A model to describe the micro-structure of macromolecular microsphere composite (MMC) hydrogel is proposed in the framework of self-consistent mean field theory (SCMFT), which is usually used to investigate copolymer. Based on the SCMFT approximation, a system of equations associated with the complex topology of MMC hydrogel is derived and solved by a new kind of relaxation algorithm successfully. From the numerical simulation of the model, we find that the two model parameters play important roles in describing the micro-structure of MMC hydrogel, the interactions between two species (polymer chains and MMS spheres) and the volume fraction of MMS spheres. The role of other model parameters on the structure of the MMC hydrogel is also discussed. The numerical results are consistent with the observation from the chemical experiments. Moreover, we also show some new micro-structures obtained by using the SCMFT model, but discovered in chemical experiments.

Keywords: Macromolecular microsphere composite (MMC) hydrogel; micro-structure; self-consistent mean field theory; pseudo-spectral method.

1. Introduction

Hydrogels have a wide range of industrial applications due to their high performance mechanical properties, high compressive strength as well as shape recoverability. They consist of three-dimensional randomly crosslinked polymer networks that absorb substantial amounts of aqueous solution. They can exhibit both solid-like and liquid-like properties so that they are widely applied to drug delivery, biosensors, tissue engineering, micro-electromechanical system devices, etc. However, hydrogels synthesized by traditional methods often cannot exhibit desired properties. They break down under low stress force easily. The essential reason for this phenomenon is that the crosslinking points are distributed randomly and the polymer chains between crosslinking points are of different lengths so that they cannot dissipate external energy efficiently. As a consequence, improving both the
mechanical strength and robustness of hydrogels is one of the primary challenges in materials design and engineering.

Recently, novel hydrogel has been synthesized and named Macromolecular Microsphere Composite (MMC) Hydrogel by Wang’s group.\textsuperscript{7} Compared to the tradition hydrogels with randomly distributed crosslinkers, both the density of crosslinking points and the number of polymer chains between them have been greatly increased. In the new hydrogel, polymer chains are chemically grafted onto macromolecular microspheres (MMSs), instead of physically attached as traditional ways do. There are a sufficiently large number of polymer chains grafted on each MMS, which definitely enhance its mechanical properties. The neighboring MMSs are connected through the polymer chains when they begin to polymerize graft longer and longer. In addition, these chains are entangled and can stretch out while swelling. The proposed scheme for the formation of MMC hydrogel is shown in Fig. 1 illustrating the swelling behavior of the hydrogel.\textsuperscript{7}

However, it is such an expensive and time-consuming work to make chemically synthesized experiments. With the aid of computational method, it leads to a new era. Unfortunately, there are very few quantitative studies directed at such hydrogels with the wonderful mechanism, especially its structure. In the past, mathematical models were introduced to understand and predict the mechanism observed experimentally, primarily from the macroscopic perspective. They included models which were used to study the behavior of swelling according to the Flory’s theory.\textsuperscript{8} Later a diffusion model for the dynamics of swelling gels was first proposed by Tanaka\textsuperscript{9} and then further developed by Doi.\textsuperscript{10} Recently, Suo has explored a new theoretical formalism to describe mass transport of small molecular species coupled with deformation of hydrogel.\textsuperscript{11} Almost all of these studies largely focus on the mechanical

![Fig. 1. The scheme for the formation of MMC hydrogel.\textsuperscript{7}](image-url)
function of hydrogel from macroscopic perspective. However, this definitely gives rise to a potential problem that they ignore the structures, on which the mechanical function of these hydrogel depends upon. In order to deal with potential problem, the self-consistent mean field theory (SCMFT) model is proposed to study the micro-structure of MMC hydrogel in this paper.

Actually, one obvious computational way to simulate the structure of MMC hydrogel is to employ molecular dynamics (MD) method. However, it is quite expensive for such large and complex systems, like hydrogels, to extract significant information about the structure and thermodynamics at realistic conditions. Hence, we need to seek another efficient method. It is convenient to adopt mesoscopic method to predict the behavior of micro-structure of this system by using SCMFT.

Compared to MD simulations, SCMFT, which is a mean field approximation based on coarse-grained descriptions, has a great computational advantage in describing the entire structure as well as interactions among different species of molecules. To some extent, it is a powerful and flexible phenomenological theory and has been applied to study the equilibrium micro-phase behavior. SCMFT is usually used to investigate the micro-structure of copolymer, AB-diblock and ABC-triblock copolymer, etc. Here MMC hydrogel possesses complex topology with many grafted polymer chains from one MMS and MMSs are connected with each other through entangle polymer chains. So we will establish a model of SCMFT with this special topology structure. Moreover the usual computational method of SCMFT does not work for this special topological soft matter. Now we will present a new kind of relaxation algorithm based on the computational method of SCMFT to simulate the structure. Through the new model and computational method we obtain the similar micro-structures as the ones from chemical experiments. Furthermore, we also discover some new micro-structures which have not been observed in chemical experiments. When we finish this work, we find another method to investigate morphologies of micelles of polymers, which is the dissipative particle dynamics (DPD). It is possible to be a good choice to simulate the micro-structure of MMC hydrogel.

This paper is organized as follows. In Sec. 2, we establish a mathematical model for MMC hydrogels based on self-consistent field theory and special topology structure. Then, we design a new algorithm to simulate the SCMFT model and obtain the micro-structure of the MMC hydrogel in Sec. 3. Last we show the numerical results and draw a conclusion in Secs. 4 and 5, respectively.

2. Theoretical Model

In this section, we will derive a SCMFT model to capture the essential characteristics of micro-structure of the MMC hydrogel. As shown in Fig. 1, the main characteristics of topology structure of MMC hydrogel is as follows: polymer chains are grafted onto the MMSs, and MMSs are connected with each other through entangled polymer chains. This structure leads to high mechanical performance. To synthesize MMC hydrogels experimentally, there are four critical parameters, namely the
concentration of MMS, the irradiation time of MMS, the monomer concentration and the temperature of reaction. Here we are much more interested in the concentration of MMS and one of the monomer molecules in the equilibrium state while taking other parameters as constants in the following discussion.

We assume that the system consists of \( n_p \) polymer chains with same chemical monomers and \( n_m \) MMS spheres. To simplify the model, we hypothesize the distribution of these chains on each MMS sphere is uniformly independent identity distribution and the number of the polymer chains on each spheres is also the same. These polymer chains are modeled as flexible Gaussian chain consisting of \( N \) segments, each of which contains volume \( v_p \) and a statistical length \( b \) (Kuhn length). Each MMS is considered as a same sphere with volume of \( v_m \). The boundary condition is periodic boundary since we assume that the system is large enough so that the influence of boundaries on the polymer chains can be ignored.

According to the continuous Gaussian chain model, each of grafted polymer chains is described by a continuous curve \( r(s) \) representing all possible configurations of the macromolecules. The main characteristic of micro-structure as mentioned above that polymer chains grafted on spheres uniformly and independently can be described by the variables, which is increased continuously along the length of the chain and \( s = N \) indicates it is at the MMSs surface and \( s = 0 \) is at its flexible extreme. Then the conformational entropy of these polymer chains has a distribution which is proportional to a Gaussian statistical weight \( e^{-\beta U_0} \), where \( \beta U_0 \) is the elastic energy, namely,

\[
\beta U_0 = \sum_{j=1}^{n_p} \frac{3}{2N b^2} \int_0^1 ds \left| \frac{dr(s)}{ds} \right|^2 = \frac{1}{4 R_g^2} \sum_{j=1}^{n_p} \int_0^1 ds |r'(s)|^2,
\]

where \( \beta \) equals to \( 1/k_B T \) and \( R_g = b \sqrt{N/6} \) denotes the radius of gyration of a polymer chain. The interaction between MMSs and polymer chains are considered to be non-bonded, which can be determined by the parameter \( \chi \) in the Flory—Huggins Lattice theory. Then the interaction energy \( \beta U_1 \) denotes:

\[
\beta U_1 = \rho_0 \int dr x \hat{\rho}_m(r) \hat{\rho}_p(r).
\]

Here \( \rho_0 \) is a reference constant of segment density (without the loss of generality we choose \( \rho_0 = 1 \)) and the function \( \hat{\rho}_p(r) \) is introduced to represent microscopic segment density of polymer chains. So is \( \hat{\rho}_m(r) \), the density of the spheres. They can be defined respectively as following:

\[
\hat{\rho}_m(r) = v_m \sum_{j=1}^{n_m} \delta(r - r_j(1)),
\]

\[
\hat{\rho}_p(r) = v_p N \sum_{j=1}^{n_p} \int_0^1 ds \delta(r - r_j(s)).
\]
Here $r_j$ (1) denotes the position of a MMS. And in our system, the volume of polymer chain segment $v_p$ is considered as a reference constant volume. The formula of micro-density $\rho_m(r)$ also describes the characteristics mentioned above that the polymer chains are grafted on the MMS sphere and the fixed extreme is connected to the sphere while the other extreme is flexible.

Similar to the method in the Ref. 1, the relevant partition function in canonical ensemble for this system can be written as:

$$
\mathcal{Z} = \frac{1}{n_p! n_m! \lambda_T^{3(n_p N + n_m)}} \prod_{j=1}^{n_p} \prod_{l=1}^{n_m} \mathcal{D}r_j \mathcal{D}r_l \exp(-\beta U_0 - \beta U_1) \delta[1 - \hat{\rho}_p(r) - \hat{\rho}_m(r)] \\
\times \prod_{j=1}^{n_p} \prod_{l=1}^{n_m} \mathcal{D}r_j \mathcal{D}r_l \exp(-\beta U_0 - \beta U_1) \delta[1 - \hat{\rho}_p(r) - \hat{\rho}_m(r)],
$$

where $\mathcal{D}r$ denotes the functional integral over all possible configurations of the polymer chains, and $\mathcal{D}r$ represents the normal integral over the position of the MMSs. The last term $\delta$ functional satisfies the local incompressibility constraint, namely, the sum of all microscopic segment volume fractions is equal to unity at all positions within the volume $V$. The parameter $\lambda_T$ represents the thermal wavelength, $m$ is the mass of an atom, and $\hbar$ is the Planck constant.

By using the Hubbard–Stratonovich transformation, the “particle-based” partition function can be transformed into the form of “field-based”. We invoke the identity:

$$
\int \mathcal{D}\rho \delta[\rho - \hat{\rho}] F[\hat{\rho}] = F[\rho]
$$

and

$$
\delta[\rho - \hat{\rho}] = \int \mathcal{D}w \exp \left[ \int d\mathbf{r} w(\mathbf{r})(\rho(\mathbf{r}) - \hat{\rho}(\mathbf{r})) \right],
$$

where $\rho$ is the average total corresponding microscopic densities $\hat{\rho}$.

By inserting the above formulas Eq. (5) and Eq. (6) into Eq. (4) and then according to the field theory, the equilibrium saddle-points are distributed along the imaginary axis in the complex field $w$ plane, so that the fields can be re-scaled as $W_m = iNw_m$, $W_p = iNw_p$, $\xi = iN\xi$, and the canonical partition function can be rewritten as follows:

$$
\mathcal{Z} \propto \int \mathcal{D}\rho_p \mathcal{D}\rho_m \mathcal{D}W_p \mathcal{D}W_m \mathcal{D}\xi \exp(-\beta H).
$$

The effective Hamiltonian above is expressed as:

$$
\frac{N\beta H}{\rho_0 V} = \frac{1}{V} \int d\mathbf{r} \chi N \rho_m(\mathbf{r}) \rho_p(\mathbf{r}) - W_p(\mathbf{r}) \rho_p(\mathbf{r}) - W_m(\mathbf{r}) \rho_m(\mathbf{r}) \\
- \xi(\mathbf{r})(1 - \rho_p(\mathbf{r}) - \rho_m(\mathbf{r})) - n_p \ln VQ_p - n_m \ln VQ_m.
$$
We put the details of calculation of Eqs. (7) and (8) in the Appendix since it is very complex. Here $Q_m$ and $Q_p$ are the partition functions for a single MMS and a polymer chain respectively, whose explicit expressions will be given later.

To solve this complex system, we approximate it by the saddle approximation method and then obtain the following self-consistent mean field equations for MMC hydrogels:

$$W_p(r) = \chi N \rho_m(r) + \xi(r), \quad (9)$$
$$W_m(r) = \chi N \rho_p(r) + \xi(r), \quad (10)$$
$$\rho_m(r) + \rho_p(r) = 1, \quad (11)$$
$$\rho_p(r) = \frac{n_p}{Q_p} \int_0^1 ds q(r,s) q^+(r,s), \quad (12)$$
$$\rho_m(r) = \frac{1}{Q_m} v_m q(r,0) q^+(r,1). \quad (13)$$

Here we emphasize that the (SCMFT) system, Eqs. (9)–(13), is very significant. It makes the many-body system to be replaced by a one-body problem with a chosen good external field. The external field replaces the interaction of all the other particles to an arbitrary particle. If we compute directly the partition function, Eq. (4) of the system, the great difficulty is the treatment of combinatorics generated by the interaction terms, Eq. (2). The goal of mean field system, Eqs. (9)–(13), is to resolve these combinatorial problems.

Here $q(r)$ and $q^+(r)$ in Eqs. (12) and (13) are the propagators for the conformations of polymer chains, both of which obey the modified diffusion equation.

$$\frac{\partial q}{\partial s} = R_g^2 \nabla^2 q - W_p(r) q(r,s),$$
$$q(r,0) = \exp(-v_m W_m(r)/N). \quad (14)$$

It is noticed that since the volume of the polymer chain segment is treated as a reference constant, we can set it as unity. Thus the volume $v_m$ of the MMS sphere is the actual quantity compared to the reference quantity, the volume $v_p$ of the segment of polymer chain.

The reverse propagator $q^+$ (starting from the free tail end of polymer chain) satisfies the following equations:

$$\frac{\partial q^+}{\partial s} = -R_g^2 \nabla^2 q^+ + W_p(r) q^+(r,s),$$
$$q^+(r,1) = \frac{\sigma}{q(r,0)}. \quad (15)$$

The distribution of the ends of chains on the MMS is specified by the local grafting density $\sigma$, which can be explained as the area fraction of surface occupied by the grafting end at MMS. To simplify the problem, we assume the grafting density $\sigma$ to be a constant. In the following we choose $\sigma = 1/(4\pi R^2)$, where $R = (5 \sim 15) * R_g$ is
the radius of the MMS. In the following computing we set \( R_g = 1 \). What is more, the initial condition of the propagator again reflects the specific structure that polymer chains are grafted on spheres. Next, the formulas for \( Q_m \) and \( Q_p \) are given respectively by:

\[
Q_m = \frac{1}{V} \int d\mathbf{r} \exp(-v_m W_m(\mathbf{r})/N) q(\mathbf{r}, 1),
\]

\[
Q_p = \frac{1}{V} \int d\mathbf{q}(\mathbf{r}, 1).
\]

Here the three algebraic equations, Eqs. (9)–(11) determine the quantities \( W_p, W_m, \xi \). Equations (12) and (13) can be solved by Eqs. (14) and (15).

In fact, in order to emphasize the relationship between the mathematical model and observable quantities from chemical experiment, we can rewrite the free energy form and the corresponding self-consistent field equations in the following. Since the exerted fields are obtained according to the saddle approximation method, an additive constant to the free energy should have no effect on final phase state. Hence, the free energy can be rescaled by disordered phase \( H_0 \). It makes the free energy to be:

\[
\frac{N\beta \tilde{H}}{\rho_0 V} = \frac{1}{V} \int d\mathbf{r} [\chi N(\rho_m(\mathbf{r}) - f_m)(\rho_p(\mathbf{r}) - f_p) - W_p(\mathbf{r})(\rho_p(\mathbf{r}) - f_p)

- W_m(\mathbf{r})(\rho_m(\mathbf{r}) - f_m) - \xi(\mathbf{r})(1 - \rho_p(\mathbf{r}) - \rho_m(\mathbf{r}))]

- n_p \ln V Q_p - n_m \ln V Q_m,
\]

(17)

where \( f_p \) and \( f_m \) are constants, representing the average volume fraction of the polymer chains and the MMS spheres respectively. More specifically, \( f_m \) can be treated as the macro observed quantity, the value of the MMS spheres. It has a significant influence on the final regular phase according to the simulation. And it is consistent with the experimental result that the concentration of the MMS spheres can affect the formulation of MMC hydrogel.\(^7\) In the following simulation, we choose \( n_m \) is 10 \( \sim \) 50, and \( n_p \) is \( (5 \sim 25) \ast n_m \). Similarly, the formula for Eqs. (9)–(13) can be rewritten based on Eq. (17). In Eqs. (9) and (10), the density item \( \rho_k (k = m, p) \) should be replaced by \( \rho_k - f_k \). That is,

\[
W_p(\mathbf{r}) = \chi N(\rho_m(\mathbf{r}) - f_m) + \xi(\mathbf{r}),
\]

(18)

\[
W_m(\mathbf{r}) = \chi N(\rho_p(\mathbf{r}) - f_p) + \xi(\mathbf{r}),
\]

(19)

\[
\rho_m(\mathbf{r}) + \rho_p(\mathbf{r}) = 1,
\]

(20)

\[
\rho_p(\mathbf{r}) = \frac{n_p}{Q_p} \int_0^1 ds q(\mathbf{r}, s) q^+(\mathbf{r}, s),
\]

(21)

\[
\rho_m(\mathbf{r}) = \frac{1}{Q_m} \frac{v_m}{N} q(\mathbf{r}, 0) q^+(\mathbf{r}, 1).
\]

(22)
By introducing the parameters \( f_m \) and \( f_p \), it enables us to compare our simulation with experimental results. In addition, these formulas will be quite useful in the following numerical simulation. As there are two kinds of species in this system which are taken to be incompressible, we enforce the condition \( f_m + f_p = 1 \). With Eq. (20), addition of Eqs. (18) and (19) yields:

\[
\xi(r) = \frac{(W_p(r) + W_m(r))}{2}.
\]  

In the following simulation, we choose \( n_m = 10 \sim 50 \), and \( n_p = (5 \sim 25) \ast n_m \). \( v_m = (1.2 \sim 9) \ast v_p \) and \( v_p = 1 \).

3. Numerical Method

As mentioned above, Eqs. (9)–(13) are obtained by the saddle approximation, which is the saddle-point configurations of fields \( [W_p, W_m, \rho_p, \rho_m, \xi] \). For such a complex system with nonlinear and multiple solutions, analytical solution is almost unavailable. Hence we should design an iterative procedure for the saddle-point values. Here we only concern the state of equilibrium. The potential fields \( W_p, W_m \) can be treated as dynamical variables during the relaxation algorithm. The initial conditions of the propagator based on our topology structure of systems make it difficult to obtain stable solution, since the density fields of these two matters are highly coupled. To solve this problem, we use the relaxation algorithm to update field instead of the traditional relaxation algorithm as following. The expression for updating these fields from relaxation step \( n \) to \( n + 1 \) is:

\[
W_{m}^{n+1} - W_{m}^{n} = \lambda' \frac{\delta H}{\delta \rho_{m}^{n}} + \lambda \frac{\delta H}{\delta \rho_{m}^{n}},
\]

\[
W_{p}^{n+1} - W_{p}^{n} = \lambda' \frac{\delta H}{\delta \rho_{m}^{n}} + \lambda \frac{\delta H}{\delta \rho_{p}^{n}},
\]  

where the relaxation parameters are chosen such that they satisfy \( \lambda' < \lambda \) and \( \lambda > 0 \).

In numerical calculation, we set \( \lambda = 0.5 \) and \( \lambda' = 0.2 \). Basically, we should take the influence of both the polymer chain and sphere to update the new field. What is more, the choosing of parameters \( \lambda \) and \( \lambda' \) will impact the robustness of this algorithm. The larger the parameters are, the more unstable the algorithm is.

In general, the iterative algorithm contains the following steps:

(1) Set the random initial values for \( W_p, W_m \) and pressure \( \xi \).
(2) Solve the modified diffusion equations numerically to calculate propagator \( q(r) \) and \( q^+(r) \) according to Eqs. (14) and (15).
(3) Update the density to obtain \( \rho_{p}^{n}(r) \) and \( \rho_{m}^{n}(r) \) based on Eqs. (21) and (22).
(4) Update the external field at the \( n \)th step iteration \( W_{n} \) to get value at the \( (n + 1) \)th iteration \( W_{n+1} \).
(5) Update the pressure field via:

\[
\xi^{n+1}(r) = \frac{(W_{p}^{n+1} + W_{m}^{n+1})}{2}.
\]
(6) The procedure is repeated from step 2 until a saddle-point configurations is found.

After updating the pressure field, $V^{-1} \int \xi(r) dr$ is subtracted in order to improve the algorithm’s stability. In fact, it has no effect on the final equilibrium structure since it is invariant to a constant shift. Here we also remark that we can choose the random initial values for $W_p, W_m$ since the result of this numerical method is independent of the initial value.

At the same time, the most demanding step in the above algorithm is to solve the modified partial differential equations to obtain propagator $q$ and $q^+$ computationally. As the volume is taken to be large enough, the diffusion equation, Eqs. (14) and (15) are solved under periodic boundary conditions. An efficient way is using pseudo-spectral method.\(^{19,20}\) The expression for propagating at $q(r, s)$ to $q(r, s + ds)$ is:

$$q(r, s + ds) = \exp\left(-\frac{ds}{2} W_p\right) \exp(ds \nabla^2) \exp\left(-\frac{ds}{2} W_p\right) + \mathcal{O}(ds^3). \quad (26)$$

To simplify numerical computation, the terms of order $\mathcal{O}(ds^3)$ are ignored and then the explicit expression is:

$$q(r, s + ds) \approx \exp\left(-\frac{ds}{2} W_p\right) \hat{F}^{-1} \left[ \exp(-ds k^2) \hat{F} \left[ \exp\left(-\frac{ds}{2} W_p\right) q(r, s) \right] \right]. \quad (27)$$

The first factor $\exp(-ds/2W_p)$ is applied to $q(r, s)$ in real space. The Fourier transform $\hat{F}$ is used and the operator $\exp(ds \nabla^2)$ can be transformed into $\exp(-ds k^2)$ in reciprocal space. In the last step, the inverse Fourier transform $\hat{F}^{-1}$ is adopted again in real space to obtain $q(r, s + ds)$. There are two reasons for using such split-step Fourier algorithm: (1) it can be much faster because of the well-developed FFT skills; the publicly available FFTW libraries can be employed in the code and (2) this method is unconditionally stable in all dimensions and has high order of accuracy.

Remark: Now we point out that it is very important and necessary for the rigorous mathematical proof of this computation method used here. According to our known information, it is very effective for the pseudo-spectral method and similar relaxation algorithm articles used here in Refs. 19 and 20 and references therein. But there are no rigorous mathematical theory. So it is also our work to study later.

4. Result
4.1. Numerical result

With this algorithm, we have studied the possible morphological structures of MMC hydrogel system. Here we show a few examples of the micro-structure of the MMC hydrogels by numerical computation.

The parameter space has a great influence on the phase behavior of the MMC hydrogel system. Specifically, it is characterized by two kinds of primary
parameters: interaction parameter $\chi N$ and the total volume fraction of the MMS $f_m$. When the total fraction of the MMS is high, we can hardly observe polymer chain in the morphology, which is consistent with the beginning of the experiment (here we note that all experimental results in this paper are provided by Prof. Huiliang Wang’s research group in School of Chemical Sciences, Beijing Normal University). With the growing of the polymer chains, they become longer and longer, which means, to some extent, the parameter $\chi N$ becomes larger. The micro-structure tends to be more stable and oriented. From Fig. 2 we can see that the polymer exhibit a certain oriented and lamella structure. If we increase the total mass of MMSs in the system, we get the morphology depicted in Fig. 3. Similarly, if we decrease the value of MMSs, namely,
the fraction of polymer chains is decreased, the result is shown in Fig. 4. As the time goes by, the polymer chains tend to connect with each other to form lamella structure so that the MMSs are surrounded by them. If we change the initial number of the MMSs and polymer chains, we can obtain other structures shown in Fig. 5, where the color blue stands for the density profile of polymer chains, and the red describes the one of MMSs. From Fig. 5 we can see that the polymer chains are ordered in array and MMS spheres are packed on them. Now we remark that the values of $f_p$ and $f_m$ here are just empirical parameters to show these physical phenomena.

4.2. Discussion

As mentioned above, the parameter space has a great influence on the final phase behavior of this MMC hydrogel. According to the experiments, there are four critical
parameters, the concentration of MMS, the irradiation time of MMS, the monomer concentration and the temperature of reaction. Now, we first consider the influence of two parameters: the concentration of MMS and the monomer concentration. Here, we also investigate the length of the monomer chain and the interaction between MMS and polymer monomer.

4.2.1. Interaction force $\chi N$

Figure 6 illustrates the different phase morphologies with various ratios of interaction force $\chi N$ and total number fraction of MMSs $f_m$. It shows that with the increasing of MMSs, it is much easier to form sphere arranged orderly. However, if there are too many MMSs in the systems compared to the total volume fraction of polymer chains, it tends to form disordered phase structure. That is to say, the final phase state is unstable. At the same time, from the viewpoint of chemistry, MMSs just act as crossing-link points while polymer chains connect the neighboring spheres. Thus they can disperse stress effectively and show perfect mechanical properties. When the interaction force is between 0.2–0.5, the system can produce the stripe state and sphere perforate cylinder state during the simulation for longer polymer chains. These well-organized structures can lead to perfect mechanism according to the experimental results. Furthermore, we also test how the length of chains $N$ affects the final phase diagram. It shows that the longer the chain is, the more likely phase structures tend to be lamella phase. When the polymer chains are very long, it is hard to observe the MMS spheres apparently since MMS spheres are packed by the polymer chains. To our surprise, the numerical simulation shows that it is not true.

![Figure 6](image-url)

**Fig. 6.** Phase diagram of MMC hydrogels as a function of interaction force $\chi N$ and total fraction of MMSs $f_m$. The polymer chain length is $N = 80$. Circle denotes the sphere state, “+” denotes the strip state, diamond denotes the lamella state, and “*” denotes the disordered state.
that the longer the polymer chain is, the better the well-organized structure will be. When the length exceeds a certain value, there appears a disorder state again.

4.2.2. Ratio of spheres

In chemical experiments these MMSs can be replaced by micelles, so the volume of the sphere is important. In the following, we try to carry out the analysis on the influence of the volume of MMS to the final state. Now we introduce a parameter \( \alpha \) to be:

\[
\alpha = \frac{\text{the radius of MMS}}{\text{the length of each segment of a polymer chain}}.
\]

In Sec. 2, we know that \( N \) is the number of the segment of a polymer chain. From Fig. 7, we can see that the MMC hydrogels are always ordered as \( N \) increases from small to large for some fixed \( \alpha \). While they change from ordered to disordered as \( \alpha \) increases from small to large for some fixed \( N \). Therefore, it indicates that the larger the radius of MMS is, the more easily the phase structure tends to be disordered. Indeed, the chemical experiments shows that the volume of the sphere can be small since they just act as crossing-link points. It is reported that the radius of MMS is at the range of \( 30-100 \) nm. Besides, during the whole process, the total mass, number and shape of the MMSs stay the same, while the graft polymer chain grows longer. According to Fig. 7, it is hard to get the ideal MMC hydrogel when we use the larger MMS sphere compared to the length of each segment of a polymer chain.

Fig. 7. It plots phase diagram of MMC hydrogels as a function of parameter \( \alpha \), which denotes the ratio of the radius of MMS sphere and the length of each segment of a graft polymer chain. Circle means the ordered and lamella phases (including the sphere state, strip state and sphere perforate cylinder state) while “+” means the disordered phase.
5. Conclusions

A model for MMC hydrogels has been proposed in the framework of SCMFT to study the micro-structure of novel hydrogel. Using this model, we develop an efficient numerical algorithm combined with pseudo-spectral algorithm for modified diffusion equations to investigate some interesting and stable morphological structures. Two model parameters play important roles on the formation of various morphologies. The numerical findings reported in this paper are consistent with the experimental results from Wang’s group. But some of chemical experiments have not been published.

We ignore water molecules in the system in the SCMFT model here. The effects are important to the transition from other ordered phases. Furthermore, it would be wonderful to assess the importance of water molecules in this system, which is responsible for gel swelling. In addition, the topology in the structure of MMC hydrogel, such as the curvature of the grafted MMSs, would affect the morphology of the system as well. In our model, we assume that the density of the grafted polymer chain on each MMS is distributed as a constant, which may lead to the symmetry phenomena which we observed in Fig. 5. Hence a specific arrangement of these polymer chains would be a new direction.

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Appendix

Based on the property of the functional $\delta$, we can calculate the partition function as follows:

\[
\mathcal{Z} \propto \prod_{j=1}^{n_p} \int \mathcal{D} \mathbf{r}_j \prod_{l=1}^{n_m} \int d\mathbf{r}_l \exp(-\beta U_0 - \beta U_1) \delta[1 - \hat{\rho}_p(\mathbf{r}) - \hat{\rho}_m(\mathbf{r})]
\]

\[
\propto \prod_{j=1}^{n_p} \int \mathcal{D} \mathbf{r}_j \prod_{l=1}^{n_m} \int d\mathbf{r}_l \exp(-\beta U_0 - \beta U_1) \mathcal{D} \rho_p \delta[\rho_p(\mathbf{r}) - \hat{\rho}_p(\mathbf{r})]
\]

\[
\times \mathcal{D} \rho_m \delta[\rho_m(\mathbf{r}) - \hat{\rho}_m(\mathbf{r})] \delta[1 - \rho_p(\mathbf{r}) - \rho_m(\mathbf{r})]
\]
\[
\alpha \prod_{j=1}^{n_p} \int \mathcal{D} r_j \prod_{l=1}^{n_m} \int dr_l \exp(-\beta U_0 - \beta U_1) \times \int \mathcal{D} \rho_p \int \mathcal{D} w_p \exp \left( i \int dr_p(r)(\rho_p(r) - \hat{\rho}_p) \right) \\
\times \int \mathcal{D} \rho_m \int \mathcal{D} w_m \exp \left( i \int dr_m(r)(\rho_m(r) - \hat{\rho}_m) \right) \times \int \mathcal{D} \xi \exp \left( i \int dr \xi(r)(1 - \rho_m(r) - \rho_p(r)) \right) \\
\alpha \prod_{j=1}^{n_p} \int \mathcal{D} r_j \prod_{l=1}^{n_m} \int dr_l \exp(-\beta U_0) \exp \left( -\int dr \chi \rho_m(r) \rho_m r \right) \times \int \mathcal{D} \rho_p \int \mathcal{D} \rho_m \int \mathcal{D} w_p \int \mathcal{D} w_m \int \mathcal{D} \xi \times \exp \left( i \int dr_p(r) \rho_p(r) \right) \exp \left( i \int dr_m(r) \rho_m(r) \right) \times \exp \left( i \int dr \xi(r)(1 - \rho_p(r) - \rho_m(r)) \right) \\
\times \exp \left( -i \int dr_p(r) \hat{\rho}_p(r) \right) \exp \left( -i \int dr_m(r) \hat{\rho}_m(r) \right) \\
\alpha \prod_{j=1}^{n_p} \int \mathcal{D} r_j \prod_{l=1}^{n_m} \int dr_l \left( -\chi \int dr \rho_m(r) \rho_p(r) \right) \times \int \mathcal{D} \rho_p \int \mathcal{D} \rho_m \int \mathcal{D} w_p \int \mathcal{D} w_m \int \mathcal{D} \xi \exp \left( -\chi \int dr \rho_m(r) \rho_p(r) \right) \\
\times \exp \left( i \int dr_p(r) \rho_p(r) \right) \exp \left( i \int dr_m(r) \rho_m(r) \right) \times \exp \left( i \int dr \xi(r)(1 - \rho_p(r) - \rho_m(r)) \right) \\
\times \exp \left( -i \int dr_m(r) \hat{\rho}_m(r) \right) \exp \left( -i \int dr \rho_p(r) \right) \exp \left( -\chi \int dr \rho_m(r) \rho_p(r) \right) \\
\times \exp \left( i \int dr \xi(r)(1 - \rho_p(r) - \rho_m(r)) \right) \\
\times \exp \left( -i \int dr \rho_m(r) \rho_m r \right) \exp \left( -\chi \int dr \rho_m(r) \rho_p(r) \right) \\
\times \exp \left( i \int dr_p(r) \rho_p(r) \right) \exp \left( i \int dr_m(r) \rho_m(r) \right) \times \exp \left( i \int dr \xi(r)(1 - \rho_p(r) - \rho_m(r)) \right) \\
\alpha \prod_{j=1}^{n_p} \int \mathcal{D} r_j \prod_{l=1}^{n_m} \int dr_l \exp(-\beta U_0 - \beta U_1) \times \int \mathcal{D} \rho_p \int \mathcal{D} \rho_m \int \mathcal{D} w_p \int \mathcal{D} w_m \int \mathcal{D} \xi \exp \left( -\chi \int dr \rho_m(r) \rho_p(r) \right) \\
\times \exp \left( i \int dr_p(r) \rho_p(r) \right) \exp \left( i \int dr_m(r) \rho_m(r) \right) \times \exp \left( i \int dr \xi(r)(1 - \rho_p(r) - \rho_m(r)) \right) \\
\times \exp \left( -i \int dr_m(r) \hat{\rho}_m(r) \right) \exp \left( -i \int dr \rho_p(r) \right) \exp \left( -\chi \int dr \rho_m(r) \rho_p(r) \right) \\
\times \exp \left( i \int dr \xi(r)(1 - \rho_p(r) - \rho_m(r)) \right) \\
\times \exp \left( -i \int dr_m(r) \hat{\rho}_m(r) \right) \exp \left( -i \int dr \rho_p(r) \right) \exp \left( -\chi \int dr \rho_m(r) \rho_p(r) \right) \\
\times \exp \left( i \int dr \xi(r)(1 - \rho_p(r) - \rho_m(r)) \right) \\
\times \exp \left( -i \int dr_m(r) \hat{\rho}_m(r) \right) \exp \left( -i \int dr \rho_p(r) \right) \exp \left( -\chi \int dr \rho_m(r) \rho_p(r) \right) \\
\times \exp \left( i \int dr \xi(r)(1 - \rho_p(r) - \rho_m(r)) \right)
\[
\times \prod_{j=1}^{n} \int \mathcal{D}r_j \exp \left( -\frac{1}{4R_g^2} \sum_{j=1}^{n} \int_{0}^{1} |r_j'(s)|^2 - i \int_{0}^{1} \sum_{j=1}^{n} w_p(r_j(s))v_p N \right) \\
\times \prod_{l=1}^{m} \int \mathcal{D}r_l \exp \left( -iv_m \sum_{j=1}^{m} w_m(r_j(1)) \right) \\
\propto \int \mathcal{D}\rho_p \int \mathcal{D}\rho_m \int \mathcal{D}w_p \int \mathcal{D}w_m \int \mathcal{D}\xi \exp \left( -\chi \int \mathcal{D}r \rho_m(r) \rho_p(r) \right) \\
\times \exp \left( i \int \mathcal{D}r \sigma_p(r) \right) \exp \left( i \int \mathcal{D}r \rho_m(r) \right) \\
\times \exp \left( i \int \mathcal{D}r \sigma_m(r) \right) \\
\times \left( \int \mathcal{D}r \exp \left( -\frac{1}{4R_g^2} \int_{0}^{1} ds |r'(s)|^2 \exp -i \int_{0}^{1} dw_p(r(s))v_p N \right) \right)^{n_p} \\
\times \left( \int \mathcal{D}r \exp(-iv_m w_m(r(1))) \right)^{n_m}.
\]

Set \( W_m = iNw_m, \ W_p = iNw_p, \ \xi = iN\xi, \) and
\[
\int \mathcal{D}r \exp \left( -\frac{1}{4R_g^2} \int_{0}^{1} ds |r'(s)|^2 \right).
\]

Then the partition function can be written as:
\[
\mathcal{Z} \propto \int \mathcal{D}\rho_p \int \mathcal{D}\rho_m \int \mathcal{D}w_p \int \mathcal{D}w_m \int \mathcal{D}\xi \exp \left( -\chi \int \mathcal{D}r \rho_m(r) \rho_p(r) \right) \\
\times \exp \left( \int \mathcal{D}r \sigma_p(r) \right) \exp \left( \int \mathcal{D}r \rho_m(r) \right) \\
\times \exp \left( \int \mathcal{D}r \sigma_m(r) \right) \\
\times \left( \int \mathcal{D}r \exp \left( -\frac{1}{4R_g^2} \int_{0}^{1} ds w_p(r(s))v_p \right) \right)^{n_p} \\
\times \left( \int \mathcal{D}r \int \mathcal{D}r \exp(-v_m W_m(r)) \right)^{n_m}.
\]

We can simplify it as follows:
\[
\mathcal{Z} \propto \int \mathcal{D}\rho_p \int \mathcal{D}\rho_m \int \mathcal{D}w_p \int \mathcal{D}w_m \int \mathcal{D}\xi \exp(-\beta H), \]

where \( H \) is the Hamilton of this system, which is:
\[
\frac{N\beta H}{\rho_0 V} = \frac{1}{V} \int \mathcal{D}r [\chi N \rho_m(r) \rho_p(r) - W_p(r) \rho_p(r) - W_m(r) \rho_m(r) \]
\[
- \xi(r)(1 - \rho_p(r) - \rho_m(r))] - n_p \ln VQ_p - n_m \ln VQ_m.
\]

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References