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On the Modeling of Polyelectrolyte Gels

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Summary: Ionic polymer gels are very attractive actuation materials with a great similarity to biological contractile tissues. They consist of a polymer network with bound charged groups and a liquid phase with mobile ions. Absorption and delivery of solvent lead to a considerably large change of volume. This swelling mechanism results from the equilibrium of different forces such as osmotic pressure forces, electrostatic forces and viscoelastic restoring forces and can be triggered by chemical (change of salt concentration or pH in the solution), thermal or electrical stimulation. In the present work, chemically and electrically stimulated electrolyte polymer gels in a solution bath are investigated. To describe the different phenomena occurring in these gels adequately, the modeling can be conducted on different scales. If only the global macroscopic behavior is of interest, the statistical theory which is capable to describe the global swelling ratio, is sufficient. By refining the scale, the mesoscopic coupled multi-field theory can be applied. Here, the chemical field is described by a convection-diffusion equation for the different mobile species. The electric field is directly obtained by solving the Poisson equation in the gel and solution domain. The mechanical field is formulated by the momentum equation. By further refining the scale, the whole structure can be investigated on the microscale by the discrete element (DE) method. In this model, the material is represented by distributed particles comprising a certain amount of mass; the particles interact with each other mechanically by a truss or beam network of massless elements. The mechanical behavior, i.e. the dynamics of the system, is followed by solving the Newton's equations of motion while the chemical field, i.e. the ion movement inside the gel and from the gel to the solution, is described by diffusion equations for the different mobile particles. All three formulations can give chemical, (electrical) and mechanical unknowns and all rely on the assumption that the concentration differences between the different regions of the gel and between gel and solution form the osmotic pressure difference, which is a main cause for the mechanical deformation of the polyelectrolyte gel film.

Keywords: discrete elements; hydrogels; multi-field formulation; simulations; statistical theory

Introduction

Electrolyte polymer gels are ductile-elastic materials. They consist of a polymer network with ionizable groups and a liquid phase with mobile ions, see Figure 1. A considerably large change of volume - by absorption or delivery of solvent - can be triggered by different stimuli such as change of temperature, of pH-value or salt concentration in the solution (chemical stimulation) or by an applied electric field (electric stimulation). Due to this capability, electrolyte polymer gels are designated as actuators for technical applications where large swelling and shrinkage is desired, such

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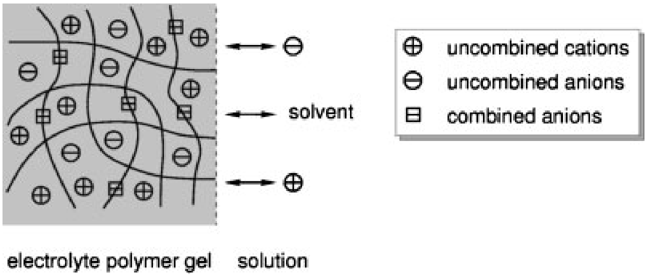


Figure 1.
Schematic of a polymer gel.

as for artificial muscles or other chemo-electro-mechanical actuators.[1]

Modeling

The swelling behavior of these gels results from the equilibrium of different forces: osmotic pressure forces, electrostatic forces, viscoelastic restoring forces, etc. To describe the different phenomena and processes adequately, the modeling can be performed on different scales (Figure 2). If only the global macroscopic behavior is of interest, the statistical theory is sufficient. To gain a more precise insight into the phenomena occurring in gels, the coupled chemo-electro-mechanical formulation is a good choice. If also the micromechanical behavior and large deformations should be taken into account, the discrete element formulation is predestined. Note that a refinement of the modeling from macroscopic to microscopic always involves an increase of computational effort. In the following the different formulations will be presented in detail.

Statistical Theory

In the 1950s, Flory and Rehner[2] were the first who formulated the theory of ''swelling of network structures''. Here, the change of ambient conditions can be represented by a change of the Gibbs free energy ΔF. The total free energy has different contributive terms:

- Free energy of mixing ΔF_M
- Free energy of elastic deformation ΔF_{el}
- Free energy of ion concentration differences ΔF_{ion} (see e.g. Ricka and Tanaka,[3] Schröder et al.,[4] etc.)

The equilibrium state is characterized by a minimum of the total free energy, i.e., the chemical potentials $\Delta\mu_1$ of the solvent in both phases – gel and solution – are identical.

$$\begin{aligned}\Delta\mu_1 &= \left(\frac{\partial \Delta F_M}{\partial n_1}\right)_{p,T} + \left(\frac{\partial \Delta F_{el}}{\partial n_1}\right)_{p,T} \\ &\quad + \left(\frac{\partial \Delta F_{ion}}{\partial n_1}\right)_{p,T} \\ &= \underbrace{\Delta\mu_{1,M}}_{\textit{mixture potential}} + \underbrace{\Delta\mu_{1,el}}_{\textit{elastic potential}} \\ &\quad + \underbrace{\Delta\mu_{1,M}}_{\textit{mobile ion potential}} = 0\end{aligned} \qquad (1)$$

In the unswollen state, solvent and polymer matrix are completely separated. In the swollen state, both polymer and

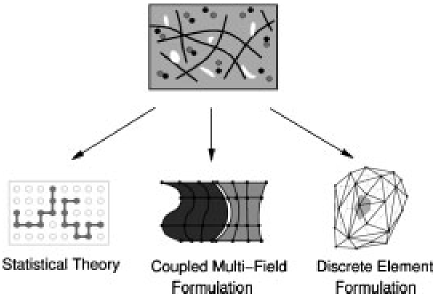


Figure 2.
Modeling of polymer gels on different scales.

solvent are in the gel part. The mixture potential $\Delta\mu_{1,M}$ reads

$$\Delta\mu_{1,M} = RT\left(\ln(1-\phi_p) + \phi_p + \chi\phi_p^2\right) \qquad (2)$$

where ϕ_p is the volume fraction of polymer in the gel, and χ is the Flory-Huggins gel-solution interaction parameter. The total swelling ratio q is given by the product of the initial swelling q_0 and the relative swelling q_r

$$q = q_0 \quad q_r = \phi_p^{-1} \qquad (3)$$

The elastic potential can be formulated in different ways, see e.g. Flory and Rehner,[2] Treloar.[5] The mobile ion potential, depending on the concentration differences in both phases may be given as

$$\Delta\mu_{1,ion} = -RT\nu_1 \sum_{\alpha=1}^{N_f} \left(c_\alpha^{(g)} - c_\alpha^{(s)}\right) \qquad (4)$$

where $c_\alpha^{(g)}$ are the concentration in gel (g) and solution (s), respectively and N_b and N_f are the numbers of bound and mobile (free) species; ν_1 is the molar volume of the solvent. Additionally, the ion distribution in both domains must meet the neutrality condition

$$\sum_{\alpha=1}^{N_f+N_b} (z_\alpha c_\alpha) = 0 \qquad (5)$$

In order to model also dissociation effects, the concentrations of the bound groups and mobile ions are variable in space and time. To incorporate the hysteretic behavior, refer to Günther et al.[6]

The relationship between concentrations c_α and electric potential Ψ is given by the Donnan equation

$$\frac{c_\alpha^{(g)}}{c_\alpha^{(s)}} = \exp\left(-z_\alpha \frac{F}{RT}\left(\Psi^{(g)} - \Psi^{(s)}\right)\right) \qquad (6)$$

where F is the Faraday constant, R the universal gas constant, T the temperature and z_α the valence of the ions. By eliminating the electric potential the relationship between different concentrations is obtained:

$$\left[\frac{c_\alpha^{(g)}}{c_\alpha^{(s)}}\right]^{-\frac{1}{z_\alpha}} = \left[\frac{c_\beta^{(g)}}{c_\beta^{(s)}}\right]^{-\frac{1}{z_\beta}} \qquad (7)$$

Finally the total swelling ratio is obtained by using Equation (1) combined with Equation (2)–(7).

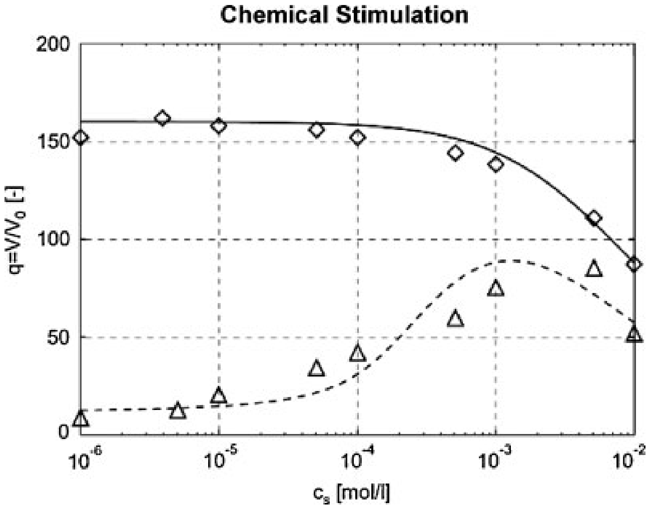


Figure 3.
Stationary swelling ratio $q = V/V_0$ of PAAm/PNa$^+$A$^-$ gel ($\diamond$) and of PAAm/PAA gel (Δ) as a function of the salt concentration c_s in the solution. The symbols represent measured values. The solid line shows the calculated values for completely dissociated fixed charges. The dashed line shows the curve for weak fixed charge groups (variable dissociation).

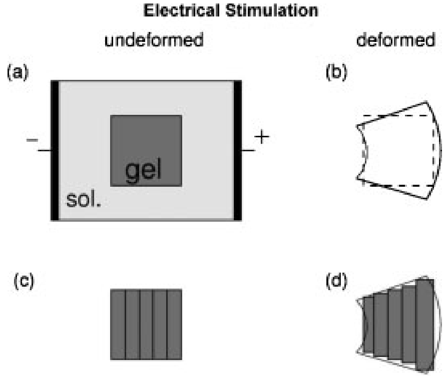


Figure 4.
Polymer gel in a solution bath with applied electric field. (a): In undeformed state, (b): in deformed state. (c): Subdivision of gel film in various parts for application of local statistical theory. (d): Gel film parts with locally different swelling ratios.

This method only works for chemical stimulation where the ion concentrations for each species α is independent of the position in space (Figure 3).

If an electric field is applied, the concentrations are dependent on the local position in the gel. In this case, the gel has to be subdivided into various small parts to realize different actual concentrations, see Figure 4(c). By measuring the difference of the electric potential at variable positions in the gel by a microelectrode technique,[1] the concentrations required for the mobile ion potential can be determined by Equation (6). Finally, locally different swelling ratios are obtained by using Equation (1), see Figure 4(d).

Coupled Multi-Field Formulation

The mesoscopic coupled chemo-electro-mechanical formulation has been developed to gain a more precise insight into the phenomena occurring in polyelectrolyte gels - i.e. ion movement, development of an inner electric field, etc.[7,8] The ion concentrations and the electric potential inside these materials can be computed by the chemical and the electrical field equation. Based on the osmotic pressure - resulting from the concentration differences - the swelling/bending of the polymer gel film may be obtained.

Chemical Field

The chemical field is described by the convection-diffusion equation for all the species α

$$\dot{c}_\alpha = \left[D_\alpha c_{\alpha,i} + z_\alpha c_\alpha \mu_\alpha \Psi_{,i}\right]_{,i} \tag{8}$$

where c_α is the concentration of the species α, D_α the diffusion constant, $\mu_\alpha = \frac{F}{RT} D_\alpha$ the unsigned mobility, and Ψ is the electric potential. i denotes the spatial direction x_i and the subscript, i the spatial derivative $\partial/\partial x_i$. Note that in Equation (8), the terms stemming from the chemical conversion have been neglected.

Electrical Field

The electrical field is described by the Poisson equation

$$\Psi_{,ii} = -\frac{F}{\varepsilon_r \varepsilon_0} \sum_{\alpha}^{N_f+N_b} (z_\alpha c_\alpha) \tag{9}$$

where ε_0 is the permittivity of free space, ε_r the dielectric constant of the material, and F the Faraday constant. Note that the whole domain (gel and solution) is solved together and thus no additional conditions prescribing the jump (e.g. obtained by the Donnan Equation (6)) of the electric potential have to be given. In the regions outside the boundary layers, also the neutrality condition, Equation (5), is fulfilled.

Mechanical Field

The mechanical field is formulated by the momentum equation. Due to the relatively slow (swelling) process, the influence of the inertia term is very small and the second order in time contribution can therefore be neglected. The momentum equation reads

$$f\dot{u}_i = \sigma_{ij,j} + \rho b_i \tag{10}$$

where u_i is the displacement vector, σ_{ij} the stress tensor, C_{ijkl} the elasticity tensor, f the friction coefficient, b_i the body force vector and ρ the mass density. Equation (10) is coupled by the strain tensor ε_{ij} and the prescribed strain $\overline{\varepsilon}_{ij}$ via the elasticity tensor:

$$\begin{aligned} \sigma_{ij} &= C_{ijkl}(\varepsilon_{kl} - \overline{\varepsilon}_{ij}) \qquad \text{where} \\ \overline{\varepsilon}_{ij} &= d_{kl}\,\Delta\pi \\ &= d_{kl}\,RT\sum_{\alpha=1}^{N_f}(c_\alpha^{(g)} - c_\alpha^{(s)}) \end{aligned} \tag{11}$$

$\Delta\pi$ represents the osmotic pressure, and $c_\alpha^{(g)/(s)}$ are the concentrations in the gel and in the solution, respectively.

To simulate the chemo-electro-mechanical multi-field, there are two different strategies:

1. For gel and solution the chemo-electrical field is solved simultaneously while the mechanical field is solved for the gel only while the surrounding solutions is not considered.
2. Gel and solution are modeled chemo-electro-mechanically, i.e. in the mechanical simulation, gel and solution are also solved together while they own different material properties.

In Figure 5, the chemo-electro-mechanical coupling scheme is shown. For one time step, all the involved fields are used in iteration loops until a converged solution is obtained. Then, the same procedure for the next time step will be applied.

Numerical Simulation with Coupled Multi-Field Formulation

In the numerical simulation, chemical as well as electrical stimulation has been considered. In Figure 6 (top), the stationary solution of the concentrations (left) as well as the electric potential (right) in gel and solution is depicted. The concentration of fixed anionic charges in the gel $c_{A^-} = c^g$ is $1M$; the concentration of the monovalent ions $(z = \pm 1)$ at the outside boundaries of the solution are set to $c_s = c^{-(s)} = c^{+(s)} = 1M$. For the electrical simulation, an electric potential of $+1$ V has been prescribed at the anode side of the solution. The steady-state results of the chemical stimulation, Figure 6 (top), have been set as initial conditions. The stationary solution of the electrical stimulation is depicted in Figure 6 (bottom).

Discrete-Element Formulation

The Discrete Element Method (DEM)[9] is an explicit dynamic numerical method for

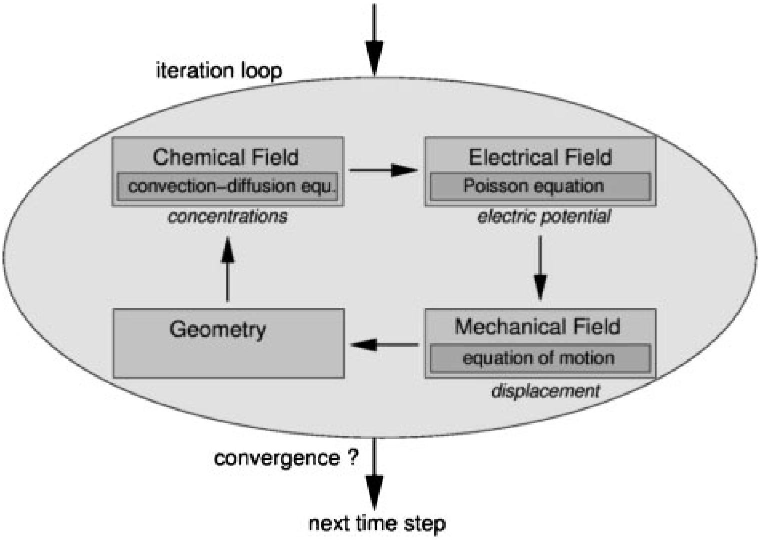
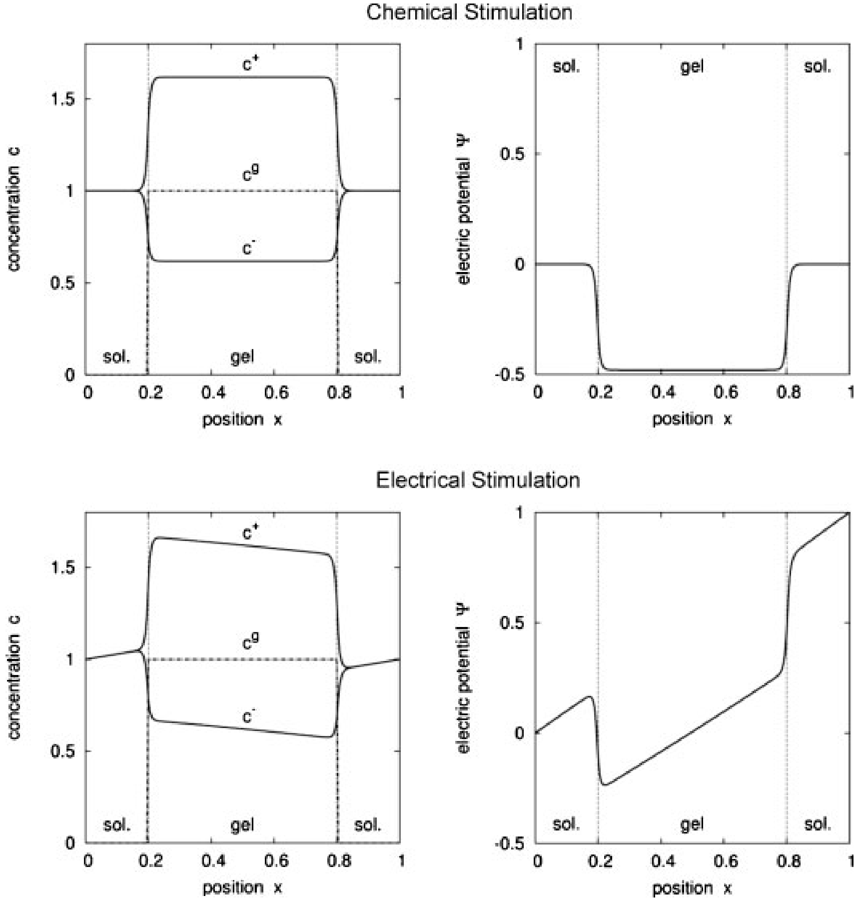


Figure 5.
Chemo-electro-mechanical coupling scheme.


Chemical Stimulation

Electrical Stimulation

Figure 6.
Stationary solution of the concentrations (left) and the electric potential (right) for chemical (top) as well as electrical stimulation (bottom).

the solution of interacting particle systems. In the most general case, a material is described by discrete point masses m_i and a set of interactions between them. The state of the system is described by the Newton's equations for central forces and moments for each particle i:

$$m_i \ddot{\boldsymbol{x}}_i = \sum_j \boldsymbol{F}_{ij}, \tag{12}$$

$$\Theta_i \ddot{\boldsymbol{\omega}}_i = \sum_j \boldsymbol{M}_{ij}. \tag{13}$$

The forces $\boldsymbol{F}_{ij}$ and the moments $\boldsymbol{M}_{ij}$ stem from the interactions of i with its neighboring particles j. The state vectors of the positions $\boldsymbol{x}_\mathrm{i}$ and rotations $\boldsymbol{\omega}_\mathrm{i}$ are obtained by an explicit numerical integration technique.

Through an appropriate choice of interactions, various types of problems can be addressed. For example the interactions could be simple spring and damper elements, which lead to a central force network. To obtain particles which occupy a certain area or volume in space, contact laws could be defined between the nodes. Any general non-linear interaction could be considered in the system. The meshless approach of the DEM allows to model problems including large deformations with geometrical and physical non-linearities, large displacements even with free motion and localisation phenomena like damage

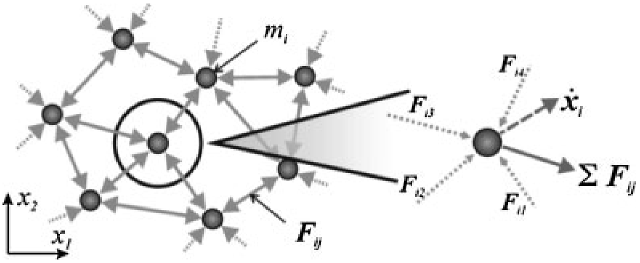


Figure 7.
Material representation as point masses and interactions in the frame of the Discrete Element Method.

and fracture (Figure 7) Through the direct control over the applied interactions the local state of the system is always accessible in a simulation.

In the DE simulation, the gel only is investigated. The boundary conditions, i.e. the gel-solution boundary, are computed at each time step by solving the Donnan Equation (7) together with the neutrality condition Equation (5). The concentration change in the gel creates a variation of the differential osmotic pressure $\Delta\pi$ and thus a change of the swelling ratio, resulting in a modification of the gel geometry.[10] Due to the number of moles of bound charges n_A in the gel remaining constant, the concentration of fixed charges c_A is dependent on the actual volume V

$$c_A = c_{A,0}\frac{V_0}{V} \tag{14}$$

where the index 0 represents the unknowns in reference state.

In Figure 8, the anionic (top) and the cationic (right) concentration for different times ($t = 0$, $t > 0$ and $t \to \infty$) is depicted. The figures represent the change of the mobile concentrations in the gel ($c_{A,0} = 2\text{M}$) while at $t = 0$ the concentration in the solution has been decreased from 2M to 1M. The resulting change of the geometry due to the concentration change is depicted in Figure 9.

Conclusion

In this paper, an overview over different formulations for the modeling of the swelling behavior of polyelectrolyte gels has been presented. If the global macro-

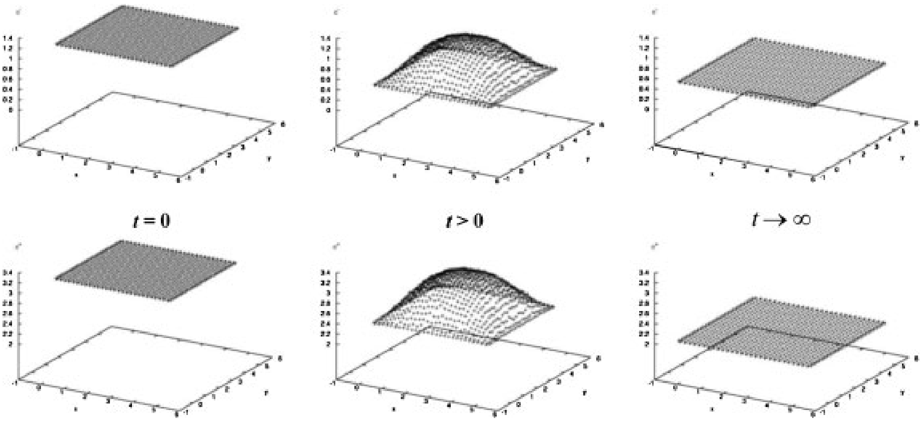


Figure 8.
Anionic c^- (top) and cationic c^+ (bottom) concentrations in the gel at different times.

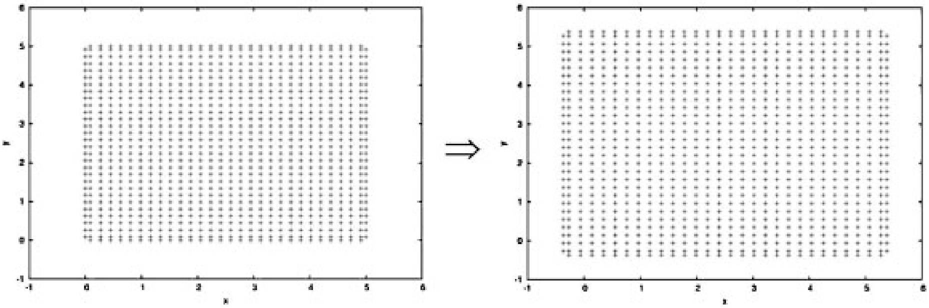


Figure 9.
Gel deformation: Initial gel configuration (left), stationary configuration (right).

scopic, mechanical response is the only property of interest, the use of the simple statistical theory leads to sufficient results for chemical stimulation. To consider the electrical stimulation, also experimental measurements for the electric potential have to be taken into account to obtain locally different swelling ratios. To give a more precise insight into the phenomena occurring in polyelectrolyte gels, such as ion movement, electric potential, etc., the coupled chemo-electro-mechanical multi field formulation is appropriate. This mesoscopic formulation is capable to capture the whole gel and solution domain for chemical, thermal and electrical stimulation without prescribing any jumps of concentration or electric potential (Donnan equilibrium) at the interface. The discrete element approach is a microscopic approach. In its present form, it is also predestined for chemical stimulation. Like the statistical theory, also the gel only has to be considered while prescribing the Donnan equilibrium at the gel boundary. Advantages of the discrete element representation are e.g. the direct physical access to the system during all the time steps of the simulation, and the possibility to describe large deformations and strains.

[1] R. W. Gülch, J. Holdenried, A. Weible, T. Wallmersperger, B. Kröplin, "*SPIE Proceedings of Smart Structures and Materials 2000: EAPAD*", Y. Bar Cohen, Ed., **2000**, 3987, pp. 193–202.
[2] P.J. Flory, J. Rehner, Jr., *J. Chem. Phys.* **1943**, *11*, pp. 521–526.
[3] J. Rička, T. Tanaka, *Macromolecules* **1984**, *17*, pp. 2917–2921.
[4] U. P. Schröder, "*Physical Properties of Polymeric Gels*", J. P. Cohen Addad, Ed., John Wiley and Sons, **1996**, pp. 19–38.
[5] L. R. G. Treloar, Oxford University Press, **1958**.
[6] M. Günther, G. Gerlach, T. Wallmersperger, "*SPIE Proceedings of Smart Structures and Materials" 2007*: EAPAD, Y. Bar Cohen, Ed., **2007**.
[7] T. Wallmersperger, B. Kröplin, R. W. Gülch, *Mechanics of Materials* **2004**, *36*, 5–6, pp. 411–420.
[8] T. Wallmersperger, B. Kröplin, J. Holdenried, R. W. Gülch, *SPIE Proceedings of Smart Structures and Materials 2007*: EAPAD, Y. Bar Cohen, Ed., **2001**, 4329, 2001.
[9] B. Bicanic, Wiley and Sons. E. , Stein, R. , deBorst, T. J. R. Hughes, Eds., **2004**, 311–337
[10] T. Wallmersperger, F. Wittel, B. Kröplin, "*SPIE Proceedings of Smart Structures and Materials 2006: EAPAD*", Y. BarCohen, Ed., **2006**, 6168, 61681H.