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Model for the phase separation of poly(*N*-isopropylacrylamide)–clay nanocomposite hydrogel based on energy-density functional

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The time-dependent Ginzburg-Landau (TDGL) mesoscopic method is utilized to simulate the phase separation of the poly(*N*-isopropylacrylamide)–clay nanocomposite hydrogel in the three-dimensional case, where the Cahn-Hilliard-Cook equation with a proposed free energy, which consists of the stretching and mixing energy based on Flory's mean theory, is considered. The main features of the presently proposed model include the following: (i) the proposed free energy consists of both the stretching and mixing energy; (ii) the processes of polymer chains detaching from and reattaching on crosslinks are considered in the proposed free energy; (iii) polymer chains have inhomogeneous chain lengths, which are divided into different types. A stabilized semi-implicit difference scheme is used to numerically solve the corresponding Cahn-Hilliard-Cook equation. Numerical results show the process of the phase separation and are consistent with morphology of the nanocomposite hydrogel.

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I. INTRODUCTION

Nanocomposite hydrogels are one kind of polymeric-based soft matter, using inorganic nanoparticles as crosslinks, such as nanoclay, silica, and graphene oxide [1].

The poly(*N*-isopropylacrylamide)–clay (PNIPA–clay) nanocomposite hydrogels and various modified hydrogels were extensively studied recently, due to their well-known thermal-stimulus responsive properties [2–7]. Haraguchi's group investigated the syntheses, the properties and the mechanism of PNIPA–clay nanocomposite hydrogels systematically [3,8–10]. Precisely, the hydrogels can be prepared by *in situ* free-radical polymerization of *N*-isopropylacrylamide (NIPA) with the inorganic clay and the clay is extensively exfoliated with the clay platelets dispersed uniformly throughout the polymer matrix, acting as effective multifunctional crosslinks. PNIPA chains are grafted on the clay surfaces on one or both sides to form polymer networks, as shown in Fig. 1. Compared with the conventional organic crosslinked hydrogels, the PNIPA–clay nanocomposite hydrogels exhibit extraordinarily large elongations before breaking, high equilibrium swelling ratios and rapid deswelling rates with temperature changes.

These properties indicate that the PNIPA chains in the nanocomposite hydrogels can be treated as long and flexible chains with nearly random configurations [3].

In past decades, many studies were carried out for the PNIPA–clay nanocomposite hydrogels. However, most of them were experiment-based and few theoretical studies have been conducted. The purpose of this paper is to construct a theoretical model for the thermally induced phase separation of the PNIPA–clay nanocomposite hydrogel.

The time-dependent Ginzburg-Landau (TDGL) mesoscopic method is widely utilized to simulate the phase separation of the binary mixtures. The well-known Cahn-Hilliard equation is one model of the TDGL method, describing the conserved dynamics. Furthermore, the Cahn-Hilliard-Cook equation [11], namely, the Cahn-Hilliard equation combined with a stochastic term representing a thermal noise, has been proved to be one of the most appropriate models for simulating the order-disorder phase separations and pattern formations of a uniform thermodynamic system [12,13], since the phase separation process starts by the growth of the enrichment of local composition fluctuations toward the equilibrium concentrations of the coexisting phases [14]. The Cahn-Hilliard and the Cahn-Hilliard-Cook equations have been extensively studied, where there exists a remarkable amount of work on both analysis and numerical schemes [13,15–17].

The TDGL method has recently been used to investigate the phase separation of polymer nanocomposites and hydrogels. For instance, Kyu's group has investigated the

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FIG. 1. The structure model for the PNIPA-clay nanocomposite hydrogel: schematic representation of nanocomposite hydrogel consisting of uniformly exfoliated clay and polymer chains.

photopolymerization-induced phase separation by coupling the photopolymerization kinetics with the TDGL method [18,19]. Zhang's group has used the TDGL method to simulate the phase separation process of macromolecule micro-sphere composite (MMC) hydrogel by solving the Cahn-Hilliard-Cook equation [20]. However, the free energies in the previously published work include a major assumption that all polymer chains in the system have the same chain length. Moreover, during the phase separation, there exists deformation of polymer chains since water molecules would run into and out of polymer networks, and thus polymer chains may detach from and reattach on crosslinks, which were not considered in the previous work.

The free energy is the vital part to simulate the phase separation of hydrogels since the Cahn-Hilliard equation is developed by the variational derivative of the free-energy functional [15]. Theoretical models with respect to the free energy of the hydrogel system have been extensively studied. For instance, Hino [21] added the mixing, elastic, and electrostatic contribution into the total Helmholtz energy. Suo's group [22] considered the free energy as the sum of the mixing energy and the stretching energy. Li [23] expressed the total change of free energy of the ionized thermal-stimulus responsive hydrogels as the sum of the mixing, elastic deformation, and ionic contributions to the change of free energy. Otake [24] decomposed the free energy of a gel into the four parts, the mixing energy, the elastic energy, the free energy arising from osmotic pressure, and the energy representing the hydrophobic interaction. Therefore, it is concluded that the mixing energy, describing the interactions between polymers and solvents, and the stretching energy, describing the physical deformation of polymer chains, are the necessary integral parts of the free energy of the hydrogels.

The models mentioned above for the free energy of the hydrogel systems are mostly concentrated on the states of the hydrogel in equilibrium with the aqueous environment, and on the mechanical forces by searching for the global minimum of the free-energy function. To the authors' knowledge, up to data, a few researchers have utilized the free-energy

functionals to describe the dynamics of swelling and volume transitions of gels based on the variational principle [25,26].

Motivated by the lack of theoretical studies on the PNIPA-clay nanocomposite hydrogels, the present work constructs a theoretical model for the thermally induced phase separation of the PNIPA-clay nanocomposite hydrogel in the three-dimensional domain and numerical experiments are conducted to simulate the process of the phase separation. In the present work, the theoretical models for the free energy of hydrogel systems are combined with the TDGL method and the free energy of the classical Cahn-Hilliard-Cook equation is adapted to simulate the time-dependent process of the phase separation of the hydrogels. It is noted that, in the adapted free energy, the assumption that all polymer chains in the system have the same chain length is removed, namely, the polymer chains in the present work are allowed with inhomogeneous chain lengths. Moreover, the chain detachment and reattachment are considered.

The adapted free-energy functional is inspired by the free energy induced by Q. Wang [27]. Nevertheless, there are two main differences between the presently proposed model and the model derived by Q. Wang. On one hand, the model derived by Q. Wang is an analytical one to investigate the stress-strain behavior of the nanocomposite hydrogels, which is concentrated on the states of the hydrogel in equilibrium. However, the adapted Cahn-Hilliard-Cook equation presented here is utilized to describe the time-dependent process of the thermally induced phase separation. On the other hand, the model derived by Q. Wang does not give the exact expression of the mixing energy since the mixing energy is assumed to be constant throughout the mechanical deformation. However, in the present work, the mixing energy is derived based on Flory's lattice theory. The mixing energy changes during the time-dependent process and is relevant to the inhomogeneous chain lengths and polymer detachment/reattachment process.

An important contribution of the present work is on adapting the free energy for the Cahn-Hilliard-Cook equation to simulate the process of the phase separation of the PNIPA-clay nanocomposite hydrogels. Compared with the previous work, the proposed free energy makes great improvements, not only allowing polymer chains with inhomogeneous chain length, but also including both the mixing and stretching energy with the chain detachment and reattachment. The derived Cahn-Hilliard-Cook equation is a good complement to the existing theories.

The main features of the present work include that (i) the proposed free energy consists of both the stretching and mixing energies, where the stretching energy reflects the physical deformation of polymer chains during the phase separation and the mixing energy describes the interaction between polymer chains and solvents; (ii) the process of polymer chains detaching from and reattaching on crosslinks is considered in the proposed free energy; (iii) polymer chains have inhomogeneous chain lengths, which are divided into different types; (iv) numerical results of this model are consistent with the morphology of the PNIPA-clay nanocomposite hydrogel.

The rest of the paper is organized as follows. In Sec. II, we describe the Cahn-Hilliard-Cook equation and develop the model for the nanocomposite hydrogel. The free-energy-density functional is formulated in Sec. III. Several numerical

results are presented and discussed in Sec. IV by solving the Cahn-Hilliard-Cook equation with a stabilized semi-implicit difference scheme and the fast Fourier transformation method. The numerical results demonstrate the pattern formation during the phase separation process and they are consistent with the chemically experimental results of the PNIPA-clay nanocomposite hydrogels. Conclusions are given in Sec. V.

II. MODEL FOR THE NANOCOMPOSITE HYDROGEL

A. Cahn-Hilliard-Cook equation for hydrogels

For the incompressible system, the Cahn-Hilliard-Cook equation can be expressed as

$$\frac{\partial \phi(\mathbf{x}, t)}{\partial t} = \nabla \cdot \left(M \nabla \frac{\delta U[\phi]}{\delta \phi} \right) + \theta \xi(\mathbf{x}, t), \quad (1)$$

where ϕ is the unknown function subject to the periodic boundary conditions, representing the volume fraction of polymer segments, namely, $\phi = V_0/V$ with V_0 the volume of the dry hydrogel and V the volume of the whole system. M is the mobility and $U[\phi]$ is the Ginzburg-Landau type energy functional,

$$\frac{U[\phi]}{k_B T} = \int \left(\frac{W(\phi)}{k_B T} + \kappa |\nabla \phi|^2 \right) d\mathbf{x}, \quad (2)$$

where $W(\phi)$ is the free-energy density of the nanocomposite hydrogel and $\kappa |\nabla \phi|^2$ accounts for the surface energy. The function $\xi(\mathbf{x}, t)$ is a stochastic term representing a thermal noise, whose strength is scaled by $\theta > 0$.

In this paper, the mobility M is taken to be a constant for simplicity. Then Eq. (1) turns into

$$\frac{\partial \phi}{\partial t} = H \Delta \frac{\delta U[\phi]}{\delta \phi} + \theta \xi(\mathbf{x}, t), \quad (3)$$

where $H = k_B T M$ is the diffusion coefficient. The stochastic term $\xi(\mathbf{x}, t)$ satisfies the fluctuation-dissipation theorem,

$$\mathbb{E}[\xi(\mathbf{x}_1, t_1) \xi(\mathbf{x}_2, t_2)] = -2H \Delta \delta(\mathbf{x}_1 - \mathbf{x}_2) \delta(t_1 - t_2), \quad (4)$$

where $\mathbb{E}$ denotes the mathematical expectation operator, k_B the Boltzmann constant and T the absolute temperature. It has been proved that to satisfy the condition Eq. (4), $\xi(\mathbf{x}, t)$ should have the form [12]

$$\xi(\mathbf{x}, t) = -\sqrt{2H} \nabla \cdot \eta(\mathbf{x}, t), \quad (5)$$

where $\eta = (\eta_1, \eta_2, \eta_3)$ with η_1, η_2, η_3 independent three-dimensional Gaussian white noises, satisfying $\mathbb{E}[\eta_l(\mathbf{x}, t)] = 0$ and $\mathbb{E}[\eta_l(\mathbf{x}_1, t_1) \eta_l(\mathbf{x}_2, t_2)] = \delta(\mathbf{x}_1 - \mathbf{x}_2) \delta(t_1 - t_2)$, $l = 1, 2, 3$.

B. Model description

In this section, the model is developed to describe the nanocomposite hydrogels and the process of the phase separation. Several necessary assumptions should be emphasized first, and some of them are based on the properties of the PNIPA-clay nanocomposite hydrogels mentioned in Sec. I.

(1) The exfoliated clay sheets, connecting long and flexible PNIPA chains with different types of lengths, act as crosslinks in the nanocomposite hydrogels. The crosslinks are such small nanoparticles with the same structure that their volumes are not counted in the model. The same distance is assumed

FIG. 2. The process of swelling and shrinking during the phase separation. During swelling, polymer chains stretch and some of them can be detached from the crosslinks (green and black chains). During shrinking, polymer chains gather together and some previously detached polymer chains would be reattached on the same crosslinks (yellow and black chains).

between every two crosslinks and the same bond is assumed between every polymer chain and crosslink.

(2) During the phase separation, the PNIPA-clay nanocomposite hydrogels are not subjected to mechanical constraints, namely, they are isotropic and the deformations of polymer chains are the same in all directions.

(3) During the phase separation, some of the nanocomposite hydrogels would swell and some polymer chains would undergo stretching deformation, which requires equal and opposite chain forces acting on the chain ends. Polymer chains would detach from crosslinks, namely, the clay sheets, if the chain forces are larger than the bonds between them.

Some of the nanocomposite hydrogels would shrink and the detached polymer chains would gather together. Then, previously detached polymer chains would be reattached on the same crosslinks. The case that chains graft on the middle crosslinks during reattachment is not considered in the present model.

The swelling and shrinking processes are shown in Fig. 2, where the grey circles denote the crosslinks and colored lines denote the polymer chains.

According to Kuhn's polymer theory, each polymer chain consists of a number of Kuhn segments with b the Kuhn length [28]. Polymer chains of inhomogeneous chain length can be classified into m types and each type has the same Kuhn segment number. Here, n_j denotes the number of the Kuhn segments in every one of the j th ($1 \leq j \leq m$) type of chains. Assume that $n_1 < n_2 < \dots < n_j < \dots < n_m$. N_j denotes the number of the j th type of chains, N the number of polymer chains in the whole system and $P_j(n_j)$ the probability distribution of N_j . Obviously, $N = \sum_{j=1}^m N_j$ and $P_j(n_j) = \frac{N_j}{N}$. According to Gaussian statistics, $P_j(n_j)$ can be written as [27,29]

$$P_j(n_j) = \tilde{P}(n_j) \bar{P},$$

where the factor $\bar{P}$ is enforced to obtain $\sum_{j=1}^m P_j(n_j) = 1$, and

$$\begin{aligned} \bar{P}(n_j) \approx & \rho \left(\frac{3}{2\pi n_j} \right)^{\frac{1}{2}} \exp \left(-G - \frac{\rho}{\sqrt{\pi}} \left[\sqrt{6n_j} e^{-G} \right. \right. \\ & + 3\sqrt{\pi} \frac{D}{b} \operatorname{erf}(\sqrt{G}) - \sqrt{6} e^{-Gn_j} \\ & \left. \left. - 3\sqrt{\pi} \frac{D}{b} \operatorname{erf}(\sqrt{Gn_j}) \right] \right). \end{aligned} \quad (6)$$

Here, D and d denote the distance between every two crosslinks before and during the deformation, respectively. And $G = \frac{3D^2}{2n_j b^2}$, $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$. ρ is denoted as the probability that the segment with length b can attach on the crosslink, which is only related to the properties of the crosslink. In the present work, ρ is equal to 1 for simplicity. The detailed derivation is in the Appendix.

Obviously, according to the definitions, $d = \lambda D$ with λ the deformation of each direction. Since the volume of crosslinks is not counted, D and d are approximated as the end-to-end distance of each polymer chain before and during the deformation respectively. To hold a polymer chain at the end-to-end distance d , equal and opposite chain forces are required to act on the chain ends. Denote f_j as the chain force of the j th type of chains. For a flexible polymer chain, the chain force is proportional to d , which can be written as [28]

$$f_j = \frac{3k_B T}{n_j b^2} d = \frac{3k_B T}{n_j b^2} (\lambda D). \quad (7)$$

Denote f_0 as the bond between each polymer chain and crosslink. Then, the critical Kuhn segment number n_c of a polymer chain connected by crosslinks in the hydrogel, by solving the equation $f_c = f_0$, is written as

$$n_c = \frac{3k_B T d}{f_0 b^2} = \frac{3k_B T \lambda D}{f_0 b^2}, \quad (8)$$

which can be seen as the Kuhn segment number of the c th type of chains. It means that, if $n_j \leq n_c$, $f_j \geq f_0$, the bond cannot hold the j th ($j \leq c$) type of chains at the end-to-end distance d , then they are detached from the crosslinks. Meanwhile, for the $\tilde{j}$ th ($c < \tilde{j} \leq m$) type of chains, $f_{\tilde{j}} < f_0$, the chains are connected by crosslinks (even though some of the chains may be detached from the crosslinks before, they would be reattached on the same crosslinks).

III. FREE ENERGY

In this section, the free-energy density is deduced, which consists of the stretching energy density and the mixing energy density. Several necessary notes are provided first.

(1) The dry hydrogel is taken as the reference state.

(2) The stretching energy comes from the deformation of polymer chains, without considering the interaction or entanglement of them. All the polymer-solvent interactions are included in the mixing energy, namely, there is no polymer-solvent interaction in the stretching energy.

(3) When a polymer chain is detached from the crosslink, it becomes dangling and its stretching energy would not be included in the stretching energy of the hydrogel. And when

a polymer chain is reattached on the crosslink, its stretching energy is counted.

A. Mixing energy

Since the critical Kuhn segment number n_c [Eq. (8)] is related to the deformation λ , there exists three possible cases.

(1) Case 1: When $n_c \geq n_m$, all m types of polymer chains are detached from crosslinks. The whole system consists of water and free polymer chains.

(2) Case 2: When $n_1 \leq n_c < n_m$, the j th ($j \leq c$) type of chains are detached from crosslinks and the $\tilde{j}$ th ($c < \tilde{j} \leq m$) type of chains are connected by crosslinks and form networks. The whole system consists of water, free polymer chains and networks.

(3) Case 3: When $n_c < n_1$, no polymer chains are detached, namely, all polymer chains are connected by crosslinks and form networks. Thus the whole system consists of water and networks.

The mixing energy density, corresponding to the three cases mentioned above, is obtained on the basis of Flory's lattice theory [28,30]. It consists of two contributions, one is from the entropy, the other is from the interactions between species. According to the lattice theory, the number of lattice sites that the nanocomposite hydrogel occupies is $n = N_s + \sum_{j=1}^m n_j N_j$, where N_s denotes the number of water molecules. Then the volume of the whole system $V = n \cdot v_m$, with v_m the volume of one lattice. Therefore, the volume fraction of water molecules $\phi_s = N_s/n$ and the volume fraction of the j th type of polymer chains $\phi_{pj} = (N_j n_j v_m)/V$, which can be written as

$$\phi_{pj} = \frac{N_j n_j}{\sum_{l=1}^m N_l n_l} \phi = \frac{P_j(n_j) n_j}{\sum_{l=1}^m P_l(n_l) n_l} \phi. \quad (9)$$

Obviously, $\sum_{j=1}^m \phi_{pj} = \phi = 1 - \phi_s$.

For each water molecule, the entropy change on mixing is

$$\Delta S_s = k_B \ln \Omega_{\text{mix}} - k_B \ln \Omega_0 = -k_B \ln \phi_s,$$

where $\Omega_0 = n\phi_s$ and $\Omega_{\text{mix}} = n$, which denote the number of states of one water molecule before and during mixing respectively. For each one of the j th type of polymer chains, the relation is similar. Then the entropy contributions from each molecule are summed to get the total entropy of mixing, and the contribution of entropy to the mixing energy can be obtained by $F_{\text{mix}} = -T \Delta S_{\text{mix}}$.

Assume that the interactions between polymer chains and water molecules remain the same when polymer chains are detached and reattached, namely, the term in the mixing energy which comes from interactions between species is the same in the above three cases. Combine the two contributions, the mixing energy density of Case 1, where there are m types of free polymer chains in the system, can be written as

$$\begin{aligned} W_{\text{mix},1} = & \frac{k_B T}{v_m} \left[(1 - \phi) \ln(1 - \phi) + \sum_{j=1}^m \frac{\phi_{pj}}{n_j} \ln \phi_{pj} \right. \\ & \left. + \chi \phi(1 - \phi) \right], \end{aligned} \quad (10)$$

with χ the parameter describing the interactions of polymer chains and solvents.

In Case 2, where the network and individual polymer molecules both exist in the system, the mixing energy density is

$$W_{\text{mix},2} = \frac{k_B T}{v_m} \left[(1 - \phi) \ln(1 - \phi) + \sum_{j=1}^c \frac{\phi_{pj}}{n_j} \ln \phi_{pj} + \chi \phi(1 - \phi) \right]. \quad (11)$$

In Case 3, due to the absence of individual polymer molecules in the system, the mixing energy density can be written as

$$W_{\text{mix},3} = \frac{k_B T}{v_m} [(1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi)]. \quad (12)$$

B. Stretching energy

The stretching energy density, also called the elastic energy density, describes the deformation of the nanocomposite hydrogel. It can be written as $F = -TS$ with T the temperature and S the entropy [30], and the difference between the stretching energies is

$$\Delta F_{\text{stre}} = (-TS_{\text{stre}}) - (-TS_{\text{stre},0}),$$

where $S_{\text{stre},0}$ and S_{stre} represent the entropy before and during the deformation respectively and $S = k_B \ln \Omega$ with Ω the number of possible states.

For the j th type of polymer chains, the probability that any given chain has the coordinate (x_i, y_i, z_i) within the range $(\Delta x, \Delta y, \Delta z)$, can be written as

$$w_i = W(x_i, y_i, z_i, n_j) \Delta x \Delta y \Delta z,$$

where

$$W(x_i, y_i, z_i, n_j) = \left(\frac{3}{2\pi n_j b^2} \right)^{\frac{3}{2}} \exp \left(-\frac{3(x_i^2 + y_i^2 + z_i^2)}{2n_j b^2} \right)$$

is a three-dimensional random walk by the Gaussian function.

During the phase separation, the deformation of polymer chains occurs. If a chain has the coordinate (x_i, y_i, z_i) after the deformation, then it must have the coordinate $(x_i/\lambda_x, y_i/\lambda_y, z_i/\lambda_z)$ before the deformation, where λ_x , λ_y and λ_z denote the deformation in the x , y and z direction respectively. Then the number of possible states of the j th type of polymer chains is

$$\Omega_j = N_j! \prod_i (w_i^{v_i}/v_i!),$$

where

$$v_i = v_i(x_i, y_i, z_i, n_j) = N_j W(x_i/\lambda_x, y_i/\lambda_y, z_i/\lambda_z, n_j) \times \Delta x \Delta y \Delta z / (\lambda_x \lambda_y \lambda_z)$$

represents the number of the j th type of polymer chains, which have end-to-end vector components from x_i to $x_i + \Delta x$, y_i to $y_i + \Delta y$, and z_i to $z_i + \Delta z$ after deformation. Introduce

Stirling's approximation for the factorials,

$$\begin{aligned} \ln \Omega_j &= \sum_i v_i \ln(w_i N_j / v_i) \\ &= -N_j [(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)/2 - \ln(\lambda_x \lambda_y \lambda_z)]. \end{aligned}$$

During the phase separation, the polymer chains with no more than n_c Kuhn segments are detached in the nanocomposite hydrogel, and thus the entropy can be written as

$$\begin{aligned} S_{\text{stre}} &= \sum_{j=c+1}^m S_{\text{stre},j} = \sum_{j=c+1}^m k_B \ln \Omega_j \\ &= \sum_{j=c+1}^m -k_B N_j [(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)/2 - \ln(\lambda_x \lambda_y \lambda_z)]. \end{aligned}$$

Since $S_{\text{stre},0} = 0$ with $\lambda_x = \lambda_y = \lambda_z = 1$ before the deformation, the difference between the stretching energies is

$$\begin{aligned} \Delta F_{\text{stre}} &= (-TS_{\text{stre}}) - (-TS_{\text{stre},0}) \\ &= \sum_{j=c+1}^m k_B T N_j [(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)/2 - \ln(\lambda_x \lambda_y \lambda_z)] \\ &= k_B T [(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)/2 - \ln(\lambda_x \lambda_y \lambda_z)] \sum_{j=c+1}^m N_j \\ &= k_B T N [(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)/2 - \ln(\lambda_x \lambda_y \lambda_z)] \\ &\quad \times \sum_{j=c+1}^m P_j(n_j). \end{aligned}$$

Assume that the volume of the nanocomposite hydrogel is V , then the stretching energy density is

$$\begin{aligned} W_{\text{stre}} &= \Delta F_{\text{stre}} / V \\ &= \frac{k_B T N}{V} [(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)/2 - \ln(\lambda_x \lambda_y \lambda_z)] \\ &\quad \times \sum_{j=c+1}^m P_j(n_j) \\ &= \frac{k_B T N}{V_0} \cdot \frac{V_0}{V} [(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)/2 - \ln(\lambda_x \lambda_y \lambda_z)] \\ &\quad \times \sum_{j=c+1}^m P_j(n_j), \end{aligned}$$

where V_0 is the volume of the dry hydrogel. Obviously, $\phi = V_0/V$, $\lambda_x \lambda_y \lambda_z = 1/\phi$, and $\lambda_x = \lambda_y = \lambda_z = (1/\phi)^{\frac{1}{3}}$ due to the isotropy.

To simplify the parameters, the volume of one Kuhn segment is assumed to be equal to v_m . Then V_0 can be approximated as

$$V_0 \approx v_m \sum_{j=1}^m n_j N_j = v_m N \sum_{j=1}^m n_j P_j(n_j),$$

and

$$\frac{N}{V_0} \approx \frac{N}{v_m N \sum_{j=1}^m n_j P_j(n_j)} = \frac{1}{v_m \sum_{j=1}^m n_j P_j(n_j)}.$$

Then the stretching energy density can be written as a function of ϕ ,

$$\begin{aligned} W_{\text{stre}} &= \frac{k_B T \phi}{v_m \sum_{j=1}^m n_j P_j(n_j)} \left[\frac{3}{2} \left(\frac{1}{\phi} \right)^{\frac{2}{3}} - \frac{3}{2} + \ln \phi \right] \\ &\quad \times \sum_{j=c+1}^m P_j(n_j) \\ &= \frac{k_B T}{v_m \sum_{j=1}^m n_j P_j(n_j)} \left[\frac{3}{2} \phi^{\frac{1}{3}} - \frac{3}{2} \phi + \phi \ln \phi \right] \\ &\quad \times \sum_{j=c+1}^m P_j(n_j). \end{aligned} \quad (13)$$

IV. NUMERICAL SIMULATION

A. Solving the model

In this section, the free-energy density is smoothed and regularized, then the stabilized semi-implicit difference scheme is presented to solve the TDGL equation.

Since chemical experiments[8] indicated that the chain lengths in the PNIPA-clay nanocomposite hydrogel are with a narrow distribution, the value of m should not be very large. Thus, the case that there are two types of polymer chains in the hydrogel is considered in this paper for simplicity, namely, $m = 2$. Other cases with larger m are similar and the strategy used in this section is suitable for all cases of m taking discrete finite values.

According to Eq. (8) with $\lambda = \lambda_x = \lambda_y = \lambda_z = (1/\phi)^{\frac{1}{3}}$, n_c can be rewritten as a function of ϕ ,

$$n_c = \frac{3k_B T \lambda D}{f_0 b^2} = \frac{3k_B T D}{f_0 b^2} \phi^{-\frac{1}{3}}.$$

In the case $m = 2$, compare n_c with the Kuhn segment number n_1 and n_2 , there are three cases, corresponding to the cases in Sec. III and the critical cases are that $n_c = n_j$, namely, $\phi = [(3k_B T D)/(f_0 b^2)]^3 / n_j^3 \triangleq A_j$, ($j = 1, 2$).

(1) Case 1: When $n_1 < n_2 \leq n_c$, namely, $\phi \leq A_2$, all polymer chains are detached from crosslinks.

(2) Case 2: When $n_1 \leq n_c < n_2$, namely, $A_2 < \phi \leq A_1$, only the polymer chains with n_1 Kuhn segments are detached from crosslinks, and the polymer chains with n_2 Kuhn segments are connected by crosslinks and form networks.

(3) Case 3: When $n_c < n_1 < n_2$, namely, $\phi > A_1$, all polymer chains are connected by crosslinks and form networks.

Then the free-energy density, as a function of ϕ , can be written as a piecewise function. To simplify the expressions, let $K_j = P_j(n_j) n_j / [P_1(n_1) n_1 + P_2(n_2) n_2]$, ($j = 1, 2$), then $\phi_{p1} = K_1 \phi$, $\phi_{p2} = K_2 \phi$. Combine Eq. (13) with Eqs. (10), (11), and (12), the normalized piecewise free-energy density can be written as

$$\begin{aligned} \frac{W v_m}{k_B T} &= G(\phi) + \left[\alpha_1(\phi) \frac{K_1}{n_1} \ln K_1 + \alpha_2(\phi) \frac{K_2}{n_2} \ln K_2 \right] \phi \\ &\quad + \chi \phi (1 - \phi) + \left[\beta_1(\phi) \frac{K_1}{n_1} + \beta_2(\phi) \frac{K_2}{n_2} \right] \left(\frac{3}{2} \phi^{\frac{1}{3}} - \frac{3}{2} \phi \right), \end{aligned} \quad (14)$$

where

$$G(\phi) = (1 - \phi) \ln(1 - \phi) + \tilde{K}(\phi) \phi \ln \phi,$$

with $\tilde{K}(\phi) = \alpha_1(\phi) \frac{K_1}{n_1} + \alpha_2(\phi) \frac{K_2}{n_2} + \beta_1(\phi) \frac{K_1}{n_1} + \beta_2(\phi) \frac{K_2}{n_2}$. $\alpha_i(\phi)$ and $\beta_i(\phi)$ are piecewise functions of ϕ with $\alpha_i(\phi) = \begin{cases} 0 & \text{if } \phi > A_i \\ 1 & \text{if } \phi \leq A_i \end{cases}$ and $\beta_i(\phi) = \begin{cases} 1 & \text{if } \phi > A_i \\ 0 & \text{if } \phi \leq A_i \end{cases}$ ($i = 1, 2$).

However, the processes of chain detachment and reattachment are actually not abrupt and they should be continuous in the statistical sense, since it is impossible that all the polymer chains of one type are detached or reattached at the same time. To model this continuous process, an infinite differentiable function is used to smooth the discontinuity point of the free-energy density approximately. Namely, the infinite differentiable functions $\bar{\alpha}_i(\phi)$ and $\bar{\beta}_i(\phi)$ are used to replace $\alpha_i(\phi)$ and $\beta_i(\phi)$, where

$$\bar{\alpha}_i(\phi) = \frac{1}{2} \tanh \left(\frac{5(-\phi + A_i)}{\epsilon} \right) + \frac{1}{2} \quad (15)$$

and

$$\bar{\beta}_i(\phi) = \frac{1}{2} \tanh \left(\frac{5(\phi - A_i)}{\epsilon} \right) + \frac{1}{2}. \quad (16)$$

Obviously, $\bar{\alpha}_i(\phi)$ and $\bar{\beta}_i(\phi)$ are smooth and satisfies

$$\bar{\alpha}_i(\phi) \approx \begin{cases} 0 & \text{if } \phi > A_i + \epsilon \\ 1 & \text{if } \phi \leq A_i - \epsilon \end{cases}$$

and

$$\bar{\beta}_i(\phi) \approx \begin{cases} 1 & \text{if } \phi > A_i + \epsilon \\ 0 & \text{if } \phi \leq A_i - \epsilon, \end{cases}$$

where the smoothing parameter $\epsilon > 0$. Following Zhu's work [31] and references therein, the logarithmic terms in W can be regularized from domain $(0, 1)$ to $(-\infty, +\infty)$, namely, $G(\phi)$ can be regularized as

$$\hat{G}(\phi) = \begin{cases} \tilde{K}(\phi) \phi \ln \phi + \frac{(1-\phi)^2}{2\xi} + \\ (1 - \phi) \ln \xi - \frac{\xi}{2}, & \text{when } \phi \geq 1 - \xi, \\ G(\phi), & \text{when } \xi \leq \phi \leq 1 - \xi, \\ (1 - \phi) \ln(1 - \phi) + \tilde{K}(\phi) \left(\frac{\phi^2}{2\xi} + \right. \\ \left. \phi \ln \xi - \frac{\xi}{2} \right), & \text{when } \phi \leq \xi, \end{cases}$$

where the parameter $\xi > 0$. Obviously, when $\xi \rightarrow 0$, $\hat{G}(\phi) \rightarrow G(\phi)$.

Thus, the smoothed and regularized free-energy density $\hat{W}$ is written as

$$\begin{aligned} \frac{\hat{W} v_m}{k_B T} &= \hat{G}(\phi) + \left[\bar{\alpha}_1(\phi) \frac{K_1}{n_1} \ln K_1 + \bar{\alpha}_2(\phi) \frac{K_2}{n_2} \ln K_2 \right] \phi \\ &\quad + \chi \phi (1 - \phi) + \left[\bar{\beta}_1(\phi) \frac{K_1}{n_1} + \bar{\beta}_2(\phi) \frac{K_2}{n_2} \right] \\ &\quad \times \left(\frac{3}{2} \phi^{\frac{1}{3}} - \frac{3}{2} \phi \right). \end{aligned} \quad (17)$$

FIG. 3. The evolution of the piecewise energy density $(W v_m)/(k_B T)$ with ϕ .

Substitute the energy functional Eq. (17) into Eqs. (2) and (3) with Eq. (5), then the TDGL equation is written as

$$\frac{\partial \phi}{\partial t} = H \Delta \frac{\delta U[\phi]}{\delta \phi} - \theta \sqrt{2H} \nabla \cdot \eta, \quad (18)$$

where $U[\phi]$ is the energy functional given by Eq. (2), namely,

$$\frac{U[\phi]}{k_B T} = \int \left(\frac{\hat{W}(\phi)}{k_B T} + \kappa |\nabla \phi|^2 \right) d\mathbf{x}.$$

The variational derivative of $U[\phi]$ with respect to ϕ can be written as

$$\frac{\delta U[\phi]}{\delta \phi} = f(\phi) - 2\kappa \Delta \phi, \quad (19)$$

where $f(\phi) = \left(\frac{\hat{W}}{k_B T} \right)'(\phi)$.

FIG. 4. The evolution of the smoothed and regularized free-energy density $(\hat{W} v_m)/(k_B T)$ with ϕ .

FIG. 5. The local magnification of $(\hat{W} v_m)/(k_B T)$.

Treating the linear part of ϕ implicitly and the nonlinear part explicitly, the time-discretized form is

$$\begin{aligned} \frac{\phi^{n+1} - \phi^n}{\Delta t} &= H \Delta [f(\phi^n) + s(\phi^{n+1} - \phi^n) - 2\kappa \Delta \phi^{n+1}] \\ &\quad - \theta \sqrt{2H} \nabla \cdot \eta^n \\ &= H [\Delta f(\phi^n) + s \Delta (\phi^{n+1} - \phi^n) - 2\kappa \Delta^2 \phi^{n+1}] \\ &\quad - \theta \sqrt{2H} \nabla \cdot \eta^n, \end{aligned} \quad (20)$$

where the stabilization term $s \Delta (\phi^{n+1} - \phi^n)$ is added to enhance the stability [32]. Furthermore, due to the periodic boundary conditions, the fast Fourier transformation method is applied to solve the equation and accelerate the computation [33].

B. Numerical results

In this section, the numerical results of the proposed Cahn-Hilliard-Cook equation are presented to show the process of the phase separation. We consider the proposed equation in a

FIG. 6. Evolutions of ϕ at time $t = 0$.

FIG. 7. Evolutions of ϕ at time $t = 20$.

dimensionless form and the parameters are set as $H = 1$, $\kappa = 0.5$, $\chi = 1.35$, $v_m = 1$, $b = 1$, $\epsilon = 0.02$, $s = 400$, $\xi = 0.002$, $n_1 = 11$, $n_2 = 15$, and $D = \sqrt{13}b$. The bonding strength is chosen as $(f_0 b)/(k_B T) = 1.8$, according to Rubinstein's theory [28].

Then we compare the piecewise free-energy density $(W v_m)/(k_B T)$ [Eq. (14)] with the smoothed and regularized free-energy density $(\hat{W} v_m)/(k_B T)$ [Eq. (17)] in Figs. 3 and 4, which shows that the discontinuity points are smoothed and the smoothed and regularized free-energy density $(\hat{W} v_m)/(k_B T)$ has two minimums from Fig. 4 and the local magnification in Fig. 5, in which case the phase separation would occur.

The numerical experiments are carried out on the domain $\Omega = [0, 30] \times [0, 30] \times [0, 30]$ with $128 \times 128 \times 128$ mesh nodes, strength of the thermal noise is set as $\theta = 10^{-3}$ and the time step $\delta t = 0.005$. We first give the initial data as

$$\begin{aligned} \phi(\mathbf{x}, 0) &= \phi(x, y, z, 0) \\ &= 0.4 + 0.05 \cos(2x/30) \\ &\quad \times \cos(2y/30) \cos(2z/30). \end{aligned} \quad (21)$$

FIG. 8. Evolutions of ϕ at time $t = 50$. FIG. 9. Evolutions of ϕ at time $t = 70$.

The evolutions of ϕ at different times during the phase separation are shown in Figs. 6–10, revealing that the polymer chains get together and merge into bigger blocks, which indicates the process of the phase separation. In Figs. 6–10, only the isosurfaces of $\phi > 0.4$ are plotted, namely, the concentrated polymer segments are shown (the red or the gray domain), and ϕ with smaller values, approximately, the solvent molecules are neglected (the vacant domain). The time evolution of the free-energy functional $U[\phi]/k_B T$ is shown in Fig. 11, and the corresponding local magnification is shown in Fig. 12, which demonstrates that the stabilized semi-implicit scheme Eq. (20) satisfies the discrete energy dissipation law in this case and the system is in the equilibrium state when $t = 100$.

C. Comparison with experimental results

In this section, the proposed Cahn-Hilliard-Cook equation is utilized to simulate the phase separation of the PNIPA–clay nanocomposite hydrogels when the system is cooled down sufficiently. The energy evolution is studied and the numerical results are compared with the chemical experimental results.

The morphology of the PNIPA–clay nanocomposite hydrogels was investigated by scanning electron microscope (SEM) [7]. For SEM analysis, the swollen hydrogels are cooled down

FIG. 10. Evolutions of ϕ at time $t = 100$.

FIG. 11. Time evolution of the free energy $U[\phi]/k_B T$ with the initial data [Eq. (21)].

sufficiently, where the hydrogels become thermodynamically unstable and tend to separate into two phases of the polymer-poor phase and the polymer-rich phase, namely, the thermally induced phase separation occurs. The quenching process causes the solvent to crystallize and the crystallized solvent is further removed by freeze-drying. After that, the polymer-rich phase solidifies to a porous structure. Haraguchi's group [8] has shown that the swollen PNIPAA-clay nanocomposite hydrogels were uniform and exhibited high transparency at the room temperature. Thus, to describe the phase separation, we choose the initial condition for ϕ as $\phi(\mathbf{x}, 0) \equiv \phi_0$ to simulate the initial uniform system. And other parameters are the same as those in Sec. IV B.

Since the SEM micrograph shows the state of the nanocomposite hydrogel after the phase separation, it makes sense to compare the equilibrium state of our numerical results with the SEM micrograph. From the energy evolution in Figs. 13 and 14, the system is in the equilibrium state when $t = 5000$. Figure 15 shows the SEM micrograph of

FIG. 12. The local magnifications of Fig. 11.

FIG. 13. Time evolution of the free energy $U[\phi]/k_B T$ with the initial volume fraction of the polymer $\phi_0 = 0.4$.

the PNIPAA-clay nanocomposite hydrogel with the scale of $50 \mu\text{m}$, given by Ma [7], and Figs. 16, 17, and 18 show the numerical simulation results at $t = 5000$ observed from different angles. The isosurfaces of $\phi > 0.4$ are plotted, namely, the concentrated polymer segments are shown (the red or the gray domain), and the solvent molecules are neglected (the vacant domain). It is shown that the pattern reveals porous microstructure, which is consistent with the SEM micrograph.

We can compare our numerical results with the SEM micrograph by estimating the porosity. Porosity is a measure of the void spaces in a material and is defined as a fraction of the volume of voids over the total volume. Namely,

$$\text{Porosity } P_r = \frac{\text{volume of voids}}{\text{total volume}}.$$

We first estimate the porosity of the PNIPAA-clay nanocomposite hydrogel from the SEM micrograph. It can be seen from Fig. 15 that the pores with

FIG. 14. The local magnification of Fig. 13.

FIG. 15. The SEM micrograph of the PNIPA–clay nanocomposite hydrogel. (Reproduced from Ref. [7] with permission.)

average diameter approximately $50 \mu\text{m}$ were formed and the average thickness of the polymer-rich phase was about $16.7 \mu\text{m}$. Approximating that the whole hydrogel system is composed of hollow cylinders, the porosity of the PNIPA–clay nanocomposite hydrogel, roughly estimated from the SEM micrograph, is equal to

$$\begin{aligned} p_r^{\text{SEM}} &= \frac{\text{volume of the pores}}{\text{volume of hollow cylinders}} \\ &= \frac{\pi(25 \mu\text{m})^2}{\pi(25 \mu\text{m} + 16.7 \mu\text{m})^2} \\ &\approx 0.3594, \end{aligned}$$

since the radius of the pores are about $25 \mu\text{m}$ and the radius of the whole cylinders are about $25 \mu\text{m} + 16.7 \mu\text{m} = 41.7 \mu\text{m}$.

For the equilibrium state of our numerical simulation results, we define the polymer-poor phase as the phases

FIG. 17. Isosurface plot of $\phi > 0.4$ at $t = 5000$ from a different angle.

with $\phi < 0.05$. Since the polymer-poor phase is removed by freeze-drying after the quenching process, we can estimate the void space as the polymer-poor phase, namely, the porosity of the PNIPA–clay nanocomposite hydrogel estimated from the numerical results is equal to

$$\begin{aligned} p_r^{\text{NumR}} &= \frac{\text{volume of the polymer-poor phase}}{\text{volume of the whole hydrogel system}} \\ &\approx 0.3596. \end{aligned}$$

It is very close to the porosity estimated from the SEM micrograph. Thus, the numerical results are consistent with the chemical experiments.

The proposed Cahn-Hilliard-Cook equation simulates the time-dependent process of the phase separation when the PNIPA–clay nanocomposite hydrogel is cooled down sufficiently. Here, we plot the cross sections of $x = 15$, $y = 15$, and $z = 15$ to show evolutions of ϕ at different times during the phase separation in Figs. 19–23, where the red (dark gray)

FIG. 16. The isosurface plot of $\phi > 0.4$ at $t = 5000$.

FIG. 18. Isosurface plot of $\phi > 0.4$ at $t = 5000$ from a different angle.

FIG. 19. Evolutions of ϕ for the initial volume fraction of the polymer $\phi_0 = 0.4$ at time $t = 5$.

domains indicate the larger values of ϕ , corresponding to the polymer-rich phase. The time evolutions of ϕ reveal that the hydrogel separates into two phases, namely, the polymer-poor phase and the polymer-rich phase, indicating the process of the phase separation.

V. CONCLUSIONS

In this work, the phase separation of the PNIPAA-clay nanocomposite hydrogel in the three-dimensional case has been investigated using the Cahn-Hilliard-Cook equation.

The contribution of the present work is on proposing a new free-energy functional to the classical Cahn-Hilliard-Cook equation. It consists of the stretching energy and the mixing energy, describing the physical deformation of polymer chains during the phase separation and the interactions between polymer chains and solvents respectively. The processes of polymer chains with inhomogeneous chain lengths detaching from and reattaching on crosslinks during the phase separation are considered in the proposed free-energy functional. Com-

FIG. 21. Evolutions of ϕ for the initial volume fraction of the polymer $\phi_0 = 0.4$ at time $t = 20$.

pared with the previous work, the proposed free energy in the derived Cahn-Hilliard-Cook equation makes great improvement. It is a good complement to the existing theories.

A stabilized semi-implicit difference scheme is utilized to numerically solve the Cahn-Hilliard-Cook equation. Numerical results reveal the porous microstructure in the equilibrium state, consistent with the SEM micrograph of PNIPAA-clay nanocomposite hydrogels. The proposed model simulates the time-dependent process of the phase separation, which shows that the hydrogel separates into two phases of the polymer-poor phase and the polymer-rich phase.

The novelty of the present work is that some adaptations have been made to the classical free energy of the Cahn-Hilliard-Cook equation. The processes of polymer chains with inhomogeneous chain lengths detaching from and reattaching on crosslinks during the phase separation are considered, such that the proposed model is a good extension to the existing theories. However, the deformations of the hydrogel

FIG. 20. Evolutions of ϕ for the initial volume fraction of the polymer $\phi_0 = 0.4$ at time $t = 10$.

FIG. 22. Evolutions of ϕ for the initial volume fraction of the polymer $\phi_0 = 0.4$ at time $t = 40$.

FIG. 23. Evolutions of ϕ for the initial volume fraction of the polymer $\phi_0 = 0.4$ at time $t = 50$.

during the phase separation is assumed to be isotropic here. According to Doi's work [25], the anisotropic deformations are essential to describe the phase coexistence, leading to important effects, such as hysteresis and incubation. The stretching energy will be generalized in our future work to take the anisotropic deformation into consideration.

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APPENDIX: DERIVATION OF EQ. (6)

According to Gaussian statistics, when one end of a chain is attached to one crosslink, the chance that the n_j th Kuhn segment along the chain is at the position D within a distance ΔD can be considered as a 1D random-walk problem. The

probability is

$$P_1 = \left(\frac{3}{2\pi sb^2} \right)^{\frac{1}{2}} \exp \left(-\frac{3D^2}{2sb^2} \right).$$

Here, we assume that the perturbation ΔD can be approximated as a circle with radius b , namely, $\Delta D \approx b$.

Denote ρ as the probability that the n_j th segment with length b can attach on the crosslink and ρ is only related to the properties of the crosslink. The probability that the n_j th Kuhn segment attach on another crosslink (with one end attached on one crosslink) can be written as

$$P_2 = P_1 \rho = b\rho \left(\frac{3}{2\pi sb^2} \right)^{\frac{1}{2}} \exp \left(-\frac{3D^2}{2sb^2} \right).$$

Similarly, the probability that the 1st to the $(n_j - 1)$ th Kuhn segments cannot attach on the crosslink is

$$P_3 = \prod_{s=1}^{n_j-1} \left[1 - b\rho \left(\frac{3}{2\pi sb^2} \right)^{\frac{1}{2}} \exp \left(-\frac{3D^2}{2sb^2} \right) \right].$$

Then the probability that the polymer chain with n_j Kuhn segments is bridged by two crosslinks with distance D can be written as

$$\tilde{P}(n_j) = P_2 P_3.$$

Since

$$\begin{aligned} P_3 &= \exp \left\{ \sum_{s=1}^{n_j-1} \ln \left[1 - b\rho \left(\frac{3}{2\pi sb^2} \right)^{\frac{1}{2}} \exp \left(-\frac{3D^2}{2sb^2} \right) \right] \right\} \\ &\approx \exp \left(\frac{\sqrt{6}\rho}{\sqrt{\pi}} \{ -\sqrt{n_j} e^{-G} + e^{-G n_j} - \sqrt{\pi G n_j} [\text{erf}(\sqrt{G}) - \text{erf}(\sqrt{G n_j})] \} \right), \end{aligned}$$

with $G = \frac{3D^2}{2n_j b^2}$ and $\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$.

Thus,

$$\begin{aligned} \tilde{P}(n_j) &= \rho \left(\frac{3}{2\pi n_j} \right)^{\frac{1}{2}} \exp \left\{ -G - \frac{\rho}{\sqrt{\pi}} \left[\sqrt{6 n_j} e^{-G} + 3\sqrt{\pi} \frac{D}{b} \text{erf}(\sqrt{G}) - \sqrt{6} e^{-G n_j} - 3\sqrt{\pi} \frac{D}{b} \text{erf}(\sqrt{G n_j}) \right] \right\}. \end{aligned}$$

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