Effects of microstructural parameters on phase transition temperature of hydrogels in chemo-mechanical coupling fields

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Abstract. The stability of hydrogels can be considered as the stability of polymer networks of the gels. The external environment can lead to the change of the polymer networks stability and the phase transition of hydrogels occurs. In this paper, a new free density energy function considering the chain entanglements and functionality of junctions is presented via combining Gent hyperelastic model and Edwards-Vilgis slip-link model with Flory-Huggins theory. A numerical method is developed to solve the phase transition temperature of the hydrogels based on the given new free energy function. Influences of four microstructure parameters on phase transition temperature of hydrogels are investigated by taking PNIPAM hydrogel as an example. Analytical results show that the microstructure parameters might affect the phase transition of the hydrogels significantly.

Keywords: Hydrogel, Microstructural parameters, Phase transition, Chemo-mechanical coupling field

1. Introduction

The responsive hydrogel produces mechanical deformation under stimulations of multi-physical fields, which include temperature [1], ion concentration [2], pH value [3] and electric field [4]. Due to these interesting behaviors, these materials have found novel applications in tissue engineering and drug delivery systems [5], sensors and actuators [6], microfluidics and micro-valves [7]. The sensitive hydrogel possess the characteristic of generating large deformation within a temperature change in a certain range under Multi-field coupling conditions for most of the applications. During the process of large deformation, phase transition may occur [8].

Phase transition of hydrogel refers to a phenomenon that equilibrium swelling volume of hydrogel will show large discontinuous change at one point with the continuous change of external conditions such as temperature or solvent composition. The equilibrium swelling volume of a gel shows a great and discontinuous change at a certain point. Back in 1950s, Flory [9] predicted the existence of phase transition of hydrogel. In 1968, Dusek [10] et al explained the possible reasons of phase transition of hydrogel from mechanism. Until the late 1970s, Tanaka [11] et al has observed the phase transition of hydrogel for the first time during the experiment in the study of acrylamide gel. Subsequently, researchers studied the volume phase transition of NIPAAm gel through experiments [12,13]. However, since the phase transition temperature is affected by many factors, such as mechanical boundary conditions or chemical potential of external solution, the numerical study of phase transition of hydrogel is not popular. To study the phase transition under multi-field numerically, finite element method should be developed. Hong et al. [14] have established FEM (finite element method) for
hydrogels in the equilibrium state. Zhang et al. [15] constructed FEM for transient analysis of concurrent large deformation and mass transport in hydrogels. Based on neutral hydrogel, Cai et al. [8] analyzed the relationship between deformation and temperature with a hybrid parameter. This hybrid parameter is expressed as the function of temperature and polymer concentration. This model can be used to study the deformation behaviour of thermo-sensitive hydrogel under different geometrical and mechanical constraints. Ma et al. [17,18] presented a more precise free energy density function by considering chain entanglements and functionality of junctions. The influence of chain entanglements and junction functionality on the chemo-mechanical behaviour of hydrogels is simulated by this function. Based on the previous work, Cai [8], Ding [19] et al achieved the transition temperature of neutral gel more accurately by solving the energy extreme. In 2016, Mazaheri et al. [19,20] eliminated the numerical instability in the vicinity of phase transition temperature due to multiple solution problems via polynomial expanding, and exhibited phase transition of PH-sensitive hydrogel. However, these studies focused on the numerical explanation of phase transition of hydrogel: some of the studies considered ideal chemical crosslinking condition only with neglecting the effects of sliding phenomenon in actual network composition and microstructure parameters [21] constituting hydrogel to phase-transition temperature of hydrogel; some leads to the error between the solution of phase transition temperature and the experimental data. In this paper, the entanglement effect of high polymer chains and the effect by microstructure parameters of hydrogel on the phase transition are synthetically considered, and a numerical method closer to the reality by solving phase transition of hydrogel. The influence of network sliding and microstructure parameters of hydrogel on the phase-transition temperature of hydrogel has also been studied. Accurate solution of the phase-transition temperature of hydrogel will provide theory and data support for the application of thermos-sensitive gels.

2. Free energy model of hydrogel

Based on Flory-Huggins polymer solution theory, the free energy of a polyelectrolyte gel could be generated from three molecular processes, including stretching of the polymer network, mixing of the networks and the solvents, and mixing of the solvents and mobile ions. It is assumed that the ionizable groups on the polymer chains do not dissociate and the fixed charge on the chains is constant. Based on prior work [8,22], (i) the stretching of the network, (ii) the mixing of the networks and the solvents and (iii) the mixing of the solvents and mobile ions will contribute to the Helmholtz Free energy of the hydrogel.

\[
\psi = \psi_e + \psi_m + \psi_i
\]  
(1)

where \(\psi\) is the total free energy density function of coupled system, \(\psi_e\) is stretch free energy of elastomeric network, \(\psi_m\) is mixture free energy of network and solvent, \(\psi_i\) is mixture free energy of ion and solvent.

\[
\psi_e = \frac{1}{2} N_c RT \left\{ \sum_{i=1}^{3} \lambda_i^2 - 3 - \frac{4}{f} \log J + \frac{N_c}{N_v} \sum_{i=1}^{3} \left[ \frac{(1+\eta)\lambda_i^2}{1+\eta \lambda_i^2} + \ln \left( 1+\eta \lambda_i^2 \right) \right] \right\}
\]  
(2)

\[
\psi_m = \frac{RT}{v_f} \left( v_f C_s \ln \frac{v_f C_s}{J} + \frac{v_f C_s}{J} \chi \right)
\]  
(3)

\[
\psi_i = RT \sum_{\beta=+,-} C'_\beta \ln \left( \frac{C'_\beta}{\sum_{\beta=+,-} C'_\beta} \right)
\]  
(4)
where \( N_c \) is the mole number of the cross-linked polymer chains; \( R \) is the universal gas constant; \( T \) is the absolute temperature; \( \lambda_i (i = 1, 2, 3) \) are the stretches in principal direction; \( f \) is the junction functionality of the cross-links; \( J \) is the swelling ratio of the gel; \( N_s \) denotes the mole number of the slip-links; \( \eta \) is the slippage parameter; \( \nu \) and \( C_s \) are, respectively, the molar volume and mole number of the solvent molecules and \( \chi \) is the Flory parameter charactering the interaction between the solvent and the polymer; \( C^\gamma \) donates mole number of the species \( \gamma \), where the subscripts “+” and “-” denote the cations and anions respectively.

It first assumes that solid polymer, solvent and ion cannot be compressed. Compared to the volume changed by imbibing molecules, the volume changed by physical association of molecules is small due to the low stress level in hydrogel. And because the ion volume is much less than solvent volume, the incompressibility condition is given

\[
J = 1 + \nu J C_s
\]

This paper introduces another free energy density function, since the solvent chemical potential must be constant under the equilibrium state, by using a Legendre transformation.

\[
\hat{\psi} = \psi - \mu C_s
\]

To analyze more general deformations due to the effect of mechanical loading, the function above is written by principal invariants \( I_i (i = 1, 2, 3) \). Based on nonlinear continuum mechanics, as large deformation occurred in gel under multi-physical fields, the principal invariants of Cauchy-Green \( C (C = F^T F) \) are given by

\[
I_i = trC, \quad I_2 = trC^2, \quad I_3 = deC = J^2
\]

Use the Eqs. (1)-(7), we obtain the energy density function as

\[
\hat{\psi}(F, \mu) = \frac{1}{2} N_c RT \begin{align*}
\left[ I_1 - 3 \frac{4}{f} \log J + \frac{N_c}{N_s} \left( \frac{1 + \eta}{1 + \eta \eta_1 + \eta^2 \eta_2 + \eta^3 J^2} \right) \right] \\
- \frac{RT}{\nu_s} \left[ (J - 1) \log \left( \frac{J}{J - 1} \right) - \frac{J - 1}{J} \chi \right] \\
+ RT \sum_{\gamma = +, -} C^\gamma \log \frac{\nu_s C^\gamma}{J - 1} - \frac{\mu}{\nu_s} (J - 1)
\end{align*}
\]

For thermo-sensitive hydrogels, dimensionless mixing parameter in free energy function \( \chi \) is approximately presented as a function of temperature \( T \) and volume fraction of polymer \( \phi \) [4, 5].

\[
\chi(T, \phi) = \chi_0 + \chi \phi
\]

where

\[
\chi_0 = A_0 + B_0 T, \quad \chi_1 = A_1 + B_1 T, \quad \phi = \frac{1}{1 + \nu J C_s} = \frac{1}{J}
\]

Parameters \( A_0, A_1, B_0, B_1 \) vary from gel to gel, and their specific values can be obtained by providing fits to experimental data, which was shown in Table 1 [22].

| Table 1 | Material parameters for the temperature sensitive hydrogel |
|---------|----------------------------------------------------------|
| \( A_0 \) | \( B_0 \) | \( A_1 \) | \( B_1 \) |
| -12.947 | 0.04496 \( K^{-1} \) | 17.92 | \( -0.569 K^{-1} \) |
When \( J = 1 \), Eq. (8) is singular which is caused by the formulae of the free energy of mixing. It leads to singularity in the numerical calculation if a solvent-free state is used as a reference. According to the processing method by Hong et al. [1], state of gel with certain solvent containing is chosen as a reference. Keep dry gel in electrochemical environment with chemical potential as \( \mu \) without other loadings. The gel swells after absorbing water, and the free stretch ratio is \( \lambda \). We have derived the free energy density function with reference to the initial state by introducing deformation gradient formula \( \mathbf{F} = \mathbf{F}_0 \mathbf{F}' \) for the current state of relative drying state.

\[
\psi' \left( \mathbf{F}', \mu \right) = \lambda^{-3} \psi \left( \mathbf{F}, \mu \right) 
\]

(11)

The total free energy density function can be obtained by rearranging equation (12).

\[
\psi' \left( \mathbf{F}', \mu \right) = \frac{1}{2} N_c R T \left[ \frac{\lambda^{-1} \mu}{\lambda_0^3} - \frac{3}{\lambda_0^3} \right] - \frac{4}{J \lambda_0^3} (3 \ln \lambda_0 + \ln J')
\]

\[
+ \frac{\lambda_0^3}{R T} \left[ \frac{(1+\eta)(\lambda_0^5 + 2 \lambda_0^4 \eta + 3 \lambda_0^3 \eta^2 J'^2)}{1+ \lambda_0^5 \eta + \lambda_0^4 \eta^2 + \lambda_0^3 \eta^3 J^2} \right]
\]

\[
+ \log \left( 1 + \lambda_0^5 \eta + \lambda_0^4 \eta^2 + \lambda_0^3 \eta^3 J^2 \right)
\]

\[
+ \frac{RT \lambda_0^3}{V_s} \sum_{\gamma = c+, c-} C_\gamma \log \left( \frac{v_\gamma C_\gamma}{\lambda_0^3 J' - 1} \right) - \frac{\mu}{V_s} \left( J' - \lambda_0^3 \right)
\]

\[
\psi' \left( \mathbf{F}', \mu \right) = \lambda^{-3} \psi \left( \mathbf{F}, \mu \right) 
\]

(12)

It has been shown that swollen hydrogels can be modeled as hyperelastic materials. Build a hyperelastic framework and let \( P'_{ik} \) denotes the first Piola–Kirchhoff stress tensor. For hyperelastic materials, \( P'_{ik} \) is given by

\[
P'_{ik} = \frac{\partial \psi}{\partial F'_{ik}} 
\]

(13)

Let \( \sigma_{ij} \) denotes the Cauchy stress tensor, \( \sigma_{ij} \) and \( P'_{ik} \) are connected by \( \sigma_{ij} = J'^{-1} P'_{ik} F_{ik} \).

In initial swelling state in gel, the true stress should meet \( \sigma_{ij} = 0 \) in gel in the initial chemical environment without any external-force constrain. The relationship between stretch ratio \( \lambda_0 \) in free expansion state and mole number \( \bar{c} \) of cation and anion in surrounding solution can be got.

\[
N_c \left( \lambda_0^5 - 2 \lambda_0^3 J' \right) + \frac{1}{V_s} \left( \log \left( 1 - \lambda_0^3 \right) + \lambda_0^3 + \lambda_0^6 \bar{c} \right)
\]

\[
N_c \left( 1 + \eta \right) \left[ \frac{\lambda_0^{-1} + 4 \eta \lambda_0 + 3 \eta^2 \lambda_0^3}{1 + 3 \eta \lambda_0^2 + 3 \eta^2 \lambda_0^4 + 3 \eta^3 \lambda_0^6} + \frac{\eta \lambda_0^{-1} + 2 \eta^2 \lambda_0 + \eta^3 \lambda_0^3}{1 + 3 \eta \lambda_0^2 + 3 \eta^2 \lambda_0^4 + 3 \eta^3 \lambda_0^6} \right]
\]

\[
+ N_c \left( 1 + \eta \right) \left[ \frac{3 \lambda_0^5 + 6 \eta \lambda_0^4 + 3 \eta^2 \lambda_0^6}{1 + 3 \eta \lambda_0^2 + 3 \eta^2 \lambda_0^4 + 3 \eta^3 \lambda_0^6} \right]
\]

\[
\left( \frac{z^c C^c}{\lambda_0^3 - 1} \right)^2 + 4 \bar{c}^2 - 2 \bar{c}
\]

(14)

3. Phase transition

Phase transformation of hydrogels has obtained many scholars' attention [23,24]. Some thermosensitive hydrogels show a phase transition temperature, near where the hydrogels have the greatest
volume transition but have the minimum change of temperature. The swelling process of gel can be regarded as a kind of hydration reaction. Different phases have different amount of hydration, which is closely related to the polymer structure and the mixed degree of the solvent and polymer network. Affected by many factors, such as mechanical boundary conditions and chemical potential of external solution, it is very difficult to obtain the accurate value of phase transition temperature so far. There are two equal local minima in free energy density function $\psi$ at phase transition temperature, which respectively corresponds to two different deformation gradient $F_1$ and $F_2$ under specific chemical potential $\mu$ and temperature $T^*$. 

$$\hat{\psi}(F_1, \mu, T^*) = \hat{\psi}(F_2, \mu, T^*)$$

In this case, the temperature $T^*$ is named phase transition temperature. We studied phase transition temperature of thermo-sensitive hydrogels by using the numerical method. To study the phase transition temperature of hydrogel, we take the case of dry neutral PNIPAM gel cube, whose functionality is 4 and the fixed charge density is 0. We adopt 8-node brick elements to model the gel cube. In the modeling, the hydrogel block is constrained to prevent rigid-body motion but is allowed to swell freely. Based on Eq. (14), the free energy density function of the cubic under free swelling can be written as:

$$\frac{\mu \psi}{RT} = \frac{1}{2} N_c \nu \left( I_1 - 3 - \log J \right) - \left[ \left( J^{-1} \right) \log \left( \frac{J - 1}{J - 1} \right) - \frac{J - 1}{J} \left( \chi_0 + \chi_1 \right) \right]$$

where $J$ is volume swelling ratio; due to isotropic free swelling of gel, stretch ratio in three directions are equal, then $I_1 = 3J^{2/3}$. Under the above condition, according to Eq.(14), in pure water the free swelling stretch ratio $\lambda_0$ should be met with the following formula,

$$N_c \nu \left( \lambda_0^{-1} - 2\lambda_0^{3/4} / 4 \right) + \log(1 - \lambda_0^{3/2}) + \lambda_0^{-3} + \frac{\chi_0 - \chi_1}{\lambda_0^6} + \frac{2\chi_1}{\lambda_0^2} = 0$$

In order to observe the phase transition temperature, we establish the relations between dimensionless free energy density function and expanding volume ratio at different temperatures, as shown in Figure 1.

It can be seen that at low temperature, when $T$ is equal to 303 K, the free energy function has only one local minimum (at the larger expansion volume ratio), which indicates that the hydrogel keep a stable expansion state at this temperature. At high temperature, when $T$ is equal to 307 K, the free energy function also has only one local minimum (at the minor expansion volume ratio), which indicates that the hydrogel keep a stable contracting state at this temperature. However, when $T$ is about 305 K, the free energy function has two local minimums and one local maximum (for two stable states and one unstable state, respectively). The smaller minimum corresponds to the stable equilibrium state, the larger the minimum corresponds to the metastable equilibrium state, and the maximum corresponds to the unstable state. Figure 2 illustrates the relationship between the hydrogel stretch ratio and the temperature under the condition of free expansion.

The phase transition temperature is located between the two temperature extreme points A and B (Figure 2). In the temperature range of phase transition, the phase transition temperature, extreme points A and B correspond to three stretch ratios, i.e., the three equilibrium states of the hydrogel at the same temperature. Based on the analysis of Figure 1, one is the unstable state. It should be pointed out that only one steady state can be obtained in the finite element simulation, which means it cannot be simulated from one state to another at the same time. At a specific temperature $T^*$, there are two local minimum values in the free energy function corresponding to the two equilibrium states of the hydrogel. If the two local minimum values are equal, the temperature $T^*$ is the phase transition temperature.
4. Effect of microstructure parameters on phase transition

For a general situation, we can use eq. (12) to find out the phase transition temperature. The method is searching for the global minimum of the developed energy function at every temperature. Then, the phase transition temperature could be found out. The effects of microstructural parameters on the phase transition temperature of the hydrogels in chemo-mechanical fields are involved. For simplicity, the molar concentrations of mobile ions in the surrounding solution are normalized by $1/\nu$, and the stress is normalized by $RT/\nu$ in this article. Several dimensionless parameters ($N_c\nu$, $N_s\nu$, $f$ and $\eta$) are introduced. For the hydrogels, $(N_c + N_s)\nu$ varies from $10^{-3}$ to $10^{-1}$, and the values of $\eta$ possess an allowable range of 0.1 to 0.6.
Table 2 Variations of the phase transition temperature to the polyelectrolyte gel for different functionality

| \( f \)  | 2.00 | 3.00 | 4.00 | 5.00 | 6.00 | 7.00 | 8.00 | \( \infty \) |
|---------|------|------|------|------|------|------|------|------|
| \( T^* \)(K) | 304.46 | 304.60 | 304.71 | 304.76 | 304.79 | 304.82 | 304.84 | 304.94 |

It can be seen from Table 2 that the phase transition temperature of the gel is significantly related to the functional degree of the gel. The higher the functional degree, the higher the phase transition temperature of the gel, and vice versa. The effect of gel temperature closure energy was significant when the functional degree was lower than that of gel temperature. Because the essence of gel phase transition is the change of gel stability, that is, the change of network mechanical property stability. When the function degree is small, the change of \( f \) will significantly change the osmotic volume elastic modulus of the gel, so the phase change temperature will change significantly. As the official energy gradually increases, its contribution to the elastic energy of the gel gradually increases, but the relative influence of the same change value of \( f \) on the elastic energy of the gel decreases, until the functional degree of the gel approaches to infinity, the phase change temperature gradually approaches to a certain fixed value.

Table 3 Variations of the phase transition temperature to the polyelectrolyte gel for different molar concentration of polymer network

| \( N'\nu \) | 0.01 | 0.02 | 0.03 | 0.04 | 0.05 | 0.06 |
|-----------|------|------|------|------|------|------|
| \( T^* \)(K) | 305.07 | 304.33 | 303.72 | 303.17 | 302.64 | 302.13 |

We can observe that when the constant total mole number of polymer networks increases from 0.01 to 0.06, the phase transition temperature has a sharp decrease. As the hydrogel is consist of polymer network. The molar concentration of polymer network might lead to a significant change of hydrogel properties, which may cause the sharp decrease of the phase transition temperature.

Table 4 Variations of the phase transition temperature to the polyelectrolyte gel for different sliding parameters

| \( \eta \) | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 |
|-----------|------|------|------|------|------|------|
| \( T^* \)(K) | 305.06 | 305.13 | 305.17 | 305.19 | 305.20 | 305.21 |

In Table 4, we can focus on the change of phase transition temperature under different sliding parameters. It can be seen from the Table that the phase transition temperature of the gel increases with the increase of the sliding parameters. When the sliding parameter is low, this effect is most obvious, that is, when \( \eta = 0.01 \) sliding parameters has most significant influence on the phase transition temperature. When the sliding parameters increase to \( \eta = 0.04 \), the sliding chain has little effect on the phase transition temperature of the gel.

In Table 5, we can also see that the phase transition temperature of the gel is significantly different for the slip-links with different volume fraction. When the molar concentration of polymer network is high, the phase transition temperature goes up as the volume fraction of the slip-links goes up. While the molar concentration of polymer network is low, the higher the volume fraction of the sliding chain, the higher the gel phase transition temperature. At a certain molar concentration of polymer network, the phase transition temperature does not vary with the volume fraction of the slip-links.
Table 5 Variations of the phase transition temperature to the polyelectrolyte gel for different volume fraction of the slip-links

| ϕ   | 0   | 0.2 | 0.4 | 0.6 | 0.8 | 1   |
|-----|-----|-----|-----|-----|-----|-----|
| T^*(K)(Nυ=0.05) | 302.63 | 302.55 | 302.50 | 302.43 | 302.40 | 302.39 |
| T^*(K)(Nυ=0.03) | 303.73 | 303.69 | 303.69 | 303.70 | 303.70 | 303.73 |
| T^*(K)(Nυ=0.01) | 305.07 | 305.09 | 305.12 | 305.17 | 305.22 | 305.31 |

5. Conclusions
Responsive hydrogels exhibit phase transition behavior under specific conditions. In this paper, a free energy density function is introduced which takes into account the entanglement effects of chain of polymer network constituting hydrogel and microstructure parameters of hydrogel. The free energy minimums of hydrogels under different conditions are compared by programming, and the phase transition temperature of the PNIPAM hydrogel is accurately calculated by numerical methods. The effect of microstructure parameters of hydrogel on the transition temperature is discussed, and some conclusions are as follows:

1. The stability of the hydrogel can be regarded as the mechanical stability of the network structure constituting hydrogel in phase transition. The stability can be judged by the free energy minimum of hydrogel.

2. The swelling process of hydrogel can be regarded as a hydration reaction. Different phases have different hydration, which are closely related to the structure of polymers and the microstructural parameters of solvent/polymer networks. The molar concentration of the polymer network is negatively correlated to the gel transition temperature. The functionality of hydrogel network and the sliding parameters of the hydrogel network is positively correlated to the transition temperature of hydrogel. The slip links affect the gel transition temperature, and is affected by the molar concentration of the polymer network.

The free energy function of hydrogel applied by this thesis contains topological information of network entanglement and the influence of microstructure parameters of hydrogel, which can truly reflect the phase transition of hydrogel in chemo-mechanical coupling field. The investigation to phase transition temperature can provide effective numerical reference for the research of hydrogel devices under complex mechanics.

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