

COMPUTATIONAL ASPECTS OF TRANSIENT DIFFUSION-DRIVEN SWELLING

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Key words: Transient Diffusion, Swelling, Open System, Hydrogel.

Summary. The boundary value problem coupling large deformation to transient mass transport in form of diffusion is governed by the balance principles for an open system. As a model material, hydrogel — a polymer capable of absorbing large amounts of water, swelling in the process — is chosen. The free Helmholtz energy additively combines elastic and mixing effects. The mass flux is constituted by Fick's law of diffusion. The implementation of a related mixed finite element method — formulated in terms of displacements and a chemical potential — poses several numerical challenges to which solutions are proposed. Finally, the implemented finite element method is illustrated in stationary as well as transient settings and further examples are given to demonstrate typical swelling behaviour.

1 INTRODUCTION

Diffusion plays an important role in many biological as well as technological processes, e.g. osmosis and diffusion welding, but also corrosion. In any case, a simulation of diffusion processes can provide additional insight into the exact details. An ideal class of materials to study diffusion are hydrogels. A hydrogel consists of multiple cross linked polymer molecules, in between which water molecules can be stored¹ swelling the gel in the process.

First modelling approaches on polymeric gels are commonly attributed to Tanaka and

his colleagues². They formulated a linear elastic model for a polymer fibre network and later connected it to diffusion by modelling the friction in the gel. More recently, non-linear approaches to accurately capture the effects of swelling, have been proposed.

The theory outlined here closely follows the works of Bouklas et al.³ and Hong et al.¹.

2 THEORY

The summary of theoretical modelling aspects is split into two parts: The definition of the boundary value problem, necessary for the implementation of the finite element method, and the material model, based on which stresses and flux terms are specified.

2.1 Definition of the boundary value problem

Hydrogel is considered as an open system containing a mixture of polymer and water. Small molecules enter the system either through the boundary in terms of the referential flux \mathbf{J} or through the source r_0 . The balance equations in local form are then given by

$$\dot{\rho}_0 = m_M [r_0 - \nabla_{\mathbf{X}} \cdot \mathbf{J}] , \quad \dot{\rho}_0 \dot{\mathbf{x}} + \rho_0 \ddot{\mathbf{x}} = \nabla_{\mathbf{X}} \cdot \mathbf{P} + \rho_0 \mathbf{b} \quad (1)$$

with the mass per molecule denoted as m_M . It is important to note that the rate of the referential density $\dot{\rho}_0$ does not vanish (as in closed systems), such that an additional term appears in the balance of linear momentum. A theory incorporating all dynamical effects has to deal with these strongly coupled governing equations. In the context of diffusion however, the dynamical effects can be neglected with the argument of decoupling the underlying time scales. For macroscopic problems typical times for diffusion are in the order of thousand seconds, while dynamical effects operate on a much shorter time frame.

The balance of mass can be recast into a particle-based balance relation by constituting the density in terms of the concentration and assuming no reaction between the polymer and the small molecules takes place. The boundary value problem is then given by

$$\begin{aligned} \nabla_{\mathbf{X}} \cdot \mathbf{P} + \rho_0 \mathbf{b} &= 0 & \text{in } \mathcal{B}_0, & \quad \mathbf{P} \cdot \mathbf{N} = \mathbf{t}_0 & \text{on } \partial \mathcal{B}_0^t, \\ \frac{\partial C}{\partial t} + \nabla_{\mathbf{X}} \cdot \mathbf{J} &= r_0 & \text{in } \mathcal{B}_0, & \quad \mathbf{J} \cdot \mathbf{N} = -j_0 & \text{on } \partial \mathcal{B}_0^j. \end{aligned} \quad (2)$$

2.2 Material model

The derivation of the material model follows the concept of standard dissipative materials. The free Helmholtz energy is additively combined of an elastic contribution Ψ^{el} , a mixing term Ψ^{m} and a bulk term Ψ^{blk} penalising compression, i.e.

$$\begin{aligned} \Psi^{\text{el}} &= \frac{1}{2} N k_B T [\mathbf{F} : \mathbf{F} - 3 - 2 \ln(\det(\mathbf{F}))] , & \Psi^{\text{blk}} &= \frac{1}{2} K [\det(\mathbf{F}) - [1 + \Omega C]]^2 , \\ \Psi^{\text{m}} &= \frac{k_B T}{\Omega} \left[\Omega C \ln \left(\frac{\Omega C}{1 + \Omega C} \right) + \frac{\chi \Omega C}{1 + \Omega C} \right] , \end{aligned} \quad (3)$$

where N describes the number of polymer chains per volume, k_B the Boltzmann constant, T the temperature, Ω the molecular volume of the solvent, χ the Flory parameter and K the bulk modulus.

The stresses and driving forces follow from the second law of thermodynamics. Contrary to the procedure for closed systems, an open system also requires to take the entropy of the mass entering the system into account. To this end, the free energy in the system needs to decrease, such that the external mechanical work and the work performed by the small molecules can be considered. After identifying the stresses and driving forces, the inequality

$$\int_{\mathcal{B}_0} \mathbf{J} \cdot \nabla_{\mathbf{x}} \mu \, dV \leq 0 \quad (4)$$

remains to be fulfilled. In straight forward fashion the mass flux \mathbf{J} is constituted to create a quadratic form as

$$\mathbf{J} = -\mathbf{M} \cdot \nabla_{\mathbf{x}} \mu, \quad \mathbf{M} := \frac{C D}{k_B T} \mathbf{F}^{-1} \cdot \mathbf{F}^{-t}, \quad (5)$$

where the mobility tensor \mathbf{M} follows from Fick's law of diffusion.

3 IMPLEMENTATION

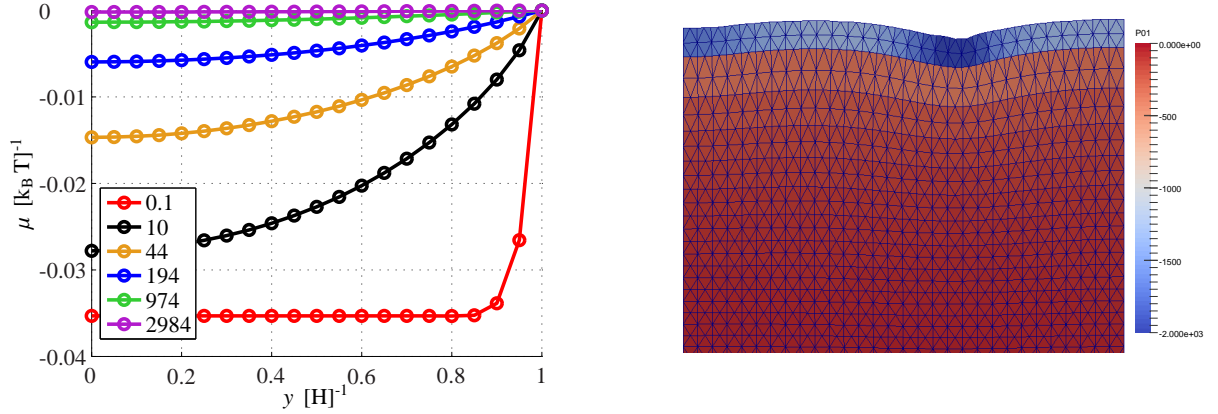
The finite element method is derived in standard manner. As field variables the displacement \mathbf{u} and the chemical potential μ are chosen. It is beneficial to choose the chemical potential instead of the concentration as field variable, to prevent higher order derivatives of the shape functions. Consequently, the Legendre transformation is applied to switch from $\Psi(\mathbf{F}, C)$ to $\hat{\Psi}(\mathbf{F}, \mu)$. This results in an implicit relation for the concentration, which is solved by a Newton-Raphson scheme on quadrature point level. The discretisation follows the isoparametric Galerkin approach using quadratic shape functions for the displacement field and linear shape functions for the chemical potential.

An important problem regarding the implementation of this model is the huge difference in scales between the displacement field and the chemical potential, which cannot be overcome by solely choosing an appropriate set of units. Instead, the chemical potential, the time and the balance equations are each normalised by characteristic material parameters. Another point to keep in mind is the singularity for $C = 0$, which requires an initial swelling $C_0 \neq 0$ prior to the simulation. C_0 can be determined analytically by assuming a homogeneous and stress-free state of initial swelling.

4 CONSTRAINED SWELLING

A layer of gel with thickness H is initially swollen with concentration C_0 and then bound to a rigid substrate. Assuming an infinite length of the layer, the problem reduces to two dimensions. The top surface of the gel is then brought in contact with an infinite reservoir

of water molecules, which start to diffuse into the gel, swelling it. Figure 1(a) shows how the water molecules slowly penetrate into the gel with increasing time. In Figure 1(b) the top surface is additionally slightly perturbed, which leads to the formation of wrinkles. The observed surface instability is invariant of the perturbation type, but strongly depends on the stiffness of the surface layer.



(a) Chemical potential μ over height y of the layer and for selected points of (normalised) time (different colours).

(b) Display of surface instability. Contour plot of the Piola stress P_{xx} in MPa.

Figure 1: Constrained swelling of a hydrogel layer.

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