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Inhomogeneous and homogeneous swelling behavior of temperature-sensitive poly-(N-isopropylacrylamide) hydrogels

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Abstract

The aim of this work is to develop a model to continuously predict inhomogeneous and homogeneous swelling behavior of temperature-sensitive poly-(N-isopropylacrylamide) hydrogels. Employing this model, some benchmark homogeneous problems such as free, unidirectional constrained and biaxial constrained swelling as well as swelling of core-shell structures are investigated. The main advantage of the model is its ability to solve inhomogeneous deformations due to a stable behavior in the vicinity of the phase transition temperature. Therefore, inhomogeneous swelling of a spherical shell on a hard core with application to microfluidics is analytically and numerically investigated for various thicknesses of the shell. Based on the solved examples, it is shown that the model possesses continuity and stability in the vicinity of the phase transition temperature.

Keywords

temperature-sensitive poly-(N-isopropylacrylamide) hydrogels, homogeneous and inhomogeneous swelling, stability, phase transition temperature

Introduction

Smart materials respond to environmental stimuli with particular changes in some variables, for example, temperature, moisture, electric or magnetic fields, pH, and stress. Among these environmental stimuli, temperature is almost the most important one. For example, in shape memory alloys (Arghavani et al., 2010; Brinson and Lammering, 1993), shape memory polymers (Baghani et al., 2012a, 2012b; Lagoudas et al., 2012; Meng and Hu, 2010), and elastomeric hydrogel (Cai and Suo, 2011), temperature is the main external stimulus. Among these smart materials, in this article, we focus on temperature-sensitive elastomeric hydrogels.

An elastomeric hydrogel is a covalently cross-linked network which can absorb large amount of water resulting in a swelled network. The amount of water in the network is affected by environmental conditions such as temperature (Chang et al., 2007; Depa et al., 2012; Wang et al., 2005), pH (Kurnia et al., 2012; Marcombe et al., 2010), mechanical load (Chester and Anand, 2010; Doi, 2009), ionic and salt concentration (Hong et al., 2010), light (Ahn et al., 2008; Zrínyi et al., 2001), and electric field (Li, 2009; Osada and Gong, 1998). Due to their specific structure, elastomeric hydrogels have found novel applications especially in tissue engineering and drug delivery systems (Hoffman, 2002), sensors and actuators (Randhawa et al., 2011; Richter et al., 2009; Wei et al., 2013; Westbrook and Qi, 2007; Xia et al., 2010), microfluidics and microvalves (Eddington and Beebe, 2004), and oilfield packers (Bhavsar et al., 2008). They have a promising future for application in microscales due to their fast response in micron size. An important class of hydrogels is those of temperature sensitive which have found applications in microfluidics and microvalves (Chester and Anand, 2011).

In many applications, a constitutive model is required to describe the hydrogel response under

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complicated thermo-mechanical conditions. As an example, in a microvalve, swelling of the hydrogel is constrained by the valve body. If the swelled hydrogel is in contact with the valve body, the contact force produced by the swelling phenomenon plays an important role in thermo-mechanical valve response. Therefore, a coupled thermo-mechanical theory is required to describe the behavior of the hydrogel in complicated problems.

The coupled nonlinear field theory of the hydrogel has attracted a great deal of interest, especially in last decade (Baek and Pence, 2011; Baek and Srinivasa, 2004; Chester and Anand, 2010; Dolbow et al., 2004; Duda et al., 2010; Hong et al., 2008, 2010; Wallmersperger et al., 2009). Particularly, coupled thermo-mechanical behavior of the temperature-sensitive hydrogels has been investigated in recent years (Birgersson et al., 2008; Cai and Suo, 2011; Chester and Anand, 2011).

Ji et al. (2006) developed a constitutive model in the scope of finite-strain kinematics for thermally induced volume transitions in stimulus-responsive hydrogels. Considering a sharp front separating swelled and collapsed phases, they modeled permeation of the fluid in the network using extended finite element method (FEM). They investigated thermally induced swelling of spherical and cylindrical specimens. Birgersson et al. (2008) presented a model for transient deformation of a neutral hydrogel due to the temperature gradient by employing a biphasic approach.

Chester and Anand (2011) developed a large deformation constitutive model for the coupled thermo-mechanical behavior of thermally responsive elastomeric gels. Limiting to isotropic materials and using Flory–Huggins model for the free energy change due to mixing, they employed a non-Gaussian model for the change in configurational entropy to account for the limited extensibility of the polymer chains.

Based on the experimental data for the interaction parameter of the swelling network presented by Afroze et al. (2000), Cai and Suo (2011) developed a constitutive model for the temperature-sensitive poly-(N-isopropylacrylamide) (PNIPAM) hydrogel. Their model was developed for weakly and covalently cross-linked PNIPAM. Employing the Flory–Rehner model and considering the experimental results, they assumed that the interaction parameter of PNIPAM to be a function of both temperature and the polymer volume fraction. Comparing the model results with those of experiments, the model was validated. However, in the vicinity of the phase transition temperature (PTT), multiple-solutions and snap-through instability were observed which results in limitations for using the model in finite element (FE) implementations and also in inhomogeneous swelling problems.

In this work, considering the Flory–Huggins model for the free energy change due to mixing, and a neo-Hookean model for the free energy change of the swelling network, we present a constitutive model for thermo-mechanical behavior of the PNIPAM hydrogel. In the mixing part of the free energy, the interaction parameter of the network is assumed to be a function of both temperature and polymer volume fraction. The modified model is validated by experimental results available in the literature and resolves the multiple-solutions and instability problems in the vicinity of PTT.

The article is organized as follows. First, the model is explained, and the governing formulations are presented in section "Model description." Thereafter, the validity and stability of the model in the vicinity of PTT are investigated in section "Results and discussion." In subsection "Homogeneous deformations," some examples of the homogeneous swelling are solved and validated by comparing two different sets of experimental data available in the literature. Then, inhomogeneous swelling of the spherical hydrogel shells on a fixed rigid core is analytically studied for temperature-sensitive PNIPAM hydrogel, and the results are presented in subsection "Analytical solution." Also, numerical implementation of the modified model for the inhomogeneous swelling of the spherical hydrogel shells on a fixed rigid core considering contact is presented in subsection "Numerical implementation." Finally, we present a summary and draw conclusions in section "Summary and conclusion."

Model description

Consider an element of a dry network of hydrogel in the reference state in which the element coordinate is denoted by $\mathbf{X}$. Under different thermo-mechanical conditions, the network deforms into the current state. In the current state, the element coordinate is defined as a function of its reference coordinate shown by $\mathbf{x}(\mathbf{X})$ which describes the network deformation. Thus, the deformation gradient can be defined as

$$\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}} \tag{1}$$

The right Cauchy-Green deformation tensor is also defined as

$$\mathbf{C} = \mathbf{F}^T\mathbf{F} \tag{2}$$

where the superscript "^{T}" denotes the transpose of the tensor. In the equilibrium conditions (regardless of time-dependent diffusion phenomenon), employing variational approach, the change in the Helmholtz free energy density of an arbitrary element of the hydrogel per unit reference volume at a specified temperature is expressed as (Cai and Suo, 2011)

$$\delta W = \mathbf{P} : \delta\mathbf{F} + \mu\delta c \tag{3}$$

where $\mathbf{P}$, μ, and c are the first Piola–Kirchhoff stress tensor, chemical potential, and number of fluid molecules absorbed by the network per unit volume of the dry polymer, respectively. Defining Helmholtz free energy density function as $W = W(\mathbf{F}, c, T)$, equation (3) yields

$$\delta W = \frac{\partial}{\partial \mathbf{F}} W(\mathbf{F}, c, T) : \delta \mathbf{F} + \frac{\partial}{\partial c} W(\mathbf{F}, c, T) \delta c \quad (4)$$

where T is the absolute temperature. Now, by comparing equations (3) and (4), we have

$$\mathbf{P} = \frac{\partial}{\partial \mathbf{F}} W(\mathbf{F}, c, T), \quad \mu = \frac{\partial}{\partial c} W(\mathbf{F}, c, T) \quad (5)$$

Considering a small density of cross-linking for the hydrogel, we assume an additive decomposition of the free energy density in the form of (see, for example, Cai and Suo, 2011; Chester and Anand, 2010, 2011; Hong et al., 2008, 2009; Li et al., 2012, among others)

$$W = W_{stretch}(\mathbf{F}, T) + W_{mixing}(c, T) \quad (6)$$

where $W_{stretch}(\mathbf{F}, T)$ and $W_{mixing}(c, T)$ are the free energy density due to elastic deformation and mixing, respectively, and assumed to be a function of $\mathbf{F}$ and c, respectively (Cai and Suo, 2012). We assume that the change in the hydrogel volume originates only from the fluid molecules diffusion through the network. In this regard, the change of the volume is equal to the absorbed fluid content of the network. Thus, the swelling constraint which relates the absorbed fluid content of the network to its deformation is (Hong et al., 2008)

$$J = 1 + \nu c \quad (7)$$

where ν and J are volume of a fluid molecule and the determinant of $\mathbf{F}$, respectively. To apply this constraint to the material behavior, we use Lagrange multiplier method by introducing the free energy function as (Hong et al., 2008, 2010)

$$W = W_{stretch}(\mathbf{F}, T) + W_{mixing}(c, T) + \Pi(J - 1 - \nu c) \quad (8)$$

where Π is the Lagrange multiplier, which should be defined from boundary conditions. Now, in terms of this modified free energy, we have

$$\mathbf{P} = \frac{\partial}{\partial \mathbf{F}} W_{stretch}(\mathbf{F}, T) + \Pi \frac{\partial}{\partial \mathbf{F}} J,$$
$$\mu = \frac{\partial}{\partial c} W_{mixing}(c, T) - \Pi \nu \quad (9)$$

For equilibrium state, the chemical potential is equal to zero; thus, the Lagrange multiplier and stresses can be obtained as

$$\Pi = \frac{1}{\nu} \frac{\partial}{\partial c} W_{mixing}(c, T), \quad \mathbf{P} = \frac{\partial}{\partial \mathbf{F}} W_{stretch}(\mathbf{F}, T) + \frac{1}{\nu} \frac{\partial}{\partial c} W_{mixing}(c, T) \frac{\partial}{\partial \mathbf{F}} J \quad (10)$$

where the obtained result for stress is equal to $\mathbf{P} = \frac{\partial}{\partial \mathbf{F}} W(\mathbf{F}, T)$, in which we eliminate c from W by using swelling constraint. Thus, in equilibrium state, the free energy and related stresses components can be obtained by direct implementation of the swelling constraint in the free energy function to eliminate c from equations. We use a neo-Hookean model to describe the elastic deformation of the network which is expressed in terms of the deformation as (Cai and Suo, 2011)

$$W_{stretch} = \frac{1}{2} NKT(I_1 - 3 - 2\log(J)) \quad (11)$$

where N and K are density of the polymer chains and Boltzmann constant, respectively. In addition, I_1 is the first invariant of $\mathbf{C}$. Also, based on the Flory–Huggins theory, the mixing part of the free energy density is (Flory and Rehner, 1943; Huggins, 1942)

$$W_{mixing} = KT\left(c \log\left(\frac{\nu c}{1 + \nu c}\right) + \frac{\chi c}{1 + \nu c}\right),$$
$$\chi = \chi_0 + \phi \chi_1, \quad \chi_0 = A_0 + B_0 T, \quad \chi_1 = A_1 + B_1 T \quad (12)$$

where ϕ is the polymer volume fraction. Also, χ is the interaction parameter of the network which is a function of temperature and the polymer volume fraction for the temperature-sensitive PNIPAM hydrogel. In addition, A_0, B_0, A_1, and B_1 are material parameters adopted for the experiments reported by Afroze et al. (2000). Using swelling constraint, equation (7), the total free energy density is

$$W = \frac{1}{2} NKT(I_1 - 3 - 2\log(J)) + \frac{KT}{\nu}(J - 1)\left(\log\left(\frac{J - 1}{J}\right) + \frac{\chi}{J}\right) \quad (13)$$

The stress components at the equilibrium state can be calculated by considering the free energy function and boundary conditions. Minimizing this free energy at a specified temperature for free swelling condition, as done by Cai and Suo (2011), we obtain the equilibrium state and plot the numerical results in Figure 1(a) and (b). In these figures, swelling ratio is defined as the ratio of the current volume to the dry network volume. As depicted in Figure 1(a) and discussed in detail by Cai and Suo (2011), this free energy experiences instability in the vicinity of PTT, due to the appearance of multiple-solutions. Producing more than one solution makes the formulation numerically unstable. Such

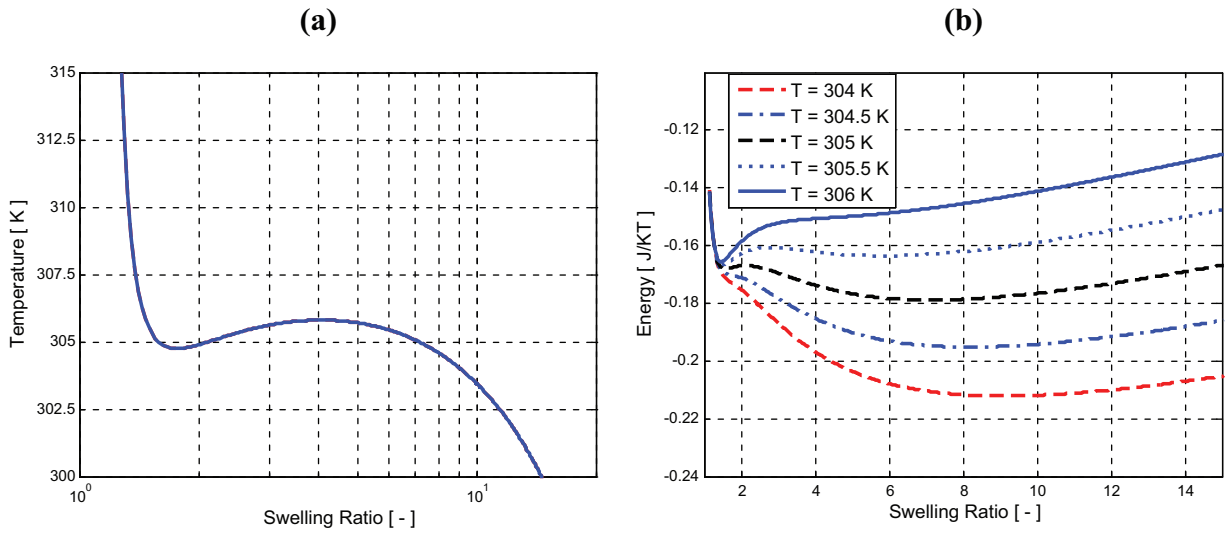

Figure 1. Free swelling for hydrogel with $N\nu = 0.01$ using Cai and Suo model: (a) equilibrium swelling ratio curve and (b) free energy density of the network in the vicinity of PTT at different given temperatures.

thing is shown in Figure 1(b), where in the vicinity of PTT, 305.5 K, we have three solutions. In addition, in the multiple-solution region, choosing the appropriate equilibrium point from the obtained solutions is a major challenge. This problem is similar to the snap-through instability effect reported for other soft materials (Liu et al., 2012; Park et al., 2012).

Moreover, multiple-solution problem becomes more prominent in implementing the constitutive model in a FE framework or even in solving inhomogeneous boundary value problems which involve solving ordinary or partial differential equations. To overcome such instability in the FEM, collocation methods are commonly employed to trace the equilibrium branches such as the arc-length method which is computationally expensive in a numerical scheme (Hong et al., 2009; Riks, 1972).

Due to the numerical instability problem described in this section, the Cai and Suo model is a numerically expensive choice to be implemented in FE framework or employed in an inhomogeneous problem. The main idea of this work is to modify the free energy function proposed by Cai and Suo (2011) to eliminate the snap-through instability and the multiple-solution problem in the vicinity of PTT for temperature-sensitive PNIPAM hydrogels. To attain this, we investigate the source of the multiple-solution problem in the free energy function. Examining different loading conditions in various examples, it is shown that the logarithmic term in the mixing free energy is the source of generating multiple-solutions. To avoid this problem, instead of this ill-posed term, we use a polynomial expression for the mixing part of the free energy. Since $J>1$, we write the polynomial expansion of the logarithmic term as

$$\log\left(\frac{J-1}{J}\right) = \log\left(1-\frac{1}{J}\right) = -\frac{1}{J}-\frac{1}{2J^2}-\frac{1}{3J^3}-\cdots \tag{14}$$

Plotting the free energy for the free swelling problem and also other states of complicated loading conditions (in section "Results and discussion," some complicated loading conditions are discussed in detail), the instability is eliminated by choosing the first three terms of the expansion series. Also, in section "Results and discussion," it is shown that the calculated numerical results are in an acceptable agreement with the experimental data available in the literature for different sets of experiments. Since the swelling ratio is often larger than unity, using the first terms of the series seems to be appropriate for approximation of the mixing free energy. On the other hand, choosing more than four terms may result in regeneration of the instability. Thus, to have maximum precision beside instability elimination, we choose the first three terms in the series approximation. Finally, the modified model for the total free energy of the hydrogel is

$$\begin{aligned} W &= \frac{1}{2}NKT(I_1-3-2\log(J)) + \frac{KT}{\nu}(J-1)\\ &\quad\left(-\frac{1}{J}-\frac{1}{2J^2}-\frac{1}{3J^3}+\frac{\chi}{J}\right)\\ &= \frac{1}{2}NKT(I_1-3-2\log(J)) + \frac{KT}{\nu}(J-1)\\ &\quad\left(-\frac{1}{J}-\frac{1}{2J^2}-\frac{1}{3J^3}+\frac{\chi_0}{J}+\frac{\chi_1}{J^2}\right) \end{aligned} \tag{15}$$

The numerical illustration of the model for free energy of the free swelling is shown in Figures 2 and 3

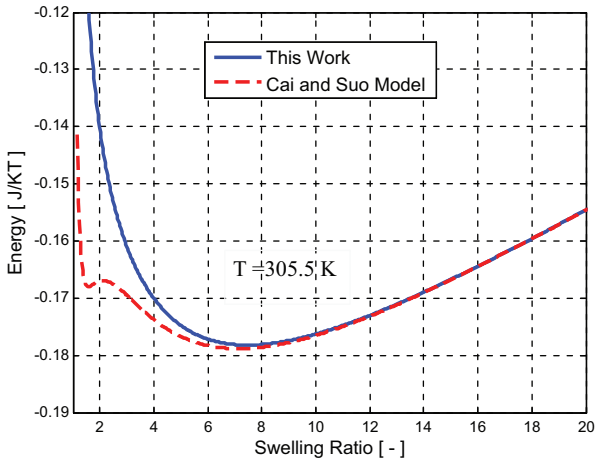

Figure 2. Free energy changes at 305.5 K for the free swelling using the modified model and Cai and Suo model.

at different temperatures in the vicinity of PTT. Elimination of the multiple-solution problem in the vicinity of PTT is depicted in Figure 2 which shows the free energy function in terms of the swelling ratio for both the Cai and Suo model and the modified model. In Figure 2, the free energy function is shown at 305.5 K, which is a critical temperature in which the multiple-solution problem is dominant. As shown, the model possesses one minimum point which results in stability of the solution in this temperature. As observed from Figure 3, the free energy only possesses one minimum at different temperatures which corresponds to a unique solution. Also, according to Figure 3, the model has a continuous behavior which eliminates the snap-through instability in the vicinity of PTT. It is worth to mention that the modified model is not designed for predicting an ideal sharp transition between the swollen and the collapsed phases through changing the temperature. The goal is to predict the behavior of PNIPAM hydrogels continuously with an acceptable precision where the numerical cost decreases in simulating the phase transition behavior. In other words, the merit of the modified model is its ability to be employed in inhomogeneous swelling problems in a FE framework.

Now in terms of the modified free energy function, we can obtain nominal stress, namely, **P**, by differentiating equation (15). If we have three nominal principal stretches, $\lambda_i,\ i = 1, 2, 3$, nominal stress components P_i are obtained as

$$\begin{aligned}
\frac{P_1\nu}{KT} &= N\nu\left(\lambda_1 - \frac{1}{\lambda_1}\right) \\
&+ \left(\frac{-1/2 + (\chi_0 - \chi_1)}{\lambda_2\lambda_3\lambda_1^2} + \frac{-1/3 + 2\chi_1}{\lambda_2^2\lambda_3^2\lambda_1^3} - \frac{1}{\lambda_2^3\lambda_3^3\lambda_1^4}\right) \\
\frac{P_2\nu}{KT} &= N\nu\left(\lambda_2 - \frac{1}{\lambda_2}\right) \\
&+ \left(\frac{-1/2 + (\chi_0 - \chi_1)}{\lambda_3\lambda_1\lambda_2^2} + \frac{-1/3 + 2\chi_1}{\lambda_3^2\lambda_1^2\lambda_2^3} - \frac{1}{\lambda_3^3\lambda_1^3\lambda_2^4}\right) \\
\frac{P_3\nu}{KT} &= N\nu\left(\lambda_3 - \frac{1}{\lambda_3}\right) \\
&+ \left(\frac{-1/2 + (\chi_0 - \chi_1)}{\lambda_1\lambda_2\lambda_3^2} + \frac{-1/3 + 2\chi_1}{\lambda_1^2\lambda_2^2\lambda_3^3} - \frac{1}{\lambda_1^3\lambda_2^3\lambda_3^4}\right)
\end{aligned} \tag{16}$$

The first terms in equation (16) come from the elastic deformation free energy, while the second terms come from the mixing terms in the energy function.

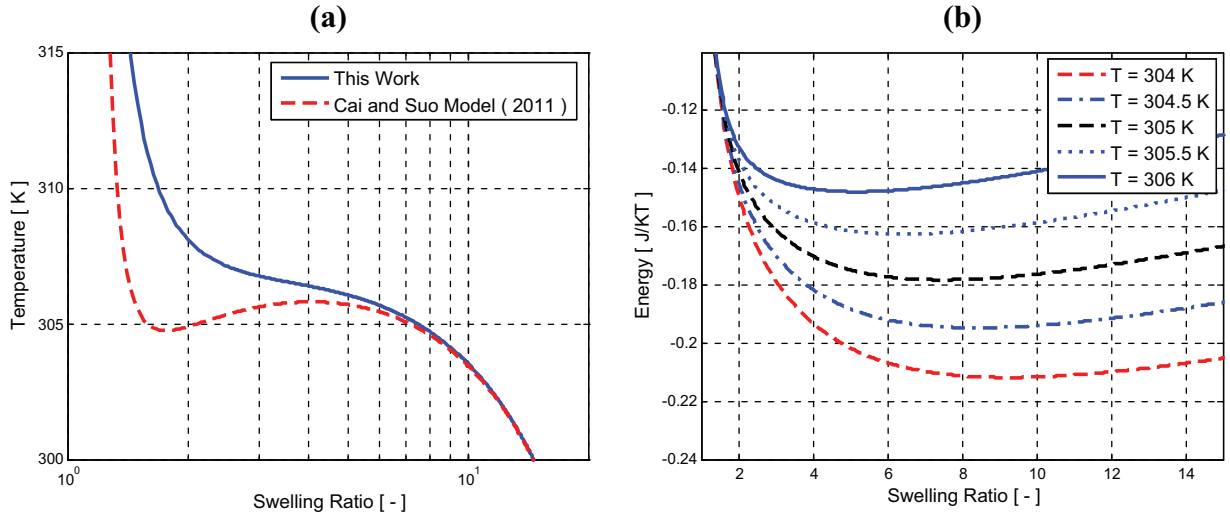

Figure 3. Free swelling for hydrogel with $N\nu = 0.01$: (a) equilibrium swelling ratio curve using modified model and Cai and Suo model and (b) free energy of the network in the vicinity of PTT at different given temperatures for the model.

Results and discussion

In this section, the modified model is used to solve some benchmark problems involving homogeneous or inhomogeneous swelling of the temperature-sensitive PNIPAM hydrogels. First, in section "Homogeneous deformations," some homogeneous examples are solved, and the results are compared to the experimental data available in the literature. Then, in section "Inhomogeneous deformations," inhomogeneous swelling of the hydrogel is studied for a spherical shell of PNIPAM on a hard core. In this problem inhomogeneous deformation occurs due to the existence of the hard core which is solved in this work for the first time.

Homogeneous deformations

Free swelling. Since free swelling of temperature-sensitive PNIPAM hydrogels has been investigated experimentally in the literature, we also investigate this problem in this work to validate the modified model. Due to the isotropic behavior of the hydrogel, for free swelling conditions, we have

$$\lambda_1 = \lambda_2 = \lambda_3 = \lambda = \left(\frac{V}{V_0}\right)^{1/3} \tag{17}$$

where V/V_0 is the swelling ratio. To determine the equilibrium state, one should find the minimum of the free energy in terms of the swelling ratio at a specified temperature. Differentiating the free energy with respect to the swelling ratio, the equilibrium state is recognized. The results are shown for different values of the cross-linking density in Figure 4(a) and (b). Figure 4(b) is a detailed view of Figure 4(a) in the vicinity of PTT. The model results are compared to those of the experimental data conducted by Oh et al. (1998) and Suzuki and Ishii (1999) as well as those predicted by the Cai and Suo model. As shown in Figure 4(a) and (b), the modified model is in good agreement with the experimental data and also has a continuous behavior without encountering any instability. The results of the model are equal to those of the Cai and Suo model in the regions far from PTT, while in the vicinity of PTT, the model is more successful in predicting the experimental results, especially for larger values of $N\nu$ as observed from Figure 4(b). It is worth to mention that the modified model may not predict sharp phase transition especially for small values of $N\nu$ in which this phenomenon is dominantly observed, for example, for $N\nu = 0.0035$ in Figure 4. As another example, for the experiment of Hirokawa and Tanaka (1984) with a sharp phase transition, as shown in Figure 5, we are capable of eliminating the instability beside predicting a continuous behavior for the value of $N\nu = 0.005$.

Unidirectional constrained swelling. In this section, the modified model is employed to solve another popular problem in the hydrogel swelling, namely, unidirectional constrained swelling. In this problem, the stretch in the constraint direction is fixed and equal to λ_1, while the other two stretches vary with the temperature changes ($\lambda_2 = \lambda_3$). Using the experimental data reported by Suzuki et al. (1997), we consider a cubic piece of the hydrogel immersed in the water at 303 K at the free swelling condition that reaches equilibrium stretch λ_0. Thereafter, the cube can be stretched while

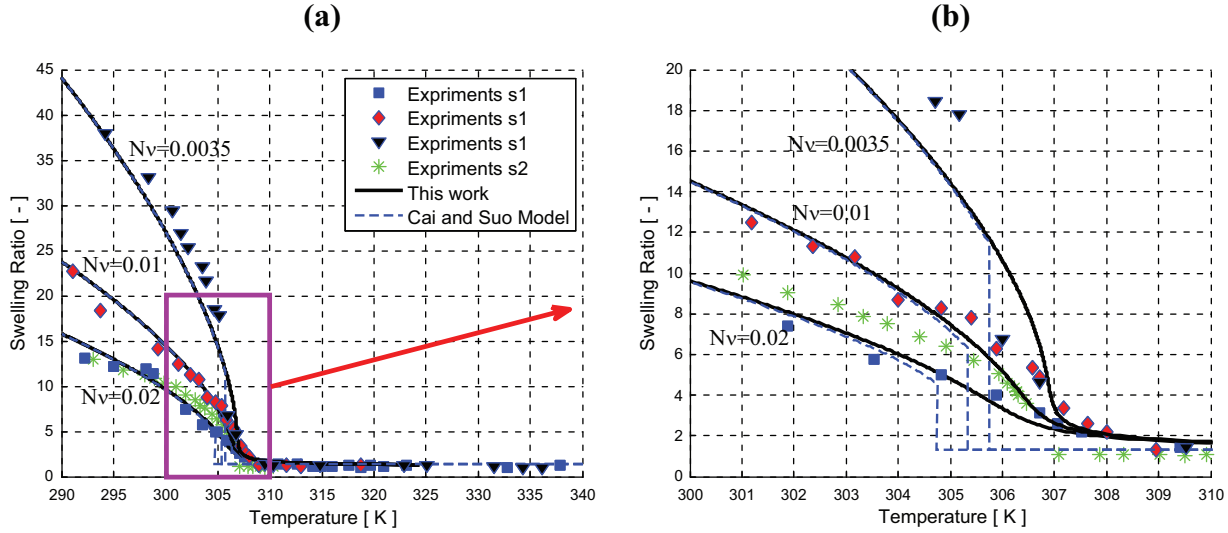

Figure 4. (a) Comparison between modified model and experiments as well as Cai and Suo model for free swelling and (b) detailed view of the comparison in vicinity of PTT. Experimental data s1 and s2 are reported from Oh et al. (1998) and Suzuki and Ishii (1999), respectively.

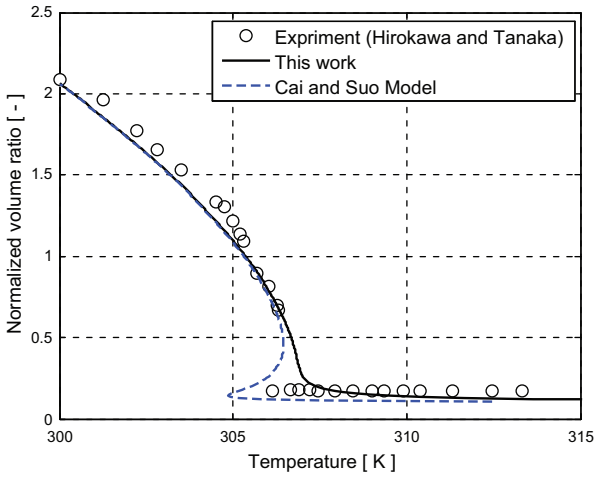

Figure 5. Comparison between modified model and experiments as well as Cai and Suo model for free swelling with a sharp phase transition. Experimental data are reported from Hirokawa and Tanaka (1984).

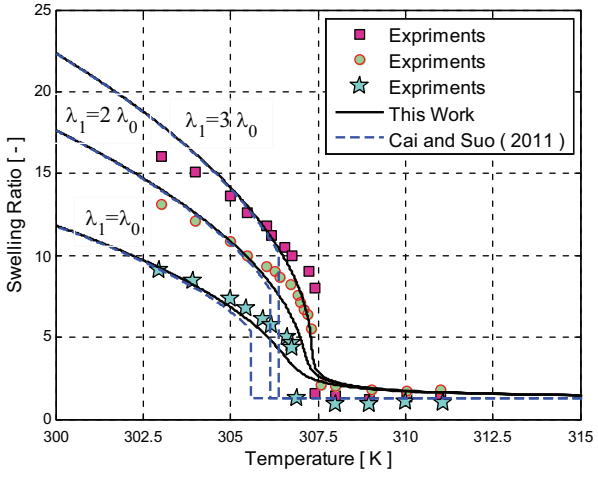

Figure 6. Comparison between this work model and experiments (Suzuki et al., 1997) as well as Cai and Suo model for unidirectional constraint swelling.

the longitudinal stretch is fixed and equal to $\lambda_1 = n\lambda_0 (n = 1, 2, 3)$. Then, the stretches in other two directions may vary with the temperature changes. Substituting the longitudinal stretch in the model, similar to section "Free swelling," the equilibrium state is calculated for different values of λ_1. The calculated results as well as the Cai and Suo model and the experimental data are shown in Figure 6. As depicted in Figure 6, the modified model is in good agreement with the experimental data. Also, a continuous behavior is predicted by the model and the instability due to the multiple-solution problem in the vicinity of PTT is disappeared.

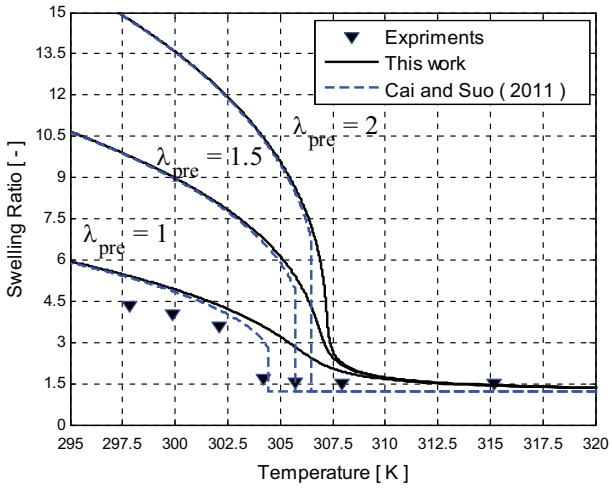

Figure 7. Comparison between the proposed model and experiments (Vidyasagar et al., 2008) as well as Cai and Suo model under biaxial constraint swelling for different values of the pre-stretches, λ_{pre}.

Biaxial constrained swelling. An interesting benchmark problem in the literature is the swelling of the hydrogel layer on a hard sub-layer. In this regard, biaxial constrained swelling of the hydrogel is studied in this section. Since thickness of the hydrogel layer is small, one can assume that the hydrogel experiences biaxial constrained swelling. Assume that the pre-stretches of the hydrogel in two constrained directions are fixed and equal to $\lambda_1 = \lambda_2 = \lambda_{pre}$. Moreover, it is assumed that the stretch in the direction normal to the constrained plain is $\lambda_3 = \lambda$. Similar to the previous examples, by substituting different values of the pre-stretches in the modified model and minimizing the free energy function at a given temperature, the equilibrium point of the hydrogel is found in terms of the temperature as shown in Figure 7 for different values of the pre-stretches, λ_{pre}. Also, the experimental data reported by Vidyasagar et al. (2008) as well as the Cai and Suo model results are depicted in Figure 7. From Figure 7, it is concluded that the modified model successfully predicts the experimental results showing a continuous behavior. Such trend has also been observed in the experiments.

Core-shell structure volume change. Predicting the response of the core-shell structure of the temperature-sensitive hydrogel has attracted a great deal of interest in recent years (Cai and Suo, 2011; Gernandt et al., 2011; Wang and Wu, 2013). The core-shell structure includes a hydrogel core and an elastomeric shell. Therefore, the modified model is employed to simulate the behavior of the core-shell structure especially its core. The equilibrium state of the system is obtained in the following.

Consider a spherical core of the temperature-sensitive hydrogel with an elastomeric shell as shown in

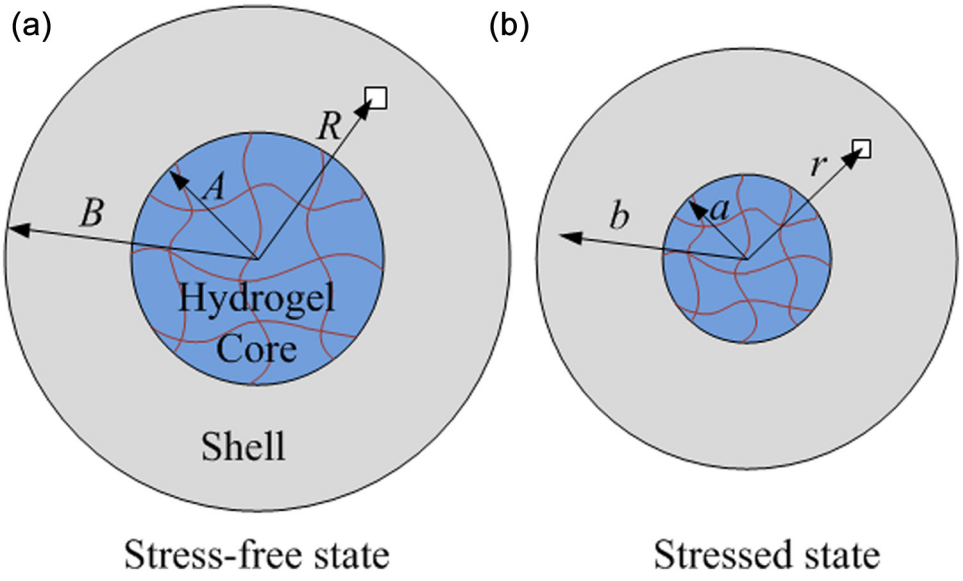

Figure 8. Schematic drawing of a core-shell structure of the temperature-sensitive hydrogel in (a) stress-free and (b) stressed states.

Figure 8. At a specified temperature, the core-shell structure is stress-free as observed in Figure 8(a). If the system experiences a temperature change, both the core and the shell are stressed due to the hydrogel core deformation, as depicted in Figure 8(b). The inner and outer radii of the shell are A and B in the stress-free state and a and b in the stressed one, respectively. Since an isotropic and homogeneous behavior is assumed for the core in the stress-free state, the stretch is equal to λ_f in the core. Also, in the stressed state, the core homogeneous stretch with respect to the dry network is

$$\lambda_1 = \lambda_2 = \lambda_3 = \lambda_f \frac{a}{A} \tag{18}$$

Subsequently, substituting equations (18) into (15), the free energy density, W_{core}, and the total free energy of the core, $W_{core,\,total}$, are respectively

$$\begin{aligned} W_{core} = {} & \frac{KT}{\nu}\left(\left(\frac{a^3\lambda_f^3}{A^3}-1\right)\left(-\frac{A^3}{a^3\lambda_f^3}-\frac{1}{2}\left(\frac{A^3}{a^3\lambda_f^3}\right)^2\right.\right. \\ & \left.\left.-\frac{1}{3}\left(\frac{A^3}{a^3\lambda_f^3}\right)^3\right)+\chi\left(1-\frac{A^3}{a^3\lambda_f^3}\right)\right) \\ & +\frac{NKT}{2}\left(3\left(\frac{a\lambda_f}{A}\right)^2-3-6\log\left(\frac{a\lambda_f}{A}\right)\right) \\ W_{core,\,total} = {} & \frac{4\pi}{3}\left(\frac{A}{\lambda_f}\right)^3 W_{core} \end{aligned} \tag{19}$$

Since deformation of the shell is assumed to be incompressible, we have

$$B^3 - A^3 = b^3 - a^3, \quad \text{or } b^3 = B^3 - A^3 + a^3 \tag{20}$$

Also, the hoop stretch, λ_θ, the radial stretch, λ_r, and subsequently the free energy density for the shell, W_{shell}, are (Cai and Suo, 2011)

$$\begin{aligned} & \lambda_1 = \lambda_2 = \lambda_\theta = \frac{r}{R}, \quad \lambda_3 = \lambda_r = \lambda^{-2} \\ & W_{shell} = \frac{G}{2}\left(2\lambda^2 + \lambda^{-1} - 3\right) \end{aligned} \tag{21}$$

Integrating the free energy density over the whole shell, the total free energy of the shell is obtained as

$$W_{shell,\,total} = 4\pi\left(a^3 - A^3\right)\int_{b/B}^{a/A} \frac{W_{shell}\lambda^2}{\left(\lambda^3-1\right)^2}\,d\lambda \tag{22}$$

The total free energy of the core-shell system is equal to the sum of total free energies of the shell and core which is a function of the outer radius of the core, namely, a. To find the equilibrium state of the system at a specified temperature, one should define the equilibrium value of a by minimizing the total free energy of the system. Substitution of all variables in terms of a and differentiation with respect to a leads to a nonlinear equation containing complicated integrals which are calculated employing numerical techniques.

Solving the nonlinear equation, the equilibrium volume ratio of the core-shell system is obtained, and the results of the modified model as well as the Cai and Suo model are shown in Figure 9. The volume ratio is defined as the ratio of current volume of the core-shell to its initial volume at stress-free state. Also, the temperature at the stress-free state is 295 K. As observed

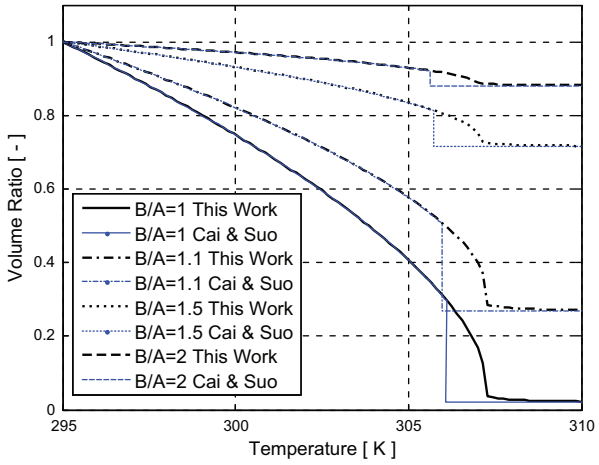

Figure 9. Comparison between modified model and Cai and Suo model results for the core-shell swelling.

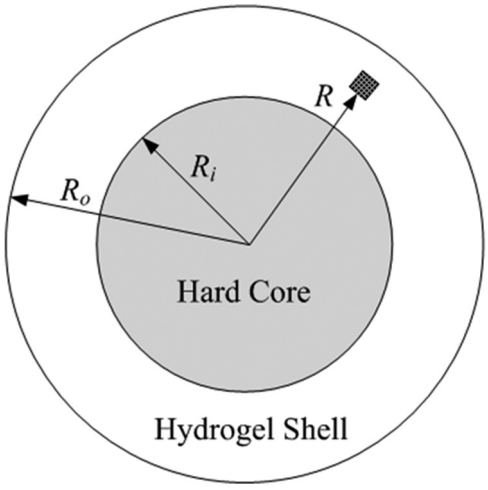

Figure 10. Schematic drawing of the hydrogel shells on a spherical core.

from Figure 9, the model possesses a continuous behavior in the vicinity of PTT compared to the Cai and Suo model.

Inhomogeneous deformations

In all the examples investigated in section "Homogeneous deformations," the swelling and deformations are homogeneous, while in many practical applications, inhomogeneous swelling of the temperature-sensitive hydrogel is of great importance in which multiple-solution problem leads to divergence of solution in the vicinity of PTT. In addition, as depicted in the plotted results of the solved examples, PTT of the Cai and Suo model is slightly dependent on the applied mechanical conditions such as constraints. This problem is prominent in inhomogeneous problems in which phase transition and consequently instability can occur in some regions of the solution. Thus, a continuous model is required to solve an inhomogeneous swelling problem. The modified model possesses the ability to solve the inhomogeneous swelling problems due to its continuous behavior.

Analytical solution. Motivated from Zhao et al. (2008), a benchmark problem in the hydrogel inhomogeneous swelling is a spherical shell on a hard core whose volume can be changed due to the environmental conditions, that is, temperature changes. The schematic drawing of this problem is shown in Figure 10. For the spherical shell, all field variables are functions of R, which is the radius of an element in the reference state as shown in Figure 10(a). Due to the symmetry, the equilibrium equation in the radial direction gives

$$\frac{dP_r}{dR} - \frac{2(P_r - P_\theta)}{R} = 0 \tag{23}$$

where P_r and P_θ are the nominal radial and hoop stresses, respectively. These stress components are obtained from equation (16) as

$$\begin{aligned} \frac{P_r \nu}{KT} &= N\nu\left(\lambda_r - \frac{1}{\lambda_r}\right) \\ &+ \left(\frac{-1/2 + (\chi_0 - \chi_1)}{\lambda_\theta^2 \lambda_r^2} + \frac{-1/3 + 2\chi_1}{\lambda_\theta^4 \lambda_r^3} - \frac{1}{\lambda_\theta^6 \lambda_r^4}\right) \\ \frac{P_\theta \nu}{KT} &= N\nu\left(\lambda_\theta - \frac{1}{\lambda_\theta}\right) \\ &+ \left(\frac{-1/2 + (\chi_0 - \chi_1)}{\lambda_\theta^3 \lambda_r} + \frac{-1/3 + 2\chi_1}{\lambda_\theta^5 \lambda_r^2} - \frac{1}{\lambda_\theta^7 \lambda_r^3}\right) \end{aligned} \tag{24}$$

Also, the stretch components in terms of the displacement field variable are

$$\lambda_r = \frac{r}{R}, \quad \lambda_\theta = \frac{d}{dR} r(R) \tag{25}$$

in which r is the radius of an element of the hydrogel in the current state. Substituting equations (24) and (25) in equation (23), a differential equation in terms of $r(R)$ is obtained which identifies the behavior of the system due to the temperature change as

$$\begin{aligned} &C_1\left(r'^5 r'' + r'^3 r''\right) + C_2 R r r'^2 r'' + C_3 R r r' r'' \\ &+ 4R^8 r r'' + 2C_2\left(R r'^4 - r r'^3\right) + \\ &2C_3\left(R r'^3 - r r'^2\right) - C_4 r r'^5 + C_4 R\left(r'^6 - r'^4\right) \\ &+ 2R^3 r^6 r'^5 + 8R^8 r'^2 - 8R^7 r r' = 0 \end{aligned} \tag{26}$$

where "$'$" stands for derivative with respect to argument R. Also, C_1, C_2, C_3, and C_4 are defined as follows

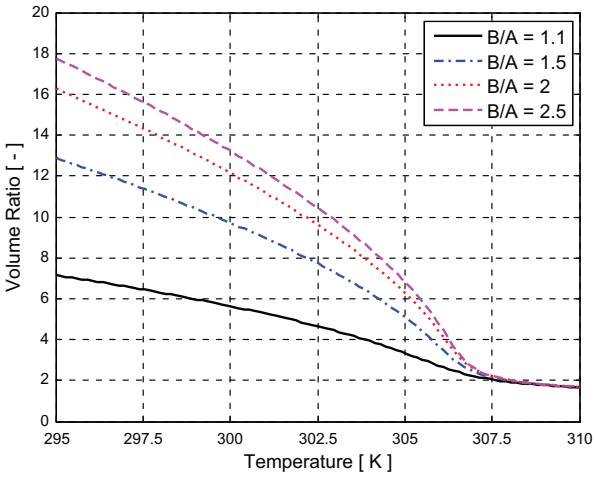

Figure 11. Swelling of a spherical shell on a hard core for different outer diameter of the shell.

$$C_1 = N\nu R^2 r^7,$$
$$C_2 = (-2A_0 + 2A_1 + 1 + 2B_1T - 2B_0T)R^3 r^4, \quad (27)$$
$$C_3 = (1 - 6B_1T - 6A_1)R^5 r^2, C_4 = 2N\nu r^7$$

The relevant boundary conditions are expressed as

$$r = \bar{\lambda}A \text{ at } R = R_i, \qquad P_r = 0 \text{ at } R = R_o \quad (28)$$

in which $\bar{\lambda}$ is the initial stretch in the inner radius, and R_i and R_o are inner and outer radii of the spherical shell in the reference state, respectively. The value of $\bar{\lambda}$ is dependent on the preparation method of the hydrogel. In this work, the value of $\bar{\lambda}$ is chosen to be 1.001 which is near unity (Zhao et al., 2008). The governing differential equation (26) should be numerically solved. To solve the present boundary value problem, a finite difference technique with Richardson extrapolation is used (Ascher et al., 1994). The calculated results are depicted in Figure 11, where volume ratio is plotted versus temperature. The volume ratio is defined as ratio of the current volume of the hydrogel shell to its dry volume. As can be seen, the modified model is capable of solving the inhomogeneous swelling with the specified boundary conditions.

Numerical implementation. To have an efficient tool for numerical investigation, the modified model is implemented in an ABAQUS user subroutine, namely, UHYPER. To show the validity of the model, inhomogeneous swelling of a hydrogel shell on a rigid pillar with the boundary conditions identical to the analytical solution presented in the previous section is solved. We present the results for different shell thickness ratio (B/A) as solved in the analytical example in section "Analytical solution" and report the normalized outer radius of the hydrogel shell (normalized by the inner radius) for both the analytical and numerical results in Figure 12. As depicted in this figure, a good agreement is observed, and the validity of the FEM solution is successfully checked. Also, deformation contours for one of the performed simulations with $B/A = 2$ are presented in Figure 13(a) and (b) at temperatures 310 and 300 K, respectively. In addition, for $B/A = 2$, we solve inhomogeneous swelling of a hydrogel shell on a rigid pillar which may experience a contact with rigid flat walls of a channel. The width of the channel, D, is selected such that $D/A = 3$, and the results are shown in Figure 14(a) and (b) at the temperatures 310 and 300 K, respectively. The inner radius of the hydrogel shell is constrained to the rigid pillar, while the outer radius of the shell experiences a contact with the walls. Thus, this problem contains a complicated coupling between temperature changes, large deformations and mechanical contact. As shown in Figure 14, the shell does not touch the walls at 310 K, and the channel remains fully open. Decreasing the temperature results in volume change of the hydrogel shell which in turn comes into contact with the channel walls at 300 K as shown in Figure 14(b). Thus, the modified model is suitable for application in the FE framework for other complicated problems.

Summary and conclusion

In this work, the equilibrium behavior of the temperature-sensitive PNIPAM hydrogel was studied. Following Cai and Suo (2011), the aim of this work was to develop a model to continuously predict the behavior of the temperature-sensitive PNIPAM hydrogels to be implemented in inhomogeneous swelling of the temperature-sensitive PNIPAM hydrogel. To develop this model, an additive decomposition of the free energy was assumed. If the Flory–Huggins theory is employed for mixing part of the free energy, snap-through instability appears in the vicinity of PTT which is undesirable for the inhomogeneous problems or in the FE framework. Use of the modified model results in eliminating multiple-solution problem. Also, the model possesses a continuous behavior in the vicinity of PTT which is appropriate for numerical simulations with a lower computational cost. The interaction parameter of the network was assumed to be a function of both the temperature and polymer volume fraction. Employing the model, some benchmark homogeneous problems were investigated. Free, unidirectional constrained and biaxial constrained swellings as well as swelling of core-shell structure were studied, and it was shown that the results were in good agreement with the experimental data.

The main advantage of the modified model is its ability to be employed in the inhomogeneous deformations. Therefore, as a benchmark problem, the

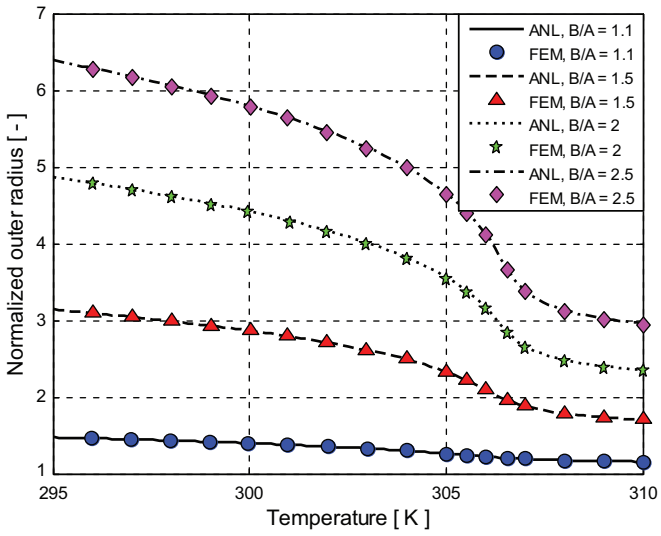

Figure 12. Analytical (ANL) and numerical (FEM) results for inhomogeneous swelling of a spherical shell on a hard core for different outer diameter of the shell.

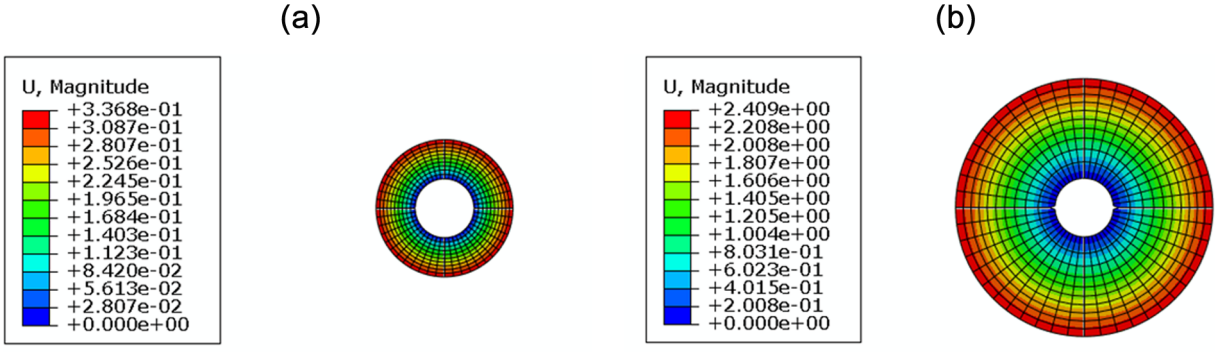

Figure 13. Swelling of a spherical shell on a hard core simulated by ABAQUS via a user subroutine at temperatures (a) 310 and (b) 300 K.

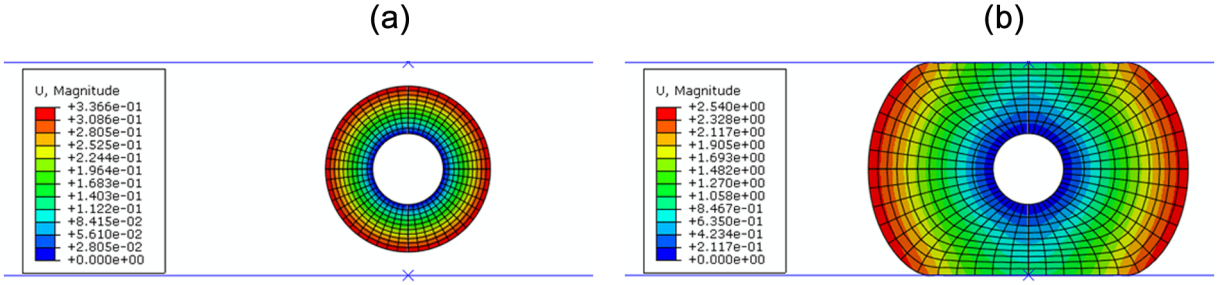

Figure 14. Swelling of a spherical shell on a hard core considering contact between the shell and a channel with rigid flat walls at temperatures (a) 310 and (b) 300 K.

inhomogeneous swelling of a spherical shell on a hard core was analytically studied, and the results were presented for various thicknesses of the shell. Also, the model was implemented in ABAQUS via a user subroutine, and the inhomogeneous swelling of a spherical shell on a hard core, identical to the analytical one, was solved; the results were successfully compared. In the next step, a simulation was conducted for the

complicated problem of contact between the hydrogel shell and a channel with rigid walls where the results were reasonable. Based on the results, it is concluded that the proposed model is capable of being implemented in the homogeneous and inhomogeneous problems without encountering any instability or multiple-solution problem which is a major concern especially in numerical simulations.

Declaration of Conflicting Interests

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