LARGE DEFORMATION AND SOLVENT PERMEATION IN POLYMER GELS

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Abstract. *A polymer gel is a two-component material composed of an elastic solid, which is given by a cross-linked polymer network, and a solvent or fluid, filling the interstitial space of the network. It displays unusual and complex behavior as a result of the coupling between large deformation and fluid permeation. The coupling between these two phenomena gives rise to very interesting and complex behaviors discussed elsewhere in the literature. In this paper we present a theory for the coupling between large deformation and solvent permeation in polymer gels. This work extends a previous contribution of the authors by introducing a new derivation for the spatial version of the basic equations for polymer gel dynamics. Further, the problem of pressure-driven fluid flow through a gel-filled channel is considered. Our interest here is to investigate how the network elastic response affects the solvent flow profile under steady-state conditions. We show that there is a class of elastic materials for which the flow profile is not affected by the applied pressure gradient. This class includes both neo-Hookean and Mooney materials but excludes Gent materials.*

Keywords: *solvent permeation, polymer gels, large deformations*

1 INTRODUCTION

A polymer gel is a two-component material composed of an elastic solid, which is given by a cross-linked polymer network, and a solvent or fluid, filling the interstitial space of the network. It displays unusual and complex behavior as a result of the coupling between large deformation and fluid permeation. The coupling between these two phenomena gives rise to very interesting and complex behaviors discussed elsewhere in the literature.

Following Duda, Souza & Fried (2010), we present a theory for the coupling between large deformation and solvent permeation in polymer gels. The basic equations for polymer gel dynamics presented in both referential and spatial versions. These equations involve the notions of fluid and osmotic pressures and total and network stresses. Further, we study the problem of pressure-driven fluid flow through a gel-filled channel. This problem was investigated by Cogan & Keener (2005) using a different description of the gel system. As Nakagaki & Guy (2008) and Guy, Nakagaki & Wright (2011) note, this problem is a subject of considerable interest for various biological materials.

The remainder of this paper is organized as follows. In Section 2, we present main ingredients of the theory developed by Duda, Souza & Fried (2010). The notions of total and network stresses are discussed in Section 3. In Section 4, we introduced a general constitutive theory suitable for describing isotropic polymer gels. the problem of pressure-driven fluid flow through a gel-filled channel is addressed in Section 4. Concluding remarks are presented in Section 5.

2 PRELIMINARIES

A *polymer gel* is a material body consisting of a *polymer network* imbibing a fluid; hereafter, for short, we drop the modifier 'polymer', and refer to the fluid as the *solvent*. The network is modeled as a continuous elastic body identified point-wise with the 3-dimensional space region $\mathcal{B}$ it occupies in a fixed reference configuration.

The gel undergoes two interdependent processes: a mechanical (macroscopic) processes due to deformation and a chemical (microscopic) process due to fluid permeation. The state of $\mathcal{B}$ at time t is then defined in terms of its placement $\mathbf{y}(\cdot, t)$, the solid content $c_S(\cdot, t)$ and the fluid content $c(\cdot, t)$, which respectively assign to each material point $\mathbf{X}$ in $\mathcal{B}$ the corresponding spatial location $\mathbf{y}(\mathbf{X}, t)$ and the referential network mass density $\rho(\mathbf{X}, t)$ and solvent number density $c(\mathbf{X}, t)$.

2.1 Field equations

We now present equations that govern the fluid uptake by $\mathcal{B}$ under the action of mechanical loads. This set of equations, which is a particular version of the general equations obtained by Duda, Souza & Fried (2010) via the combination of basic balances with a thermodynamically consistent constitutive theory, is comprised by the constraint of local volume preservation, which represents the conventional assumption that the solid and solvent are both incompressible, and a pair of field equations that describe the features of the problem associated with mechanics and permeation. The equations are conveniently organized as follows:

- Incompressibility constraint:

$$\det \mathbf{F} = \frac{\phi_0}{\phi} = \phi_0 + \upsilon c; \tag{1}$$

- Force balance:

$$\mathrm{Div}\,\mathbf{S} = \mathbf{0}, \qquad \mathbf{S} = \frac{\partial \hat{\psi}(\mathbf{F}, c)}{\partial \mathbf{F}} - \pi \mathbf{F}^{*}, \qquad \mathbf{F}^{*} = (\det \mathbf{F})\mathbf{F}^{-\top}; \tag{2}$$

- Network conservation:

$$\dot{\rho} = 0; \tag{3}$$

- Solvent content balance:

$$\frac{\partial c}{\partial t} = -\mathrm{Div}\mathbf{J}, \qquad \mathbf{J} = -\hat{\mathbf{M}}(\mathbf{F}, c)\nabla\mu, \qquad \mu = \frac{\partial \hat{\psi}(\mathbf{F}, c)}{\partial c} + \pi\upsilon. \tag{4}$$

Here and henceforth, $\mathbf{F} = \nabla \mathbf{y}$ is the deformation gradient, ϕ_0 the polymer volume fraction at the reference configuration, ϕ is the polymer volume fraction at the actual configuration, υ is the volume occupied by an individual solvent molecule, $\mathbf{S}$ is the Piola stress tensor, $\hat{\psi}$ and $\hat{\mathbf{M}}$ are the constitutive response functions determining the free-energy density and mobility, π is a Lagrange multiplier field required to maintain the constraint described in Eq. (1), $\mathbf{J}$ is the solvent flux relative to the solid, and μ is the chemical potential of the solvent in the solid. Further, the mobility response must obey the reduced dissipation inequality

$$\hat{\mathbf{M}}(\mathbf{F}, c)\nabla\mu \cdot \nabla\mu \geq 0 \tag{5}$$

for all $(\mathbf{F}, c)$ compatible with Eq. (1) and $\nabla\mu$. External body force, inertial effects, and solvent supply are neglected here. Importantly, mechanics and permeation are coupled via the incompressibility constraint. Additional couplings may also arise through the response functions $\hat{\psi}$ and $\hat{\mathbf{M}}$.

2.2 Boundary conditions

Along with the aforementioned governing equations, initial and boundary conditions must also be imposed. Whereas the former involves the prescription of the initial distribution of the solvent concentration c, the latter requires the prescription of conditions that describe mechanical and permeation interactions between the solid and the environment:

- Mechanical conditions: At the interface $\partial\mathcal{B}$ between the solid and the environment either $\mathbf{Sn}$ or the motion $\mathbf{y}$ is prescribed;
- Permeation conditions: At the interface $\partial\mathcal{B}$ between the solid and the environment either $\mathbf{J} \cdot \mathbf{n}$ or the chemical μ is prescribed.

Here, $\mathbf{n}$ is the unit normal to $\partial\mathcal{B}$. For instance, if we suppose that $\mathcal{B}$ is immersed in an environment wherein the chemical potential of the solvent is constant and equal to μ_a and assume that at the interface $\partial\mathcal{B}$ between the solid and the environment a traction $\mathbf{s}$ is prescribed and chemical equilibrium prevails, the corresponding boundary conditions yield

$$\mathbf{Sn} = \mathbf{s}, \qquad \mu = \mu_a. \tag{6}$$

2.3 Mechanochemical equilibrium

Observe that Eq. (2) expresses mechanical equilibrium. Chemical equilibrium, on the other hand, requires that c be time-independent and that $\mathbf{J} = \mathbf{0}$. These imply that Eq. $(4)_1$ is trivially satisfied and that Eq. $(4)_2$ reduces to $\nabla\mu = \mathbf{0}$. For the environment described above, this condition and Eq. $(6)_2$ imply that

$$\mu = \mu_a \tag{7}$$

on $\mathcal{B}$. Mechanochemical equilibrium states are therefore governed by Eq. (1), Eq. (2), Eq. $(4)_3$, and Eq. (7), along with the boundary conditions Eq. $(6)_1$. As Eq. (7) holds on $\mathcal{B}$, the Eq. $(6)_2$ is satisfied. Further, if the mechanical loading is conservative, that is, if there exists a potential energy $\mathcal{L}[\mathbf{y}]$, mechanochemical equilibrium states correspond to critical points of the net potential-energy functional of $\mathcal{B}$

$$\mathcal{F}[\mathbf{y}, c] = \int_{\mathcal{B}} (\hat{\psi}(\mathbf{F}, c) - \mu_a c\,)\, dV + \mathcal{L}[\mathbf{y}], \tag{8}$$

subject to the constraint described by Eq. (1). On the basis of the energy criterion for stability, an equilibrium state is stable if it is a local minimum of $\mathcal{F}$ and otherwise is unstable. Take notice that in the case the body is impermeable, equilibrium states correspond to critical points of Eq. (8) subject to the constraint in Eq. (1), in which case μ_a is the Langrange multiplier associated with the constraint that the solvent content is fixed.

2.4 Fluid and osmotic pressures

The theory described above is fully specified by the response functions $\hat{\psi}$ and $\hat{\mathbf{M}}$. Throughout this paper, we adopt the Frenkel–Flory–Rehner hypothesis (Flory (1953)) and suppose that $\hat{\psi}$ is given by

$$\hat{\psi}(\mathbf{F}, c) = \mu_0 c + \hat{\psi}_e(\mathbf{F}) + \hat{\psi}_m(c) \tag{9}$$

where μ_0 is the chemical potential of the pure solvent, and $\hat{\psi}_e$ and $\hat{\psi}_m$ are the response functions for the elastic and mixing energy densities. Thus, $\hat{\psi}$ incorporates three contributions: the energy of the "unmixed" pure solvent ($\mu_0 c$); the elastic energy due to network deformation ($\hat{\psi}_e(\mathbf{F})$); and the energy of mixing ($\hat{\psi}_m(c)$).

We now explore the consequences of Eq.(9) leading to the notions of fluid and osmotic pressures, and total and network stresses.

It follows from Eqs. $(4)_3$ and (9) that the Lagrange multiplier π can be written as

$$\pi = p + \Pi, \tag{10}$$

where

$$p := \frac{\mu - \mu_0}{\upsilon}, \qquad \Pi = \hat{\Pi}(c) := -\frac{\hat{\psi}_m'(c)}{\upsilon}. \tag{11}$$

where here and henceforth, f' denotes the derivative of f with respect to its argument. The quantities p and Π are often called the fluid and mixing osmotic pressures (e.g. Doi (2013)).

3 TOTAL AND NETWORK STRESSES

The use of the notions of fluid and osmotic pressures implies that the Piola stress tensor $\mathbf{S}$ and the Cauchy stress tensor $\mathbf{T}$ can be written as

$$\mathbf{S} = \mathbf{S}_{\mathrm{n}} + \mathbf{S}_{\mathrm{f}}, \qquad \mathbf{T} = \mathbf{T}_{\mathrm{n}} + \mathbf{T}_{\mathrm{f}} \tag{12}$$

where

$$\mathbf{S}_{\mathrm{n}} = \hat{\mathbf{S}}_{\mathrm{n}}(\mathbf{F}) = \frac{\partial \hat{\psi}_e(\mathbf{F})}{\partial \mathbf{F}} - \Pi(c)\,\mathbf{F}^*, \quad \mathbf{S}_{\mathrm{f}} = -p\mathbf{F}^*, \quad \mathbf{T}_{\mathrm{n}} = \hat{\mathbf{T}}_{\mathrm{n}}(\mathbf{F}) := \hat{\mathbf{S}}_{\mathrm{n}}(\mathbf{F})(\mathbf{F}^*)^{-1}, \quad \mathbf{T}_{\mathrm{f}} = -p\mathbf{I}, \tag{13}$$

where Eq. (1) and $\mathbf{S} = \mathbf{T}\mathbf{F}^*$ have been used.

Eqs. $(12)_1$ and $(13)_2$ suggest that the *total* Piola stress $\mathbf{S}$ is given by the sum of two contributions, one due to the network $\mathbf{S}_{\mathrm{n}}$ and other due to the interstitial fluid $\mathbf{S}_{\mathrm{f}}$. From Eq. $(12)_2$, the same holds for the *total* Cauchy stress $\mathbf{T}$. Therefore, the total Cauchy stress in the gel results from two contributions, one due to the network, $\mathbf{T}_{\mathrm{n}}$, and other due to the solvent, $-p\mathbf{I}$. The network contributions arise from the elastic free energy of the gel and the osmotic pressure, whereas solvent contribution arises from the volumetric constraint (See, for instance, Doi (2013)). Notice that, for a dry material point, p corresponds to the standard pressure that appears due to incompressibility. In this case, the network and fluid contributions to the stress are, indeed, the active and reactive parts of the stress.

4 GOVERNING EQUATIONS IN THE SPATIAL DESCRIPTION

We now derive the basic equations for gel dynamics in the spatial description. Our aim is to arrive at the equations presented by Doi (2009), which were derived in a different manner.

We begin by observing that the spatial version of the network mass conservation can be written as

$$\frac{\partial \rho_s}{\partial t} + \operatorname{div}(\rho_s \mathbf{v}) = 0, \tag{14}$$

where ρ_s is the spatial mass density of the network and $\mathbf{v} = \dot{\mathbf{y}}$ is the spatial velocity field. The spatial counterpart of Eq. (1) states that ρ_s is related to the polymer volume fraction ϕ by $\rho_s = \rho_p \phi$, where ρ_p, the specific density of the network component, is constant. Thus, it follows from Eq. (14) that the polymer volume fraction ϕ evolves according to the equation

$$\frac{\partial \phi}{\partial t} + \operatorname{div}(\phi \mathbf{v}) = 0. \tag{15}$$

On the other hand, the spatial version of Eq. $(2)_1$ involving the Cauchy stress tensor $\mathbf{T}$ yields

$$\operatorname{div}\mathbf{T} = \mathbf{0}, \qquad \mathbf{T} = \mathbf{T}_{\mathrm{n}} - p\mathbf{I}, \qquad \mathbf{T}_{\mathrm{n}} = \frac{\partial \hat{\psi}_e(\mathbf{F})}{\partial \mathbf{F}}(\mathbf{F}^*)^{-1} - \Pi(c)\mathbf{I}, \tag{16}$$

where Eq. (13) has been used. The spatial version of Eq. $(4)_1$ is given by

$$\frac{\partial c_s}{\partial t} + \operatorname{div}(c_s \mathbf{v}) = -\operatorname{div}\mathbf{j}, \qquad \mathbf{j} = (\mathbf{F}^*)^{-\top}\mathbf{J}, \tag{17}$$

where $c_s = c/\det\mathbf{F}$ is the solvent content per unit spatial volume, and $\mathbf{j}$ is the solvent flux per unit spatial area. In view of the definition of c_s and the constraint described by Eq. (1), it follows that Eq. $(17)_1$ reduces to

$$\text{div}\,(\upsilon\mathbf{j} + \mathbf{v}) = 0. \tag{18}$$

In view of Eqs. $(4)_2$ and $(11)_1$, it follows that

$$\mathbf{j} = -\upsilon\mathbf{M}_s\,\text{grad}p, \qquad \mathbf{M}_s = (\mathbf{F}^*)^{-\top}\hat{\mathbf{M}}(\mathbf{F}, c)\mathbf{F}^{\top}, \tag{19}$$

where grad$p$ is the spatial gradient of p.

The equations of Doi (2009) involve the solvent velocity field $\mathbf{v}_s$ rather than the solvent flux $\mathbf{j}$. These quantities are related by

$$\mathbf{j} = c_s(\mathbf{v}_s - \mathbf{v}), \tag{20}$$

which in conjunction with the relation $\upsilon c_s = (1-\phi)$, Eq. (18) and Eq. (19) imply that

$$\text{div}\,((1-\phi)\mathbf{v}_s + \phi\mathbf{v}) = 0, \tag{21}$$

and that

$$\mathbf{v}_s - \mathbf{v} = -\mathbf{K}\,\text{grad}p \tag{22}$$

where the tensor $\mathbf{K}$ is a function of $\mathbf{F}$.

The final set of equations for gel dynamics presented by Doi (2009) is comprised by Eqs. (15), (16), (21) and (22), representing, respectively, mass conservation, mechanical equilibrium, incompressibility condition, and Darcy's Law.

5 ISOTROPIC POLYMER GELS

We now consider a theory appropriate to describe isotropic polymer gels. Accordingly, we suppose that the elastic contribution to $\hat{\psi}$ is isotropic and takes the generic form

$$\hat{\psi}_e(\mathbf{F}) = \tilde{\psi}_e(I_1, I_2), \tag{23}$$

where $I_1 = \text{tr}\,\mathbf{B}$ and $I_2 = (I_1^2 - \text{tr}\,\mathbf{B}^2)/2$ are the first and second principal invariants of the left Cauchy-Green tensor $\mathbf{B} = \mathbf{F}\mathbf{F}^{\top}$. Notice that the mixing energy $\hat{\psi}_m$ is already isotropic since, in view of the incompressibility constraint, it can be seen as function of $\det\mathbf{F}$ and hence of $I_3 = \det\mathbf{B}$, , the third invariant of $\mathbf{B}$. Further, we consider that the mobility in Eq. $(19)_2$ is given by

$$\mathbf{M}_s = \hat{m}(c)\mathbf{I}, \qquad \hat{m}(c) > 0, \tag{24}$$

which implies that assumed mobility response is isotropic. From Eq. (1), both $\hat{\psi}_m$ and $\hat{m}$ can be viewed as a function of ϕ or $I_3 = \det\mathbf{B}$.

With aforementioned constitutive assumption for $\hat{\psi}_e$, the relations described by Eqs. $(13)_1$ and $(13)_3$ specialize to

$$\mathbf{S}_{\text{n}} = \alpha_1\mathbf{F} + \alpha_2(I_1\mathbf{I} - \mathbf{B})\mathbf{F} - \Pi\mathbf{F}^*, \qquad \mathbf{T}_{\text{n}} = (\beta_0 + \Pi)\mathbf{I} + \beta_1\mathbf{B} + \beta_{-1}\mathbf{B}^{-1}, \tag{25}$$

where

$$\alpha_1 = 2\frac{\partial\tilde{\psi}_e}{\partial I_1}, \quad \alpha_2 = 2\frac{\partial\tilde{\psi}_e}{\partial I_2}, \quad \beta_0 = \frac{2I_2\alpha_2}{\sqrt{I_3}}, \quad \beta_1 = \frac{2\alpha_1}{\sqrt{I_3}}, \quad \beta_{-1} = -2\sqrt{I_3}\alpha_2. \tag{26}$$

Take notice that $\beta_0 = -\beta_{-1}\, I_2/I_3$. On the other hand, the foregoing choice for $\mathbf{M}_s$ implies that Eq. (19) determining the solvent flux $\mathbf{j}$ specializes to

$$\mathbf{j} = -\upsilon\hat{m}(c)\text{grad}\, p. \tag{27}$$

According the constraint described in Eq. (1), there is a one-to-one relation between c and ϕ. Hence, any function of c can be written as a function of ϕ, and vice-versa. From now we view both m and Π as functions of ϕ.

6 PRESSURE-DRIVEN FLOW THROUGH A GEL-FILLED CHANNEL

We now apply the foregoing theory of isotropic polymer gels present to consider the problem of pressure-driven flow through a gel-filled channel. Our interest here is to investigate the influence of the gel properties on the characteristics of this flow under steady-state conditions.

Specifically, consider the space between two infinitely long parallel plates separated by a gap d and completely filled by a gel which is fixed to and impermeable at the plates. We introduce a Cartesian coordinate system with the x-axis chosen parallel to the flow, the y-axis orthogonal to the plates, and z-axis orthogonal to the (x, y)-plane. We take the plates to be located at $y = 0$ and $y = d$. Suppose that the gel is in a stress-free state with polymer volume fraction constant and equal to ϕ_0. Then, a pressure gradient is applied to the system gel is causing the solvent to flow. Thus, we suppose that the pressure p is given up to an arbitrary and constant pressure p_0, that is,

$$p(x, y) = -ax + p_0, \tag{28}$$

with the constant a given. Substituting Eq. (28) into (27), it follows that the x-component of the solvent flux, is given by

$$j_x = \hat{m}(\phi)a, \qquad \hat{m}(\phi) = \upsilon\, m(\phi). \tag{29}$$

Observe that the y and z-components of $\mathbf{j}$ are equal to zero. Since the the solvent flux is fully characterized by j_x, its detailed features depends on the function $\hat{m}$ and polymer fraction distribution ϕ. Whereas $\hat{m}$ represents a material property, the polymer volume fraction ϕ needs to be determined by invoking the equations that govern the interaction between mechanics and permeation.

We assume the gel undergoes a special time-independent deformation in which the spatial (x, y, z) and referential (X, Y, Z) coordinates of a gel particle are related by

$$X = x + f(y), \qquad Y = g(y), \qquad Z = z, \tag{30}$$

with $g' > 0$. Since the gel is fixed to the plates, the functions f and g must obey the boundary conditions

$$f(0) = f(d) = 0, \qquad g(0) = 0, \qquad g(d) = d. \tag{31}$$

We also assume that f is symmetric with respect to the central line between the two plates. Notice that Eq. (30) represents the inverse of the placement $\mathbf{y}$ in Cartesian coordinates. Therefore the matrix representation of $\mathbf{F} = \nabla\mathbf{y}$, when expressed relative to the spatial configuration, is given by

$$[\mathbf{F}] = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & \eta & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{32}$$

showing that $\mathbf{F}$ is a superimposition of an uniaxial extension with stretch $\eta := 1/g'$ on a simple shear with amount $\gamma := -f'/g'$.

An important consequence of the Ansatz described in Eq. (30) follows from the use of the incompressibility constraint of Eq. (1). In fact, considering $\det\mathbf{F} = 1/g'$ into eq. (1), it follows that

$$\phi = \phi_0\, g', \tag{33}$$

which shows that ϕ depends on y only. In addition, as a consequence of Eqs. $(30)_2$ and $(31)_2$, we may write

$$Y = \frac{1}{\phi_0}\int_0^y \phi(\bar{y})\,\mathrm{d}\bar{y}, \tag{34}$$

which provides some elementary insight regarding how the vertical component of the inverse placement depends on the distribution of the polymer volume fraction in the spatial configuration (normalized by the referential polymer volume fraction).

We now show that the fluid content balance is trivially satisfied under the conditions discussed so far. In fact, Eq. (18) reduces to $\operatorname{div}\mathbf{j} = 0$ since $\mathbf{v} = \mathbf{0}$. Further, since the y and z-components of $\mathbf{j}$ vanish, whereas the x-component of $\mathbf{j}$ given by Eq. (29) depends only on y, a property inherited from ϕ. Altogether, the Eq. (18) is trivially satisfied. The same applies to the impermeability boundary condition. Thus, no new information can be extracted from the fluid content balance and the task of determining ϕ remains. Therefore the mechanical part of the problem must be considered.

By using Eq. (32) we conclude that

$$[\mathbf{B}] = \begin{bmatrix} 1+\gamma^2 & \eta\gamma & 0 \\ \eta\gamma & \eta^2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad [\mathbf{B}^{-1}] = \begin{bmatrix} 1 & -\gamma/\eta & 0 \\ -\gamma/\eta & (1+\gamma^2)/\eta^2 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{35}$$

Consequently, the network stress tensor $\mathbf{T}_{\mathrm{n}}$ in Eq. $(25)_2$ admits the matrix representation

$$[\mathbf{T}_{\mathrm{n}}] = \begin{bmatrix} \sigma_x^{\mathrm{n}} & \tau_{xy}^{\mathrm{n}} & 0 \\ \tau_{xy}^{\mathrm{n}} & \sigma_y^{\mathrm{n}} & 0 \\ 0 & 0 & \sigma_z^{\mathrm{n}} \end{bmatrix}, \tag{36}$$

with components

$$\begin{aligned} \sigma_x^{\mathrm{n}} &= \beta_0 - \Pi + \beta_1(1+\gamma^2) + \beta_{-1}, \qquad \tau_{xy}^{\mathrm{n}} = \beta_1\gamma\eta - \beta_{-1}\gamma/\eta, \\ \sigma_y^{\mathrm{n}} &= \beta_0 - \Pi + \beta_1\eta^2 + \beta_{-1}(1+\gamma^2)/\eta^2, \qquad \sigma_z^{\mathrm{n}} = \beta_0 - \Pi + \beta_1 + \beta_{-1}, \end{aligned} \tag{37}$$

where β_0, β_1 and β_{-1} are defined by Eqs. (26), and the principal invariants of $\mathbf{B}$ are given by

$$I_1 = 2 + \gamma^2 + \eta^2, \qquad I_2 = 1 + \gamma^2 + 2\eta^2, \qquad I_3 = \eta^2. \tag{38}$$

By using Eq. $(16)_2$, the matrix representation of the total stress tensor $\mathbf{T}$ can now be written as

$$[\mathbf{T}] = \begin{bmatrix} \sigma_x & \tau_{xy} & 0 \\ \tau_{xy} & \sigma_y & 0 \\ 0 & 0 & \sigma_z \end{bmatrix}, \tag{39}$$

with components

$$\begin{aligned} \sigma_x &= \sigma_x^{\mathrm{n}} - p, \qquad \tau_{xy} = \tau_{xy}^{\mathrm{n}}, \\ \sigma_y &= \sigma_y^{\mathrm{n}} - p, \qquad \sigma_z = \sigma_z^{\mathrm{n}} - p, \end{aligned} \tag{40}$$

where p is given by Eq. (28). Observe that Π can be viewed as a function of y through ϕ. Therefore, it follows from x-component of $\operatorname{div}\mathbf{T} = \mathbf{0}$ that the shear stress profile is linear, with $(\tau_{xy})' = -a$. From Eq. (37) and assuming the symmetry of f, it follows that

$$\tau_{xy} = -a(y - d/2). \tag{41}$$

The y-component of $\operatorname{div}\mathbf{T} = \mathbf{0}$ provides the relation

$$\sigma_y^{\mathrm{n}} = k \quad \text{where} \quad k \quad \text{is constant.} \tag{42}$$

Now we explore the consequences of Eqs. (41) and (42) by considering Eqs. (37), (38) and (40). Observe that τ_{xy} and σ_y^{n} can be written in terms of the amount of shear γ and stretch η as

$$\tau_{xy} = K(\gamma,\eta)\gamma, \qquad \sigma_y^{\mathrm{n}} = \hat{\sigma}_y^{\mathrm{n}}(\gamma,\eta) \tag{43}$$

where

$$K(\gamma,\eta) := 2\left[\frac{\partial\tilde{\psi}_e}{\partial I_1} + \frac{\partial\tilde{\psi}_e}{\partial I_2}\right], \qquad \hat{\sigma}_y^{\mathrm{n}}(\gamma,\eta) := 2\eta\left[\frac{\partial\tilde{\psi}_e}{\partial I_1} + 2\frac{\partial\tilde{\psi}_e}{\partial I_2}\right] - \Pi. \tag{44}$$

Thus, Eq. (41) results in

$$\tau_{xy} = -a(y - d/2) = K(\gamma(y),\eta(y))\,\gamma(y). \tag{45}$$

Moreover, considering that $\eta = \phi_0/\phi = \sqrt{I_3}$, it follows from Eq. (42) that

$$k = \hat{\sigma}_y^{\mathrm{n}}(\gamma(y),\eta(y)). \tag{46}$$

Although the constant k is unknown, its evaluation requires the introduction of the boundary condition described in Eq.$(31)_3$ and Eq. (34)

$$d = \frac{1}{\phi_0}\int_0^d \phi(y)\, dy. \tag{47}$$

It can be seen that Eq. (41) implies that

$$\tau_{xy} = -a(y - d/2) = (\beta_{-1} - \beta_1 I_3) f'. \tag{48}$$

As we obtained that $\beta_0 = -\beta_{-1} I_2/I_3$ and that $\phi_0/\phi = \sqrt{I_3},$ Π can be written as a function of I_3. Therefore it follows from Eq. (42) that

$$k = \beta_1 I_3 - 2\beta_{-1} - \Pi(I_3). \tag{49}$$

Granted knowledge of the pressure gradient a, the distance between the plates d, the initial polymer volume fraction ϕ_0, and the material properties defined by υ and the free energy response $\tilde{\psi}$, the Eqs. (47), (48) and (49) represent a system to obtain f', ϕ and k. The following remarks are in order:

- When a pressure gradient is applied, a shear stress τ_{xy}, given by Eq. (41), is developed to ensure mechanical equilibrium. This stress is accompanied by the shear strain f', as showed by Eq. (45).
- The determination of f' requires the knowledge of the material properties through the "shear modulus" $(\beta_1 I_3 + \beta_{-1}),$ which is a function of I_1, I_2 and I_3. In view of Eq. (38) and the relation $\phi_0/\phi = \sqrt{I_3},$ this modulus may depend on f' and ϕ.
- The polymer volume fraction is obtained by solving Eq. (49) subject to the constraint described by Eq. (48). This solution "feels" the pressure gradient if and only if the elastic contribution $\sigma_y^e = \beta_1 I_3 - 2\beta_{-1}$ to σ_y "feels" it through f'. In this case, $\beta_1 I_3 - 2\beta_{-1}$ can not depend exclusively on I_3.

In summary, whereas the shear stress, which is sustained by the elasticity of the network, always feels the pressure gradient, the component σ_y^{n} of σ_y sustained by the network can the pressure gradient only for special kinds of elastic behavior. If this condition is not attained, the pressure gradient cannot influence the the polymer volume fraction.

To clarify the issue raised above, suppose that $\beta_1 I_3 - 2\beta_{-1} =: h(I_3)$. In this case, Eq. (49) reduces to $h(I_3) - \Pi(I_3) = k,$ with k unknown. As k is constant, so is I_3. Thus, ϕ is constant and, by Eq. (47), equals to ϕ_0. Consequently, $k = h(I_3) - \Pi(I_3)$. The shear strain distribution f' is obtained by solving Eq. (45), which may result in a nonlinear equation. In this case, the solvent flux in Eq. (29) is constant and given by $j_x = \hat{m}(\phi_0)\, a$. This corresponds to a "plug flow". Neither the elastic nor the mixing properties affects the flow.

On using Eq. (26), one can notice that the condition $\beta_1 I_3 - 2\beta_{-1} = h(I_3)$ holds for both the neo-Hookean and Mooney elastic energies. However, there are many examples of elastic energies proposed for modeling gels which violate that condition. See, for instance, Dobrynin & Carrillo (2010), Drozdov & Christiansen (2013), Gent (1996), Palmer & Boyce (2008), Sasson *et al.* (2012), Yan & Jin (2012), and Urayama, Ogasawara & Takigawa (2006).

6.1 Solvent redistribution

We now consider the problem of obtaining the polymer volume fraction ϕ for the case in which the elastic and mixing energies densities are given by

$$\tilde{\psi}_e(I_1, I_2) = -\frac{GJ_m}{2}\ln\left(1 - \frac{I_1 - 3}{J_m}\right), \quad \tilde{\psi}_m(\phi) = \frac{k_B T \phi_0}{\upsilon}\frac{(1-\phi)}{\phi}\left(\ln(1-\phi) + \chi\phi\right) \tag{50}$$

which represent, respectively, Gent and Flory-Huggins models for the elastic and mixing energy densities. Here, G is the shear modulus at the reference state, J_m the phenomenological parameter that accounts for the finite extensibility of polymer in the network, k_B and T the Boltzmann constant and absolute temperature, υ the volume occupied by a solvent molecule, and χ the Flory-Huggins interaction parameter.

With the aforementioned choices, a single calculation using Eqs. (1), $(11)_2$, $(38)_1$ and (44), shows that in the present case Eqs. (45) and (46) can be written as

$$\frac{G_0 J_m}{J_m - (\eta(y)^2 + \gamma(y)^2 - 1)}\gamma(y) = -a(y - d/2) \tag{51}$$

and

$$\frac{G_0 J_m}{J_m - (\eta(y)^2 + \gamma(y)^2 - 1)}\eta(y) + \frac{k_B T}{\upsilon}(\ln(1-\phi(y)) + \phi(y) - \chi\phi(y)^2) = k, \tag{52}$$

which, supplemented by Eq. (47) and the relation $\eta = \phi_0/\phi$, provide a system of equations for $\gamma(y)$, $\phi(y)$ and k. To solve these equations, we proceed in steps as described below:

1. Use Eq. (51) to write $\gamma(y)$ as a function of y and $\phi(y)$;
2. With the result just described, rewrite Eq. (52) as $f(y, \phi(y)) - k = 0$;
3. Assume that the function ϕ can be approximated by a polynomial of order n, that is,

$$\phi(y) \approx \phi_a(y) = \sum_{i=0}^{n} a_i y^i; \tag{53}$$

4. Solve the system of $n + 2$ equations given by

$$\begin{aligned} &f(y_j, \phi_a(y_j)) - k = 0, \quad y_j \in [0, d], \quad j = 1, n+1, \quad y_j \neq y_l, \quad j \neq l \\ &\int_0^d \phi_a(y)\, dy - \phi_0 d = 0 \end{aligned} \tag{54}$$

for $(a_0, a_1, ..., a_n, k)$.

Figure 1. displays the polymer fraction distributions for increasing values of ad/G and $\phi_0 = 0.01$, $J_m = 10.$, $k_B T/(\upsilon G) = 100.$, and $\chi = 0.2$. The results were obtained by using the procedure described above for $n = 5$ and an equally-spaced distribution of points in the interval $[0, d]$. The values of the fixed physical parameters, although typical, were chosen for illustrative purpose only. The mentioned figure shows the polymer content (solvent content) in the center of the channel diminishes (increases) as ad/G increases.

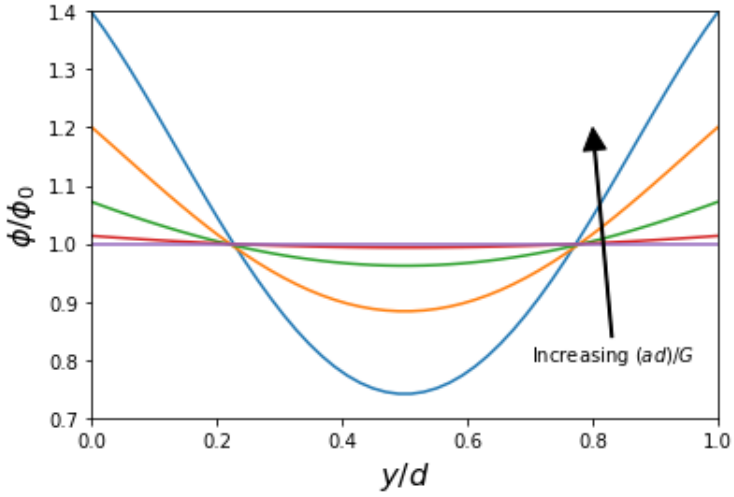

Figure 1: Polymer volume fraction distribution for different values of $(ad)/G$. The following parameters remained fixed: $\phi_0 = 0.01$, $J_m = 10.$, $k_BT/(\upsilon G) = 100.$, $\chi = 0.2$ and $n = 5$.

CONCLUSION

We have presented a theory for the interplay between large deformation and solvent permeation in polymer gels. After introducing the notions of osmotic pressures and network stress, we presented an alternative derivation for the spatial version of the basic equations for gel dynamics presented elsewhere in the literature. These equations were applied to the analysis of pressure-driven fluid flow through a gel-filled channel. We derived that the shear stress τ_{xy} is a function of the pressure gradient a. Whether the same conclusion applies or not to the normal stress σ_y^{n} depends on the elastic response. When it does not apply, the polymer volume fraction, and hence the flow profile, is not affected by the pressure gradient. This is the case for both neo-Hookean and Mooney elastic materials.

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