

1 Polyelectrolytes Gel Model Derivation.

1.1 Conservation Law.

We here consider the gel as a three-phase medium composed of a solid polymer network with fixed charges, a solvent (i.e. water molecules, interstitial fluid) and solutes (freely moving charges).

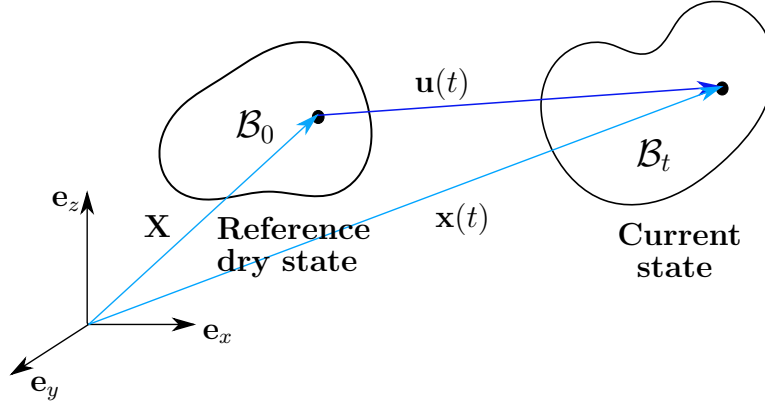


Figure 1: Sketch of the dry and current state of the gel.

As the tissue deforms, the material element originally located at \mathbf{X} in the initial configuration \mathcal{B}_0 is displaced to the point \mathbf{x} in the current configuration \mathcal{B}_t , see Figure 1. Such a transformation is described by the deformation gradient tensor $\mathbb{F} = \partial \mathbf{x} / \partial \mathbf{X}$; the information about the change in volume is encoded in $J = \det \mathbb{F}$, while $\mathbf{u} = \mathbf{x} - \mathbf{X}$ is the displacement vector. As in [6], we consider the reference, or initial, state \mathcal{B}_0 , which is stress free, to be equivalent to the dry state of the gel, i.e. only solid phase present. Since we assume the solid phase to be incompressible, any change in the volume can only be related to the migration of solvent and solute molecules, whose nominal ¹ concentrations will be denoted by C_s and C_i respectively, $i = 1, \dots, N$ with N being the number of free ion species. This lead to the molecular incompressibility condition:

$$J = 1 + v_s C_s + \sum_{i=1}^N v_i C_i \quad (1)$$

¹variable value in the reference configuration.

where v_m are the characteristic molecular volume of each species in the solution. When considering the interstitial fluid, the contribution of ions to the volume can be neglected [12, 13] so that Equation (1) reduces to:

$$J = 1 + v_s C_s. \quad (2)$$

Consequently, the volume fractions of fluid ϕ_f and solid ϕ_n phases in the swollen gel are defined as:

$$\phi_f = \frac{v_s C_s}{1 + v_s C_s}, \quad \phi_n = \frac{1}{1 + v_s C_s}. \quad (3)$$

where again we are neglecting the contribution of ions to the total volume. While C_m denotes the number of each molecule per unit volume in the initial configuration for the m -th species in the solution, the actual concentration in the current state is denoted by $c_m = C_m/J$. Throughout the derivation of the model, we will be using the index $i = 1, \dots, N$ to denote the ionic species only, while $m \in \{s, 1, \dots, N\}$ refers to all mobile species, i.e. both the solvent and solutes.

Mass conservation must apply to all mobile species and in the initial configuration this reads:

$$\dot{C}_m + \nabla_0 \cdot \mathbf{J}_m = 0, \quad (4)$$

where \mathbf{J}_m is the nominal flux per unit area in the dry state, \dot{C}_m is the derivative of C_m with respect to time, i.e. $\dot{C}_m \equiv \partial_t C_m$ and ∇_0 denotes the gradient in the Lagrangian coordinates \mathbf{X} . Their counterparts in the actual configuration are denoted by \mathbf{j}_m and ∇ and are defined according to the following rules:

$$\mathbf{J}_m = J \mathbb{F}^{-1} \mathbf{j}_m, \quad \nabla_0(\cdot) = \mathbb{F}^T \nabla(\cdot). \quad (5)$$

When considering tissues or hydrogels, inertial and gravitational effects are commonly neglected, so that the conservation of momentum for the gel reads:

$$\nabla_0 \cdot \mathbb{S} = 0, \quad (6)$$

where \mathbb{S} is the first Piola-Kirchoff tensor, which represents the stress state of the gel in the initial configuration. The counterpart in the current configuration is the Cauchy stress tensor \mathbb{T} , which is related to \mathbb{S} as follows:

$$\mathbb{T} = J^{-1} \mathbb{S} \mathbb{F}^T. \quad (7)$$

The presence of free moving ions generates an electric field which is denoted by \mathbf{E} and \mathbf{e} in the initial and current configuration respectively. Introducing the electrostatic potential Φ , we have that:

$$\mathbf{E} = -\nabla_0 \Phi, \quad \mathbf{e} = -\nabla \Phi. \quad (8)$$

As in [7], we consider the gel to be a dielectric material². Consequently, the presence of the electric field generates an electric displacement \mathbf{H} ³, which must obey Gauss law of electrostatics:

$$\nabla_0 \cdot \mathbf{H} = Q, \quad (9)$$

where Q is the local total charge, which accounts for both fixed and moving charges:

$$Q = e \left(\sum_i z_i C_i + z_f C_f \right), \quad (10)$$

where e is the elementary charge, C_f is the concentration of fix charges and z_m is the valence of the corresponding charged species. As for above, we can move from nominal quantities to the corresponding value in the current configuration by applying the following rules:

$$\mathbf{H} = J\mathbb{F}^{-1}\mathbf{h}, \quad (11)$$

$$\mathbf{E} = \mathbb{F}^T \mathbf{e}, \quad (12)$$

where \mathbf{h} is the electric displacement in the current configuration.

1.2 Energy Balance Inequality.

The energy imbalance inequality reads:

$$\frac{d}{dt} \left\{ \int_R \psi \right\} \leq W(R) + M(R) \quad (13)$$

where R is an arbitrary control volume of the system, ψ is the Helmholtz free energy, $W(R)$ is the rate at which the environment does work on R and

²a material that does not conduct electricity but can be polarized in the presence of an electric field.

³the vector field that accounts for both the electric field and the polarization of the dielectric material.

$M(R)$ is the inflow of mass due to transport. Considering a control volume R in the reference configuration \mathcal{B}_0 , the system exchanges mass due to the diffusion of each mobile species, so that $M(R)$ is given by:

$$M(R) = \sum_{m=s,1,\dots,N} - \int_{\partial R} \mu_m \mathbf{J}_m \cdot \mathbf{n} \quad (14)$$

where \mathbf{n} is the unit normal vector to the surface ∂R and μ_m is the chemical potential associated with each species. Widely used in the thermodynamics of mixture, the chemical potential is a measure of the rate of change in free energy associated with adding one more molecule to a unit volume.

The term $W(R)$, i.e. the rate of work done on the system, is instead decomposed in two contributions, the rate of electrical $W_{el}(R)$ and mechanical work $W_{mec}(R)$. Following [3], $W_{el}(R)$ is defined as:

$$W_{el}(R) = - \int_{\partial R} \Phi \dot{\mathbf{H}} \cdot \mathbf{n} \quad (15)$$

Following the work of Gurtin [5], we account both for the presence of macro-stresses \mathbb{S} and micro-stresses $\boldsymbol{\xi}$, which arise due to the system heterogeneity [11]⁴. As before we only consider the dominant contribution of the solvent while neglecting the solute, so that $W_{mec}(R)$ reads:

$$W_{mec}(R) = \int_{\partial R} (\boldsymbol{\xi} \cdot \mathbf{n}) \dot{C}_s + \int_{\partial R} \mathbb{S} \mathbf{n} \cdot \dot{\mathbf{u}} \quad (16)$$

where $\mathbf{u} = \mathbf{x} - \mathbf{X}$ is the displacement vector, which is related to the deformation tensor by $\mathbb{F} = \mathbb{I} - \nabla_0 \mathbf{u}$. Substituting this result back into the formula (13) and applying the divergence theorem we obtain the following inequality:

$$\int_R \dot{\psi} - \mathbf{E} \cdot \dot{\mathbf{H}} + \sum_{i=1}^N \left[e \Phi z_i \dot{C}_i + \nabla_0 (\mu_i \mathbf{J}_i) \right] + \nabla_0 (\mu_s \mathbf{J}_s - \boldsymbol{\xi} \dot{C}_s - \mathbb{S}^T \dot{\mathbf{u}}) \leq 0 \quad (17)$$

Since this must hold for any choice of the volume R , the inequality must hold also locally:

$$\dot{\psi} - \mathbf{E} \cdot \dot{\mathbf{H}} + \sum_{i=1}^N \left[e \Phi z_i \dot{C}_i + \nabla_0 (\mu_i \mathbf{J}_i) \right] + \nabla_0 (\mu_s \mathbf{J}_s - \boldsymbol{\xi} \dot{C}_s - \mathbb{S}^T \dot{\mathbf{u}}) \leq 0. \quad (18)$$

⁴Assuming only interface is between solid and solvent phase.

Further accounting for Equations (4)-(6), we obtain that:

$$\begin{aligned} \dot{\psi} - \mathbf{E} \cdot \dot{\mathbf{H}} + \sum_{i=1}^N [e\Phi z_i - \mu_i] \dot{C}_i - (\mu_s + \nabla_0 \cdot \boldsymbol{\xi}) \dot{C}_s - \mathbb{S} : \dot{\mathbb{F}} \\ - \boldsymbol{\xi} \cdot \nabla_0 \dot{C}_s + \sum_m \nabla_0 \mu_m \cdot \mathbf{J}_m \leq 0. \end{aligned} \quad (19)$$

As exhaustively discussed in previous studies [1, 5], the energy inequality imposes restrictions on the constitutive equation of the free energy ψ . Adapting their results to our specific problem, we have that:

$$\psi = \psi(\mathbb{F}, \mathbb{F}_e, C_s, C_i, \nabla_0 C_s, \mathbf{H}), \quad (20)$$

which precludes any explicit dependency of ψ on the chemical potential or the viscous deformation gradient \mathbb{F}_v . By differentiating the incompressibility condition (2), we obtain:

$$\sum_m v_m \dot{C}_m - J \mathbb{F}^{-T} : \dot{\mathbb{F}} = 0, \quad (21)$$

If we now substitute (20) into (19), and include the constraint (21) using as Lagrange multipliers p , we are left with the augmented form of the energy imbalance inequality:

$$\begin{aligned} \left(\frac{\partial \psi}{\partial \nabla_0 C_s} - \boldsymbol{\xi} \right) \cdot \nabla_0 \dot{C}_s + \left(\frac{\partial \psi}{\partial C_s} - \mu_s - \nabla_0 \cdot \boldsymbol{\xi} + p v_s \right) \dot{C}_s \\ + \sum_i \left(\frac{\partial \psi}{\partial C_i} + e\Phi z_i - \mu_i + p v_i \right) \dot{C}_i + \left(\frac{\partial \psi}{\partial \mathbf{H}} - \mathbf{E} \right) \cdot \dot{\mathbf{H}} \\ + \left(\frac{\partial \psi}{\partial \mathbb{F}} - \mathbb{S} - p J \mathbb{F}^{-T} \right) : \dot{\mathbb{F}} + \sum_m \nabla_0 \mu_m \cdot \mathbf{J}_m \leq 0. \end{aligned} \quad (22)$$

1.3 Construction of the Free Energy.

Having the general form of ψ , Equation (20), it remains to construct its precise form. Following a standard approach in ψ -depending modeling, we assume that the total free energy can be additively decomposed with each physical mechanisms contributing independently. We here consider six distinct contributions:

- the energy of the electric field ψ_1 ;
- the energy of solvent and solutes' molecules not interacting with the solid phase ψ_2 ;
- the energy of mixing the solid phase with the solution, ψ_3 ;
- the energy of mixing the solvent with the solutes in solution, ψ_4 ;
- the interfacial energy between dissimilar phases, ψ_5 ;
- the energy of the solid phase not interacting with the solution, ψ_6 .

Assuming the solid phase to be an ideal and linear dielectric material, with constant permittivity ϵ , the free energy of polarization reads [2, 7]:

$$\psi_1 = \frac{1}{2\epsilon J} \mathbf{H} \mathbb{F}^T \cdot \mathbb{F} \mathbf{H}. \quad (23)$$

The specific energy density ψ_2 has the standard form:

$$\psi_2 = \sum_m \mu_m^0 C_m \quad (24)$$

where μ_m^0 denotes the chemical potential of non interacting solvent and ions molecules. According to Flory-Huggins theory [4, 9] of mixtures, the mixing energy is given by:

$$\psi_3 = \frac{k_B T}{v_s} \left(v_s C_s \ln \frac{v_s C_s}{1 + v_s C_s} + \chi \frac{v_s C_s}{1 + v_s C_s} \right), \quad (25)$$

where k_B is the Boltzmann's constant, T is the temperature and χ is the Flory-Huggins parameter, which is a measure of the enthalpy of mixing.

Assuming the solution is dilute, the contribution ψ_4 reads [7, 12, 13]:

$$\psi_4 = k_B T \sum_{i=1}^N C_i \left(\ln \frac{C_i}{C_s} - 1 \right). \quad (26)$$

For non dilute solution the form proposed by Hong [7] is:

$$\psi_4 = k_B T \sum_m C_m \left(\ln \frac{C_m}{\sum_i C_i + C_s} - 1 \right). \quad (27)$$

As proposed by Hong et al. [8], we include in the energy the effect of interface tension. Assuming that the contribution of mobile ions is negligible, only the solid-solvent interface contributes to the energy:

$$\psi_5 = \frac{\gamma}{2} J |\nabla C_s|^2, \quad (28)$$

where the constant γ plays a role analogous to a surface tension.

For the strain energy we consider the gel to be an hyper-elastic Neo-Hookean material:

$$\psi_6(\mathbb{F}) = \frac{G}{2} (\mathbb{F} : \mathbb{F} - 3 - 2 \ln J) \quad (29)$$

where G is the shear constant of the material.

1.4 Entropy Production σ .

Having specified how the system interacts with its environment, we can now discuss how it dissipates energy. We here consider only the contribution due to the transport of the solution (diffusion of solvent and solutes). The thermodynamic fluxes associated with these two phenomena are \mathbf{J}_m , $m = s, 1, \dots, N$, and \mathbb{L}_v . Consequently, the entropy production is of the form:

$$\sigma = \sum_m \zeta_m \cdot \mathbf{J}_m, \quad (30)$$

where ζ s represent the thermodynamic forces associate with each flux. On the other hand, $\nabla_0 \dot{C}_s$, \dot{C}_s , \dot{C}_i , $\dot{\mathbf{H}}$ and $\dot{\mathbb{F}}$ are the independent physical variables that describe the evolution of reversible process. In order for the energy imbalance inequality (22) to hold for any choice of the these fields and given the constraint (20) on ψ , we have that the terms highlighted in blue in

Equation (22) must be identically zero.

$$\boldsymbol{\xi} = \gamma J \mathbb{B}^{-1} \nabla_0 C_s, \quad (31)$$

$$\begin{aligned} \mu_s = p v_s + \mu_s^0 - \gamma J \nabla^2 C_s + k_B T \left[\ln \frac{C_s v_s}{1 + C_s v_s} + \frac{1}{1 + C_s v_s} \right. \\ \left. + \frac{\chi}{(1 + C_s v_s)^2} + \ln \frac{v_s C_s}{\sum_m v_m C_m} - \frac{v_s \sum_\alpha C_\alpha}{\sum_m C_m v_m} \right], \end{aligned} \quad (32)$$

$$\mu_i = p v_i + \mu_i^0 + e \Phi z_i + k_B T \ln \frac{v_i C_i}{\sum_m v_m C_m} - k_B T \frac{\sum_a C_a v_i}{\sum_m v_m C_m}, \quad (33)$$

$$\mathbf{E} = \frac{1}{\epsilon J} \mathbb{F}^T \mathbb{F} \mathbf{H}, \quad -\epsilon J \nabla^2 \Phi = Q, \quad (34)$$

$$\begin{aligned} \mathbb{T} = -p \mathbb{I} + \underbrace{\gamma \left[\frac{1}{2} |\nabla C_s|^2 \mathbb{I} - \nabla C_s \otimes \nabla C_s \right]}_{\mathbb{T}^{kort}} + \underbrace{\epsilon \left[\frac{1}{2} |\nabla \Phi|^2 \mathbb{I} - \nabla \Phi \otimes \nabla \Phi \right]}_{\mathbb{T}^{Max}} \\ + \frac{G}{J} (\mathbb{B} - \mathbb{I}), \end{aligned} \quad (35)$$

So that the energy imbalance inequality reduces to:

$$\sum_m \nabla_0 \mu_m \cdot \mathbf{J}_m \leq 0. \quad (36)$$

In the framework of linear non-equilibrium thermodynamics, when considering isothermal transformation, the second law of thermodynamics can be rewrite as:

$$W(R) + M(R) - \frac{d}{dt} \left\{ \int_R \psi \right\} = T \int_R \sigma \, dV, \quad (37)$$

Substituting Equations (31)-(35) into (37) and moving from the integral to the local form, we obtain:

$$\sigma = - \sum_m \frac{1}{T} \nabla_0 \mu_m \cdot \mathbf{J}_m. \quad (38)$$

Comparing Equation (38) and (30), it is evident that the thermodynamics forces are:

$$\zeta_m = - \frac{1}{T} \nabla_0 \mu_m. \quad (39)$$

Assuming to be in regime of linear non-equilibrium thermodynamics, we have that forces linearly depend on fluxes:

$$\zeta_k = -\frac{1}{T}\nabla_0 \mu_m = \sum_{k=s,1,\dots,N} H_{mk} \mathbf{J}_m. \quad (40)$$

Since the entropy production depends on the deformation, it is more suitable to move from the Lagrangian to the Eulerian coordinates. So that Equation (40) can be rewritten as:

$$\nabla \mu_m = - \sum_{k=s,1,\dots,N} T J H_{mk} \mathbb{B}^{-1} \mathbf{j}_m = \sum_{k=s,1,\dots,N} \ell_{mk} \mathbf{j}_m. \quad (41)$$

where the coefficient ℓ_{mk} are now constant, i.e. they are independent of the deformation. These can be correlated to drag coefficients, which are commonly used in the theory of mixtures [12, 13]. Let us first rewrite the fluxes as $\mathbf{j}_m = c_m(\mathbf{v}_m - \mathbf{v}_n) = c_m \bar{\mathbf{v}}_m$, where \mathbf{v}_m is the velocity of the m -th component in the current configuration, \mathbf{v}_n is the velocity of the network also in the current configuration and $\bar{\mathbf{v}}_m$ is the relative velocity of the m -th component with respect to the network. Then Equation (41) can be written as:

$$-c_j \nabla \mu_j = \sum_b h_{jb} \bar{\mathbf{v}}_j = \sum_{i \neq j} f_{ji} (\bar{\mathbf{v}}_i - \bar{\mathbf{v}}_j) + f_{js} (\bar{\mathbf{v}}_s - \bar{\mathbf{v}}_j) + f_{jn} \bar{\mathbf{v}}_j, \quad (42)$$

$$-c_s \nabla \mu_s = \sum_i f_{si} (\bar{\mathbf{v}}_i - \bar{\mathbf{v}}_s) + f_{sn} \bar{\mathbf{v}}_s, \quad (43)$$

where f_{mi} and h_{mn} are the drag coefficients related to the interaction between fluid constituents and the polymer network respectively. Based on the Onsanger's reciprocal relation we have that:

$$f_{mb} = f_{bm}. \quad (44)$$

A common assumption in the study of mixture theory is that the solute-solute drag can be neglected so that $f_{ij} = 0$ for $i, j = 1, \dots, N$ [10, 12]. The remaining drag coefficient are instead defined by:

$$f_{sn} = \frac{1}{k}, \quad f_{js} = \frac{k_B T c_j}{D_j^0}, \quad f_{js} + f_{jn} = \frac{k_B T c_j}{D_j}, \quad (45)$$

where k is the hydraulic permeability of the solvent in the network, D_j^0 is the diffusion coefficient of the solute in pure solution, while D_j is the diffusion coefficient in the gel.

Using (42)-(45), the relative velocities are of the form:

$$\bar{\mathbf{v}}_s = -K \left(\nabla \mu_s + \sum_i \frac{D_i}{D_i^0} \frac{C_i}{C_s} \nabla \mu_i \right), \quad (46)$$

$$\bar{\mathbf{v}}_j = -\frac{D_j}{k_B T} \nabla \mu_j + \frac{D_j}{D_j^0} \bar{\mathbf{v}}_s, \quad (47)$$

and the coefficient K is defined as:

$$\frac{1}{K} = \frac{1}{c_s k} + \sum_i \frac{k_B T}{D_i^0} \left(1 - \frac{D_i}{D_i^0} \right) \frac{c_i}{c_s}. \quad (48)$$

If we now move back to the initial configuration, we have that the fluxes \mathbf{J}_m have the form:

$$\mathbf{J}_m = J \mathbb{F}^{-1} \mathbf{j}_m = \mathbb{F}^{-1} C_m \bar{\mathbf{v}}_s, \quad (49)$$

where $\bar{\mathbf{v}}_s$ are defined by Equations (46)-(47). Substituting now Equations (49) into the conservation of mass laws (4), we recover the following governing equations:

$$\partial_t C_s = \nabla_0 \cdot \left[K \mathbb{F}^{-1} \left(C_s \nabla \mu_s + \sum_i \frac{D_i}{D_i^0} C_i \nabla \mu_i \right) \right], \quad (50)$$

$$\partial_t C_i = \nabla_0 \cdot \left[\frac{D_i}{k_B T} C_i \mathbb{F}^{-1} \nabla \mu_i - \frac{D_i}{D_i^0} \frac{C_i}{C_s} \mathbf{J}_s \right]. \quad (51)$$

1.5 Study of the free-swelling equilibrium.

In this section we consider the homogeneous equilibrium of a free swelling polyelectrolytes, under the assumption that all gradient vanish. Let us consider for simplicity the case in which there are only two charged ions C_+ and C_- with charges +1 and -1 respectively and same molecular volume v . As the gel swells in contact to the bath, the chemical potential and the stress tensor are constant along the interface. In order to identify the right boundary condition, we first need to study the bath.

1.5.1 The bath

In the bath, the set of Equations (31)-(35) reduces to:

$$\mu_s = pv_s + \mu_s^0 + k_B T \left[\ln \frac{v_s C_s}{\sum_m v_m C_m} - \frac{v_s \sum_\alpha C_\alpha}{\sum_m C_m v_m} \right], \quad (52)$$

$$\mu_\pm = pv + \mu_\pm^0 \pm e\Phi + k_B T \ln \frac{v C_\pm}{\sum_m v_m C_m} - k_B T \frac{\sum_a C_a v}{\sum_m v_m C_m}, \quad (53)$$

$$\mathbf{E} = \frac{1}{\epsilon J} \mathbb{F}^T \mathbb{F} \mathbf{H}, \quad -\epsilon J \nabla^2 \Phi = C_+ - C_-, \quad (54)$$

$$\mathbb{T} = -p\mathbb{I} + \epsilon \left[\frac{1}{2} |\nabla \Phi|^2 \mathbb{I} - \nabla \Phi \otimes \nabla \Phi \right]. \quad (55)$$

As in Yu, we consider the reservoir to be infinite so that the concentration of ions is fixed away from the interface with the gel and equal to c_0 in the current configuration. Note that at equilibrium, electro-neutrality imposes that $c_0^+ = c_0^- = c_0 = C^+/J = C_-/J$, where $J = \sum_m v_m C_m$. Consequently the set of equations reduces to:

$$p = 0, \quad (56)$$

$$\mu_s = \mu_s^0 + k_B T [\ln v_s c_s - v_s c_s - 2v_s c_0], \quad (57)$$

$$\mu_\pm = \mu_\pm^0 \pm e\Phi + k_B T \ln v c_0 - v k_B T (2c_0 + c_s). \quad (58)$$

Assuming that in the outer solution $J \sim v_s C_s$, so that $v_s c_s \sim 1$, and that $\Phi = 0$, we are left with the conditions:

$$p = 0, \quad (59)$$

$$\mu_s = \mu_s^0 + k_B T [-1 - 2v_s c_0], \quad (60)$$

$$\mu_\pm = \mu_\pm^0 + k_B T \ln v c_0 - v k_B T (2c_0 + 1). \quad (61)$$

1.5.2 The gel.

We now consider the gel and impose the continuity condition at the interface, so that at equilibrium Equations (31)-(35) reduces to:

$$0 = pv_s + k_B T \left[2c_0 v_s + \ln \frac{C_s v_s}{1 + C_s v_s} + \frac{1}{1 + C_s v_s} + \frac{\chi}{(1 + C_s v_s)^2} + \ln \frac{v_s C_s}{\sum_m v_m C_m} - \frac{\sum_\alpha (v_s - v_\alpha) C_\alpha}{\sum_m C_m v_m} \right], \quad (62)$$

$$z_f C_f + C_+ - C_- = 0, \quad (63)$$

$$0 = pv \pm e\Phi + 2k_B T c_0 + k_B T \ln \frac{C_\pm}{c_0 \sum_m v_m C_m} - k_B T \frac{C_s (v - v_s)}{\sum_m v_m C_m}, \quad (64)$$

$$0 = -p\mathbb{I} + \frac{G}{J} (\mathbb{B} - \mathbb{I}). \quad (65)$$

For the free swelling case the deformation tensor $\mathbb{F} = \lambda \mathbb{I}$ so that $\mathbb{B} = \lambda^2 \mathbb{I}$. As in the paper by Yu, we now assume that $v = v_s$ so that the equations further simplify to:

$$0 = pv + k_B T \left[2c_0 v + \ln \frac{C_s v}{1 + C_s v} + \frac{1}{1 + C_s v} + \frac{\chi}{(1 + C_s v)^2} + \ln \frac{v C_s}{\sum_m v_m C_m} \right], \quad (66)$$

$$z_f C_f + C_+ - C_- = 0, \quad (67)$$

$$0 = pv \pm e\Phi + 2k_B T c_0 + k_B T \ln \frac{C_\pm}{v c_0 \sum_m C_m}, \quad (68)$$

$$p = \frac{G}{\lambda^3} (\lambda^2 - 1). \quad (69)$$

Using Equations(68), we have that the electric potential has the form:

$$\Phi = \frac{k_B T}{2e} \ln \frac{C_-}{C_+}. \quad (70)$$

while the concentrations C_+ and C_- , using also Equation (66):

$$C_- = c_0 \frac{(v C_s)^2}{1 + C_s v} \exp \left(\frac{e\Phi}{k_B T} \right) \exp \left(\frac{1 + C_s v + \chi}{(1 + v C_s)^2} \right), \quad (71)$$

$$C_+ = c_0 \frac{(v C_s)^2}{1 + C_s v} \exp \left(-\frac{e\Phi}{k_B T} \right) \exp \left(\frac{1 + C_s v + \chi}{(1 + v C_s)^2} \right), \quad (72)$$

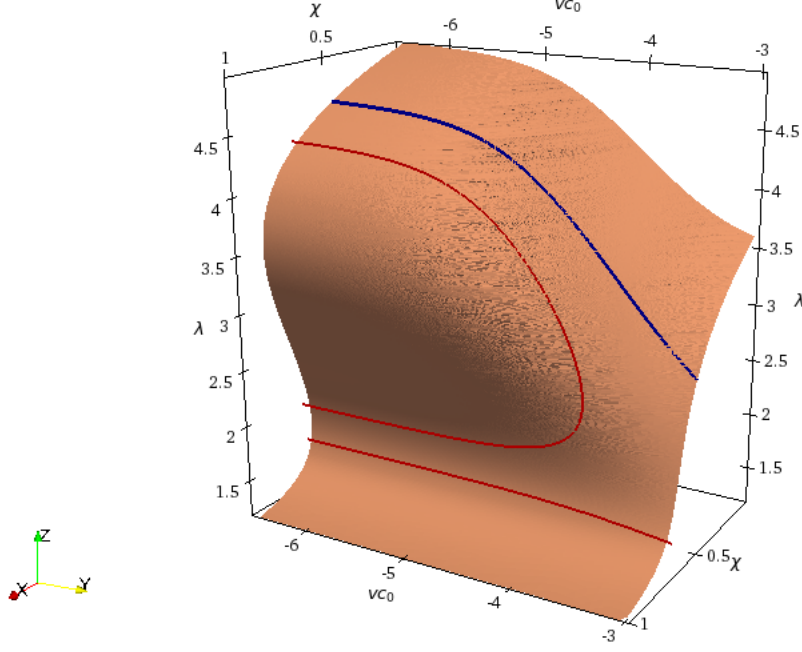


Figure 2: Two-parameters bifurcation analysis: equilibrium manifold. The red line corresponds to the section of the manifold for $\chi = 0.7$, while the blue line $\chi = 0.5$.

which implies that:

$$C_+ C_- = c_0^2 \frac{(vC_s)^4}{(1 + C_s v)^2} \exp \left(2 \frac{1 + C_s v + \chi}{(1 + vC_s)^2} \right). \quad (73)$$

Combining (73) with the electro-neutrality condition, we have:

$$C_{\pm} = \mp \frac{z_f C_f}{2} + \sqrt{\left(\frac{z_f C_f}{2} \right)^2 + c_0^2 \frac{(vC_s)^4}{(1 + C_s v)^2} \exp \left(2 \frac{1 + C_s v + \chi}{(1 + vC_s)^2} \right)}. \quad (74)$$

Using the incompressibility condition, we have that:

$$\lambda^3 = 1 + vC_s + 2v \sqrt{\left(\frac{z_f C_f}{2} \right)^2 + c_0^2 \frac{(vC_s)^4}{(1 + C_s v)^2} \exp \left(2 \frac{1 + C_s v + \chi}{(1 + vC_s)^2} \right)}. \quad (75)$$

Finally substituting the definition of p into Equation (20), we have:

$$0 = \frac{Gv}{k_B T \lambda^3} (\lambda^2 - 1) + 2c_0 v + \ln \frac{C_s v}{1 + C_s v} + \frac{1 + vC_s + \chi}{(1 + C_s v)^2} + \ln \frac{vC_s}{\lambda^3 - 1}. \quad (76)$$

Note that the two conditions (75) and (76) uniquely define the equilibrium swelling ratio for any value of c_0 . Fixing the values of the other parameter to match with the work of Yu and varying vc_0 and χ , we obtained the manifold showed in Figure 2.

2 Non-dimensional formulation of the model

$$D_i = D_i^0, \quad k = \frac{D_0(1 + v_s C_s)^\beta}{k_B T c_s} \Rightarrow K = \frac{D_0(1 + v_s C_s)^\beta}{k_B T}. \quad (77)$$

Variables rescaling:

$$\begin{aligned} k_B T \hat{\mu} + \mu_0 - k_B T &= \mu, & \hat{C}_i &= v C_i, & \hat{\Phi} &= \frac{\Phi e}{k_B T}, & G_1 \hat{p} &= p \\ G_1 \hat{\mathbb{T}} &= \mathbb{T}, & \hat{\mathbf{x}} L &= \mathbf{x}, & \hat{t} \tau &= t, & e \hat{Q} &= v Q, & \hat{K} &= \frac{k_B T}{D_0} K \\ & & \hat{\mathbf{j}} &= \frac{v L}{D_0} \mathbf{j}, & \hat{\mathbb{L}} &= \tau \mathbb{L} \end{aligned}$$

We also need to rewrite the problem in terms of the current configuration, so that the governing equation become:

$$\partial_t c_s + c_s \text{tr}(\mathbb{L}) = -\nabla \cdot \mathbf{j}_s, \quad (78)$$

$$\partial_t c_i + c_i \text{tr}(\mathbb{L}) = -\nabla \cdot \mathbf{j}_i, \quad (79)$$

$$\mathbf{j}_s = -c_s K \left(\nabla \mu_s + \sum_i \frac{C_i}{C_s} \nabla \mu_i \right) \quad (80)$$

$$\mathbf{j}_i = -\frac{D_i c_i}{k_B T} \nabla \mu_i + c_i \bar{\mathbf{v}}_s \quad (81)$$

So that the a-dimensional set of equation is:

$$\mu_s = p \frac{G_1 v_s}{k_B T} - \frac{\gamma}{v k_B T L^2} J \nabla^2 C_s + \left[\ln \frac{C_s}{1 + C_s} + \frac{1}{1 + C_s} + \frac{\chi}{(1 + C_s)^2} + \ln \frac{C_s}{\sum_m C_m} \right], \quad (82)$$

$$\mu_i = p \frac{G_1 v_i}{k_B T} + \Phi z_i + \ln \frac{C_i}{\sum_m C_m}, \quad (83)$$

$$-\frac{\epsilon k_B T v}{L^2 e^2} J \nabla^2 \Phi = Q \quad (84)$$

$$\mathbb{T} = -p \mathbb{I} + \frac{\gamma}{G_1 v^2 L^2} \left[\frac{1}{2} |\nabla C_s|^2 \mathbb{I} - \nabla C_s \otimes \nabla C_s \right] + J^{-1} (\mathbb{B} - \mathbb{I}) + \frac{\epsilon (k_B T)^2}{G_1 L^2 e^2} \left[\frac{1}{2} |\nabla \Phi|^2 \mathbb{I} - \nabla \Phi \otimes \nabla \Phi \right], \quad (85)$$

$$\nabla \cdot \mathbb{T} = \mathbf{0} \quad (86)$$

$$\partial_t c_s + c_s \text{tr}(\mathbb{L}) = -\frac{\tau D_0}{L^2} \nabla \cdot \mathbf{j}_s, \quad (87)$$

$$\partial_t c_i + c_i \text{tr}(\mathbb{L}) = -\frac{\tau D_0}{L^2} \nabla \cdot \mathbf{j}_i, \quad (88)$$

$$\mathbf{j}_s = -c_s K \left(\nabla \mu_s + \sum_i \frac{C_i}{C_s} \nabla \mu_i \right) \quad (89)$$

$$\mathbf{j}_i = -\frac{D_i c_i}{D_0} \nabla \mu_i + \frac{c_i}{c_s} \mathbf{j}_s \quad (90)$$

We consider a 1D problem of constrained swelling, so that the problem simplifies:

$$L_d = \sqrt{\frac{\epsilon k_B T v}{e^2}} \ll L \Rightarrow \beta = \frac{L_d^2}{L^2} \ll 1 \quad (91)$$

We also assume that:

$$L_{int} = \frac{\gamma}{v k_B T} > L_d \quad (92)$$

$$\mu_s = p\mathcal{G} - \frac{L_{int}^2}{L^2} J \partial_{zz} C_s + \left[\ln \frac{C_s}{1+C_s} + \frac{1}{1+C_s} + \frac{\chi}{(1+C_s)^2} + \ln \frac{C_s}{\sum_m C_m} \right], \quad (93)$$

$$\mu_i = p\mathcal{G} + \Phi z_i + \ln \frac{C_i}{\sum_m C_m}, \quad (94)$$

$$-\beta^2 J \partial_{zz} \Phi = Q \quad (95)$$

$$\partial_z T_z = 0 \quad (96)$$

$$T_z = -p - \frac{L_i^2}{2\mathcal{G}L^2} (\partial_z C_s)^2 + J^{-1} (J^2 - 1) - \frac{\beta^2}{2\mathcal{G}} (\partial_z \Phi)^2, \quad (97)$$

$$\partial_t c_s + c_s \text{tr}(\mathbb{L}) = -\partial_z j_s, \quad (98)$$

$$\partial_t c_i + c_i \text{tr}(\mathbb{L}) = -\partial_z j_i, \quad (99)$$

$$j_s = -c_s K \left(\partial_z \mu_s + \sum_i \frac{c_i}{c_s} \partial_z \mu_i \right) \quad (100)$$

$$j_i = -\frac{D_i c_i}{D_0} \partial_z \mu_i + \frac{c_i}{c_s} j_s \quad (101)$$

where the time τ can now be defined as $\tau = L^2/D_0$, where L is the original size of the gel. We thus have that in the external layer, electro neutrality must hold. By expanding the solution in terms of β we have at the leading order:

$$Q^0 = 0 \implies \begin{cases} C_f + \sum_i C_i^0 z_i = 0, & \text{gel} \\ \sum_i c_i^0 z_i = 0, & \text{bath} \end{cases} \quad (102)$$

which implies the concentration of the ion in the solution c_i^0 can not be continuous across the layer. Assuming that there are only two ion species so

that $z_i = +1, -1$. If we now differentiate the equation (94), we obtain that:

$$\frac{\partial}{\partial z} (j_+ - j_-) = 0, \quad (103)$$

$$C_+ - C_- = C_f \quad (104)$$

$$j_s = -c_s K \left(\partial_z \mu_s + \sum_i \frac{c_i}{c_s} \partial_z \mu_i \right) \quad (105)$$

$$j_i = -\frac{D_i c_i}{D_0} \partial_z \mu_i + \frac{c_i}{c_s} j_s \quad (106)$$

$$\begin{aligned} \mu_s = p\mathcal{G} - \frac{L_{int}^2 J}{L^2} \partial_{zz} C_s + \left[\ln \frac{C_s}{1 + C_s} + \frac{1}{1 + C_s} \right. \\ \left. + \frac{\chi}{(1 + C_s)^2} + \ln \frac{C_s}{\sum_m C_m} \right], \end{aligned} \quad (107)$$

$$\mu_i = p\mathcal{G} + \Phi z_i + \ln \frac{C_i}{\sum_m C_m}, \quad (108)$$

$$\partial_z T_z = 0 \quad (109)$$

$$T_z = -p - \frac{L_i^2}{2\mathcal{G}L^2} (\partial_z C_s)^2 + J^{-1} (J^2 - 1). \quad (110)$$

While in the bath we have:

$$\frac{\partial}{\partial z} (j_+ - j_-) = 0, \quad (111)$$

$$c_+ = c_- = c_0 \quad (112)$$

$$\mu_s = p\mathcal{G} + \ln c_s, \quad (113)$$

$$\mu_i = p\mathcal{G} + \Phi z_i + \ln c_i, \quad (114)$$

$$\partial_z T_z = 0 \Rightarrow \partial_z p = 0 \quad (115)$$

$$j_s = -c_s \partial_z \mu_s + \sum_i c_i \partial_z \mu_i \quad (116)$$

$$j_i = -\frac{D_i c_i}{D_0} \partial_z \mu_i - \frac{c_i}{c_s} j_s \quad (117)$$

Substituting (117) into (111):

$$\dot{j}_s = -\partial_z c_s - 2\partial_z c_0 = 0 \Rightarrow \partial_t c_s = 0, \quad (118)$$

$$\partial_z \left(\frac{2D}{D_0} c_0 \partial_z \phi \right) = 0, \quad (119)$$

$$\partial_t c_0 = \frac{D}{D_0} \partial_{zz} c_0 \quad (120)$$

where the first equation is due to the fact that $c_s + 2c_0 \equiv 1$. If we now rescale the space with respect to β , we have:

$$\begin{aligned} \mu_s = p\mathcal{G} - \frac{L_{int}^2 J}{L_d^2} \partial_{zz} C_s + \left[\ln \frac{C_s}{1 + C_s} + \frac{1}{1 + C_s} \right. \\ \left. + \frac{\chi}{(1 + C_s)^2} + \ln \frac{C_s}{\sum_m C_m} \right], \end{aligned} \quad (121)$$

$$\mu_i = p\mathcal{G} + \Phi z_i + \ln \frac{C_i}{\sum_m C_m}, \quad (122)$$

$$-J\partial_{zz}\Phi = Q \quad (123)$$

$$T_z = -p - \frac{L_i^2}{2\mathcal{G}L_p^2} (\partial_z C_s)^2 + J^{-1} (J^2 - 1) - \frac{1}{2\mathcal{G}} (\partial_z \Phi)^2, \quad (124)$$

$$\beta \partial_t c_s + \beta c_s \dot{J} J^{-1} = -\partial_z j_s, \quad (125)$$

$$\beta \partial_t c_i + \beta c_i \dot{J} J^{-1} = -\partial_z j_i, \quad (126)$$

$$j_s = -c_s K \left(\partial_z \mu_s + \sum_i \frac{c_i}{c_s} \partial_z \mu_i \right) \quad (127)$$

$$j_i = -\frac{D_i c_i}{D_0} \partial_z \mu_i + \frac{c_i}{c_s} j_s \quad (128)$$

where we have the new parameter $\xi = L_d/L_{int} \ll 1$. If we expand C_s in term of β and ξ , with $\beta < \xi$:

$$C_s = C_s^{(0,0)} + \xi C_s^{(0,1)} + \xi^2 C_s^{(0,2)} + \beta C_s^{(1,0)} + \beta \xi C^{(1,1)} + \beta^2 C^{(2,0)} + h.o.t \quad (129)$$

Substituting into Equation (121)-(124) and imposing $\mu_s \sim O(1)$ we have:

$$\partial_{zz}C^{(0,0)} = \partial_{zz}C^{(0,1)} = \partial_{zz}C^{(1,0)} = 0 \quad (130)$$

$$\begin{aligned} \mu_s = p\mathcal{G} - \partial_{zz}C_s^{(0,2)} - \frac{L_{int}}{L}\partial_{zz}C_s^{(1,1)} - \frac{L_{int}^2}{L^2}\partial_{zz}C_s^{(2,0)} \\ + \left[\ln \frac{C_s^{(0,0)}}{1 + C_s^{(0,0)}} + \frac{1}{1 + C_s^{(0,0)}} + \frac{\chi}{(1 + C_s^{(0,0)})^2} + \ln \frac{C_s^{(0,0)}}{J^{(0,0)} - 1} \right], \end{aligned} \quad (131)$$

$$\partial_z C_s^{(0,0)} = 0 \Rightarrow C_s^{(0,0)} = const \quad (132)$$

$$\begin{aligned} T_z^{(0,0)} = -p^{(0,0)} - (\partial_z C_s^{(0,1)})^2 - \frac{L_{int}}{L}\partial_z C_s^{(1,0)}\partial_z C_s^{(0,1)} - \frac{L_{int}^2}{L^2}(\partial_z C_s^{(1,0)})^2 \\ + (J^{(0,0)})^{-1}((J^{(0,0)})^2 - 1) - \frac{1}{2\mathcal{G}}(\partial_z \Phi^{(0,0)})^2, \end{aligned} \quad (133)$$

$$\partial_z T_z^{(0,0)} = 0 \Rightarrow \partial_z p^{(0,0)} = \left(\frac{(J^{(0,0)})^2 + 1}{(J^{(0,0)})^2} \right) \partial_z J^{(0,0)} + \frac{Q}{\mathcal{G}J} \partial_z \Phi^{(0,0)} \quad (134)$$

$$\partial_z j_s = \partial_z j_+ = \partial_z j_- = 0 \quad (135)$$

In the bath, we have that:

$$\mu_s = p\mathcal{G} + \ln c_s, \quad (136)$$

$$\mu_i = p\mathcal{G} + \Phi z_i + \ln c_i, \quad (137)$$

$$-\epsilon_r \partial_{zz} \Phi = Q \quad (138)$$

$$\partial_z T_z = 0 \Rightarrow \partial_z p = \frac{Q}{\mathcal{G}} \partial_z \Phi \quad (139)$$

$$T_z = -p - \frac{\epsilon_r}{2\mathcal{G}}(\partial_z \Phi)^2, \quad (140)$$

$$\beta \partial_t c_s = -\partial_z j_s, \quad (141)$$

$$\beta \partial_t c_i = -\partial_z j_i, \quad (142)$$

So that at first order the fluxes j_m are constant in the layer, as well as

the stress T_z . In the bath we thus have that:

$$\begin{aligned} j_s^{bath} &= -2Q\partial_z\Phi = \lim_{z\rightarrow\infty} j_s^{bath} = 0 \\ \Rightarrow Q &= 0, \quad \partial_z\Phi = \text{const} \end{aligned} \quad (143)$$

$$j_{\pm}^{bath} = -\frac{D}{D_0}\partial_z c_{\pm}^{bath} \pm c_{\pm}^{bath} \frac{D}{D_0}\partial_z\Phi = j_{\pm}^{gel} \quad (144)$$

$$-p^{bath} - \frac{\epsilon_r}{2\mathcal{G}}(\partial_z\Phi)^2 = T_z^{gel} \quad (145)$$

while in the gel:

$$0 = C_s^{(0,0)}\partial_z\mu_s^{(0,0)} + \sum_i C_i^{(0,0)}\partial_z\mu_i \quad (146)$$

$$\begin{aligned} \partial_z\mu_s &= \mathcal{G} \left(\frac{(J^{(0,0)})^2 + 1}{(J^{(0,0)})^2} \right) \partial_z J^{(0,0)} + \frac{Q}{J^{(0,0)}} \partial_z \Phi^{(0,0)} - \frac{\partial_z J^{(0,0)}}{J^{(0,0)} - 1} \\ &\quad - \partial_z \left(\partial_{zz} C_s^{(0,2)} + \frac{L_{int}}{L} \partial_{zz} C_s^{(1,1)} + \frac{L_{int}^2}{L^2} \partial_{zz} C_s^{(2,0)} \right) \end{aligned} \quad (147)$$

$$\begin{aligned} \partial_z\mu_{\pm} &= \mathcal{G} \left(\frac{(J^{(0,0)})^2 + 1}{(J^{(0,0)})^2} \right) \partial_z J^{(0,0)} + \frac{Q \pm J^{(0,0)}}{J^{(0,0)}} \partial_z \Phi^{(0,0)} \\ &\quad + \frac{\partial_z C_{\pm}^{(0,0)}}{C_{\pm}^{(0,0)}} - \frac{\partial_z J^{(0,0)}}{J^{(0,0)} - 1} \end{aligned} \quad (148)$$

$$\begin{aligned} 0 &= \mathcal{G} (J^{(0,0)} - 1) \left(\frac{(J^{(0,0)})^2 + 1}{(J^{(0,0)})^2} \right) \partial_z J^{(0,0)} + \frac{(2Q - C_f)J^{(0,0)} - Q}{J^{(0,0)}} \partial_z \Phi^{(0,0)} \\ &\quad - C_s^{(0,0)} \partial_z \left(\partial_{zz} C_s^{(0,2)} + \frac{L_{int}}{L} \partial_{zz} C_s^{(1,1)} + \frac{L_{int}^2}{L^2} \partial_{zz} C_s^{(2,0)} \right) \end{aligned} \quad (149)$$

$$j_i^{gel} = -\frac{DC_i^{gel}}{D_0} \partial_z \mu_i^{gel} = \frac{D}{D_0} \partial_z c_i^{bath} \quad (150)$$

Since we have that in the bulk of the gel $j_+ - j_- = 0$, we have the additional condition that in the bath $\partial\Phi^{gel} = \text{const} = 0$. If we assume the bath to be of infinite size so that the concentration derivative goes to zero:

$$\partial_z c_{\pm} = \text{const} = \lim_{z\rightarrow\infty} c_{\pm}^{bath} = 0, \quad \mu_{\pm}^{bath} = \ln c_0. \quad (151)$$

This implies that the chemical potential is constant in the bath and thus also in the Debye layer. As the stress is zero in the outer region of the bath we

have that T_z must be zero everywhere in the layer:

$$p^{bath} = -\frac{\epsilon_r}{2\mathcal{G}}(\partial_z\Phi)^2 = 0 \quad (152)$$

$$p^{gel} = -(\partial_z C_s^{(0,1)})^2 - \frac{L_{int}}{L}\partial_z C_s^{(1,0)}\partial_z C_s^{(0,1)} - \frac{L_{int}^2}{L^2}(\partial_z C_s^{(1,0)})^2 + J^{-1}(J^2 - 1) - \frac{1}{2\mathcal{G}}(\partial_z\Phi)^2 \quad (153)$$

So that the chemical potential are constant inside and outside the gel, at first order. Consequently we have that:

$$\mu_{\pm}^{bath} = p\mathcal{G} + \Phi z_i + \ln \frac{C_{\pm}}{J-1}, \quad (154)$$

$$-\partial_Z(J^{-1}\partial_Z\Phi) = Q \quad (155)$$

If we also assume that $L_{int}^2/L_d^2 \gg 1$ we must have that at first order:

$$\partial_Z(J^{-1}\partial_Z C_s^0) = 0 \Rightarrow \partial_Z C_s^0 = Jconst = \alpha J \quad (156)$$

while the continuity of the stress tensor is given by:

$$-p^{bath} - \frac{\epsilon_r}{2v} \frac{(\partial_Z\Phi)^2}{J^2} = -p - \frac{L_i^2}{2\mathcal{G}L_p^2}\alpha^2 + J^{-1}(J^2 - 1) - \frac{1}{2v} \frac{(\partial_Z\Phi)^2}{J^2} \quad (157)$$

Also at the first order, have continuity of the electrical potential so that:

$$C_i^0 = c_0^{bath}(J-1)\exp[\Delta p\mathcal{G} - z_i\Delta\Phi] \quad (158)$$

where $\Delta = (\cdot)_{bath} - (\cdot)_{gel}$. In the bath instead the governing equations are:

$$\mu_s^b = p^b\mathcal{G} - \frac{L_{int,b}^2}{L^2}\partial_Z(J^{-1}\partial_Z C_s) + \ln \frac{C_s}{\sum_m C_m}, \quad (159)$$

$$\mu_i^b = p^b\mathcal{G} + \Phi z_i + \ln \frac{C_i}{\sum_m C_m}, \quad (160)$$

$$-\beta^2\tilde{\epsilon}\partial_Z(J_b^{-1}\partial_Z\Phi) = Q_b \quad (161)$$

$$T_z = -p - \frac{L_{int,b}^2}{2\mathcal{G}L^2} \frac{(\partial_Z C)^2}{J_b^2} - \frac{\beta^2}{2v} \tilde{\epsilon} \frac{(\partial_Z\Phi)^2}{J_b^2}, \quad (162)$$

$$\partial_t C_s = \partial_Z \cdot \left[\frac{K}{J^2} \left(C_s \partial_Z \mu_s + \sum_i C_i \partial_Z \mu_i \right) \right], \quad (163)$$

$$\partial_t C_i = \partial_Z \cdot \left[J_{bath}^{-2} \left(\frac{D_i}{D_0} C_i \partial_Z \mu_i \right) \right]. \quad (164)$$

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