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# The Phase Transition Model for Heat-Shrinkable Thermo-Sensitive Hydrogels Based on Interaction Energy

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**Abstract.** A biphase mixture continuum mechanics model is derived for neutral heat-shrinkable thermo-sensitive hydrogels in this paper. The mixing free energy of the special mixture is recalculated based on the partition function of Bose system, and it evaluates the contribution of the hydrophilic, hydrophobic interaction and hydrogen bonding to the volume phase transition behaviors. The ideas of the Flory lattice theory and the UNIFAC group contribution method are employed to get the expression of the mixing free energy. Then we deduce a particular model by combining this mixing free energy with the conservation laws equations and constitutive relations of both phases to predict the volume transition behaviors of these special hydrogels.

**AMS subject classifications**: 76A05, 76T99, 35Q92, 92E10

**Key words**: Heat-shrinkable thermo-sensitive hydrogels, volume phase transition, free energy, Flory lattice theory, group contribution method, conservation law equations.

## 1 Introduction

Hydrogel is a kind of macromolecular materials which are constructed by swelled hydrophilic polymers and the absorbed water in the interspace of polymer networks. There are complex micro-structure [26], phase transition process [27] and large deformation [25]. An environmental stimuli-responsive hydrogel or the smart hydrogel is the hydrogel which would undergo discrete or continuous volume transformations in response to infinitesimal changes of the external environment, such as the pH of the solution, the electric field, the solvent composition, the temperature, the salt concentration or the light, etc [15]. The thermo-sensitive hydrogel is a kind of smart hydrogels. It can sense

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the variation of the external temperature and respond to it by imbibing or extruding fluid from the surroundings. For a thermo-sensitive hydrogel, there is a critical temperature in which it undergoes the volume phase transition. There are heat-shrinkable hydrogels and heat-swellable thermo-sensitive hydrogels. The former will lose its water and shrink when the temperature increases, and the latter will absorb water and swell with the rising of temperature. Here, we pay our attention on the heat-shrinkable hydrogel and call its critical temperature as its LCST (lower critical solution temperature). Poly(N-isopropylacrylamide) (PNIPAAm) is a particular kind of these hydrogels because its LCST is around $33^{\circ}C$ which is very close to the temperature of human body. At the temperature lower than $33^{\circ}C$, uncross-linked PNIPAAm can be dissolved in water and form a colorless and transparent liquid solution. When the temperature is increased beyond this temperature, the solution separates into two liquid phases with different concentrations of the polymers and the thicker part turns white and turbid [23]. This particular property makes it potential to be used as sensor or inductor or in drug control and release system.

It can be explained for the volume transition of the heat-shrinkable thermo-sensitive hydrogels as follows. This kind of hydrogels contain both hydrophilic amide groups and hydrophobic alkyl groups which interact with water molecules in the solution. When the temperature is lower than its LCST, the polymer is dissolved in water. And the interaction between the polymer and water is the hydrogen bonding interaction between amide groups and hydrones. At this time, the hydrones around the polymer chains are forming a highly ordered solvent shell connected by hydrogen bonds. With the rising of temperature, the hydrophobic effect is growing, and the solvent shell is broken. When the temperature rises to a certain value, water molecules will dissolve out from hydrogels and the phase transition behaviors happen [23].

The characteristics of volume phase transition of the smart hydrogels have drawn considerable attentions. In recent decades, people have got a lot of achievements in prediction of the phase transition behaviors of thermo-sensitive hydrogels by establishing mathematical models and molecular simulation ( [14, 15] and references therein). The well-known mathematical models are the collective diffusion model [19], the hydrodynamic model [6,18], the continuum theory model [1,8,10,11], etc. The collective diffusion model was firstly proposed by Tanaka based on the assumption of the linear elasticity and the small deformation ignoring shear energy and the relative motion between the crosslinked polymer networks and the fluid in the hydrogels' swelling process [22]. This original theory was further improved by Wang et al. [21] and T.Yamaue et al. [24]. The most extensively used thermodynamic model was derived by Flory [6] in 1953 for description of the equilibrium volume transition of the hydrogels. The free energy of the hydrogels is assumed to be a sum of the mixing free energy due to the mixing process and the elastic free energy due to the swelling process and the ionic contributions. Then the chemical potentials of both phases and osmotic pressure acting on the hydrogel network can be derived according to their thermodynamical relationships with the free energy. In the continuum theory, both the solid phase and the liquid phase are assumed to be

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incompressible and continuous in the whole region of the mixture with the introduction of the concepts of the volume fraction of both phases. The conservation laws of mass, momentum and energy conservations of the two phases and the mixture were smoothly derived by Atkin et al. [1] or Hassanizadeh et al. [10,11]. They provided good theoretical framework for studying of the process of the volume phase transition of the two-phase or multi-phase mixtures.

In addition, M. Doi [5] provided a kinetic model about solid neutral hydrogels. It can be used to study the swelling and squeezing of gels. Cai et al. [3] established a phase transition model of isotropic thermo-sensitive hydrogels. It can explain the sensitive phase transition behaviors according to the variation of the temperature of square shaped and spherical hydrogels. Furthermore, they provided general theoretical framework for the phase transition behaviors of anisotropic neutral thermo-sensitive hydrogels. However, all of these models mentioned above cannot evaluate the contribution of the hydrophilic, hydrophobic effects and hydrogen bonding towards the phase transition behaviors of the hydrogels. Molecular simulation has more advantages on this aspect because it can construct nearly perfect networks with well-defined structures and study the dynamic and structural characteristics of the hydrogels. It also can provide better understanding of the mechanism of both polymer-solvent interaction and polymer network conformation. However, it is very computationally intensive and time-consuming, so it is limited to the hydrogels with relatively small structures [15].

In this paper, we will set up a model which integrates the advantages of both the previous mathematical models and molecular simulation to predict the volume phase transition behaviors of the neutral heat-shrinkable thermo-sensitive hydrogels. We start our work by recalculating the mixing free energy of these special hydrogel. We first point out the shortage of the classical Flory-Huggins mixing free energy in calculating the contribution of interaction between the polymer chains and the water molecules. After that, we introduce a new model based on the assumptions that the contribution of water molecules in the mixture to interaction energy works like the particles in the Bose system, and use it to calculate the mixing free energy of this special material. Then we apply this new model to PNIPAAm and analyze its reliability. Finally, we combine the related theoretical achievements with our new results to deduce the particular theoretical framework for these special hydrogels.

## 2 Notations

In this section, we briefly introduce some notations. Let $\mathbf{X}=(X_1,X_2,X_3)$ and $\mathbf{x}=(x_1,x_2,x_3)$ represent the position of a material point at the initial time and the present time respectively. $\alpha$ denotes the phase of polymer $(p)$ or the liquid phase-water $(f)$. $t$ and $T$ are time and absolute temperature, respectively. $T^\alpha$ is the absolute temperature of the phase $\alpha$. $\phi^\alpha$ and $\varphi^\alpha$ denotes the volume fraction of the phase $\alpha$ in the initial state and the present state. $\rho^\alpha$ is the real density of the phase $\alpha$, and $\mathbf{v}^\alpha$ means the velocity of phase $\alpha$. $\Omega$ is any

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spatial region with boundary $\Gamma$. $A_{ij}=(\frac{\partial x_i}{\partial X_j})$ is the symbol of deformation gradient tensor. The material derivative of the physical quantity $\Xi^\alpha$ is given by

$$\frac{D\Xi^\alpha}{Dt}=\Big(\frac{\partial}{\partial t}+\mathbf{v}^\alpha\cdot\frac{\partial}{\partial \mathbf{x}}\Big)\Xi^\alpha.$$

The volume fraction of the phase $\alpha$ in the present point $\mathbf{x}$ at the time $t$ is defined as

$$\phi^\alpha(\mathbf{X},t)=\varphi^\alpha(\mathbf{x}(\mathbf{X},t),t)=\frac{v^\alpha(\mathbf{x}(\mathbf{X},t),t)}{v^\alpha(\mathbf{x}(\mathbf{X},t),t)+v^\beta(\mathbf{x}(\mathbf{X},t),t)},$$

where $v^\alpha(\mathbf{x}(\mathbf{X},t),t)$, $v^\beta(\mathbf{x}(\mathbf{X},t),t)$ denote the volume occupied by the phases $\alpha$, $\beta$ at the time $t$, respectively. It is easy to get that

$$\sum_\alpha\phi^\alpha(\mathbf{X},t)=\sum_\alpha\varphi^\alpha(\mathbf{x}(\mathbf{X},t),t)=1.$$

# 3 Free energy

In this section, we will first give a brief review of the classical Flory free energy theory. Then we provide a new expression for the mixing free energy for the heat-shrinkable thermo-sensitive hydrogels.

## 3.1 Preliminaries

### 3.1.1 The classical Flory free energy of a polymer solution

According to the thermodynamics theory, the free energy plays a crucial role in describing the thermodynamical property of a system. It determines the equilibrium state of a system. And it is closely related to the chemical potential of each phase and osmotic pressure of the solution. The most widely used theory about the free energy of the polymer solution is the Flory's mean field theory in which the total increment of free energy of the ionized thermo-sensitive hydrogels, $\Delta G_{gel}$, can be expressed as [6, 15]:

$$\Delta G_{gel}=\Delta G_{mixing}+\Delta G_{elastic}+\Delta G_{ion},$$

where $\Delta G_{mixing}$, $\Delta G_{elastic}$ and $\Delta G_{ion}$ denote the mixing, elastic deformation and ionic contributions to the change of free energy, respectively. For the neutral thermo-sensitive hydrogels, it can be derived as:

$$\Delta G_{gel}=\Delta G_{mixing}+\Delta G_{elastic}.$$

By the Flory-Huggins lattice theory, the variation of mixing free energy caused by changing the solvent-solvent contact into the solvent-polymer contact may be written as [6, 12]

$$\Delta G_{mixing}=\kappa_B TN\Big(\varphi^f\ln\varphi^f+\frac{\varphi^p}{x}\ln\varphi^p+\chi\varphi^f\varphi^p\Big). \tag{3.1}$$

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Here, $N$ is the total number of the lattices occupied by polymer chains and water molecules. $\kappa_B$ is the Boltzmann constant. $x$ is the average density of crosslink of the polymer chains. $\chi$ is the Huggins parameter depending on both the absolute temperature and the volume fraction of each phase, and $\chi\kappa_B T$ denotes the energy variation created by putting a solvent molecule to the polymer networks. It is well-known that the expression (3.1) is derived from the following three assumptions [12]:

1. The polymer in the solution is aligned in the form of lattice. Each solvent molecule occupies one lattice. Each macromolecule occupies $x$ different coterminous lattices.

2. The polymer chains are flexible enough, and every configuration of the chains has the same energy.

3. The probability that each lattice is occupied by every chain segment or water molecule is equal.

In this model the entropy is employed and regarded as number of the possibilities that the spatial distribution of the polymer chains may engage in. And then the expression of the mixing free energy of the mixture was derived according to its thermodynamical relationship with entropy. It provides us a lattice theory idea, and makes it possible to do further study on modeling and analyzing the volume transition behaviors. However, the assumptions above make this model exist some disadvantages listed as following, and this model has the potentiality to be improved.

1. According to the thermodynamics and statical physics, the state of a solution means the distributional consequences of its total energy to each molecule and each group on the polymer chains. The entropy of the solution means the number of the distributional ways in a certain macro state. In this paper, macro state of the solution indicates its specified total energy, temperature and the number of the polymer chains and the hydrones. Therefore, different locations or different forms of the polymer chains may be identified as the same energy state.

2. The interactions between different groups of polymer chains are different with each other. This makes the probability of each configuration of polymer chains different.

3. The interaction of different groups with the hydrone is different, and this makes the possibility of a hydrone adjacent to them different.

For the contribution of elastic deformation to the change of free energy, Flory also established the affine model to calculate it. A lot of work have been done to improve it, here we will not come down to it.

### 3.1.2 The group contribution method

The group contribution method is one of the most widely used method to study the quantitative relationship between the configuration and the activity of molecules. It uses the

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principle that some simple aspects of the structures of chemical components are always the same in many different molecules. It regards the property of pure components or mixtures as the resultant contributions of their ingredient groups to this special property. This method is established on the Langmuir independent action principle. In this theory, there are no interactions between groups which have the fixed contribution to a particular property of the substance. On this basis, lots of properties of complex molecules will be obtained approximately at least [20].

According the group contribution method, we can predict the properties of all kinds of pure substances and mixtures from dozens of contribution parameters of the ingredient groups. Therefore, it is widely used to predict various physical and chemical properties of compounds, such as the solubility in water, activity coefficients, the boiling temperature, the standard entropy of ideal gas and the entropy of mixing, etc.

One of the frequently used group contribution methods is UNIFAC (Universal quasi-chemical Functional Group Activity Coefficients [7]) group-contribution method, which is very important to calculate activity coefficients. This method is based on the Guggenheim's liquid solution lattice theory and Wilson's local components concept. In the framework of UNIFAC group contribution method, the interaction parameters of all kinds of groups are got from existing phase equilibrium data. Then they are used to predict the phase equilibrium data of the systems which there is no experimental data.

The UNIFAC group contribution method assumes that the logarithm of activity coefficient is the sum of component part and the remaining part. The former part is determined by the difference between the sizes and shapes of molecules, and only posses the property of pure substances. And the latter is determined by the interaction energy. For the $i$-th component in any solution, we have

$$\ln\gamma_i=\ln\gamma_i^C+\ln\gamma_i^R. \tag{3.2}$$

1. The activity coefficient of the component part $\ln\gamma_i^C$ is expressed as

$$\ln\gamma_i^C=\ln\frac{\Phi_i}{x_i}+\frac{z}{2}q_i\ln\frac{\theta_i}{\Phi_i}+l_i-\Phi_i x_i-\frac{\Phi_i}{x_i}\sum x_j l_j. \tag{3.3}$$

Here,

$$\theta_i=\frac{q_i x_i}{\sum q_j x_j}, \tag{3.4}$$

$$\Phi_i=\frac{r_i x_i}{\sum r_j x_j}, \tag{3.5}$$

and satisfy

$$\sum\theta_i=1,\quad \sum\Phi_i=1,\quad l_i=\frac{z}{2}(r_i-q_i)-(r_i-1). \tag{3.6}$$

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Coordination numbers:

$$z=10,\quad r_i=\sum_k v_k^{(i)}R_k,\quad q_i=\sum_k v_k^{(i)}Q_k. \tag{3.7}$$

In the above expressions, $x_i$ is the molar fraction of the $i$-th component. $v_k^{(i)}$ is the number of the $k$-th group in the $i$-th kind molecule. $R_k$ is the van der Waals volume of the $k$-th group. $Q_k$ is the van der Waals surface area of the $k$-th group. $\theta_i$ is the van der Waals surface area fraction of the $i$-th group. $\Phi_i$ is the average volume fraction of the $i$-th component.

2. The remaining part activity coefficient $\ln\gamma_i^R$ can be got from

$$\ln\gamma_i^R=\sum_k v_k^{(i)}[\ln\Gamma_k-\ln\Gamma_k^{(i)}], \tag{3.8}$$

where

$$\ln\Gamma_k=Q_k\left[1-\ln\left(\sum_m\Theta_m\Psi_{mk}\right)-\sum_m\frac{\Theta_m\Psi_{km}}{\sum_n\Theta_m\Psi_{nm}}\right], \tag{3.9}$$

$$\Theta_m=\frac{Q_mX_m}{\sum_nQ_nX_n}, \tag{3.10}$$

$$X_m=\frac{\sum_j v_m^{(j)}x_j}{\sum_j\sum_n v_n^{(j)}x_j},\qquad j=1,2,\cdots,M;\quad n=1,2,\cdots N, \tag{3.11}$$

$$\Psi_{nm}=\exp\left(-\frac{a_{nm}}{T}\right). \tag{3.12}$$

The expression of $\ln\Gamma_k^{(i)}$ is similar to (3.9). In (3.9)-(3.12), $i$, $j$ is the number of component. $M$ is the total number of the kinds of the components. $N$ is the total number of the groups. $\Theta_m$ is the surface area fraction of groups in the solution. $X_m$ is the fraction of the $m$-th group in the solution. $T$ is the absolute temperature. The parameter $a_{nm}$ is the interaction parameter of groups. They evaluate the interaction between these groups and assumed to be independent with the temperature. Generally, $a_{nm}\neq a_{mn}$, and $a_{mm}=0$. $a_{nm}$ and $a_{mn}$ are obtained from experimental data of phase equilibrium state, and more datas of groups can be got from the table of UNIFAC-$\gamma^\infty$ group interaction parameters.

The basic assumption of the UNIFAC group contribution method is that the same group has the same contribution in different molecules or solutions. Actually, the same group definitely has different contribution to different molecules or solutions. This model treats groups in a unified way, so it can not be used when two strong groups are neighboring and can not distinguish isomers [20]. Lots of work has been done to improve its accuracy. In this paper, we only apply the key idea of the method instead of overcoming its weakness.

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So far, this method has been widely used in gas-liquid equilibria, liquid-liquid equilibria, and predicting the solubility of substances in different solvents, etc. However, it has seldom been used in the field of concentrated polymer solution. Hydrogels are some kind of concentrated polymer solution. In this paper, we propose to apply this idea to calculate the contribution of interaction between different groups in the hydrogels and to test its validity.

## 3.2 New expression of mixing free energy

In this part, we will establish a new model to calculate the mixing free energy of the heat-shrinkable thermo-sensitive hydrogels and analyze it with the related thermodynamic equilibrium theory.

### 3.2.1 Assumptions in the new model

Here the ideas of lattice theory and the UNIFAC group contribution method are employed to build the new model. The thermodynamics and statistical physics theory related with Bose system are used to study the exact contribution of the interaction energy to the volume phase transition of the neutral heat-shrinkable thermo-sensitive hydrogel. We assume that the mixture has the following properties.

1. It contains $N_0$ hydrones. $v_0$ is the volume of each hydrone. There are at most $m_0$ hydrones close to one hydrone.

2. It has $N$ polymer chains, and each one has $n_0$ units. The volume of each unit is $v$. Each unit has $s$ kinds of group in the same way. The maximum number of the hydrone next to the $i$-th group on a special unit is $m_i$.

3. The total energy contained in dry polymer networks is $E_0$. The average interaction energy between the $i$-th group and all the other kinds of groups in the dry material is $\varepsilon_i^0$. (To simplify the model, we apply the postulation $a_{nm}=a_{mn}$, which may cause errors.)

4. The interaction energy between two neighboring hydrones is 0. The interaction energy between the $i$-th group and one hydrone adjacent to it is $\varepsilon_i$. And the interaction energy between a hydrophilic group with a hydrone is negative, while a hydrophobic group with a hydrone is positive.

Then we have the following results:

1. The total volume of the solvent is $V=n_0Nv+N_0v_0$.

2. The volume fraction of polymer in the solvent is

$$\varphi=\frac{n_0Nv}{n_0Nv+N_0v_0}. \tag{3.13}$$

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3. The volume fraction of the water is

$$1-\varphi=\frac{N_0v_0}{n_0Nv+N_0v_0}. \tag{3.14}$$

Combining (3.13) and (3.14), we have

$$n_0N=\frac{1}{v}(n_0Nv+N_0v_0)\varphi=\frac{V}{v}\varphi, \tag{3.15}$$

$$N_0=\frac{1}{v_0}(n_0Nv+N_0v_0)(1-\varphi)=\frac{V}{v_0}(1-\varphi). \tag{3.16}$$

4. The variation of the energy caused by putting a hydrone, instead of other groups, into one position adjacent to one $i$-th group $\Delta E_i$ is $\varepsilon_i-\varepsilon_i^0$.

5. The total energy in the system equals the initial energy of the dry polymer networks $E_0$ and the variation in the solvent due to the replacement of the hydrones $\Delta E$, noting that total interaction energy between hydrones is 0.

We can find out that $\Delta E$ is caused by the addition of hydrones to the polymer chains. It equals the total energy that is derived from the substitution of the hydrones to any other kind of group. We define the energy of each hydrone as the energy variation caused by itself. Therefore, the hydrones in the solution act like independent, identically distributed and undistinguishable particles, the particles in a Bose system.

### 3.2.2 The expression of mixing free energy of heat-shrinkable thermo-sensitive hydrogels in the new model

In this section, the volume fraction of the polymer chains is simplified as $\varphi$. A hydrone has $s+1$ energy levels if the following three assumptions are satisfied:

1. The hydrone in the solution is regarded as particle in the Bose system;

2. The interaction of one hydrone with any kind of the polymer group is taken as a special energy level of this hydrone;

3. The interaction energy between two adjacent hydrones, zero, is assumed as its last energy level.

The coordination number or the degeneracy of the $i$-th energy is $\omega_0=\frac{1}{2}m_0N_0$, and the coordination number of the $(s+1)$-th energy level is $\omega_0=\frac{1}{2}m_0N_0$. The partition function of these $N_0$ water molecules is:

$$Z=\sum_{i=1}^{s}\omega_i\exp(-\beta\Delta E_i)+\omega_0=\sum_{i=1}^{s}m_in_0N\exp(-\beta\Delta E_i)+\frac{1}{2}m_0N_0.$$

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Therefore,

$$\ln Z = \ln\left[\sum_{i=1}^{s} m_i n_0 N \exp(-\beta\Delta E_i) + \frac{1}{2} m_0 N_0\right].$$

By formula (3.15) and (3.16), we obtain

$$\ln Z = \ln\left[\sum_{i=1}^{s} m_i \frac{V}{v}\varphi \exp(-\beta\Delta E_i) + \frac{1}{2} m_0 \frac{V}{v_0}(1-\varphi)\right].$$

So the expression of entropy of the solution can be written as:

$$S = N_0\kappa_B\left(\ln Z - \beta\frac{\partial}{\partial\beta}\ln Z\right) - \kappa_B \ln(N_0!),$$

where $\beta = \frac{1}{\kappa_B T}$. The free energy can be deduced as

$$\begin{aligned} F &= E_0 - N_0\kappa_B T \ln\frac{Z}{N_0} - \kappa_B T N_0 \\ &= E_0 - N_0\kappa_B T \ln\frac{\sum_{i=1}^{s} m_i \frac{V}{v}\varphi\exp(-\beta\Delta E_i) + \frac{1}{2}m_0\frac{V}{v_0}(1-\varphi)}{\frac{V}{v_0}(1-\varphi)} - \kappa_B T\frac{V}{v_0}(1-\varphi) \\ &= E_0 - \kappa_B T\frac{V}{v_0}(1-\varphi)\ln\left[\sum_{i=1}^{s} m_i\frac{v_0}{v}\frac{\varphi}{1-\varphi}\exp(-\beta\Delta E_i) + \frac{1}{2}m_0\right] - \kappa_B T\frac{V}{v_0}(1-\varphi). \end{aligned} \tag{3.17}$$

Let

$$m = \sum_{i=1}^{s} m_i \frac{v_0}{v}\exp(-\beta\Delta E_i),$$

then

$$F = E_0 - \kappa_B T\frac{V}{v_0}(1-\varphi)\ln\left(\frac{m\varphi}{1-\varphi} + \frac{1}{2}m_0\right) - \kappa_B T\frac{V}{v_0}(1-\varphi). \tag{3.18}$$

Thus

$$\frac{\delta F}{\delta\varphi} = \kappa_B T\frac{V}{v_0}\left\{\ln\left[\frac{(m-\frac{1}{2}m_0)\varphi + \frac{1}{2}m_0}{1-\varphi}\right] - \frac{(m-\frac{1}{2}m_0)(1-\varphi)}{(m-\frac{1}{2}m_0)\varphi + \frac{1}{2}m_0}\right\}. \tag{3.19}$$

In the equilibrium state, we have $\frac{\delta F}{\delta\varphi} = 0$. Therefore,

$$\ln\left[\frac{(m-\frac{1}{2}m_0)\varphi + \frac{1}{2}m_0}{1-\varphi}\right] - \frac{(m-\frac{1}{2}m_0)(1-\varphi)}{(m-\frac{1}{2}m_0)\varphi + \frac{1}{2}m_0} = 0. \tag{3.20}$$

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### 3.2.3 Numerical test

In this section, we will test our new expression of the mixing free energy (3.18) by applying it to a kind of heat-shrinkable thermo-sensitive hydrogels, Poly(N-isopropylacrylamide) (PNIPAAm). Because of the special property of the neutral heat-shrinkable thermo-sensitive hydrogels, different temperatures may lead to different volume fraction of the polymer chains in equilibrium state. The volume fraction of the polymer chains will increase when the temperature increases and will change sharply when the temperature changes around the LCST of the hydrogel. We plot the figure $\varphi$ against $T$ in (3.20) with different parameter settings and observe the contributions of both the hydrophilic and hydrophobic groups on the polymer chains to its volume phase transition behaviors.

The N-acrylamide (AAm) synthesized by monomers is a kind of thermo-sensitive hydrogels. A subtle change of outside temperature can lead to its discontinuous phase transformation. Poly(N-isopropylacrylamide) (PNIPAAm) is a special kind of such hydrogels [23]. The overwhelming majority of its chain segments are constituted of a hydrophilic amide group and some hydrophobic hydrocarbon-based groups [4]. The amide group consists of two small hydrophilic groups: -CO- and -NH-. It can supply about seven positions for hydrones nearby itself. (Here seven and numbers hereafter twenty, one, five, six, three, two are only assumptions based on the space geometric configurations of the chain segments of this polymer and the water molecules. They are applied only for simplification instead of deriving from the UNIFAC group contribution method. This part could be improved.) The hydrophobic groups consist of -CH=CH-, -$CH(CH_3)_2$, and could offer around twenty seats for hydrones adjacent itself. The volume of one segment is about seven times large as a hydrone. We start our numerical testing from a simplified assumption that both all the hydrophilic and hydrophobic groups have separate equivalent effect with $\sum_{i_1} m_{i_1} \frac{v_0}{v} \approx 1$ and $\sum_{i_2} m_{i_2} \frac{v_0}{v} \approx 5$. (Here and in the following paragraph, $i_1$ and $i_2$ denote the variety of the hydrophilic and hydrophobic group, separately). There are at most six hydrones near a special hydrone, then we have $\frac{m_0}{2} = 3$.

Firstly, the contribution of the hydrophilic groups, -CO- and -NH-, is taken into consideration. The hydrophobic effect is ignored from the start point. (The following interaction parameters are obtained by referring the table of UNIFAC-$\gamma^{\infty}$ group interaction parameters [20]. they are not exactly equal any values provided in the table, but they belong to their reasonable range [20].) If $-\frac{\triangle E_{i_1}}{\kappa_B}$ is set as 450, 750, 1000, 1500, 2500, 7500 separately, $m$ is taken as $\exp(\frac{450}{T})$, $\exp(\frac{750}{T})$, $\exp(\frac{1000}{T})$, $\exp(\frac{1500}{T})$, $\exp(\frac{2500}{T})$, $\exp(\frac{7500}{T})$, respectively. Fig. 1 shows the correlation of the volume fraction of polymer under equilibrium state $\varphi$ with temperature $T$ in this case.

From Fig. 1(a), (b), (c), we can see that as the temperature $T$ increases, the dependent variable $\varphi$ first increases then decreases when the hydrophilic interaction is relatively lower. Here and below, we use $T_{\max}$ to denote the temperature which gives the maximum value of $\varphi$. As shown in Fig. 1, stronger hydrophilic effect leads bigger $T_{\max}$. This may be attributed to the reason that when $T$ goes up, $m$ goes down. The effect of

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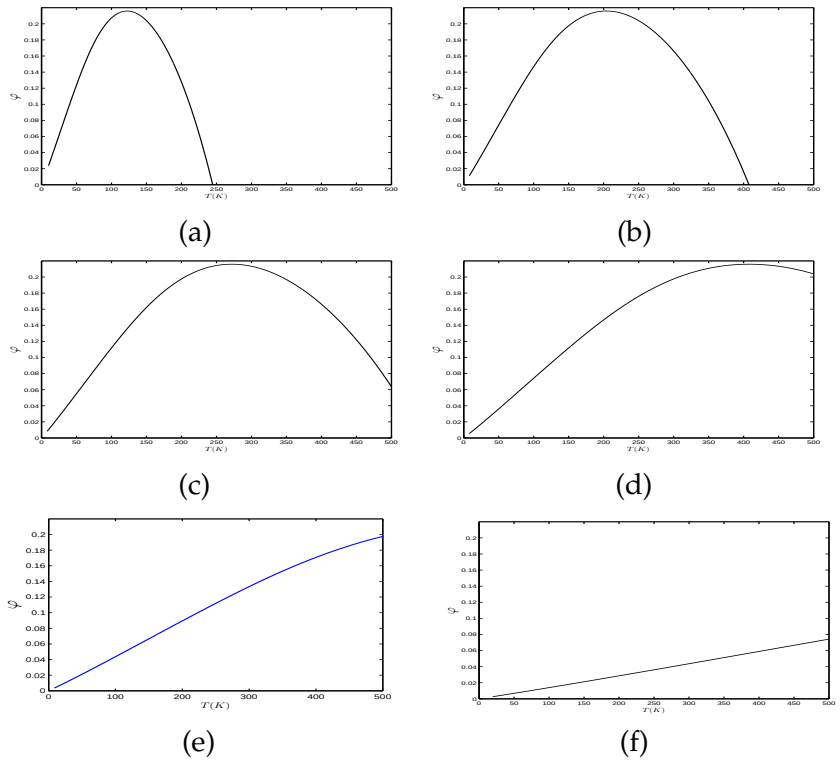



Figure 1: The correlation of the volume fraction of polymer under equilibrium state $\varphi$ with temperature $T(K)$. $m_0=3$ in all of these figures, (a): $m=\exp(\frac{450}{T})$, (b): $m=\exp(\frac{750}{T})$, (c): $m=\exp(\frac{1000}{T})$, (d): $m=\exp(\frac{1500}{T})$, (e): $m=\exp(\frac{2500}{T})$, (f): $m=\exp(\frac{7500}{T})$.

hydrophilic interaction is decreasing because of more vigorous activity of polymer segments and water molecules. $T_{\max}$ is around $300K$ when $m=\exp(\frac{1000}{T})$. This accords with the property of PNIPAAm to some extent. And $\varphi$ increases as increasing of $T$ all the time if the hydrophilic interaction is relatively higher as displayed in Fig. 1(d), (e), (f). If the hydrophilic interaction energy is much higher, $\varphi$ increases linearly as $T$ increases, and the rate of increase is lower when the interaction energy is higher.

Next we consider the contribution of hydrophobic groups. From our undisplayed numerical test, we found that, it is inappropriate to ignore the hydrophilic at any case. Since this, we select $-\frac{\triangle E_{i_1}}{\kappa_B}=1000$, and set $-\frac{\triangle \varepsilon_{i_2}}{\kappa_B}$ in every figure is 0, $-2500$, $-500$, $-100$, $-20$, $-5$, separately, $m$ in each figure is $\exp(\frac{1000}{T})$, $\exp(\frac{1000}{T})+5\exp(-\frac{2500}{T})$, $\exp(\frac{1000}{T})+5\exp(-\frac{500}{T})$, $\exp(\frac{1000}{T})+5\exp(-\frac{100}{T})$, $\exp(\frac{1000}{T})+5\exp(-\frac{20}{T})$, $\exp(\frac{1000}{T})+5\exp(-\frac{5}{T})$ accordingly. In this case, the correlation $\varphi$ with $T$ is shown as Fig. 2. It is observable from this group of figures that the role of the hydrophilic interaction is dominant, and the hydrophobic groups play the role of lessing the decreasing rate of $\varphi$ when $T>T_{\max}$. $\varphi$ declines more slowly at the range $T>T_{\max}$ with less value of $\frac{\triangle \varepsilon_{i_2}}{\kappa_B}$. This could be due to

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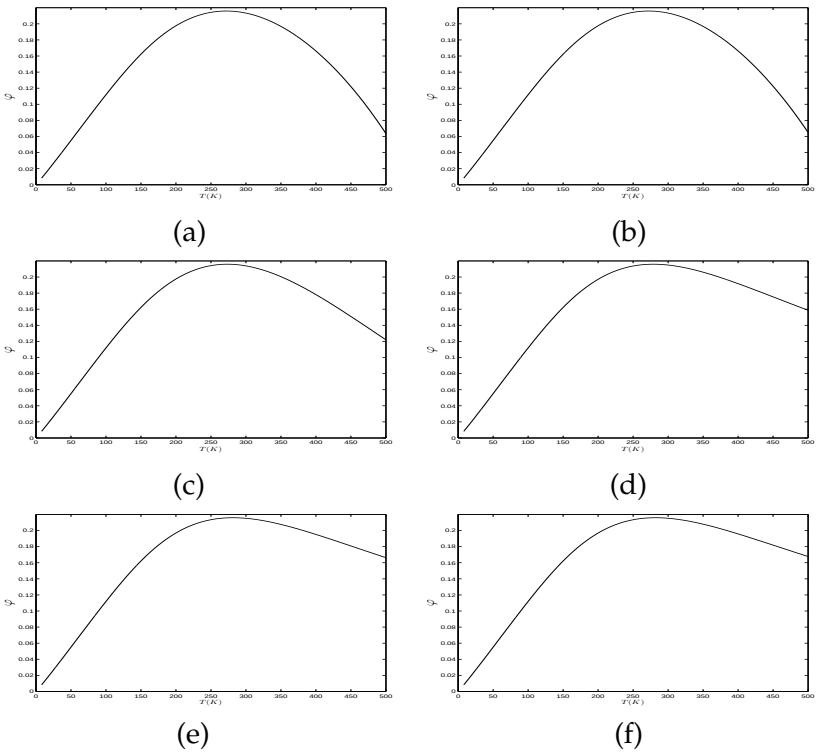



Figure 2: the correlation of the volume fraction of polymer under equilibrium state $\varphi$ with temperature $T(K)$. $m_0=3$ in all figures (a): $m=\exp(\frac{1000}{T})$, (b): $m=\exp(\frac{1000}{T})+5\exp(-\frac{2500}{T})$, (c): $m=\exp(\frac{1000}{T})+5\exp(-\frac{500}{T})$, (d): $m=\exp(\frac{1000}{T})+5\exp(-\frac{100}{T})$, (e): $m=\exp(\frac{1000}{T})+5\exp(-\frac{20}{T})$, (f): $m=\exp(\frac{1000}{T})+5\exp(-\frac{5}{T})$.

that the existence of the hydrophobic groups deactivate the hydrophilic ones, and reduce the tendency of them dissolving out from the solution. In addition, the smaller value $\frac{\triangle\varepsilon_{i_2}}{\kappa_B}$ leads relatively larger $-\frac{\triangle\varepsilon_{i_2}}{\kappa_B}$ and bigger $m$, which is a little analogous to increase the hydrophilic effect.

Finally, the correlation of these two variables $\varphi$ and $T(K)$ is discussed under the assumption that both the interaction of two hydrophilic groups and the hydrophobic interaction are different. $m$ in every small figure are set by

$$0.5\left(\exp\left(\frac{150}{T}\right)+\exp\left(\frac{450}{T}\right)\right)+3\exp\left(-\frac{5}{T}\right)+2\exp\left(-\frac{50}{T}\right),$$
$$0.5\left(\exp\left(\frac{450}{T}\right)+\exp\left(\frac{750}{T}\right)\right)+3\exp\left(-\frac{5}{T}\right)+2\exp\left(-\frac{50}{T}\right),$$
$$0.5\left(\exp\left(\frac{750}{T}\right)+\exp\left(\frac{1200}{T}\right)\right)+3\exp\left(-\frac{5}{T}\right)+2\exp\left(-\frac{50}{T}\right),$$
$$0.5\left(\exp\left(\frac{750}{T}\right)+\exp\left(\frac{1200}{T}\right)\right)+2\exp\left(-\frac{5}{T}\right)+3\exp\left(-\frac{50}{T}\right),$$

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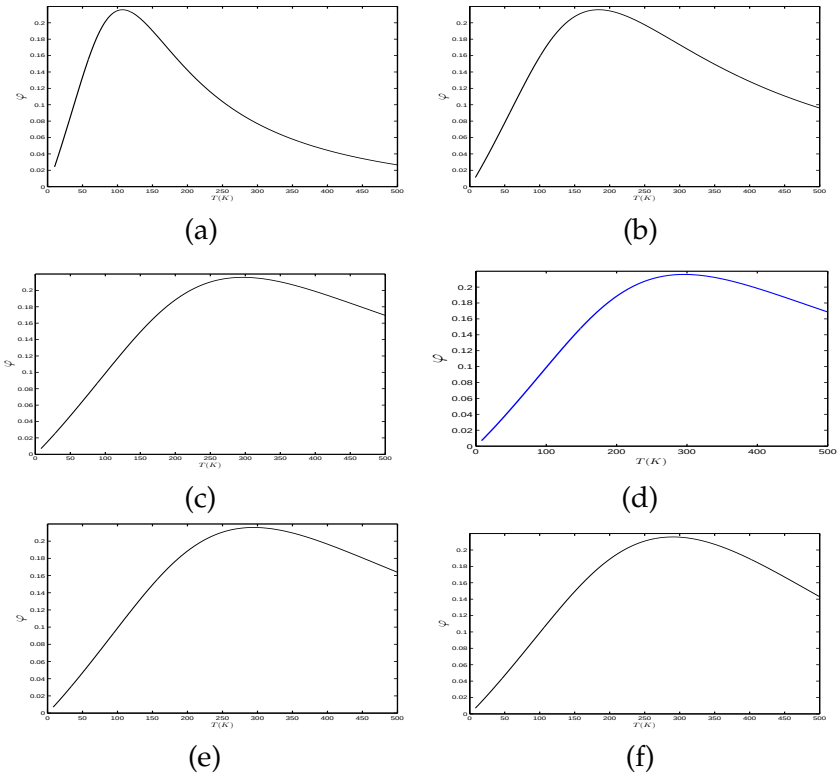



Figure 3: the correlation of the volume fraction of polymer under equilibrium state $\varphi$ with temperature $T(K)$. $m_0=3$ in every figure. (a): $m=0.5(\exp(\frac{150}{T})+\exp(\frac{450}{T}))+3\exp(-\frac{5}{T})+2\exp(-\frac{50}{T})$, (b): $m=0.5(\exp(\frac{450}{T})+\exp(\frac{750}{T}))+3\exp(-\frac{5}{T})+2\exp(-\frac{50}{T})$, (c): $m=0.5(\exp(\frac{750}{T})+\exp(\frac{1200}{T}))+3\exp(-\frac{5}{T})+2\exp(-\frac{50}{T})$, (d): $m=0.5(\exp(\frac{750}{T})+\exp(\frac{1200}{T}))+2\exp(-\frac{5}{T})+3\exp(-\frac{50}{T})$, (e): $m=0.5(\exp(\frac{750}{T})+\exp(\frac{1200}{T}))+3\exp(-\frac{50}{T})+2\exp(-\frac{150}{T})$, (f): $m=0.5(\exp(\frac{750}{T})+\exp(\frac{1200}{T}))+2\exp(-\frac{150}{T})+3\exp(-\frac{500}{T})$.

$$0.5\left(\exp\left(\frac{750}{T}\right)+\exp\left(\frac{1200}{T}\right)\right)+3\exp\left(-\frac{50}{T}\right)+2\exp\left(-\frac{150}{T}\right),$$
$$0.5\left(\exp\left(\frac{750}{T}\right)+\exp\left(\frac{1200}{T}\right)\right)+2\exp\left(-\frac{150}{T}\right)+3\exp\left(-\frac{500}{T}\right).$$

The results are shown in Fig. 3. These figures shown in this group enhance the reliability of the speculation we obtained from the previous two group figures. By comparing Fig. 3(a), (b), (c), we can also perceive that $T_{\max}$ increases with hydrophilic contribution. Fig. 3(c), (d), (e), (f) agree with the predication of the influence of the hydrophobic interaction from the aspect of how they affect the $\varphi$ when $T>T_{\max}$. Moreover, from the comparison of Fig. 3(a) with Fig. 1(a), small hydrophobic effect increase the maximum solubility of polymer chains in water $\varphi$ to the range $[0,1]$ when $T>T_{\max}$. This makes up the deficiency of this model and make the new mixing free energy (3.18) more reasonable.

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### 3.3 Conclusion of this new model

From the above figures, the new model explains the volume transition of the heat-shrinkable thermo-sensitive hydrogels to a certain extent. It evaluates the contributions of both the hydrophilic and hydrophobic interactions to the phase transitions of these hydrogels. And the changing trend of the volume fraction of the polymer chains predicted by the formula (3.20) agrees with the property of heat-shrinkable thermo-sensitive hydrogels in general. Additionally, we can observe that the maximum value of $\varphi$ is less than 0.22 for all the given $m$. This speculation needs further analysis. Therefore, chemical experiments are really anticipated to verify these predictions or modify the expression of the new mixing free energy.

Of course, this model can be improved from the following aspects:

1. obtaining more appropriate parameters from analysis the spatial geometry configuration of the polymer chains to supply better coordination number;
2. use more adequate hydrophilic and hydrophobic effect parameters;
3. combining it with the classical theoretical results used as the third part of the Flory-Huggins mixing free energy, $\chi\varphi_f\varphi_p$;
4. considering the interactions of polymer chains in detail;
5. taking the effect of the conformational energy of polymer chains into consideration.

It should be pointed out that, our model is just to calculate the contribution of the hydrophilic, hydrophobic interaction and hydrogen bonding to the volume phase transition of the neutral heat-shrinkable thermo-sensitive hydrogels. It is a little part of the interaction potential energy. If we want to calculate the free energy of the whole mixture, we have to calculate the potential energy accurately and the another part of the internal energy, the average of the kinetic energy of both phases caused by their constant random motion, firstly. Unfortunately, there are few achievements have been done on the formidable work to calculate the latter value, even though some acceptable models have been established to compute the former half work. Therefore, there is a still long arduous walk to go on this road. We hope our work can provide even a little help to this project.

## 4 Framework of transition modeling of neutral thermo-sensitive hydrogel

Here, we will give the framework of transition modeling of neutral thermo-sensitive hydrogels. A model derived from the theory of the conservation of mass, momentum, energy for both phases and the whole solution will be listed here. And the constitutive equations of the two phases and the mixture will be also summarized. Combining our results with the previous consequences, the volume phase transition processes of the

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neutral heat-shrinkable thermo-sensitive hydrogels will be simulated and analyzed in the future.

### 4.1 Governing equations

The continuum theory of mixtures has been applied extensively in the past several decades. The conservation law equations deduced from this theory have been used widely. The essential results about two-phase mixture will be summarized here. We note that the two phases are assumed as incompressible as most of the published literatures, $\nabla\cdot\mathbf{v}^\alpha=0$.

In the mixture, the mass conservation of each phase was given by Atkin and Craine [1] and Hassanizadeh et al. [11] as:

$$\frac{\partial}{\partial t}(\rho^\alpha\varphi^\alpha)+\nabla\cdot(\rho^\alpha\varphi^\alpha\mathbf{v}^\alpha)=0. \tag{4.1}$$

Here, $\nabla$ is the symbol of gradient operator about $\mathbf{x}$. Since the real density of each phase $\rho^\alpha$ is independent on the location and time, the balance equation of the volume fraction for each phase can be given by:

$$\begin{aligned}&\frac{\partial}{\partial t}\varphi^\alpha+\nabla\cdot(\varphi^\alpha\mathbf{v}^\alpha)=0, \qquad (4.2)\\ &\nabla\cdot\Big(\sum_\alpha\varphi^\alpha\mathbf{v}^\alpha\Big)=\sum_\alpha\nabla\cdot(\varphi^\alpha\mathbf{v}^\alpha)=\sum_\alpha\frac{\partial}{\partial t}\varphi^\alpha+\sum_\alpha\nabla\cdot(\varphi^\alpha\mathbf{v}^\alpha)=0.\end{aligned}$$

Let $\mathbf{v}=\sum_\alpha\varphi^\alpha\mathbf{v}^\alpha$, which means the volume-averaged velocity of the mixture, it leads to

$$\nabla\cdot\mathbf{v}=0, \tag{4.3}$$

which is the conservation of the mixture.

In the present work, equation of momentum for each component of the mixture is given by

$$\rho^\alpha\varphi^\alpha\frac{D\mathbf{v}^\alpha}{Dt}=\nabla\cdot\mathrm{P}^\alpha+\mathbf{f}^\beta,$$

where $\mathrm{P}^\alpha$ represents the stress tensor of the phase $\alpha$, and $\mathbf{f}^\beta$ denotes the reaction couple of the force given by the other phase $\beta$, which should be a variable of the volume fraction of any ingredient in the system $\varphi^\alpha$ such as

$$\sum_\beta\frac{\mathbf{f}^\beta}{\rho^\alpha\varphi^\alpha}=0.$$

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If we add the influence of external field imposed on the system, the conservation of momentum with respect to each constituent can be derived as:

$$\rho^\alpha \varphi^\alpha \frac{D\mathbf{v}^\alpha}{Dt} = \nabla \cdot \mathrm{P}^\alpha + \rho^\alpha \varphi^\alpha \mathbf{F}^\alpha + \mathbf{f}^\beta,$$
$$\frac{D\mathbf{v}^\alpha}{Dt} = \frac{\nabla \cdot \mathrm{P}^\alpha}{\rho^\alpha \varphi^\alpha} + \mathbf{F}^\alpha + \frac{\mathbf{f}^\beta}{\rho^\alpha \varphi^\alpha}. \tag{4.4}$$

For the whole system, it can be given by

$$\sum_\alpha \rho^\alpha \varphi^\alpha \frac{D\mathbf{v}^\alpha}{Dt} = \sum_\alpha \nabla \cdot \mathrm{P}^\alpha + \sum_\alpha \rho^\alpha \varphi^\alpha \mathbf{F}^\alpha. \tag{4.5}$$

Conservation of energy for each phase is given by Lustig et al. [16] and Huyghe and Janssen [13]:

$$\rho^\alpha \varphi^\alpha \frac{De^\alpha}{Dt} = \mathrm{P}^\alpha : \nabla \mathbf{v}^\alpha - \nabla \cdot \mathbf{q}^\alpha + \rho^\alpha \varphi^\alpha \bar{e}^\alpha, \tag{4.6}$$

where $e^\alpha$, $\bar{e}^\alpha$ represent the internal energy, the energy interaction with other phases of the component $\alpha$, respectively. And $\mathbf{q}^\alpha$ is conductive heat flux of the phase $\alpha$. Combining the equations of both phases, a more convenient form for the energy balance can be yielded as

$$\sum_\alpha \rho^\alpha \varphi^\alpha \frac{De^\alpha}{Dt} = \sum_\alpha \mathrm{P}^\alpha : \nabla \mathbf{v}^\alpha - \sum_\alpha \nabla \cdot \mathbf{q}^\alpha + \sum_\alpha \rho^\alpha \varphi^\alpha \bar{e}^\alpha. \tag{4.7}$$

## 4.2 Constitutive relations

The constitutive relation of a material is the equation which describes the functional relationship of the stress(stress tensor) and the strain rate(strain tensor) of this material. It expresses the property or response characteristic of this material and plays a significant role in elasticity mechanics and the theory of mixture solution, etc.

For any object, its constitutive equation can be expressed as [5]

$$\sigma_{ij} = \frac{\partial F}{\partial \mathrm{A}_{ik}} \mathrm{A}_{jk}. \tag{4.8}$$

In this equation, $\mathrm{A}_{ij} = (\frac{\partial x_i}{\partial X_j})$ denotes deformation gradient tensor of this object. $F$ is its free energy function. Here, we will just summarize the existing framework to calculate the constitutive relationship of each phase and the whole solution.

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### 4.2.1 Mixture

The free energy for the hydrogel is usually taken to follow the framework of the Flory-Huggins theory, and the Gibbs free energy of the solution can be written as [17]

$$\bar{F}(\varphi,T)=\int[F(\varphi,T)+\frac{\gamma}{2}|\nabla\varphi|^2]d\mathbf{x}, \tag{4.9}$$

where $F(\varphi,T)$ is the free energy per volume of the hydrogel which here can adopt the new expression derived from our model. $\bar{F}(\varphi,T)$ is the Gibbs free energy and $\gamma$ is a material parameter. The osmotic pressure derived by Araki and Tanaka [2] can be rewritten as

$$\begin{aligned}&\nabla p^{(os)}=\varphi\nabla\frac{\delta\bar{F}(\varphi,T)}{\delta\varphi},\\&p^{(os)}=\varphi\frac{\partial F}{\partial\varphi}-F-\varphi\gamma\nabla^2\varphi+\frac{\gamma}{2}(\nabla\varphi)^2.\end{aligned} \tag{4.10}$$

### 4.2.2 Liquid phase

For the fluid phase, the rates of strain, $E^f$, and stress tensors, $\sigma^f$, are defined as

$$\mathrm{E}^f=\frac{1}{2}[\nabla\mathbf{v}^f+(\nabla\mathbf{v}^f)^T], \tag{4.11}$$

$$\mathrm{P}^f=-(1-\varphi)p\mathrm{I}+2\mu^f\mathrm{E}^f, \tag{4.12}$$

where $\varphi=\varphi^p$ denotes the volume fraction of the polymer chains, $I$ is the unit second-order tensor, $\mu^f$ is the dynamic viscosity of the fluid, and $p$ is the total intrinsic fluid pressure expanded as

$$p=p'+p^{(os)}. \tag{4.13}$$

$p'$ in (4.13) is the remaining part of the intrinsic fluid pressure. The dynamic viscosity of the liquid in (4.12) can be approximated by [9]

$$\mu^f=0.6612(T-229)^{-1.562}.$$

### 4.2.3 Polymer phase

For the polymer phase, the main deformation of the solid part of the hydrogel, the polymer phase, is the elastic deformation. Here, the free energy related with its elastic deformation is represented as $F^p$, and the deformation gradient tensor as $A^p_{ij}$, from (4.8), we can obtain that

$$\mathrm{P}^p=-\varphi\mathrm{I}+\frac{\partial F^p}{\partial\mathrm{A}^p_{ik}}\mathrm{A}^p_{jk}. \tag{4.14}$$

Combining (4.12)and (4.14), the expression of the stress tensor of the hydrogel can be deduced as

$$\mathrm{P}=-p\mathrm{I}+\frac{\partial F^p}{\partial\mathrm{A}^p_{ik}}\mathrm{A}^p_{jk}+2\mu^f\mathrm{E}^f. \tag{4.15}$$

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# 5 Conclusions

In this paper, we set up a new model based on the assumption of Bose system, and get a new expression of the mixing free energy of the neutral heat-shrinkable thermo-sensitive hydrogels

$$F = E_0 - \kappa_B T \frac{V}{v_0}(1-\varphi)\ln\left[\sum_{i=1}^{s} m_i \frac{v_0}{v}\frac{\varphi}{1-\varphi}\exp(-\beta\Delta E_i) + \frac{1}{2}m_0\right] - \kappa_B T \frac{V}{v_0}(1-\varphi),$$

or

$$F = E_0 - \kappa_B T \frac{V}{v_0}(1-\varphi)\ln\left(\frac{m\varphi}{1-\varphi} + \frac{1}{2}m_0\right) - \kappa_B T \frac{V}{v_0}(1-\varphi).$$

The meanings of the notations in these expressions explained in Section 3.2. And the reliability of the new expression is tested by being applied to PNIPAAm. Combining it with the governing equations and constitutive equations of both phases (4.2), (4.4), (4.6), (4.11), (4.12), (4.13), (4.14) and the whole mixture (4.3), (4.5), (4.7), (4.15), it is possible to predict the contributions of the interaction to phase transition. Now there are some relevant works about the this topic ([28] and references therein).

There are still a lot of studies to do to fulfill this work:

1. improve the mixing free energy of this new model from the given aspects;
2. improve the elastic free energy of shrinkable neutral thermo-sensitive hydrogels;
3. predict the volume phase transition behaviors of these hydrogels by appropriate numerical methods [29] and compare them with experiments.

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