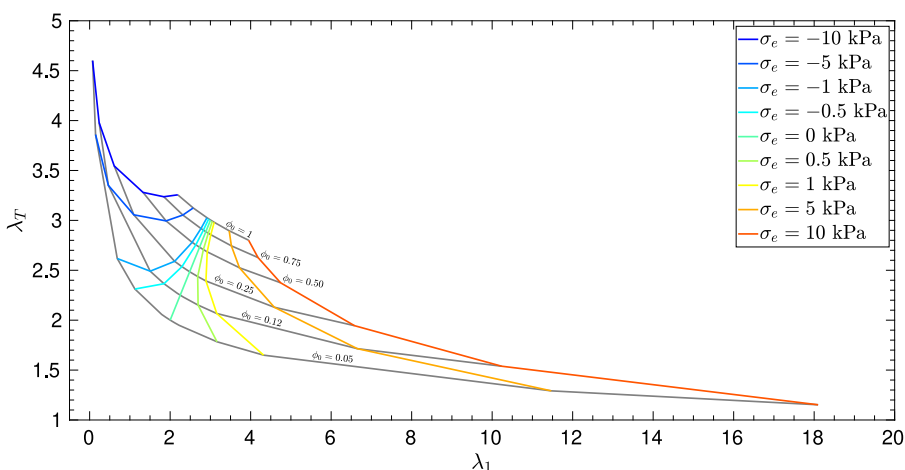


Fig. 8. Uni-axial traction test results of a parallelepiped gel in the λ_1 - λ_T plane. The iso-lines in grey represent the initial network fractions ranging $\phi_0 = [0.05, 1]$. The extreme red and blue iso-lines represent respectively the maximum positive and negative tractions studied, whereas the straight iso-line is of the zero imposed traction.

Apart from (5.76) and (5.77), the remaining set of equations that do not change compared to the earlier free-swelling case are the pair of chemical potential balances (4.67) and the pair of global constraints on the number of moles within the bath (4.69). Together these form a system of 7 algebraic equations to be resolved for 7 scalar unknowns, which characterize the homogeneous isotropic swelling problem under uni-axial traction: $(\lambda_1, \lambda_T, c_d, g_d, N_c, N_g, p)$. The system of 7 algebraic equations is resolved for the same material parameters as in Section 4 for ranges of uni-axial traction $\sigma_e = [-10, 10]$ kPa and initial network fraction $\phi_0 = [0.05, 1]$. See results in Fig. 8. For the case of $\sigma_e = 0$ kPa, i.e. essentially free-swelling, a reduction in ϕ_0 corresponds to a decrease in the stretch (λ_1 or λ_T) which is exactly the same as what can be observed in Fig. 5 for λ . For positive imposed tractions as ϕ_0 reduces λ_1 increases and λ_T decreases as expected. On the other hand, compressive tractions follow an inverse trend.

6. Conclusions and future directions

We have presented a theory for the swelling of a partially cross-linked polymer gel, based on an enriched mechano-diffusion theory of polymer gels. The equation accounts for the elastic deformation of the network and the diffusive motion of both the solvent and the free-chains in the polymer network. We focused our study on the characterization of the equilibrium solution of the swelling problem under free conditions (absence of loads and constraints) and under uniaxial traction.

The analysis we carried on shows as the mechanics of swelling for partially cross-linked polymers can be described as usually done for perfectly cross-linked polymer, by enlarging the point of view to include the liquid bath in the model. It also shows as the mechanics of swelling for perfectly cross-linked polymer arises as a special case from this theory.

We left a few interesting issues for future studies. Firstly, the analysis of the so-called residual swelling between polymer gels, occurring when two different polymer gels, one softer and one stiffer, are put in contact and due to the flow of free-chains from the softer to the stiffer polymer gel relevant changes of shapes can take place (see Pezzulla et al., 2015).

Secondly, we will aim to investigate the possibility to describe through our theory, appropriately reduced, the blossom of the flow of free-chains in dry polymer under loads, as shown in Wang et al. (2024).

Finally, we will aim to take into account breaking of chemical bonds in the polymer network, which would cause a decrease in the volume of the polymer network and an increase in the amount of free-chains in the gel, by polymer remodeling (Wang et al., 2022).

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Siddhartha H. Ommi reports financial support was provided by Government of Italy Ministry of Foreign Affairs and International Cooperation. Paola Nardinocchi reports financial support was provided by Ministry of University and Research. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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