**Dieses Dokument ist eine Zweitveröffentlichung (Verlagsversion) /
This is a self-archiving document (published version):**

Adrian Ehrenhofer, Thomas Wallmersperger

Hydrogels for engineering: normalization of swelling due to arbitrary stimulus

Erstveröffentlichung in / First published in:

SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring.
Portland, 2017. Bellingham: SPIE, Vol. 10163 [Zugriff am: 02.05.2019].

DOI: <https://doi.org/10.1117/12.2259872>

Diese Version ist verfügbar / This version is available on:

<https://nbn-resolving.org/urn:nbn:de:bsz:14-qucosa2-348901>

„Dieser Beitrag ist mit Zustimmung des Rechteinhabers aufgrund einer (DFGgeförderten) Allianz- bzw. Nationallizenz frei zugänglich.“

This publication is openly accessible with the permission of the copyright owner. The permission is granted within a nationwide license, supported by the German Research Foundation (abbr. in German DFG).

www.nationallizenzen.de/

PROCEEDINGS OF SPIE

[SPIDigitalLibrary.org/conference-proceedings-of-spie](https://spiedigitallibrary.org/conference-proceedings-of-spie)

Hydrogels for engineering: normalization of swelling due to arbitrary stimulus

Adrian Ehrenhofer, Thomas Wallmersperger

Adrian Ehrenhofer, Thomas Wallmersperger, "Hydrogels for engineering: normalization of swelling due to arbitrary stimulus," Proc. SPIE 10163, Electroactive Polymer Actuators and Devices (EAPAD) 2017, 1016321 (17 April 2017); doi: 10.1117/12.2259872

SPIE.

Event: SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring, 2017, Portland, Oregon, United States

Hydrogels for Engineering: Normalization of Swelling due to Arbitrary Stimulus

Adrian Ehrenhofer^a and Thomas Wallmersperger^a

^aInstitut für Festkörpermechanik, Technische Universität Dresden, 01062 Dresden

ABSTRACT

In engineering, materials are chosen from databases: Engineers orient on specific parameters such as Young's modulus, yield stress or thermal expansion coefficients for a desired application. For hydrogels, the choice of materials is rather tedious since no generalized material parameters are currently available to quantify the swelling behavior. The normalization of swelling, which we present in the current work, allows an easy comparison of different hydrogel materials. Thus, for a specific application like a sensor or an actuator, an adequate material can be chosen.

In the current work, we present the process of normalization and provide a course of action for the data analysis. Special challenges for hydrogels like hysteresis, conditional multi-sensitivity and anisotropic swelling are addressed. Then, the Temperature Expansion Model is shortly described and applied. Using the derived normalized swelling curves, a nonlinear expansion coefficient $\beta(F)$ is derived. The derived material behavior is used in an analytical model to predict the bending behavior of a beam made of thermo-responsive hydrogel material under an anisotropic temperature load. A bending behavior of the beam can be observed and the impact of other geometry and material parameters can be investigated.

To overcome the limitations of the one-dimensional beam theory, the material behavior and geometry can be implemented in Finite Element analysis tools. Thus, novel applications for hydrogels in various fields can be envisioned, designed and tested. This can lead to a wider use of smart materials in sensor or actuator devices even by engineers without chemical background.

Keywords: Simulation, Modeling, Hydrogels, Generalized Approach, Beam Bending, Finite Element Method

1. INTRODUCTION

When engineers choose materials for a specific application, they mostly use a material from a databases or from their own or corporate experience. Up to now, smart materials are not widely in use and not many material databases were yet compiled. This is due to the unknown capabilities and the known problems like missing long-term stability or vulnerability of the materials.^{1,2} The scientific community is on the way to overcome these problems in various ways.

In the current work, we provide a capability measure for hydrogels that can also be transferred to other smart materials. It is motivated on the basis of continuum mechanics and standard material testing procedures from mechanical engineering. The tensile test and the derived measure for linear elasticity – the Young's modulus – are the starting point of the definition.

The challenge for hydrogels is that even though swelling curves for different hydrogels are very similarly shaped, a simple parameter like the Young's modulus is not sufficient for the description of the behavior.³ This is due to the fact that the quasi-linear region is small in comparison to the linear-elastic region of the tensile

Further author information:

Adrian Ehrenhofer: E-mail: Adrian.Ehrenhofer@tu-dresden.de

Thomas Wallmersperger: E-mail: Thomas.Wallmersperger@tu-dresden.de

(a) Tensile test for a simple material. Young's modulus can be derived in the linear-elastic region, i.e. for stress $\sigma < \sigma_{\text{yield}}$.

(b) Swelling curve for a hydrogel. Using the ordinate for the stimulus is rather unusual but serves a better comparison to the simple material.

Figure 1. Comparison of the basic concept of Young's modulus for simple materials and the sensitivity measure for smart materials. These are the most basic approaches using the technical strain ε in both cases. More complex models based on continuum mechanics use the definition for large deformation gradients, e.g. the Hencky strain ε^H . They are then also valid for finite deformations.

test curve, see figure 1. However, for small stimulus changes the sensitivity measure can still provide information about the capabilities of the material.

In our previous work,⁴ we derived a sensitivity measure and showed that it is applicable for swelling due to different stimuli. This includes temperature,^{5,6} pH,^{7,8} ion concentration⁹ and light responsiveness.¹⁰ In this work, we also described the underlying swelling mechanisms for the used hydrogels.

In the current work, we provide additional background to the normalized description, see section 2. We show how it can be implemented in the framework of engineering design to facilitate the smart material choice for engineers without requiring chemical background knowledge. The Temperature Expansion Model allows this implementation into commercial Finite Element simulation tools. In section 3, the application of the model in a beam-model is depicted analytically using Euler-Bernoulli beam theory. Parametric studies of material parameters give an insight into their importance for this special application. In section 4, the conclusion and outlook for normalization and the Temperature Expansion Model are presented.

2. MATERIALS AND NORMALIZED SWELLING CURVES

In the current section, the normalization procedure from our previous work⁴ is revisited, see section 2.1. For the example of thermo-responsive poly(N-isopropylacrylamide) (PNiPAAm) gels, an analytical sigmoid sample function is described and implemented into the Temperature Expansion Model, see section 2.2. Then, special characteristics for hydrogels that pose challenges, are described in section 2.3. The capabilities of the presented approach and model are demonstrated in the following section 3 for the example of anisotropic swelling in a gradient field.

2.1 Approach on data analysis

The approach to new swelling data, in order to normalize it and to derive the sensitivity parameter, consists of several steps. The schematic of this approach is depicted in figure 2. The single steps therein are further described here.

Figure 2. Workflow for the data analysis. To gain the sensitivity of the hydrogel to a chosen stimulus, the swelling behavior for this stimulus has to be regarded separately.

2.1.1 Data extraction

When literature data, instead of own experiments, is used to identify the normalized behavior, the data has to be extracted from the respective publications. Unfortunately, only few authors give supplementary machine-readable data of the physical swelling curves for further processing. Thus, a digitizer-tool must be used to obtain the data in a processable form. In the current work, we use the Engauge Digitizer¹¹ to extract the physical swelling data points from the publications. Swelling data can be volumes/volume-swelling degrees or masses/mass-swelling degrees versus a stimulus measure. As described in our previous work,⁴ they can be translated into each other under certain assumptions.

2.1.2 Curve fitting

Normally, only few data points are given by experimenters due to the tedious measurement process. For hydrogels, the number of achievable data points is also limited since the swelling is usually very slow.^{12,13} When the swelling mechanism is known, the shape of the stimulus-swelling-curve can be predicted. It can be e.g. a classical sigmoid-shaped *phase transition* behavior (e.g. for thermo-responsiveness⁸) or equilibrating behavior (e.g. bio-responsivity^{9,14}). The adequate fitting function for the behavior can be found through different fitting mechanisms, e.g. least square fit.

Figure 3. Original swelling data from our previous work⁵ with different fitting functions: Piecewise cubic Hermite interpolation splines (PCHIP), sigmoid function based on the error function and a sigmoid based on the tanh() function.

Sigmoid based on the error function	Sigmoid based on the hyperbolic tangent function
$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (1a)$	$\tanh(x) = \frac{e^{2x} - 1}{e^{2x} + 1} \quad (2a)$
$d^{\text{sig,erf}}(S) = a_1 \text{erf}(b_1 (S + c_1)) + d_1 \quad (1b)$	$d^{\text{sig,tanh}}(S) = a_2 \tanh(b_2 (S + c_2)) + d_2 \quad (2b)$
$\varepsilon^{\text{H,sig,erf}}(F) = \bar{a}_1 \text{erf}(\bar{b}_1 (F - 1)) \quad (1c)$	$\varepsilon^{\text{H,sig,tanh}}(F) = \bar{a}_2 \tanh(\bar{b}_2 (F - 1)) \quad (2c)$

Table 1. Two possible definitions for global sigmoid functions. At first, the general definition of the shape function is shown. Then, the sigmoid functions that can be derived from them in physical form – using diameters d and stimulus S – are described. In normalized form, Hencky strain ε^{H} and stimulus ratio F are used.

In the current work, we use piece-wise cubic Hermite interpolation polynomials (PCHIP) to fit the swelling curves. In contrast to a global sigmoid function like the error function $\text{erf}()$ or hyperbolic tangent function $\tanh()$, the PCHIP curves' global shapes follow from the fitting. Therefore, this approach can be more universally applied. Additionally, the other two possibilities are depicted in table 1 since they can be used for analytical derivations. In figure 3, the two types are juxtaposed with the original data points from our previous work⁵ and the PCHIP fitting.

Please note that the fitting of the data points can be performed before or after the normalization procedure. For the sigmoid based on the error function, four parameters describe the deswelling of the hydrogel and subsequently decreasing diameter of a structure in equation 1b. The parametric study is performed for $\bar{a}_1$ and $\bar{b}_1$ since the information of the four parameters can be condensed into two parameters in equation (1c).

Figure 4. Study of the impact of the factors $\bar{a}_1$ and $\bar{b}_1$ for the example of the error function, see equation (1a). The changing sensitivity is further explained in equation (5).

For the analytical sigmoid based on the error function, a parametric study for $\bar{a}_1$ and $\bar{b}_1$ and their impact to the strain versus stimulus ratio curve is depicted in figure 4. Here, it can be seen that a change of the first parameter $\bar{a}_1$ leads to a stretching of the curve in strain direction. A change of the second parameter $\bar{b}_1$ affects the steepness as well as the curvature. The derivations have also shown, that both parameters can be used to flip the curves around the x -axis to get an ascending swelling behavior as it is observed e.g. for hydrogels with upper critical solution temperature (UCST) behavior.

2.1.3 Reference state identification

The reference point, which is needed for the derivation of the generalized measures, is arbitrary. It can be chosen e.g. as the inflexion point of a sigmoid-like swelling curve or a 50%-value of an equilibrating behavior.⁴ If it is chosen as the inflexion point, it yields the sensitivity parameter of the material.

However, in mechanical interaction, the stress-free reference state has to be taken as the starting point. It is demarked by the environmental conditions of the synthesis. Only this reference state yields a correct deformation behavior in superposition with mechanical strains. This can be understood in a way that from different synthesis conditions, the starting point of a numerical experiment has to be reached before subsequent steps can be taken.

In section 3, three reference cases are described. They serve to compare the special behavior of a PNIPAAm structure when synthesized at different temperatures.

2.1.4 Derivation of Hencky strain and stimulus ratio

With the identified physical conditions of the reference state and the respective swelling diameter, the normalized measures can be derived. They are (i) the stimulus ratio

$$F = \frac{S}{S_{\text{ref}}}, \quad (3)$$

where S denotes an arbitrary stimulus, S_{ref} its reference value, and (ii) the Hencky strain

$$\varepsilon^{\text{H}} = \ln \frac{d}{d_{\text{ref}}} \quad (4)$$

with the quotient of the actual diameter d and the diameter in reference state d_{ref} .

The choice of another reference state in the same stimulus-swelling-curve leads to different Hencky strain vs. stimulus ratio curves. From equation (3), it can be seen that a changing reference stimulus leads to a rescaling of the stimulus ratio function with the factor $1/S_{\text{ref}}$. A changing reference state however only leads to a shifting of the axis intercept with the negative factor $\ln d_{\text{ref}}$, as can be derived from equation (4). A special case of this influence is presented in section 2.3.5 when different temperature scales are used.

For the sigmoid functions described in table 1, the change of reference state leads to different function parameters $\bar{a}_1$ and $\bar{b}_1$ in equation (1c) or $\bar{a}_2$ and $\bar{b}_2$ in equation (2c), respectively.

2.1.5 Derivation of the sensitivity parameter

The sensitivity parameter is found at the reference point. It is in fact the slope of the linearized $\varepsilon^{\text{H}} - F$ -curve in its normalized form. It can be used to identify and assess the capabilities of a material. Different hydrogels from literature are investigated and their sensitivity is derived in our previous work.⁴ For the sigmoid curves (1a) and (2a), the sensitivity parameter can be derived analytically as

$$\text{Sensitivity}^{\text{erf}} = \frac{2 \bar{a}_1 \bar{b}_1}{\sqrt{\pi}} \quad (5) \quad \left| \quad \text{Sensitivity}^{\text{tanh}} = \bar{a}_2 \bar{b}_2. \quad (6)$$

The analytical solution for equation (5) is depicted in figure 5. The cutting curve between the sensitivity plane for $\text{Sensitivity} = -7.8$ which corresponds to the experimental data for PNIPAAm, is depicted. For data points on this curve, the combination of $\bar{a}_1$ and $\bar{b}_1$ yields the adequate sensitivity, whereas curvature and swelling range can be varied.

Figure 5. Impact of the factors $\bar{a}_1$ and $\bar{b}_1$ in the sigmoid based on the error function. The point P denotes the fitting data for the experimental swelling curve of PNIPAAm. The depicted curve is the cutting line between the surface and the plane with Sensitivity = -7.8.

2.2 Temperature Expansion Model for finite deformation

In our previous work,^{5,15,16} we used a linear model of isotropic volume change to describe the swelling of a poly(N-isopropylacrylamide) hydrogel specimen. The very simplistic model aimed to allow an easy implementation into Finite Element tools and the simulation of arbitrary structures. The derived model was named Temperature Expansion Model since it is based on the similarity between the isotropic swelling behavior and thermal expansion.

The material parameters were gained from a free swelling experiment. The comparison of experiments and numerical simulations with this model in clamped configuration have shown good results even though linear kinematics were considered. However, especially in superposition with mechanical stresses, effects of large deformation gradients have to be considered. Therefore, in the current work, we expand the Temperature Expansion Model to finite deformations, since hydrogel swelling generally leads to large displacement gradients. Using normalized swelling behavior instead of physical values, arbitrary stimuli can be implemented within this framework.

Thermal expansion is generally implemented in commercial Finite Element tools as thermal expansion strain $\varepsilon^{\text{therm}} = \alpha \Delta\vartheta$. Here, α denotes the thermal expansion coefficient and $\Delta\vartheta$ the temperature difference to a given reference state.

A similar approach can also be found in the formulation of osmotic pressure as $\varepsilon^{\text{osm}} = \Gamma \Delta\Pi$.¹⁷ In contrast to hydrogel models from Cai et al.¹⁸ or Mazaheri et al.,¹⁹ the Temperature Expansion Model does not consider the actual swelling related processes that occur inside the gel. It can therefore be classified as a purely macroscopic/phenomenological model. The parameters can be derived from the micro-scale using concepts of model scale transition or from experimental data.

2.2.1 Nonlinear expansion coefficient derivation

The expansion coefficient α is generally defined using the technical strain ε as a reference. This is valid since for common materials, only very small thermal deformations can be observed. For example, $\alpha_{\text{Steel}} \approx 10 \cdot 10^{-6}/\text{K}$ with a very high temperature change from melting point to room temperature $\Delta\vartheta \approx 1500 \text{ K}$ leads only to a very small strain $\varepsilon = 1.5 \cdot 10^{-2}$. For the Temperature Expansion Model, very large strains $\varepsilon^{\text{H}} \approx 2$ for small stimulus changes $\Delta F < 1$ are expected. Therefore, nonlinear material behavior has to be incorporated. The nonlinear expansion coefficient β is used in the Temperature Expansion Model to describe the strain for the according difference stimulus

$$\varepsilon^{\text{H}}(F) = \beta(F) (F - 1). \quad (7)$$

Please note that the reference stimulus ratio is always 1 due to the normalization of the stimulus and the reference point. Therefore, $\beta(F)$ is not defined at the reference point due to division by zero.

However, this value is of special interest because the sensitivity parameter (section 2.1.5) is defined as the slope of the normalized curve at the reference point. It can be derived by limit considerations for the sigmoid based on the $\tanh()$ function defined in equation (2a)

$$\beta(F = 1) = \text{Sensitivity} = \lim_{F \rightarrow 1} \frac{\varepsilon^H}{F - 1} = \lim_{F \rightarrow 1} \frac{\bar{a}_2 \tanh(\bar{b}_2 (F - 1))}{F - 1}. \quad (8)$$

For $F = 1$, this is a 0/0 division which can be solved using l'Hôpital's rule, i.e. differentiating both numerator and denominator under consideration of the chain rule

$$\beta(F = 1) = \lim_{F \rightarrow 1} \frac{\bar{a}_2 \bar{b}_2 (1 - \tanh^2(\bar{b}_2 (F - 1)))}{1} = \bar{a}_2 \bar{b}_2. \quad (9)$$

Similar considerations for the error function lead to $\beta(F = 1) = 2\pi^{-0.5} \bar{a}_1 \bar{b}_1$ since the derivative of the error function (1a) is $2\pi^{-0.5} \exp(-x^2)$. We can therefore directly identify the sensitivity from the respective parameter and add it to the undefined point in $\beta(F)$ at the inflexion point $F = 1$.

Figure 6. Variation of the factors $\bar{a}_1$ and $\bar{b}_1$ and their impact on the derived β -coefficient for the Temperature Expansion Model, compare with figure 3. For the chosen inflexion point as a reference, the maximum of the $\beta(F)$ curve is the sensitivity depicted in figure 5. Here, $\beta = \beta^{\text{erf}}$ is considered using the parameters from equation (1c).

In figure 6, the parameter study on the analytical sigmoid function is continued. It can be observed that both the change of $\bar{a}_1$ and $\bar{b}_1$ lead to a shifted minimum and therefore changed sensitivity.

For changing reference state, i.e. when another point on the physical swelling-stimulus-curve is used as reference point (see section 2.1.3), other $\beta(F)$ curves follow. In these cases, the absolute maximum/minimum of the coefficient is no longer the sensitivity. In figure 7, the PNIPAAm material behavior with three different reference points is depicted.

2.2.2 Application of the Temperature Expansion Model

The Temperature Expansion Model is applied in a way, that the Finite Element Model is constructed in the reference state according to the geometry. For a state change, the respective stimulus ratio $F = \vartheta/\vartheta_{\text{ref}}$ for the end state is calculated by using equation (3). Then, the $\beta(F)$ curve (equation (7)) is used to gain the nonlinear thermal expansion coefficient. Please note that the curve derived for the used reference state is needed.

Figure 7. For different reference states $\vartheta_{\text{ref}}^{\text{I}} = 32^\circ\text{C}$, $\vartheta_{\text{ref}}^{\text{II}} = 28^\circ\text{C}$ and $\vartheta_{\text{ref}}^{\text{III}} = 36^\circ\text{C}$, different β curves can be found. This is due to different stimulus ratio definitions with $F = \vartheta/\vartheta_{\text{ref}}$. The sensitivity is the minimum of $\beta(F)$ only if the reference state is the inflexion point of the original curve.

In figure 8, three different temperature states are depicted. For every change in temperature from starting temperature $\vartheta^{\text{start}} = \vartheta^{\text{ref}}$ to ending temperature ϑ^{end} , the adequate $F = \vartheta^{\text{end}}/\vartheta^{\text{start}}$ is multiplied by the respective $\beta(F^{\text{end}})$. It can be seen that the model works in every direction and consecutively, i.e. the change $28^\circ\text{C} \rightarrow 32^\circ\text{C}$ followed up by $32^\circ\text{C} \rightarrow 36^\circ\text{C}$ yields the same result as $28^\circ\text{C} \rightarrow 36^\circ\text{C}$.

Figure 8. Depiction of the change in state and following temperature-dependent diameter of a sphere. Here, six state changes are depicted with their respective coefficients $\beta^{28}, \beta^{32}, \beta^{36}$ from figure 7. With a chosen reference state, the respective initial diameter d and expansion coefficient $\beta(F_{\text{start} \rightarrow \text{end}})$ with adequate $F_{\text{start} \rightarrow \text{end}} = \vartheta_{\text{end}}/\vartheta_{\text{start}}$ is used.

2.3 Challenging characteristics of hydrogels

The swelling mechanisms of hydrogels lead to unique challenges for these materials. At first, single sensitive hydrogels and occurring specialties are described. These are hysteresis behaviors and anisotropy. Afterwards, the handling of multisensitivity and conditional switchability is described. Then, differences in stimulus axis scaling are discussed.

2.3.1 Swelling hysteresis

In some hydrogel materials, an equilibrium hysteresis behavior can be found.^{20,21} Please note that especially in older publications, a hysteresis that is graphically depicted could also be caused by non-equilibrium measurements. This means that the experimenters underestimated the time for the hydrogel to reach the equilibrium state, which can take days, depending on the swelling mechanism and the physical dimensions of the hydrogel sample. Hysteresis due to transient swelling processes is part of our future work.

In our current work,⁴ we concentrate on hydrogels that show equilibrium hysteresis due to physical effects, e.g. as published by Arndt et al.⁷ Then, the normalization is only applicable in one direction, i.e. in swelling or deswelling direction. By inverting the x -axis of the swelling curve, the other direction can be normalized. In the current case, this is done by taking the pOH-value instead of the pH-value. The Temperature Expansion Model can still be used to simulate the swelling between two given states. However, please note that the swelling simulations cannot easily be inverted since different initial states – depending on the material's load history – are needed.

2.3.2 Anisotropic swelling

Isotropic swelling is normally produced by isotropic stimulus input. An exception lies here at the indirect light responsiveness, i.e. when the heating effect of light is used.¹⁰ Generally, the electro-magnetic field is anisotropic, but in this special case, it is used only for its heating effect. Since heating and the following heat transfer through conduction is isotropic, the swelling is also perceived as isotropic.

However, anisotropic swelling can also be achieved with isotropic stimuli like temperature or ion concentration. Therefore, gradients in the stimulus over the hydrogel region are used and anisotropic swelling is observed. Using the Temperature Expansion Model (section 2.2), this can be simulated with a gradient in temperature throughout a hydrogel bar. An adequate example for this behavior is presented in section 3.

2.3.3 Handling of multisensitivity

Hydrogels mostly perform swelling under multiple stimuli. However, when one stimulus is dominating the behavior by several orders of magnitude, the material is mostly used in a monosensitive setup. Please note that in literature, the names for multisensitive behaviors are used inconsistently between Greek, Latin and English numeral prefixes, see table 2.

Number of sensitivities	Latin	Greek	Others
1	simsensitive	monosensitive	single sensitive
2	bisensitive	disensitive	dual sensitive
3	tersensitive	trisensitive	triple sensitive
4	quatersensitive	tetrasensitive	quadsensitive

Table 2. Denotation of the type of hydrogel with different prefixes.

When a material is synthesized especially to perform multisensitive swelling, the different kinds of behavior are of comparable size. Kim et al.⁹ provide an example swelling behavior of bisensitive hydrogel copolymers. The used material is made by copolymerization of acrylamide (AAm) with phenylboronic acid (PBA). Due to binding reactions, PBA is responsible for the swelling response to sugar molecules. These can be glucose, fructose and other sugars. For the second sensitivity, glucose or fructose concentrations between 0 and 20 mM were added by the authors.

The equilibrium swelling curves for the bisensitive hydrogel systems fructose-pH (figure 9(a)) and glucose-pH (figure 9(b)) can also be used for a monosensitive sensor or actuator setup by fixing the other value. For example,

the five curves⁹ giving the swelling degree over pH-value at constant fructose or glucose concentrations can be evaluated for constant pH and varying fructose concentration. After a two-dimensional surface fitting (see figure 9), the sensitivity of the hydrogel for pH at different glucose concentrations or e.g. the sensitivity for glucose at different pH can be evaluated.

Figure 9. Bisenstive swelling behavior of a poly(MPBA-co-AAm) hydrogel, data extracted from.⁹ The different swelling curves were fitted with a bilinear interpolant.

Multiresponsive hydrogels can be normalized as well. However, if one of the swelling directions is not sigmoid-shaped, the reference point cannot be found easily on the 2D surface. In the example, the swelling curve in pH-direction is sigmoid shaped while in sugar direction it is an equilibrating behavior. Using a 50% threshold for the sugar responsiveness and the inflexion point in the pH responsiveness, the reference points for both behaviors can be calculated.

2.3.4 Multisensitive conditional switchability

Another phenomenon occurring in multisensitive hydrogels is conditional switching, which is described e.g. by Tanaka et al.²² The multisensitive hydrogel described in this work shows a conditional switching behavior: For thermally swollen state, the PNiPAAm-co-sodium acrylate does not react on concentration stimulus. In their work, the authors describe this as an occurring diffusion barrier for $\vartheta < \vartheta^{LCST}$. Generally, materials showing such a complex behavior are complicated to handle in sensor or actuator setup. A much better use for this effect is e.g. in Chemical Information Processing.

2.3.5 Stimulus axis rescaling

Some swelling mechanisms like pH-responsiveness or ion concentration-dependent swelling show measurable volume changes only in a very large stimulus range. E.g. in the publication of Li et al.²³ the concentration for sodium ions has to change over several orders of magnitude for perceivable swelling. The choice of stimulus axis scaling has an impact on the derived normalized swelling and the sensitivity parameter. It is therefore important to provide fixed values for when to start with logarithmic scaling and when not, to make sensitivities comparable.

In the current work, we propose that the concentration has to change at least two orders of magnitude for maximum swelling, so that logarithmic stimulus axis scaling is appropriate. This is the case e.g. for all pH-responsive hydrogels.

For several used stimuli, it is possible to use different stimulus definitions, e.g. like Celsius scale $[\vartheta] = ^\circ\text{C}$ and absolute temperature $[T] = \text{K}$. While the first is generally more understandable in the context of engineering, it has the serious disadvantage of diverging stimulus ratio $F = \vartheta/\vartheta_{\text{ref}}$ at 0°C .

For comparison, the stimulus ratio in both scales is derived as

$$F^K = \frac{T}{T_{\text{ref}}} = \frac{\vartheta + 273.15 \text{ K}}{\vartheta_{\text{ref}} + 273.15 \text{ K}} = \frac{1}{\vartheta_{\text{ref}} + 273.15 \text{ K}} \vartheta + \frac{273.15 \text{ K}}{\vartheta_{\text{ref}} + 273.15 \text{ K}} \quad (10)$$

$$F^\vartheta = \frac{\vartheta}{\vartheta_{\text{ref}}} = \frac{1}{\vartheta_{\text{ref}}} \vartheta. \quad (11)$$

From the equations, it can be seen that the difference between the two descriptions is a rescaling of the F -axis in form of a stretching (lower slope) and a displacement (positive axis intersection).

Please note that for hydrogels, either definition is possible since they are never used for temperatures near freezing point. In any case, the anomaly of water at around 4 °C invalidates the Temperature Expansion Model and forms a boundary where it cannot be applied. In the current work, we use the definition from equation (11), i.e. $F = \vartheta/\vartheta_{\text{ref}}$.

3. APPLICATIONS FOR ACTUATORS

Using the normalized forms of the swelling behavior and the Temperature Expansion Model, simulations can be performed for complex structures. In the current section, anisotropic swelling caused by a spatially variable stimulus is presented. The experimental setup and research questions are presented in section 3.1. Then, an analytical model based on Euler-Bernoulli beam theory is presented in section 3.2. The results for the implemented PNIPAAm swelling behavior are depicted in section 3.3.

3.1 Anisotropic swelling under a stimulus gradient

In the current work, we present a bending structure under a temperature gradient, i.e. a linear spatial temperature distribution, see figure 10. A beam with the geometry parameters length, width and height $l \times b \times h$, which is fixed at the left side, is exposed to a linear temperature distribution in height direction. Please note that usually, the y -axis is reversed to yield positive bending displacements $w(z)$ in downwards direction.

We assume that the temperature at the top and bottom of the beam is constant $\vartheta^{\text{top}} = 32^\circ\text{C}$ and $\vartheta^{\text{bottom}} = 32.5^\circ\text{C}$. The temperature field solution of the one-dimensional Fourier problem without convection or heat sources

$$\frac{d^2\vartheta(y)}{dy^2} = 0 \quad (12)$$

under constant Dirichlet boundary conditions $\vartheta(-h/2) = \vartheta^{\text{top}}$ and $\vartheta(h/2) = \vartheta^{\text{bottom}}$ yields a linear temperature distribution. Three different reference states are assumed. Therefore three different stimulus ratio distributions, which represent this temperatures, are obtained, see figure 10(a).

The material used in the numerical experiment is PNIPAAm with the respective temperature responsive behavior described in section 2.1.2. Since LCST-behavior is observed, we expect a bending of the hydrogel beam in the downwards-direction, i.e. positive bending displacements $w(z)$. This is due to the fact that the bottom part of the beam is exposed to a temperature $\vartheta > \vartheta^{\text{LCST}}$ and therefore deswells.

Depending on the initial state of the synthesis, we can identify three testcases:

- Case I: Initial state is the reference state of the swelling at $\vartheta^{\text{I, ref}} = 32^\circ\text{C}$. The hydrogel beam is cut out of a hydrogel that is neither completely swollen, nor completely deswollen.
- Case II: As initial state, we choose the completely swollen state with $\vartheta < \vartheta^{\text{LCST}}$. The hydrogel is thus synthesized in low temperature environment and therefore in completely swollen state, e.g. in an ice bath. For the purpose of this work, $\vartheta^{\text{II, ref}} = 28^\circ\text{C}$.
- Case III: Initially, the material is completely deswollen. This equals the synthesis of the hydrogel in high temperature environment with $\vartheta > \vartheta^{\text{LCST}}$. Here, $\vartheta^{\text{III, ref}} = 36^\circ\text{C}$.

The testcases serve a better understanding of the importance of the reference state chosen for simulations.

(a) Temperature distribution with different reference states. (b) Bender structure with coordinate system and displacements $w(z)$ and tip displacement w_{Tip}

Figure 10. Anisotropic swelling is caused by the gradient of a stimulus that would lead to isotropic swelling. For a beam structure, this leads to a bending.

3.2 Analytical reference model

The expected deformation of a beam structure is bending due to constant curvature. The following equations resemble the mechanical theory used by Wallmersperger et al.²⁴ for Ionic Polymer Metal Composite benders. The differential equation in Euler-Bernoulli beam theory that describes the bending displacement $w(z)$ versus beam length direction z due to a bending moment around the x -axis M_{bx} reads

$$\frac{w''(z)}{(1 + w'(z)^2)^{3/2}} = -\frac{M_{bx}}{E I_{xx}}. \quad (13)$$

Here, the derivative is $()' = d/dz$, E denotes the Young's modulus and I_{xx} is the bending resistance which is a geometry parameter of the beam cross-section. For rectangular cross section, it equals $I_{xx} = b h^3/12$. For small deformation gradients, the equation simplifies to the well-known $w''(z) = -M_{bx}/EI_{xx}$. Boundary conditions of free end for $z = l$ and fixed for $z = 0$ lead to a displacement of

$$w(z) = \frac{E I_{xx}}{M_{bx}} \left(1 - \sqrt{1 - \left(\frac{M_{bx}}{E I_{xx}} z \right)^2} \right) \quad (14)$$

The temperature gradient and the respective swelling is coupled into the mechanical field as it is also used by Wallmersperger et al.²⁴ Therefore, the bending moment of the resulting stresses is obtained by integration of the stress in x - and y -direction

$$M_{bx}(z) = \int_{x=-\frac{b}{2}}^{\frac{b}{2}} \int_{y=-\frac{h}{2}}^{\frac{h}{2}} y \sigma^{\text{therm}}(x, y, z) dy dx. \quad (15)$$

The stress is derived using the Temperature Expansion Model, see section 2.2. Together with the stimulus ratio $F = F(y)$, which is a function in y -direction due to the y -dependent temperature, this leads to

$$\sigma^{\text{therm}}(x, y, z) = E \beta(F) \Delta F. \quad (16)$$

Thus, with a known linear distribution of F (constant gradient field, see figure 10) over the beam height, the expansion coefficient $\beta(F)$ and the subsequent σ^{therm} can be calculated. This leads to a bending moment M_{bx} which is constant in z -direction in the present case. The hydrogel beam structure forms an arc segment. Please note that equation (15) has the effect of a linearization of the nonlinear stress distribution in y -direction due to kinematic constraints, i.e. the linear distribution of strains with Bernoulli's hypothesis. The model parameters used are depicted in table 3.

Elastic modulus	Height	Width	Length
$E = 1 \text{ N/cm}^2$	$h = 1 \text{ cm}$	$b = 1 \text{ cm}$	$l = 10 \text{ cm}$

Table 3. Model parameters for the analytical reference model. In the current work, a square cross-section of the beam was assumed. The elastic modulus plays no role in the calculated bending, it was therefore chosen deliberately.

3.3 Results of the analytical reference model

The analytical reference model was implemented in Matlab using the Symbolic Toolbox for analytical derivations. With the given temperature gradient (figure 10), the expansion coefficient $\beta(y)$ in the height direction can be derived, see figure 11(a). The thermal stresses can be calculated using equation (16). The results are depicted in figure 11(b). Please note that a generic elastic modulus of $E = 1 \text{ N/cm}^2$ is used since it cancels out in the calculation of the bending.

It can be seen that the stress distributions differ depending on the used reference state. This is due to the fact that with different synthesis conditions – and therefore different initial states of the numerical experiment – pre-stresses occur. For Case II with synthesis temperature $\vartheta = 28^\circ\text{C}$, only deswelling occurs in the prescribed temperature range. In contrast, for Case III with higher synthesis temperature $\vartheta = 36^\circ\text{C}$, the temperatures inside the beam lead to swelling and thus positive thermal expansion stress. The stress distribution observed for Case I is very similar to the PCHIP fitted experimental data since it uses the same reference point. Therefore, it can be stated that the sigmoid fitting function introduced above is applicable in the chosen temperature range.

Figure 11. In height direction, for the different test cases, the expansion coefficients β and subsequent thermal stresses σ^{therm} can be derived. Please note that even though the elastic modulus cancels out in calculation of the bending, it has an influence on the depicted stresses.

The bending moment obtained through integration using equation (15) for each case leads to the bending displacement $w(z)$, see figure 12. The resulting bending moments are equal for cases I - III for the present model, even though three different reference states were used. This is due to the fact that the above mentioned pre-stresses only lead to a lengthening of the beam. Only the temperature distribution in height direction – and the resulting stress difference between the top and bottom side – leads to bending.

In comparison to the reference case with the PCHIP fitted experimental data, a very similar bending behavior is observed. The resulting difference becomes more obvious when a longer beam is depicted, since the smaller bending moment leads to a different curvature of the deformed beam.

Figure 12. Bending of the simulated beam with overall length $l = 10$ cm and height $h = 1$ cm. Due to the constant bending moment over z , the beam forms an arc.

4. CONCLUSION AND OUTLOOK

In the current work, we presented how the isotropic swelling can be generalized to be understandable to engineers without chemical background knowledge. Challenges that occur in the description for hydrogels were discussed. This includes hysteretic effects, conditional swelling, anisotropy and logarithmic rescaling.

In the following, we explained the implementation of the derived normalized swelling in the framework of the Temperature Expansion Model. Therefore, nonlinear thermal expansion coefficients $\beta(F)$, which depend on the stimulus ratio F , were derived. In this context, the stimulus ratio is used as a pseudo-temperature for arbitrary physical background.

Simulation results for the bending of a hydrogel beam under a linear temperature distribution were shown. For different reference states – which correspond to different synthesis conditions – the model yields different stress distributions over the beam-height which are caused by the locally different swelling of the hydrogel. However, the same overall bending of the beam is obtained.

ACKNOWLEDGMENTS

The present work is supported by the Deutsche Forschungsgemeinschaft (DFG) in the framework of the research training group “Hydrogel-based microsystems” DFG-GRK 1865. It is also partly supported by the Center for Advancing Electronics Dresden (cfaed) at Technische Universität Dresden.

REFERENCES

- [1] Gerlach, G. and Arndt, K.-F., [*Hydrogel sensors and actuators: engineering and technology*], vol. 6, Springer Science & Business Media (2009).
- [2] Bar-Cohen, Y., [*Electroactive Polymers as Artificial Muscles: Capabilities, Potentials and Challenges*], Ch. 23, 188–196, American Society of Civil Engineers (2000).
- [3] Liu, F. and Urban, M. W., “Recent advances and challenges in designing stimuli-responsive polymers,” *Progress in Polymer Science* **35**(1), 3–23 (2010).
- [4] Ehrenhofer, A., Elstner, M., and Wallmersperger, T., “Normalization of hydrogel swelling behavior for sensoric and actuatoric applications,” *under review at Sensors and Actuators B: Chemical* (2017).
- [5] Ehrenhofer, A., Bingel, G., Paschew, G., Tietze, M., Schröder, R., Richter, A., and Wallmersperger, T., “Permeation control in hydrogel-layered patterned PET membranes with defined switchable pore geometry - experiments and numerical simulation,” *Sensors and Actuators B: Chemical* **232C**, 499–505 (2016).
- [6] Boyko, V., Lu, Y., Richter, A., and Pich, A., “Preparation and characterization of acetoacetoxyethyl methacrylate-based gels,” *Macromolecular Chemistry and Physics* **204**(16), 2031–2039 (2003).

- [7] Arndt, K., Richter, A., Ludwig, S., Zimmermann, J., Kressler, J., Kuckling, D., and Adler, H., "Poly (vinyl alcohol)/poly (acrylic acid) hydrogels: FT-IR spectroscopic characterization of crosslinking reaction and work at transition point," *Acta Polymerica* **50**(11-12), 383–390 (1999).
- [8] Kuckling, D., Arndt, K.-F., and Richter, S., [*Hydrogel Sensors and Actuators: Engineering and Technology*], Ch. Synthesis of Hydrogels, 15–67, Springer Berlin Heidelberg, Berlin, Heidelberg (2010).
- [9] Kim, A., Mujumdar, S. K., and Siegel, R. A., "Swelling properties of hydrogels containing phenylboronic acids," *Chemosensors* **2**(1), 1–12 (2013).
- [10] Suzuki, A. and Tanaka, T., "Phase transition in polymer gels induced by visible light," *Nature* **346**(6282), 345–347 (1990).
- [11] Mitchell, M., "Engauge digitizer." A free open-source software to extract data points from a graph image. Hosted on SourceForge at: <http://digitizer.sourceforge.net> (2002).
- [12] Lucantonio, A., Nardinocchi, P., and Teresi, L., "Transient analysis of swelling-induced large deformations in polymer gels," *Journal of the Mechanics and Physics of Solids* **61**(1), 205–218 (2013).
- [13] Andersson, M., Axelsson, A., and Zacchi, G., "Swelling kinetics of poly (n-isopropylacrylamide) gel," *Journal of controlled release* **50**(1), 273–281 (1998).
- [14] Miyata, T., Urugami, T., and Nakamae, K., "Biomolecule-sensitive hydrogels," *Advanced drug delivery reviews* **54**(1), 79–98 (2002).
- [15] Ehrenhofer, A., Wallmersperger, T., and Richter, A., "Simulation of controllable permeation in pnipaaam coated membranes," in [*Proc. SPIE 9800, Behavior and Mechanics of Multifunctional Materials and Composites 2016*], *Proc. SPIE* **980016** (2016).
- [16] Ehrenhofer, Adrian; Wallmersperger, T., "Adjustable fluid and particle permeation through hydrogel composite membranes," *Accepted for publication, Journal of Intelligent Material Systems and Structures* (2017).
- [17] Wallmersperger, T., Kröplin, B., and Gülch, R. W., "Coupled chemo-electro-mechanical formulation for ionic polymer gels – numerical and experimental investigations," *Mechanics of Materials* **36**(5), 411–420 (2004).
- [18] Cai, S. and Suo, Z., "Mechanics and chemical thermodynamics of phase transition in temperature-sensitive hydrogels," *Journal of the Mechanics and Physics of Solids* **59**(11), 2259–2278 (2011).
- [19] Mazaheri, H., Baghani, M., and Naghdabadi, R., "Inhomogeneous and homogeneous swelling behavior of temperature-sensitive poly-(n-isopropylacrylamide) hydrogels," *Journal of Intelligent Material Systems and Structures* **27**(3), 324–336 (2016).
- [20] Guenther, M., Gerlach, G., and Wallmersperger, T., "Modeling of nonlinear effects in ph sensors based on polyelectrolytic hydrogels," in [*The 14th International Symposium on: Smart Structures and Materials & Nondestructive Evaluation and Health Monitoring*], 652417–652417, International Society for Optics and Photonics (2007).
- [21] Guenther, M., Gerlach, G., and Wallmersperger, T., "Non-linear effects in hydrogel-based chemical sensors: experiment and modeling," *Journal of Intelligent Material Systems and Structures* **20**(8), 949–961 (2009).
- [22] Tanaka, T., Wang, C., Pande, V., Grosberg, A. Y., English, A., Masamune, S., Gold, H., Levy, R., and King, K., "Polymer gels that can recognize and recover molecules," *Faraday Discussions* **101**, 201–206 (1995).
- [23] Li, W., Zhao, H., Teasdale, P., John, R., and Zhang, S., "Synthesis and characterisation of a polyacrylamide–polyacrylic acid copolymer hydrogel for environmental analysis of Cu and Cd," *Reactive and Functional Polymers* **52**(1), 31–41 (2002).
- [24] Wallmersperger, T., Leo, D. J., and Kothera, C. S., "Transport modeling in ionomeric polymer transducers and its relationship to electromechanical coupling," *Journal of Applied Physics* **101**(2), 024912 (2007).