The Influence of Entanglements of Net Chains on Phase Transition Temperature of Sensitive Hydrogels in Chemo-Mechanical Coupled Fields

Tao Li¹, Qingsheng Yang¹,* , Lianhua Ma² and Xiaojun Zhang²,*

Abstract: Phase transition of hydrogel, which is polymerized by polymer network, can be regarded as the transition of polymer network stability. The stability of the polymer network might be changed when the external environment changed. This change will lead to the transformation of sensitive hydrogels stability, thus phase transition of hydrogel take place. Here, we present a new free density energy function, which considers the non-gaussianity of the polymer network, chains entanglement and functionality of junctions through adding Gent hyplastic model and Edwards-Vilgis slip-link model to Flory-Huggins theory. A program to calculate the phase transition temperature was written based on new free energy function. Taking PNIPAM hydrogel as an example, the effects of network entanglement on the phase transition temperature of hydrogel were studied by analyzing the microstructure parameters of the hydrogel networks. Analytical results suggest a significant relationship between phase transition temperature and entanglement network.

Keywords: Sensitive hydrogel, entanglements, phase transition, chemo-mechanical coupling fields.

1 Introduction

Previous studies suggested that the stimulation of multi-physical fields induced sensitive hydrogel mechanical deformation. The known physical field mainly includes temperature field [Depa, Strachota, Šlouf et al. (2012)], ion concentration field [Hong, Zhao and Suo (2010)], pH value field [Kurnia, Birgersson and Mujumdar (2012); Qu, Zhao, Ma et al. (2017)], and electric field [Li (2009)]. Because of their unique characteristics, the sensitive hydrogels show new breakthrough in the field of tissue engineering [Wang, Qian, Zhao et al. (2017)], drug delivery systems [Mandru, Bercea, Gradinaru et al.]

¹ Department of Engineering Mechanics, Beijing University of Technology, Beijing, 100124, China.
² College of Civil Engineering and Architecture, Hebei University, Baoding, 071002, China.
* Corresponding Authors: Qingsheng Yang. Email: qsyang@bjut.edu.cn; Xiaojun Zhang. Email: zxj1998@hbu.edu.cn.
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(2019)], sensors [Guo, Li and Zhou (2013); Wang and Zhang (2019)], microfluidics and micro-valves [Mazaheri, Baghani, Naghdabadi et al. (2015)], and supercapacitor [Zhao, Li and Wang (2018)]. In a certain temperature range, the sensitive hydrogel produces large deformation under Multi-field coupling conditions, during which phase transition may occur [Cai and Suo (2011)].

Phase transition of hydrogel refers to a phenomenon that equilibrium swelling volume of hydrogel presents large discontinuous change at one point with the continuous change of external environment. To be specific, at a certain point, the equilibrium swelling volume of hydrogen has a high and discontinuous change. Back in 1950s, Flory et al. [Flory and Rehner (1943)] predicted the existence of phase transition of hydrogel. In 1968, Dusek et al. [Dusek and Patterson (1968)] explained the possible mechanisms of phase transition of hydrogel. Until the late 1970s, Tanaka et al. [Tanaka (1978); Tanaka, Fillmore and Sun (1980)] reported the phase transition of hydrogel for the first time in a study of acrylamide gel experimentally. Subsequently, researchers studied the volume phase transition of both nonionic gel [Hirokawa and Tanaka (1984)] and ionized gel [Hirotsu, Hirokawa and Tanaka (1987)] through experiments. Furthermore, the effect of solvent on the hydrogel [Hirotsu (1987)] has also been investigated. On that basis, many insightful explorations on the hydrogel phase transition phenomenon were carried out by using experimental methods. Jung et al. [Jung, Macconaghy, Kaar et al. (2017)] studied the influence factors of gel phase transition at the micro level. Wu et al. [Wu, Li, He et al. (2018)] studied the effect of GO content on gel phase transition in composite gel. Yao et al. [Yao, Pratyush, Balazs et al. (2018)] and Kim et al. [Kim, Kim, Lee et al. (2016)] explored the control method and application on phase transitions. However, since the phase transition temperature is affected by many factors, including mechanical boundary conditions or chemical potential of external solution, the numerical study of phase transition of hydrogel remain elusive. To study the phase transition under multi-field numerically, finite element method should be developed. Hong et al. [Hong, Liu and Suo (2009)] have established FEM (finite element method) for hydrogels in the equilibrium state. Zhang et al. [Zhang, Zhao, Suo et al. (2009)] constructed FEM for transient analysis of concurrent large deformation and mass transport in hydrogels. Based on neutral hydrogel, Cai et al. [Cai and Suo (2011)] analyzed the relationship between deformation and temperature with a hybrid parameter. This hybrid parameter is expressed as the function of temperature and polymer concentration, which can be used to understand the deformation behavior of thermo-sensitive hydrogel under different geometrical and mechanical constraints. Based on previous work, Ding et al. [Ding, Liu, Hu et al. (2013)] achieved the transition temperature of neutral gel more accurately by solving the energy extreme. In 2016, Mazaheri et al. [Mazaheri, Baghani and Naghdabadi (2016a); Mazaheri, Baghani, Naghdabadi et al. (2016b)] 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 hydrogel phase transition only considering ideal chemical crosslinking condition with neglecting...
the effects of sliding phenomenon in actual network composition and effects of microstructure parameters [Yang, Ma and Shang (2013)]. This may leads to the deviation between the solution of phase transition temperature and the experimental data. Yang et al. [Yang, Ma and Shang (2013); Ma, Yang and Yang (2015)] 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 behavior of hydrogels is simulated by this function. Following these studies, Li et al. [Li, Yang, Ma et al. (2019)] put forward a new formula to describe the large deformation of hydrogel under coupling fields by using a non-Gaussian model [Gent (2012)].

There are many experimental measurement methods for phase transition temperature of different hydrogels, but the results obtained by these measurement methods always show different values. As the phase transition temperature for a particular kind of hydrogel should be a fixed value, the measuring errors in experimental may have a negative effect for us to understand the effect of hydrogel microstructure on hydrogel phase transition from the mechanism. Further more, the numerical simulation method is also a common tool for study hydrogel phase transition. However, the current numerical simulation models either apply the ideal model by ignoring many influencing factors in the real phase transition process, or ignore the fact that the phase transition of hydrogel is a discontinuous process, which makes it impossible to obtain accurate phase transition temperature. In this paper, we aim to achieve accurate theoretical phase transition temperature of hydrogel by introducing a theoretical model, which is in conformity with the actual situation of hydrogel as closely as possible. The influence of network sliding and microstructure parameters of hydrogel on the phase-transition temperature of hydrogel has also been studied based on the proposed theoretical model. Accurate solution of the phase transition temperature of hydrogel will provide theoretical and experimental support for better application of thermos-sensitive gels.

2 Free energy density of temperature-sensitive hydrogel with phase transition

The polyelectrolyte hydrogel will show coupled deformation behavior, while immersed in solution. The hydrogel and the absorbed solution are considered to be one system, and the energy change of the system can be represented by Helmholtz free energy formula [Hong, Zhao and Suo (2010)]. Based on Flory-Huggins polymer solution theory, three molecular processes constitute the free energy of a polyelectrolyte hydrogel: stretching energy of the polymer networks, mixing energy of the networks with the solvents, and mixing energy of the solvents with the mobile ions. In this case, the total free energy density function of the coupled system $W$ can be expressed as:

$$W = W_c + W_m + W_i$$ (1)

Hydrogel is a kind of three-dimensional network structure that is cross-linked by polymer network. However, in the actual preparation of the gel, it is difficult to obtain an ideal
chemical cross-linked polymer network form, in which most of the uncross-linked polymer monomers form entangled sliding chains. In other words, there are two typical polymer network structure forms at the micro level of hydrogel, as shown in Fig. 1. The most common free energy models of hydrogels consider that, in the ideal case, the gels only form chemical crosslinking networks, while the role of sliding chains in gel deformation is ignored. As an additional structural form of cross-linked network, the sliding chain will slide relatively during the deformation process, which can improve the elastic modulus of the gel. The number of sliding chains and the difficulty degree of entanglement network will affect the increase of elastic modulus caused by sliding chains.

![Polymer network formation and microstructure of hydrogel](image)

**Figure 1:** Polymer network formation and microstructure of hydrogel

In addition, the structure of chemical crosslinking network is characterized by the functionalities $f$ of crosslinking points. Functionality refers to the number of polymer chains connected to a crosslinking point, representing the number of functional groups contained in each monomer molecule. Under the influence of the preparation conditions, the cross-linked polymer networks for hydrogel may have different functionalities. Fig. 2 shows the crosslinked form of polymer network with different functional degrees. It can be seen from the figure that the higher functional degree is, the more complex polymer network structure is and the more chain segments will be involved in the hydrogel deformation process, resulting in the increase of elastic modulus. The traditional free energy models do not take the influence of the structure.

![Diagram of crosslinking network functionality](image)

**Figure 2:** Diagram of crosslinking network functionality
of cross-linked network (namely, functionality) into account. In this paper, we try to represent the real condition of hydrogel polymer network through introducing the microstructure parameters related to the functionality of the sliding chain and gel cross-linked network and discuss the influence of the effects of microstructural parameters on phase transition temperature of hydrogels in chemo-mechanical fields. Thus, the stretch free energy of elastomeric network can be expressed as Li et al. [Li, Yang and Ma et al. (2019)]:

\[
W_c = -\frac{1}{2} N_c R T \left\{ J_{lim} \ln \left( 1 - \frac{\sum_{i=1}^{3} \lambda_i^2 - 3}{J_{lim}} \right) + \left( \frac{4}{J} - 2 \right) \ln J \right\}
\]

\[
- \frac{N_c}{N_c} \sum_{i=1}^{3} \left[ \frac{(1+\eta)\lambda_i^2}{1+\eta \lambda_i^2} + \ln \left( 1 + \eta \lambda_i^2 \right) \right]
\]

where, \( W_c \) is mixture free energy of network with solvent, \( W_i \) is mixture free energy of ion with solvent [Ma, Yang and Yang (2015)].

\[
W_m = \frac{RT}{v_s} \left( v_s C_s \ln \frac{v_s C_s}{J} + \frac{v_s C_s}{J} \kappa \right)
\]

\[
W_i = RT \sum_{\beta = +, -} C^\beta \left( \ln \frac{C^\beta}{\sum_{\beta = +, -} C^\beta} \right)
\]

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; \( v \) 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; \( C^\beta \) donates mole number of the species \( \beta \), where the subscripts “+” and “−” denote the cations and anions respectively.

First, we assume 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. Because the ion volume is much less than solvent volume, the incompressibility condition is given as:

\[
J = 1 + v_s C_s
\]
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.

\[ \dot{W} = W - \mu C_s \]  

(6)

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

\[ I_1 = \text{tr} C, \quad I_2 = \text{tr} C^2, \quad I_3 = \text{det} C = J^2 \]  

(7)

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

\[
\dot{W} = -\frac{1}{2}N_c RT \left\{ \begin{array}{c}
J_{\text{lim}} \ln \left( \frac{I_1}{J_{\text{lim}}} - 1 \right) \left( \frac{4}{J - 2} \right) \ln J \\
- \frac{N_s}{N_c} \left[ (1+\eta)(I_1 + 2\eta I_2 + 3\eta^2 J^2) \right] + \log \left( 1 + \eta I_1 + \eta^2 I_2^2 + \eta^3 J^2 \right) \\
- \frac{RT}{v_s} \left[ (J-1) \log \left( \frac{J}{J-1} \right) - \frac{J - 1}{J} \right] - \frac{\mu}{v_s} (J - 1)
\end{array} \right\} 
\]

(8)

For thermo-sensitive hydrogels, dimensionless mixing parameter in free energy function is approximately presented as a function of temperature and volume fraction of polymer \( \varphi [\text{Li (2009)}] \).

\[ \chi(T, \varphi) = \frac{Z_1}{1 + v_s C_s} = A_0 + B_0 T + \frac{(A_1 + B_1 T)}{J} \]  

(9)

The parameters vary from gel to gel, and their specific values can be obtained by providing fits to experimental data, which was shown in Tab. 1 [Afroze, Nies and Berghmans (2000)].

**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 | -0.0569 K\(^{-1}\) |

It has been shown that swollen hydrogels can be modeled as hyperelastic materials. Build a hyperelastic framework and let \( P_{ik} \) denote the first Piola-Kirchhoff stress tensor. For hyperelastic materials, is given by
Let $\sigma_{ij}$ denote the Cauchy stress tensor, and are connected by $\sigma_{ij} = J^{-1} P_{ik} F_{jk}$.

In initial swelling state in gel, the true stress should meet in gel in the initial chemical environment without any external-force constrain. The relationship between stretch ratio in free expansion state and mole number of cation and anion in surrounding solution can be got.

$$N_c \left( \lambda^{-1} - 2 \lambda^{-3} / f - \lambda^{-4} \right) + \frac{1}{v_s} \left( \log \left(1 - \lambda^{-3}\right) + \lambda^{-3} + \lambda^{-6} \right)$$

$$+ N_s (1+\eta) \left[ \frac{\lambda^{-1} + 4 \eta \lambda + 3 \eta^2 \lambda^3}{1 + 3 \eta \lambda + 3 \eta^2 \lambda^4 + \eta^3 \lambda^6} \right] + \frac{1}{v_s} \left( \frac{\eta \lambda^{-1} + 2 \eta^2 \lambda + \eta^3 \lambda^3}{(1 + 3 \eta \lambda + 3 \eta^2 \lambda^4 + \eta^3 \lambda^6)} \right)$$

$$= \sum_{\beta=+,-} \frac{C_\beta}{\lambda^3 - 1} + \frac{\mu_0}{RT v_s} \left(3 \lambda^2 + 6 \eta \lambda^3 + 3 \eta^2 \lambda^6\right) (\eta \lambda^{-1} + 2 \eta^2 \lambda + \eta^3 \lambda^3)$$

Phase transformation of hydrogels has obtained many scholars’ attention [Jung, Macconaghy, Kaar et al. (2017); Wu, Li, He et al. (2018); Yao, Pratyush, Balazs et al. (2018); Kim, Kim, Lee et al. (2016)]. Some thermo-sensitive 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. The volume phase transition is a consequence of the hydrogen bond between PNIPAM and water and hydrogen bond between water and water. It can be seen from the insertion diagram that hydrogen bond between PNIPAM and water and hydrogen bond between water and water are both easy to form at low temperature. The attraction between PNIPAM and water is due to hydrogen bond interaction, which provides a driving force for gel swelling. When there are more hydrogen bonds between PNIPAM and water formation, the driving force of gel volume swelling increases. However, formation of hydrogen bonds between solvent molecules may cancel out the driving stress, which can limit the gel swelling. When the number of hydrogen bond between PNIPAM and water is larger than that between water and water, the cancellation is partial. However, the formation of hydrogen bond between water and water reduces the translational entropy between solvent molecules, and increases the repulsive volume interaction. In this case, the gel presents as a dry swelling process at low temperature. 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. There are two equal local minima in free energy density function $W$ at phase transition temperature, which respectively corresponds to two different deformations gradients $F_1$ and $F_2$ under specific chemical potential and temperature $T^*$ conditions.

$$\dot{W}(F_1, \mu, T^*) = \dot{W}(F_2, \mu, T^*)$$  \hfill (12)

In this case, the temperature 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. Based on Eq. (8), the free energy density function of the cubic under free swelling can be written as:

$$\frac{\nu_s W}{RT} = \frac{1}{2} N_c \nu_s \left[ J_{lim} \left( 1 - \frac{I_1}{J_{lim}} \right) - \ln J \right] - \frac{1}{2} \left[ (J-1) \log \left( \frac{J}{J-1} \right) - \frac{J-1}{J} \left( \frac{\lambda_0 + \lambda_1}{\lambda_0} \right) \right]$$  \hfill (13)

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. (11), in pure water the free swelling stretch ratio $\lambda$ should be met with the following formula.

$$N_c \nu_s \left( \lambda_0^{-1} - 2\lambda_0^{-3/4} - \lambda_0^{-4} \right) + \log \left( 1 - \lambda_0^{-3} \right) + \lambda_0^{-3} + \frac{\lambda_0}{\lambda_0^2} + \frac{\lambda_1}{\lambda_0^4} = 0$$  \hfill (14)

In order to observe the phase transition temperature, we established the relations between dimensionless free energy density function and expanding volume ratio at different temperatures, as shown in Fig. 3. At low temperature, when $T$ is equal to 304 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, $T = 306$ 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. Fig. 4 illustrates the relationship between the hydrogel stretch ratio and the temperature under the condition of free expansion.

The Fig. 4 shows a comparison among our result, traditional analytical result obtained by Ding et al. [Ding, Liu, Hu et al. (2013)] and experimental data for the relationship between temperature and swelling ratio. The solid curves are obtained analytically for the free swelling of hydrogel at crosslink density $N_c \nu_s = 0.005$ and the triangle symbols represent test results reported by Suzuki et al. [Suzuki and Ishii (1999)]. These three sets of data matching well. As our analytical result shows, the phase transition temperature is located between the two temperature extreme points A and B. We define the temperature region between A and B as phase transition temperature region which is estimated
analytically. In the region of phase transition temperature, there are three swelling ratios at a certain temperature. These three swelling ratios correspond to three equilibrium states of the hydrogel at the same temperature. Based on the analysis of Fig. 3, 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. When it comes to experimental methods, phase transition temperature region has other definition. As reported [Suzuki and Ishii (1999)], the phase transition temperature could

**Figure 3:** Variations of free energy with swelling volume ratio at different temperatures

**Figure 4:** The relationship between temperature and swelling ratio
be found by slightly changing the temperature around the phase transition temperature. But hysteresis might be occurred during the process of phase transition temperature testing experiment due to the phase coexistence. That is to say, the phase transition temperature measured by heating the gel is higher than the real phase transition temperature, and vice versa. Therefore, the real phase transition temperature lies between the two phase transition temperatures measured by heating and cooling process respectively. This temperature interval is defined as phase transition temperature in the experiment, as the shadow shown in Fig. 4. The results obtained in this paper is also consistent with traditional analytical result. As the traditional analytical methods ignore the defects in the polymer network and the statistical mechanical properties of polymer network when the hydrogel has large deformation, the results obtained by the traditional analytical methods are smaller than that of the present model. As observed in Fig. 4, the present analytical results are closer to the phase transition temperature region obtained by the experiment than those provided by the traditional analytical method.

To study the free swelling of hydrogel in environmental solution, the changing regular pattern of hydrogel stretch ratio with temperature can be obtained by calculating the minimum value of the hydrogel free energy function at different temperatures, as shown in Fig. 5. As shown in Fig. 5, the gel stays in a swelling state at low temperature (swollen gel). With the increase of temperature, PNIPAM gel began to shrink. When the temperature reaches the critical temperature, there is a change from swelling to shrinkage, and at high temperature it becomes totally shrunken (shrunken gel). It is observed that when the temperature is in the lower range, the stretch ratio decreases with the increase of temperature. The lower the density of chemical crosslinking chain is, the larger the stretch ratio is. The change of the relative phase transition temperature is very small as crosslinking chain density varies. Therefore, the phase transition temperature of the

![Figure 5: Variations of the stretch ratio of the hydrogel with temperatures](image-url)
hydrogel is unaffected by the crosslinking chain density. The same temperature corresponds to multiple stretch ratios in the phase transition temperature range (as shown in Fig. 5 dotted line range), which shows that in a certain temperature range, the free swollen hydrogel has more than one stable state. In addition, the stretch ratio changes very little with temperature, and the stretch ratio of different crosslinking chain density is almost equal away from the phase transition temperature. Under high temperature conditions, the number of the hydrogen bonds decreased. Hydrophobic association of PNIPAM increases and repulsive force between PNIPAM and water increase under all conditions. On this basis, the solvents turn into undesirable solvents, which are good for gel swelling, so gel has little shrink volume under high temperature conditions.

Fig. 6 shows the relationship between the swelling ratio and the ion concentrations. The swelling deformation behavior of the hydrogel varies at different temperatures. The free stretch ratio decreases with the increase of the ion concentration of external solution. There is a phase transition ion concentration at a low temperature. For ion concentration of external solution reaches a certain value, the hydrogel generates distinct volume deformation that is a phase transition course. The gel expansion rate changes very little when the ion concentration of the external solution exceeds the critical value. Phase transition ion concentration is almost zero at high temperatures, and hydrogel expansion is insensitive to the ion concentration change of external solution.

3 Effect of microstructure parameters on phase transition

Due to the numerical instability problem described in this section, the Cai’s et al. [Cai and Suo (2011)] model is a numerically expensive choice to be implemented in FE framework or employed in an inhomogeneous problem. To eliminate the snap through instability and the
multiple-solution problem in the vicinity of PTT Region for temperature sensitive PNIPAM hydrogels researchers use a polynomial expression for the mixing part of the free energy. But in this method discontinuous phase transition cannot be observed. To study the phase transition phenomenon, a program was written to establish the relationship among the microstructure parameters of the gel, the external environment parameters (mainly chemical potential or concentration and temperature in the chemo-mechanical coupling field) and the phase transition temperature. The influence of these parameters on the gel phase transition under the effect of the chemically mechanical coupling could be explored.

The specific process is shown in Fig. 7. Firstly, the two minimum values of dimensionless free energy are obtained through choosing randomly temperature in the PTT temperature region of the hydrogel. Then the phase transition temperature can be calculated by use of dichotomy method and double sides approximate process. Where, \( T_n \) is the temperature at step n, and the initial temperature \( T_0 \) is a random value of temperature taken from the phase transition temperature region, \( P_m \) is the temperature incremental step, where the step is less than half of the region length of PTT region, \( W_A \) is dimensionless free energy in a stable collapsed phase, \( W_B \) is dimensionless free energy in a stable swollen phase, \( J_A \) is volumetric change rate of gel in a stable collapsed phase, \( J_B \) is volumetric change rate of gel in a stable swollen phase.

But it should be emphasized that the phase transition temperature is obtained by comparing the energy minimum value of the two phases in which the phase transition happens. The energy is related only to the state of the corresponding hydrogel (the energy minimum value corresponds to the stable state) and not to the intermediate steps that are taken. So the choice of initial temperature has no effect on the solution. We can take any temperature in the phase transition temperature interval as the initial temperature, and the corresponding hydrogel structure parameters as the initial conditions.

The phase transition temperature of hydrogel under different external conditions was calculated by using this developed program. In order to study the effects of different microstructure parameters on the phase transition temperature of hydrogel, the relation that phase transition temperature changing with specific parameters can be obtained by changing a single parameter and inputting it one by one. The effects of microstructural parameters \( \eta, f, N_c, v_s + N_s, \varphi \), related to the three-dimensional polymer network in the hydrogel, on the phase transition temperature of the hydrogel were examined. The specific calculated results are further discussed in detail below. For the hydrogels, \( \varphi = \frac{N_s}{N_c + N_s}, \quad N_v = (N_c + N_s)v_s \) and the values of \( \eta \) possess an allowable range of 0.1 to 0.6.

Shown in Fig. 8, the phase transition temperature of the gel is significantly related to the functional degree of the gel. The higher of the functional degree, the higher the phase transition temperature of the gel, and vice versa. The number of active functional groups on the polymer chain is called the functional degree, which refers to the average functional degree of the gel material. The function of the system has a great influence on the structure of polycondensate. For example, when \( f = 1 \), only low-molecular substances
can be formed; when \( f = 2 \), polymer chains begin to form; only when \( f > 2 \) can conditions be met for the formation of branched polymers or bulk polymers. The degree of hinge of macromolecular chain increases with the increase of function. When \( f \) increases, the phase transition temperature increases. We reasoned that in the gel with higher functionality, the crosslinking degree is higher, and the network structure of the gel is denser. It is more difficult for the polymer network to lose water and curl into clusters, so it requires a higher temperature to make more PNIPAM-H\(_2\)O hydrogen bond breaks before the phase transition occurs. Therefore, the phase transition temperature rises. The effect of gel temperature closure energy was significant when the functional degree was lower than that of gel temperature. The essence of gel phase transition is the change of

![Figure 7: Calculation flow chart of phase transition temperature](image_url)
gel stability, that is, the change of network mechanical property stability. When the function degree is small, the change of $f$ will significantly affects 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. In Fig. 8, the phase transition temperature of the gel is significantly different for the slip-links with different volume fraction. The higher the volume fraction of the sliding chain, the higher the gel phase transition temperature. However, the influence of functional degree on gel phase transition is basically the same in the trend.

As shown in Fig. 9, when the molar concentration of high polymer chain increases, there will be more entangled high polymer networks in the hydrogels of the same volume, meaning that there are more functional groups in the same volume of hydrogels. The essence of phase transition in the gel is the shrinkage of the polymer chains caused by the breakup of PNIPAM-H$_2$O bonds at high temperature. When the molar concentration increases, the number of broken PNIPAM-H$_2$O bonds for gel phase transition is easier to reach to make the gel molecular chain curled. So the phase transition temperature of the gel will go down.

Fig. 10 shows that the phase transition temperature increases slowly with the increase of hydrogel sliding parameter. As mentioned earlier, curling and stretching of high polymer that forming three-dimensional gel network is the fundamental cause for the volume phase transition of the hydrogels. The work should be done to overcome the elastic
energy stored up in the hydrogels by the curling and stretching process. For the polymer network, a sliding chain model proposed by Edwards et al. [Edwards and Vilgis (1986)] can be used to describe the elastic energy during gel deformation. The corresponding elastic entropy can be expressed as

\[ \Delta S_e = NS_0 \frac{C_1}{C_0} \sum_{i=1}^{3} \left[ \frac{(1+\eta \lambda_i^2)}{1+\eta \lambda_i^2} + \ln(1+\eta \lambda_i^2) \right]. \]

As seen from the equation that the elastic entropy decreases as the sliding parameter increases,

Figure 9: Variations of the phase transition temperature with the molarity of the polymer chains

Figure 10: Variations of the phase transition temperature with sliding parameter
and the corresponding elastic energy $W_{el} = -T \Delta S_e$ increases gradually. The working of volume phase transition against elastic energy tends to increase. In the view of microscopic, it indicates that more PAM-H$_2$O hydrogen bonds need to be broken. The temperature for inducing hydrogen bond break needs to be higher, which is the corresponding phase transition temperature of hydrogel. Therefore, the phase transition temperature increases with the increase of hydrogel sliding parameter.

In Fig. 11, we focused on the change of phase transition temperature under different slip-links volume fraction. The phase transition temperature of the gel decreases with the increase of the sliding chain volume fraction at high molar concentration. When the slip chains are close to the chemical cross-linking chains in the gel, the effect is most obvious, that is, $\varphi = 0.5$ slip-links has significant influence on the phase transition temperature. When the gel crosslinking is perfect or chemical crosslinking is very low, the sliding chain has little effect on the phase transition temperature of the hydrogel.

![Figure 11: Variations of the phase transition temperature with the volume ratio of the slip-links](image)

When the volume fraction of slip-links changes with the constant total mole number of polymer networks, we can observe that at small concentration of the surrounding solution, the higher of the slip-links volume fraction, the higher swelling ratio of the hydrogel is. This is because that formation of sliding chain mainly depends on the intermolecular force, which is smaller than the interaction of intramolecular valence bond that form entanglement chain. Hydrogel is more easily dispersed during the process of absorbing water and swelling, and then the polymer network becomes looser and the swelling of the hydrogel becomes easier, and vice versa.

### 4 Conclusions

Responsive hydrogels exhibit phase transition behavior under specific conditions. In this paper, we introduced free energy density function, which considers the entanglement effects of chain of polymer network constituting hydrogel and microstructure parameters of hydrogel. The free energy minimum of hydrogel under different conditions is compared
by program. In contrast, 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 critical conclusions are as follows:

(1) The steady state of the hydrogel can be viewed as the mechanical stability of the polymer network structure. The stability can be evaluated by the free energy minimum of hydrogel. The phase transition temperature and phase transition concentration of hydrogel can be solved by comparing the free energy minimum of hydrogel network in different coupling fields.

(2) There are errors in the measurements of experimental data due to many factors, such as temperature drift, boundary condition perturbation, preparation process of hydrogel and so on. Even because of the exhibiting of the phase coexistence, the experiment cannot measure the real phase transition temperature. As a method to study phase transition of hydrogel, analytical method can be used to obtain the certain phase transition temperature, which is fitting well with the measured phase transition temperature region. Therefore, analytical method can provide significant support for the researchers to study the phase transition of hydrogel in the coupling fields.

(3) The polymer network structure and the microstructural parameters leads to different amount of hydration in different phases. The gel transition temperature is negatively correlated to the molar concentration of the polymer network and positively correlated to the functionality of hydrogel network and the sliding parameters. The slip links affect the gel transition temperature, and is affected by the molar concentration of the polymer network. To be specific, the free energy function of hydrogel adopted in this article takes into account of topological information of network entanglement and the influence of microstructure parameters of hydrogel. Therefore, the function can be considered as the reflection on actual phase transition of hydrogel in chemo-mechanical coupling field. The phase transition temperature is discussed in this paper, and numerical reference for hydrogel devices under complex mechanics can be provided by the experimental data and simulation results.

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