A lattice model for thermally-sensitive core–shell hydrogels

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A B S T R A C T

A lattice molecular thermodynamic model for describing the swelling behavior of thermally-sensitive core–shell hydrogels was developed by integrating a close-packed lattice model for mixing free energy and a Flory Gaussian chain model for the elastic free energy. The thermodynamic model is characterized with two parameters: the temperature-dependent exchange energy parameter ε and the Topology-dependent size parameter V^*. The input values of both parameters can be obtained by experimental results of pure polymer hydrogels. With the help of proposed model, swelling behaviors of two kinds of hydrogel systems were analyzed: one is a doubly thermally-sensitive core–shell hydrogels (with two LCSTs) and the other comprises a thermally-sensitive hydrogel shell with a hard internal core. We show that the calculated results are in good agreement with the experimental data.

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1. Introduction

Smart hydrogels are soft materials which can swell through absorbing solvent and deswell through ejecting the solvent as a response to external stimuli (such as temperature, pH, ionic strength, and composition of solvent). These hydrogels have been widely applied in sensors [1,2], immobilized enzymes [3], material extraction [4,5], drug delivery devices [6–8], catalysts [9], and so on. In recent years, novel architectures (such as core–shell structures [10–18] and interpenetrating network structures [19,20]) have been designed to obtain materials with superior properties and functions. The properties of these particles, such as stability, biocompatibility, mechanical strength, and even functionalities, have been improved.

In the related theoretical filed, as early as 1953, Flory [21] established the swelling theory of such special network structures based on the polymer solution theory and the rubber theory. Until 1987, Tanaka and his coworker [22] established a thermodynamic model for hydrogels. They considered the chemical potential inside the hydrogel was equal to that of outside hydrogel at swelling equilibrium. From then on, researchers have paid more and more attention to establishing molecular thermodynamic models for hydrogels. For the homogeneous hydrogels, corresponding molecular thermodynamic models for describing their swelling behaviors have been widely reported. Considering the influence of hydrogen bonding, Shenoy et al. [23] combined an association model with a Flory–Rehner approach to develop a new model. Starting from a quasi-chemical partition function [24], which con-

sidered both the rubber elasticity theories and competition between hydrogen bonding and dispersion forces, Oliveira et al. [25] presented an oriented quasi-chemical thermodynamic model to explain the swelling behavior of hydrogels. Huang et al. [26] developed a molecular thermodynamic model based on a lattice model [27–29] for thermally-sensitive hydrogels. Then, Zhi et al. [30,31] established molecular thermodynamic models for thermal and solvent sensitive hydrogels and also multi-sensitive hydrogels. Jung et al. [32] combined modified double lattice model (MDL) theory with Flory–Erman theory to describe the reentrant swelling behavior of thermally-sensitive hydrogels.

Nevertheless, the above models are essentially proposed for homogeneous hydrogels, and the properties of the core–shell hydrogels are fundamentally different. In core–shell hydrogel system, the core and shell are constrained by and correlated with each other, and thus, the swelling process is an inhomogeneous deformation. The thermodynamic study on phase transitions of such hydrogels is rather complicated. With a general yet complex formalism of field theory, Sekimoto and Kawasaki [33] have studied the phase coexistence in hydrogels, and using the Legendre transformation, the inhomogeneous swelling behavior of covalently cross-linked polymers is investigated by Marcombe et al. [34]. Furthermore, the thermodynamic theory of Gibbs and the Flory–Huggins statistical-mechanical model were combined to establish a field theory for describing the phase transition result from a mechanical constraint [35]. Base on the field theory, Gernandt et al. [36] presented a general thermodynamic model together with a conventional thermodynamics theory of hydrogel swelling for calculating the internal structure of core–shell hydrogels. Despite the success of those models, they are generally too complex for application.

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In present work, we propose a simple yet meaning thermodynamic model to address the swelling behavior of two kinds of hydrogels. One is composed of hydrogels in both core and shell. In other words, the swelling of the core and the shell is affected by thermodynamic and solution properties and shows very complicated swelling behavior. The other is composed of non-hydrogel core and an external hydrogen shell, i.e., a hydrogel is coated onto a hard core surface (e.g., gold, polystyrene PS, silica, etc.). The swelling behavior of these core–shell hydrogels is dominated by two different contributions: the interaction between polymer chains and solvent and the elasticity of polymer networks. Here, we combine the close-packed lattice model [27–29] for mixing free energy and Flory's Gaussian chain model [21] for the elastic free energy. With proposed thermodynamic model, two sorts of core–shell hydrogels have been studied. One is composed of hydrogels in both the core and the shell with different LCSTs and the other is composed of a hard core and a thermally-sensitive gel shell. In particular, they are employed to represent poly(N-isopropylacrylamide)-poly(N-isopropylmethacrylamide) (PNIPAM–PNIPMAM) and polystyrene-poly(N-isopropylacrylamide) (PS-PNIPAM) core–shell hydrogels, respectively.

2. Molecular thermodynamic model

The swelling behaviors of hydrogels are decided by two separate and additive contributions. One is the mixing interaction between polymers and solvent and the other is the elasticity of polymer hydrogel network, which describes the cross-linking degree and other constraint. The total changes of Gibbs free energy ΔG are composed of the mixing contribution and the elasticity contribution:

$$\Delta G = \Delta G_{mix} + \Delta G_{elas} \tag{1}$$

where the ΔG_{mix} and ΔG_{elas} are the changes of mixing Gibbs free energy and elastic Gibbs free energy, respectively. The hydrogel can be regarded as a close-packed lattice mixture composed of polymer network and solvent. If ignore the effect of pressure, ΔG_{mix} value of hydrogels can be calculated by using the close-packed lattice model proposed by Yang and his coworkers [27–29]:

$$\frac{\Delta G_{mix}}{N_r kT} = \varphi_S \ln \varphi_S + \frac{\varphi_P}{r_P} \ln \varphi_P + \frac{z}{2}\left[\varphi_S \ln \frac{\theta_S}{\varphi_S} + \frac{\varphi_P q_P}{r_P} \ln \frac{\theta_P}{\varphi_P}\right]$$
$$+ \frac{z}{2T^*} \varphi_S \varphi_P - \frac{z}{4T^{*2}} \varphi_S^2 \varphi_P^2 - \frac{z}{12T^{*2}} \varphi_S^2 \varphi_P^2(\varphi_S^2 + \varphi_P^2)$$
$$- \frac{\varphi_P(r_P - 1 + \zeta_P)}{r_P} \ln \left(\frac{1 + \varphi_S(\exp(1/T^*) - 1)}{1 + \varphi_S \varphi_P(\exp(1/T^*) - 1)}\right) \tag{2}$$

In above equation, the energy parameter $T^* = kT/\varepsilon$ (ε is the exchange energy), k is the Boltzmann constant, z is the coordination number $z = 6$, the subscripts "s" and "p" represent solvent and polymer network, and r_s and r_p are the chain lengths of solvent and of polymer, respectively. In our study, the value of r_s is set as a unit. N_r is the total number of chains, i.e., $N_r = N_S + N_P$. Here, N_S and N_P stand for the chain numbers of the solvent and polymer. φ_i and θ_i are, respectively, the volume and surface fractions of component i with $i = s, p$. They can be calculated by

$$\varphi_i = N_i r_i/(N_S r_S + N_P r_P) \tag{3}$$

$$\theta_i = N_i q_i/(N_S q_S + N_P q_P) \tag{4}$$

where q_i is the surface area parameters of solvent or polymer defined by

$$q_i = [r_i(z - 2) + 2]/z \tag{5}$$

The last term of Eq. (2) denotes the contribution of chain connectivity of polymer, and the involved parameter ζ_P characterizes the long-range correlations between segments on the same polymer chain, which can be written as:

$$\zeta_P = \frac{(r_P - 1)(r_P - 2)}{r_P^2}(0.1321 r_P + 0.5918) \tag{6}$$

Since the elasticity of polymer network is entropic, it is reasonable to suppose that the macroscopic deformation is proportional to the microscopic deformation of polymer chains. The free energy difference during the structural change of polymer network can be calculated by the Gaussian model [21],

$$\Delta G_{elas} = \frac{3}{2} N_C kT(\lambda^2 - 1 - \ln \lambda) \tag{7}$$

where the N_C is the number of polymer chains in hydrogel network and the λ is the swelling ratio of hydrogel, which is defined as

$$\lambda^3 = \frac{V}{V_0} = \frac{\varphi_{P,0}}{\varphi_P} \tag{8}$$

The subscript "0" is the initial state of hydrogel network. Combining Eqs. (1)–(7), the Gibbs free energy difference, i.e., ΔG, during the swelling (or deswelling) can be expressed as:

$$\frac{\Delta G}{N_r kT} = \frac{\Delta G_{mix}}{N_r kT} + \frac{\Delta G_{elas}}{N_r kT}$$
$$= \varphi_S \ln \varphi_S + \frac{\varphi_P}{r_P} \ln \varphi_P + \frac{z}{2}\left[\varphi_S \ln \frac{\theta_S}{\varphi_S} + \frac{\varphi_P q_P}{r_P} \ln \frac{\theta_P}{\varphi_P}\right]$$
$$+ \frac{z}{2T^*} \varphi_S \varphi_P - \frac{z}{4T^{*2}} \varphi_S^2 \varphi_P^2 - \frac{z}{12T^{*2}} \varphi_S^2 \varphi_P^2(\varphi_S^2 + \varphi_P^2)$$
$$- \frac{\varphi_P(r_P - 1 + \lambda_P)}{r_P} \ln \left(\frac{1 + \varphi_S(\exp(1/T^*) - 1)}{1 + \varphi_S \varphi_P(\exp(1/T^*) - 1)}\right)$$
$$+ \frac{3N_C}{2N_r}(\lambda^2 - 1 - \ln \lambda) \tag{9}$$

The chemical potential of solvent in the core and shell can be derived from Eq. (9) as follows:

$$\frac{\Delta \mu_S}{kT} = \ln \varphi_S + \varphi_P + 3\left[\ln \frac{3}{2 + \varphi_S} + \frac{2\varphi_P}{3 - \varphi_P} - \varphi_P - + \frac{2\varphi_P^2}{6 + 3\varphi_S}\right]$$
$$+ 3\varphi_P^2\left(\frac{1}{T^*}\right) - 1.5\varphi_S \varphi_P^2(2\varphi_P - \varphi_S)\left(\frac{1}{T^*}\right)^2$$
$$- 0.5\varphi_S \varphi_P^2(4\varphi_S^2 \varphi_P - \varphi_S^3 + 2\varphi_P^3 - 3\varphi_S \varphi_P^2)\left(\frac{1}{T^*}\right)^3$$
$$- 1.1312\varphi_P^2 C_1\left(\frac{1}{C_2} - \frac{\varphi_P - \varphi_S}{C_3}\right)$$
$$- \frac{v_S N_C}{N_A V_0}\left[\frac{\varphi_P}{2\varphi_{P,0}} - \left(\frac{\varphi_P}{\varphi_{P,0}}\right)^{1/3}\right] \tag{10}$$

where $C_1 = \exp(1/T^*)$, $C_2 = 1 + \varphi_S C_1$, $C_3 = 1 + \varphi_S \varphi_{PC} C_1$. For the chemical potential outside the core–shell hydrogel, only the mixing contribution should be accounted for. Since the solvent is pure in our discussion, $\Delta \mu_S^{solv}$ is considered as zero.

3. Swelling behaviors of doubly thermally-sensitive core–shell hydrogels

3.1. Swelling equilibrium

In the initial state (or equivalently reference state), a polymer network contains no solvent water, and the core is of radius R_{core} which is also called the inner radius. We use R_{shell} to denote the total radius of the core–shell hydrogel. The schematic illustration of such state is shown in Fig. 1a. In the swelling equilibrium state, the