The micro-structure and phase transition process of macromolecular microsphere composite (MMC) hydrogel

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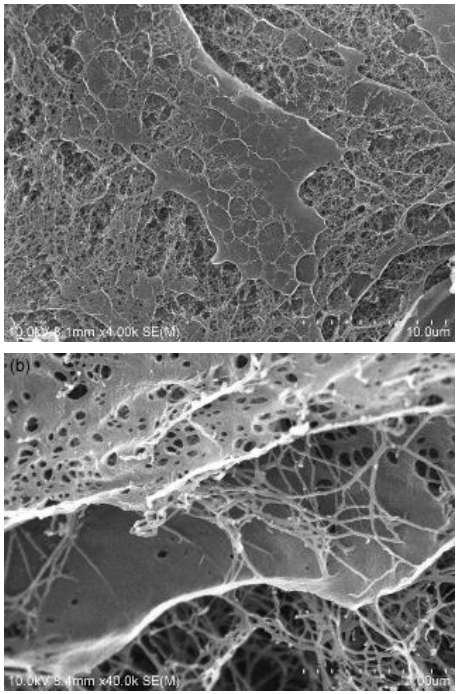
Outline

Examples in our life: bean curd(豆腐)、jelly(果冻)、contact lenses(隐形眼镜)、...

Hydrogel

Jellyfish Gel and Its Hybrid Hydrogels with High Mechanical Strength

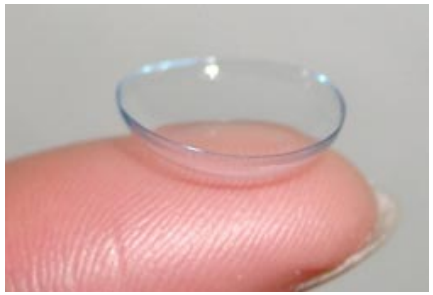


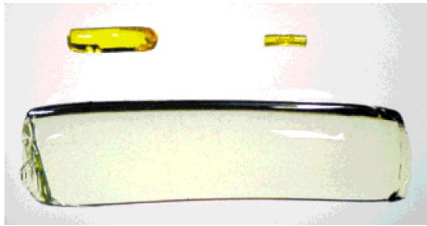
- SEM micrograms of the jellyfish mesogloea.

Introduction: What is Hydrogel?

Common uses include:

- Sustained-release drug delivery system
- Tissue engineering as scaffold
- Granule for holding soil moisture in arid areas





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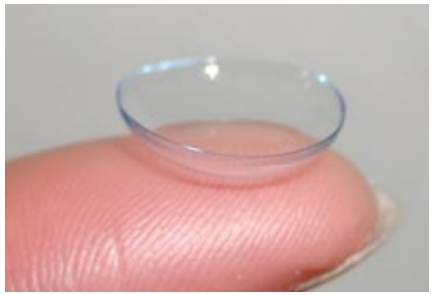
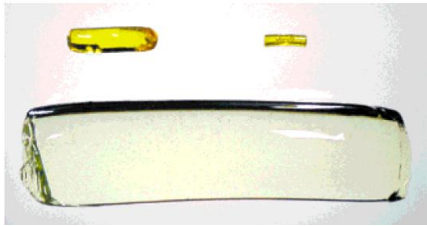
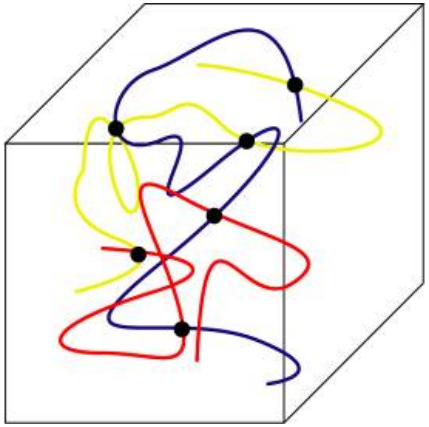




Hydrogel is a three-dimensional randomly crosslinked polymer network that absorb substantial amounts of aqueous solutions.



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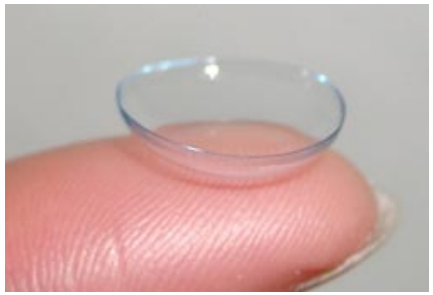

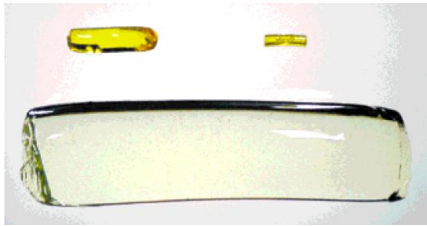

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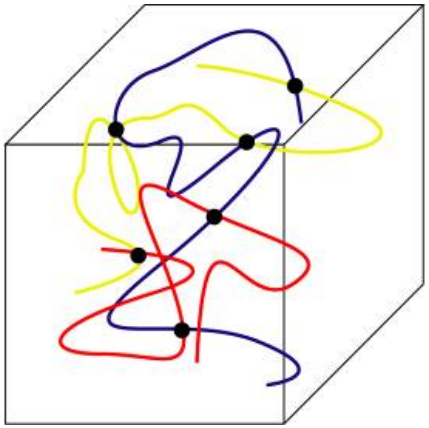
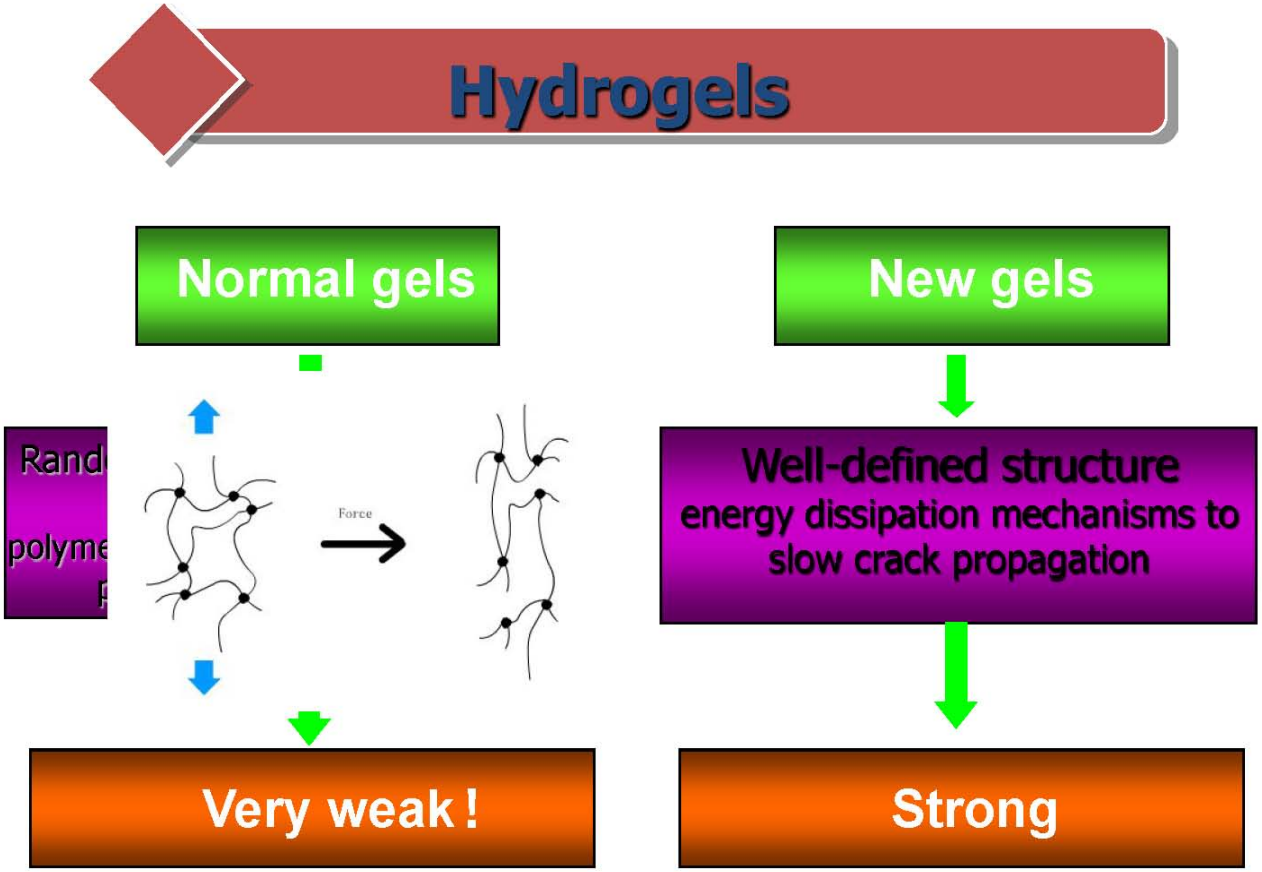


Properties

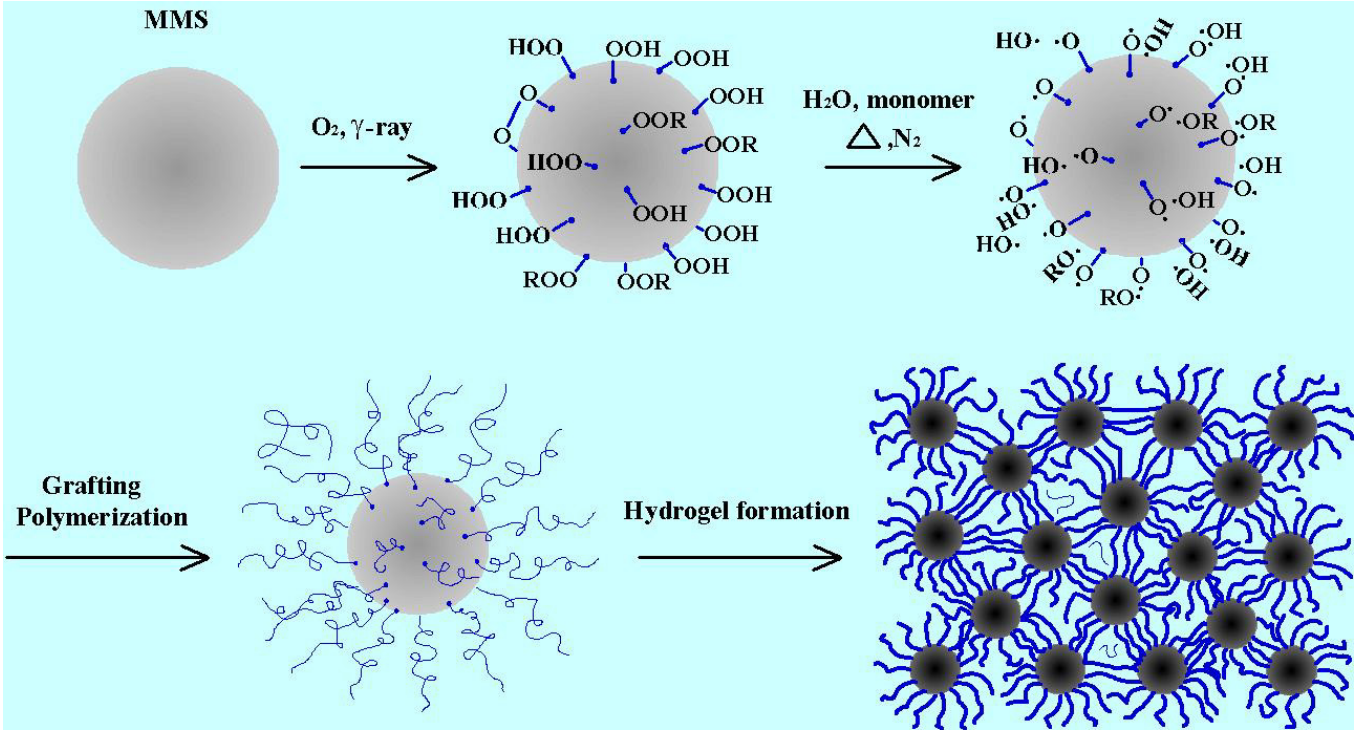
Solid & jelly-like material, highly absorbent,

Hydrogel

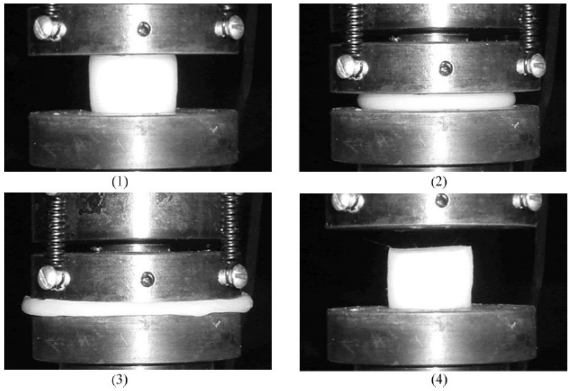


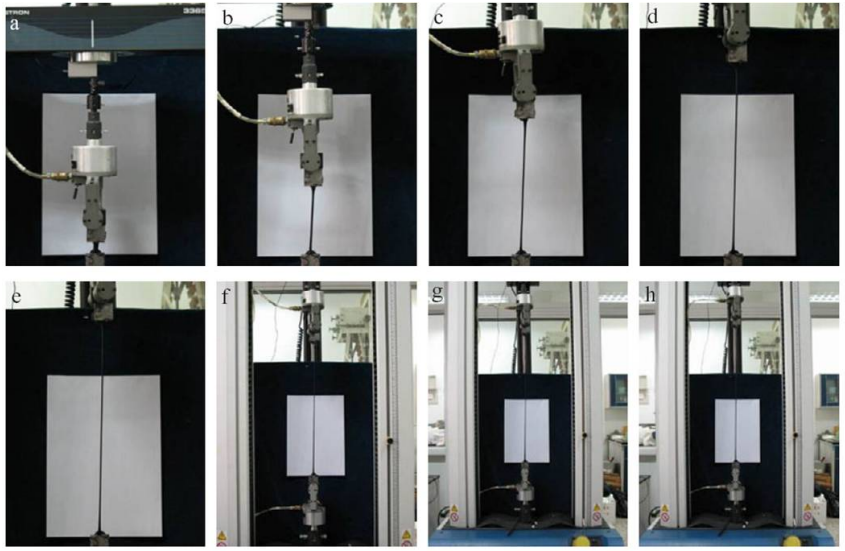
$G=10^{-1}$-10^{2} J/m^2

Macromolecular Microsphere Composite (MMC) Hydrogel

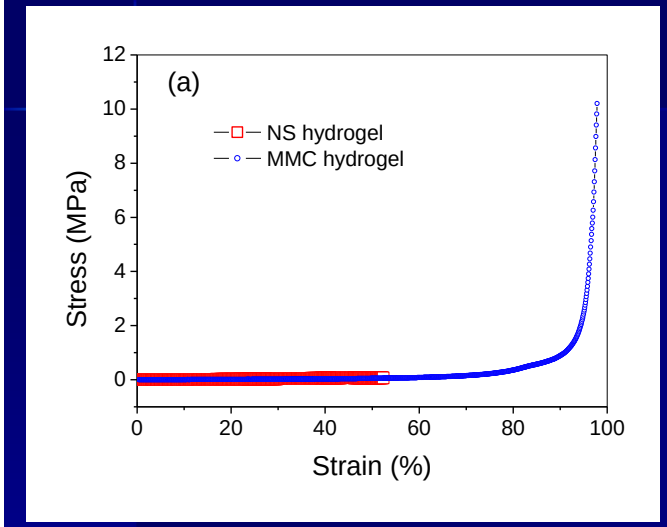


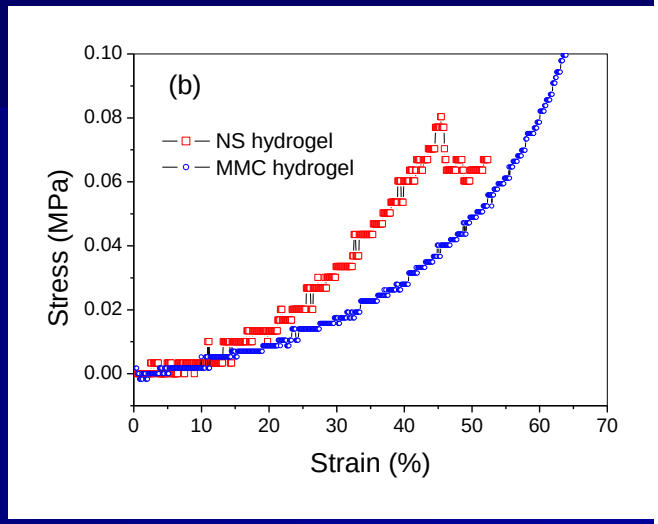
new hydrogels:compressive tests





The stress-strain curves

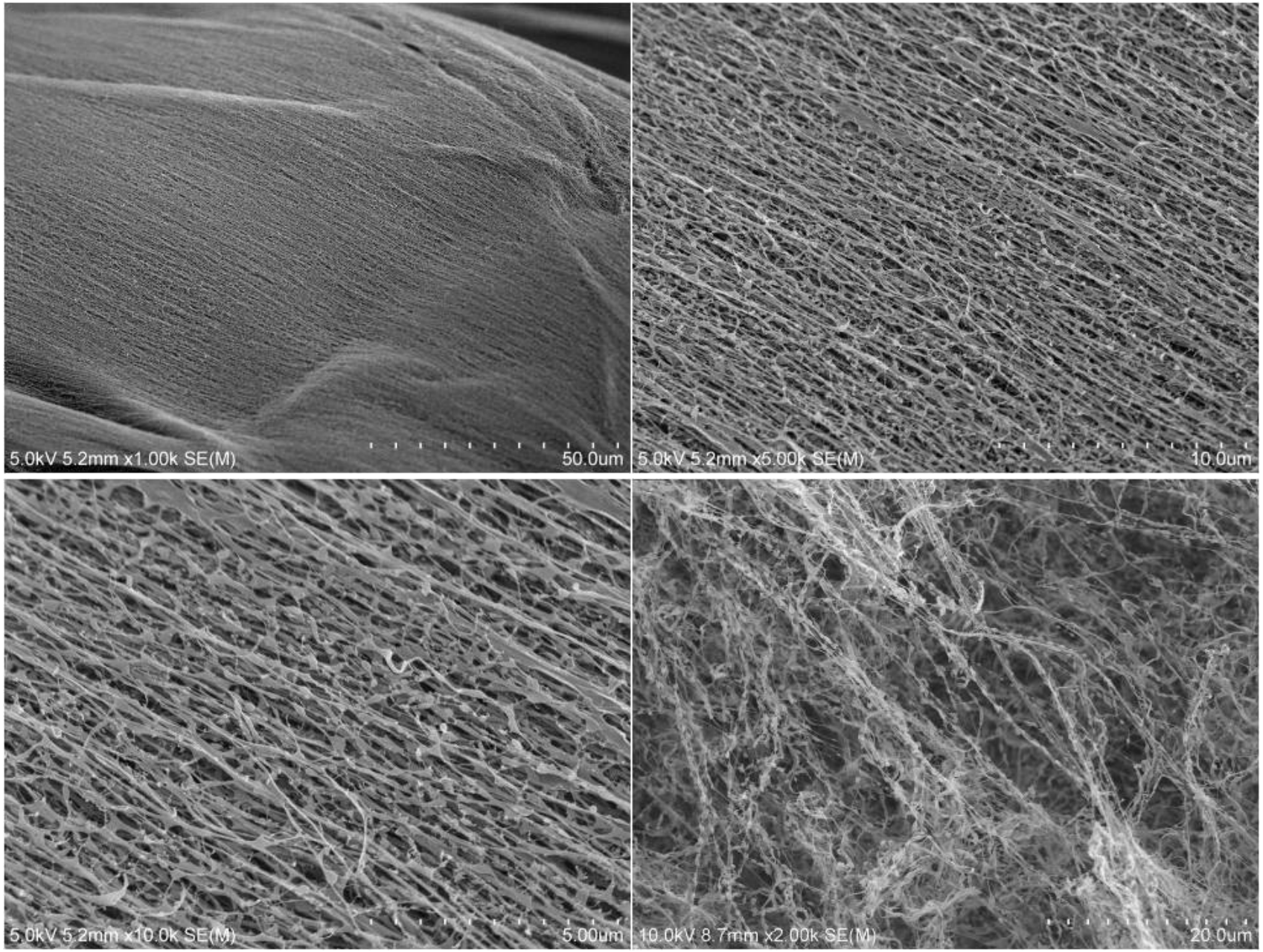




The stress-strain curves for the NS and MMC (A6) hydrogels. (a) Full range, (b) Stress at low strain.

- Advanced Materials, 2007, 19(12),1622-1626。

microstructure



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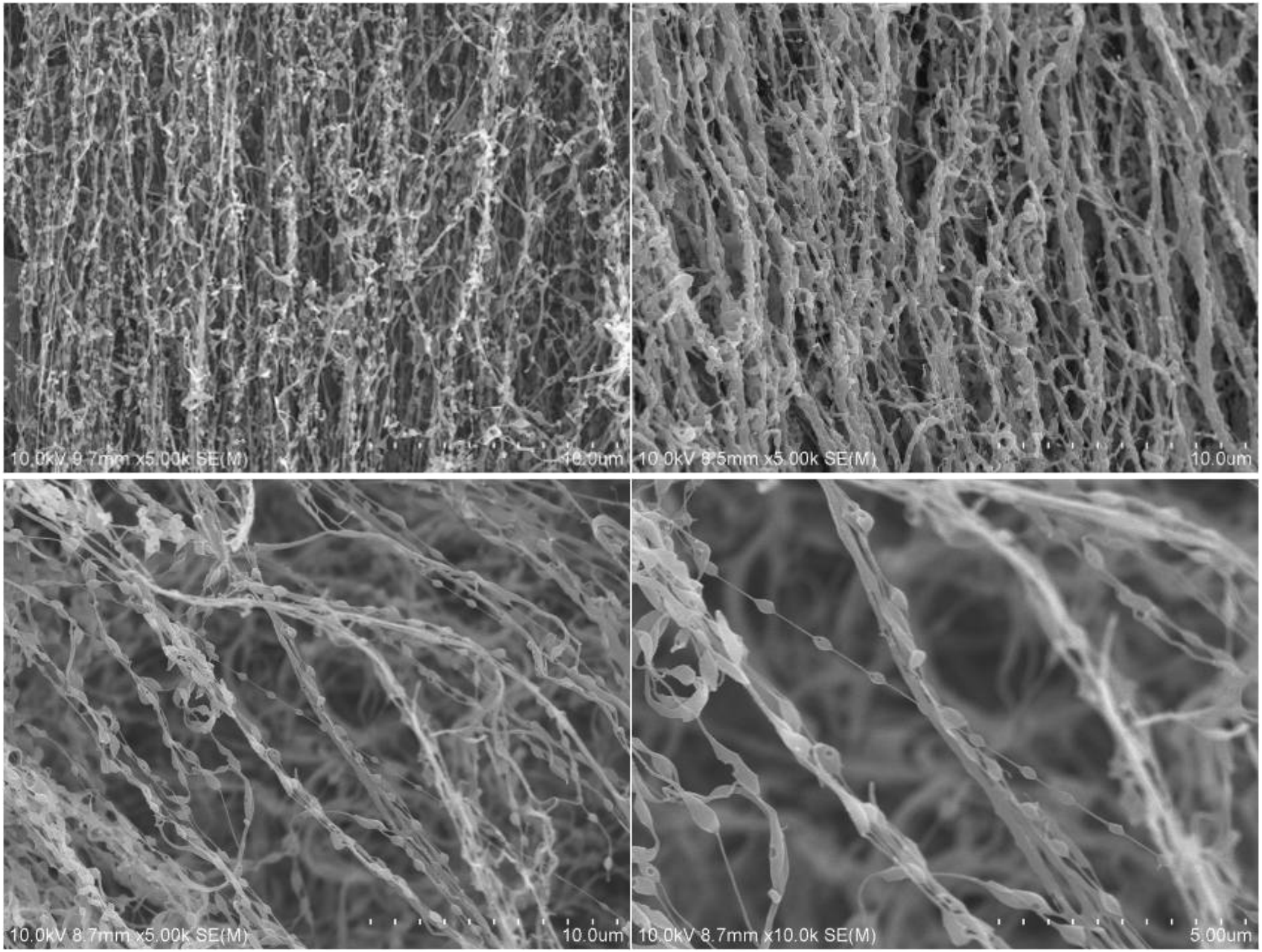


Problems:

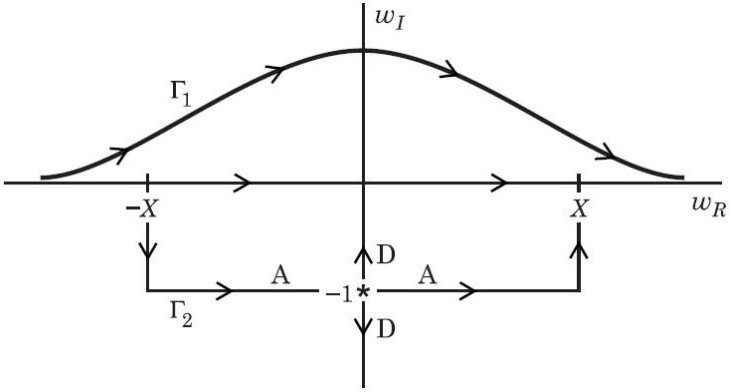
- Why the hydrogels have such high mechanical strengths?
  - Structure-Property relationship
  - Structural factors: nanoparticle size, grafting(接枝) density, polymer chain length, chain conformation, entanglement（纠缠）, hydrogen bonding……
- Theoretical studies may provide supports for optimizing the synthesis

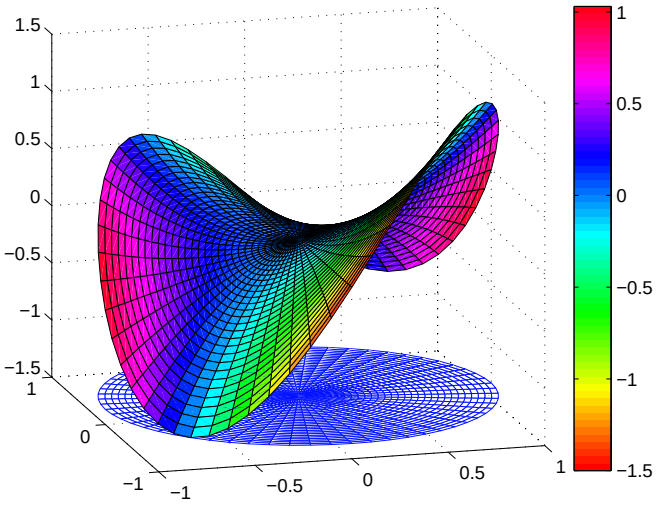
Outline

Introduction(SCFT)

- Ignore the local fluctuation of equilibrium
- Consider the largest probability equilibrium
- Saddle point approximation (physics)
- Laplace asymptotic theory of Integrals(mathematics)

Hamilton: $H = iw + \frac{1}{2}w^2$





Introduction:Polymer

Polymer: chain molecule consisting of monomers

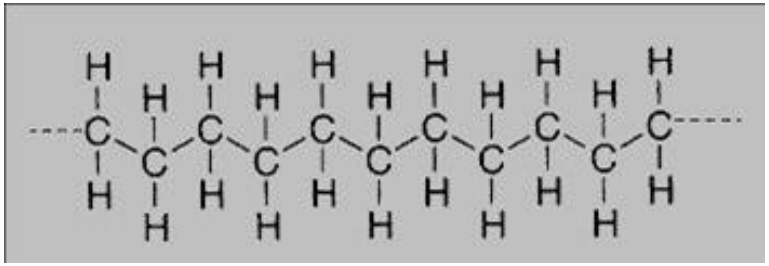


Figure: Homopolymer: identical monomers

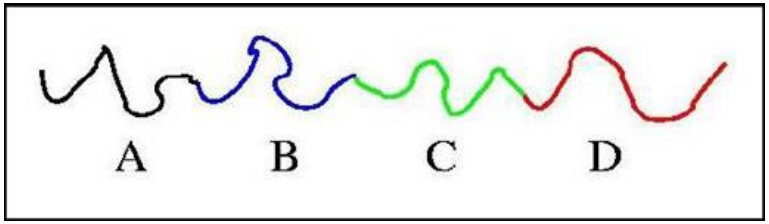


Figure: Copolymer: distinct monomers

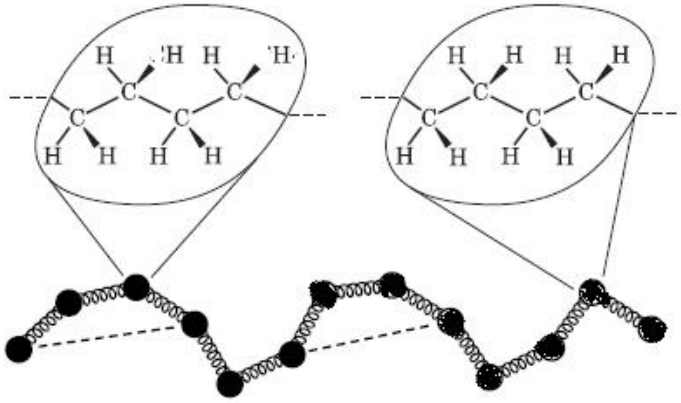


Figure: Coarse grained—Bead-spring Model

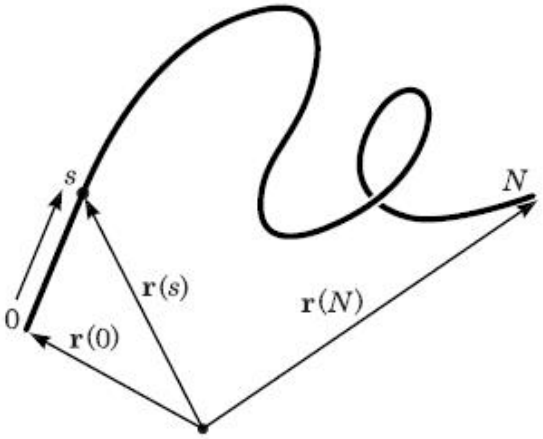
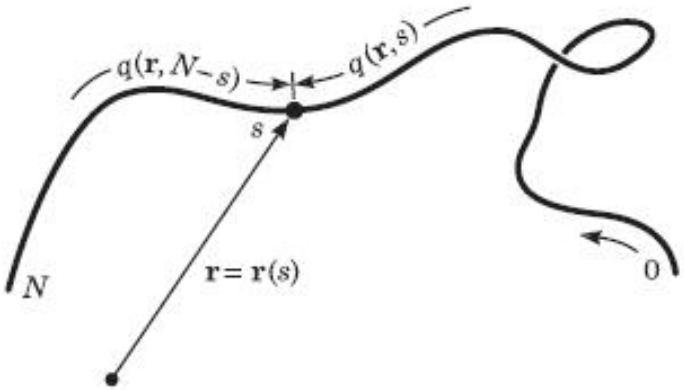


Figure: Continuous Model

Introduction: Gaussian Random-Walk Model for a Single Polymer Chain



Idea: Polymer chain $\Longleftrightarrow$ Path integral by S.F.Edwards in 1965. Polymer as a flexible Gaussian chain described by curve $\mathbf{r}(s)$ in $[0, N]$ that can be treated as path of particle doing Brown motion.

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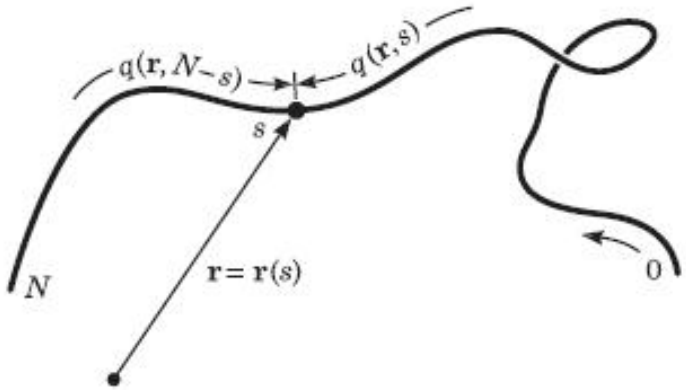

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Propagator $q(\mathbf{r}, s)$ in field $w(\mathbf{r})$ satisfies

$$\frac{\partial}{\partial s} q(\mathbf{r}, s) = R_g^2 \nabla_{\mathbf{r}}^2 q(\mathbf{r}, s) - w(\mathbf{r}) q(\mathbf{r}, s) \tag{1}$$

$$q(\mathbf{r}, 0) = 1. \tag{2}$$

where

$$0 \leq s \leq N, \quad \mathbf{r} \in V$$

$R_g^2 = \frac{b^2 N}{6}$ denotes the unperturbed radius of gyration, V represents the total domain.

Introduction: polymer system of SCFT and its application

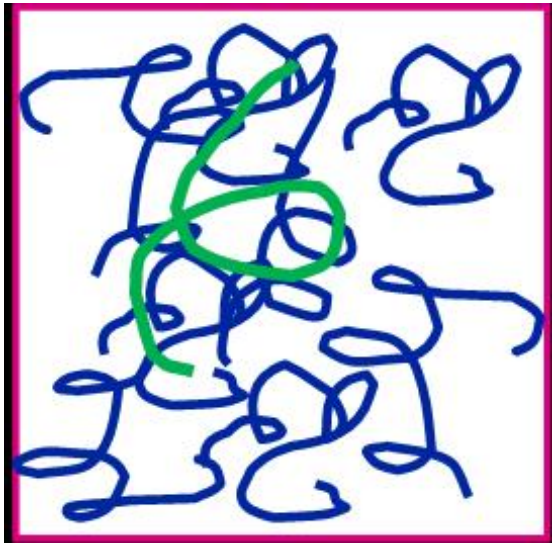

Figure: Polymers influencing one another

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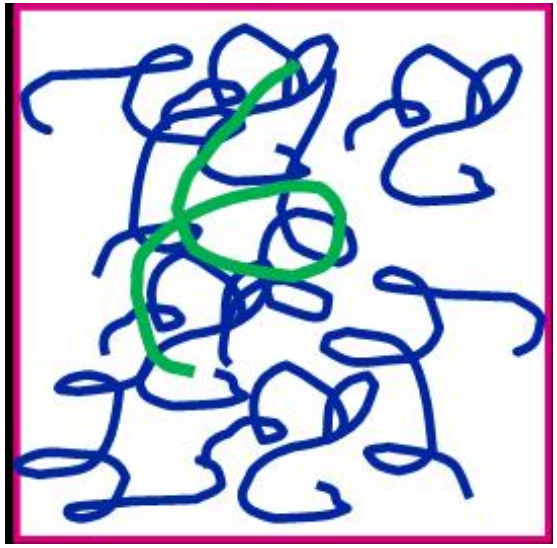

Figure: Polymers influencing one another

Figure: One polymer chain in one field creating by the whole system

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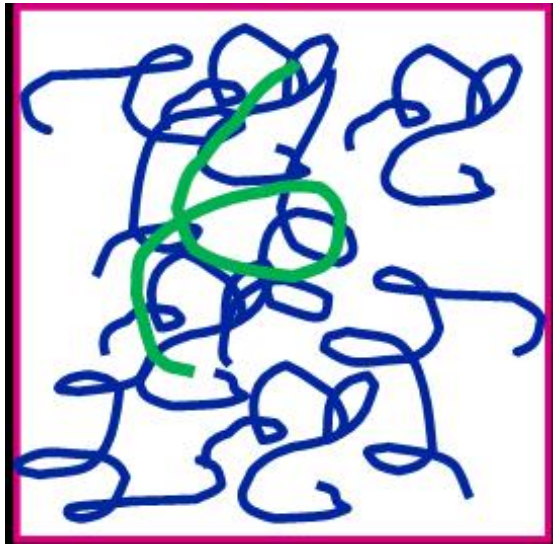

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Mean field Theory: From based particles to based field

Mean field Approximation: criterion of the dominant field

$$\left.\frac{\delta H[w]}{\delta w}\right|_{w^*} = 0$$

Outline

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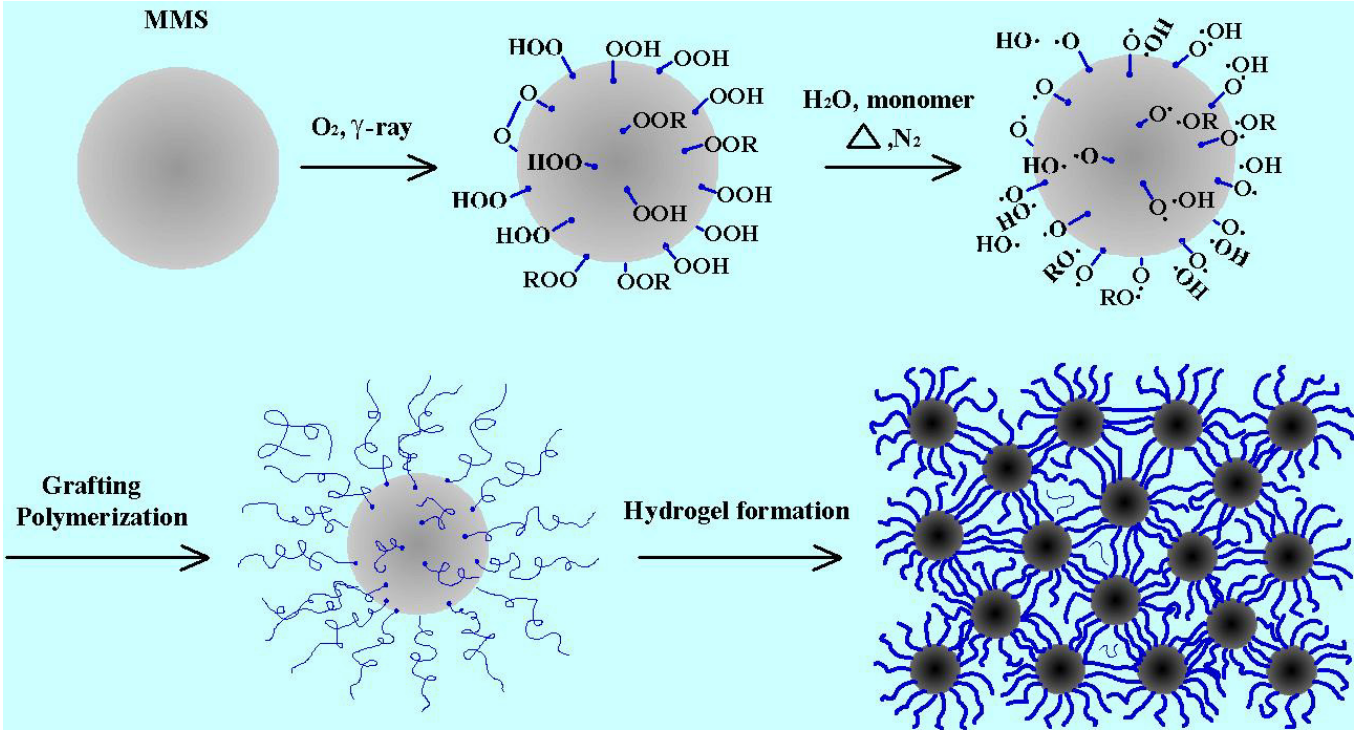

Incompressible SCFT Model

- All polymer chains are modeled as flexible Gaussian chain
- Each MMS is considered as the same sphere with volume of v_M
- The account of polymer chains on each MMSs are the same.

Incompressible Model in canonical ensemble (n, V, T)

Consisting of n_M MMSs , n_p polymer chains

Microscopic segment density:

$$\hat{\rho}_M(\mathbf{r}) = v_M \sum_{j=1}^{n_M} \delta(\mathbf{r} - \mathbf{r}_j(1)),$$

$$\hat{\rho}_p(\mathbf{r}) = v_p N \sum_{j=1}^{n_p} \int_0^1 ds \; \delta(\mathbf{r} - \mathbf{r}_j(s)).$$

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Incompressible Condition:

$$\delta[\hat{\rho}_p + \hat{\rho}_M - 1].$$

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Density as the average of microscopic segment density:

$$\rho_M(\mathbf{r}) = \langle \hat{\rho}_M(\mathbf{r}) \rangle,$$

$$\rho_p(\mathbf{r}) = \langle \hat{\rho}_p(\mathbf{r}) \rangle.$$

Incompressible SCFT Model

Partition function of the system

$$\mathcal{Z} = \frac{1}{n_p! n_M! (\lambda^3)^{n_p N + n_M}} \prod_{j=1}^{n_p} \int \mathcal{D}\mathbf{r}_j \prod_{l=1}^{n_M} d\mathbf{r}_l \ \exp\left(-\beta U_0 - \beta U_1\right) \ \delta[1 - \hat{\rho}_p(\mathbf{r}) - \hat{\rho}_M(\mathbf{r})]$$
$$\propto \prod_{j=1}^{n_p} \int \mathcal{D}\mathbf{r}_j \prod_{l=1}^{n_M} d\mathbf{r}_l \ \exp\left(-\beta U_0 - \beta U_1\right) \ \delta[1 - \hat{\rho}_p(\mathbf{r}) - \hat{\rho}_M(\mathbf{r})], \tag{3}$$

where

$$\beta U_0 = \sum_{j=1}^{n_p} \frac{3}{2Nb^2} \int_0^1 ds \left| \frac{d\mathbf{r}(s)}{ds} \right|^2 = \frac{1}{4R_g^2} \sum_{j=1}^{n_p} \int_0^1 ds \ |\mathbf{r}'(s)|^2,$$
$$\beta U_1 = \rho_0 \int d\mathbf{r} \ \chi \ \hat{\rho}_M(\mathbf{r}) \ \hat{\rho}_p(\mathbf{r}), \tag{4}$$
$$\beta = 1/k_B T.$$

Note: assuming short-range between MMSs and polymer chains interaction gives interaction potential with Flory-Huggins parameter.

Use the Hubbard-Stratonovich transformation to introduce two fields:

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

$$\delta[\rho - \hat{\rho}] = \int \mathcal{D}\psi(\mathbf{r})\ e^{i \int d\mathbf{r} \psi(\mathbf{r})[\rho(\mathbf{r}) - \hat{\rho}(\mathbf{r})]}.$$

Rewrite the partition function (3) in the form of functional integral and obtain effective Hamiltonian H:

$$\mathcal{Z} \propto \int \mathcal{D}\rho_p \int \mathcal{D}\rho_M \int \mathcal{D}W_p \int \mathcal{D}W_M \int \mathcal{D}\xi\ \exp(-\beta H), \tag{5}$$

$$\begin{aligned} \frac{N\beta H}{\rho_0 V} = \frac{1}{V} \int d\mathbf{r}\, [\chi\ N\rho_M(\mathbf{r})\ \rho_p(\mathbf{r}) - W_p(\mathbf{r})\ \rho_p(\mathbf{r}) - W_M(\mathbf{r})\ \rho_M(\mathbf{r}) \\ -\xi(\mathbf{r})(1 - \rho_p(\mathbf{r}) - \rho_M(\mathbf{r}))] \\ - n_p \ln VQ_p - n_M \ln VQ_M, \end{aligned} \tag{6}$$

Saddle point approximation

$\delta H = 0 \Longrightarrow$

$$
\begin{aligned}
W_p(\mathbf{r}) &= \chi N \rho_M(\mathbf{r}) + \xi(\mathbf{r}), && (7)\\
W_M(\mathbf{r}) &= \chi N \rho_p(\mathbf{r}) + \xi(\mathbf{r}), && (8)\\
\rho_M(\mathbf{r}) &+ \rho_p(\mathbf{r}) = 1, && (9)\\
\rho_p(\mathbf{r}) &= \frac{n_p}{Q_p} \int_0^1 ds q(\mathbf{r}, s) q^+(\mathbf{r}, s), && (10)\\
\rho_M(\mathbf{r}) &= \frac{1}{Q_M} \frac{v_M}{N} q(\mathbf{r}, 0) q^+(\mathbf{r}, 1), && (11)
\end{aligned}
$$

where

$$
\begin{aligned}
Q_M &= \frac{1}{V}\int d\mathbf{r}\exp\left(-v_M W_M(\mathbf{r})/N\right)\, q(\mathbf{r},1), \\
Q_p &= \frac{1}{V}\int d\mathbf{r}\; q(\mathbf{r},1).
\end{aligned}
\tag{12}
$$

Propagator $q(\mathbf{r},s)$ and reverse propagator $q^+(\mathbf{r},s)$ satisfy respectively

$$
\begin{aligned}
\frac{\partial q}{\partial s} &= R_g^2\nabla^2 q - W_p(\mathbf{r})q(\mathbf{r},s), \\
q(\mathbf{r},0) &= \exp\left(-v_M W_M(\mathbf{r})/N\right)
\end{aligned}
\tag{13}
$$

$$
\begin{aligned}
\frac{\partial q^+}{\partial s} &= -R_g^2\nabla^2 q^+ + W_p(\mathbf{r})q^+(\mathbf{r},s) \\
q^+(\mathbf{r},1) &= \frac{\sigma}{q(\mathbf{r},0)},
\end{aligned}
\tag{14}
$$

Boundary Condition: Periodic B.C.

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$$

Boundary Condition: Periodic B.C.

highly non-linear systems with multi-solutions, non-local and multi-parameters!

Outline

- M.W.Matsen, M.Schick Spectral methods, PRL (1994). —-Expand the spatially varying functions
  - Need the symmetry in advance !
- F.Drolet,G.H.Fredrickson Combinatorial screening algorithm in real space, PRL (1999).
  - Does not require a priori assumption of symmetry.
  - Discover new phases.
- Rasmussen,Kalosakas Pseudo-spectral Algorithm (2002).
  - Does not require a priori assumption of symmetry.
  - Use split strategy.
  - Improve the computational efficiency based FFT.

Pseudo-spectral Algorithm

Rewrite propagator PDE as

$$q(\mathbf{r}, s + ds) = \exp\left(ds(\nabla^2 - w_p(\mathbf{r}))\right) q(\mathbf{r}, s), \tag{15}$$

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$$q(\mathbf{r}, s + ds) \approx \exp\left(-\frac{ds}{2}w_p\right)\exp\left(ds\nabla^2\right)\exp\left(-\frac{ds}{2}w_p\right)q(\mathbf{r}, s), \tag{16}$$

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Algorithm:

- Set $q_0(\mathbf{r})$.
- Compute in real space $q_1 = \exp\left(-dsw_p(\mathbf{r})/2\right)q_0$.
- Use Fourier transform for q_1 to obtain $\hat{q}_1$.
- Let $\hat{q}_2 = \exp\left[-ds(2\pi M/L)^d\right]\hat{q}_1$, where M discrete points , L periodic lenght , d dimension.
- Take inverse Fourier transform on $\hat{q}_2$ to get q_2.
- Compute in real space $q_3 = \exp\left(-dsw_p(\mathbf{r})/2\right)q_2$.
- Let q_3 be $q(\mathbf{r}, s + ds)$ to update $q_0(\mathbf{r})$, take back to step 1 until $s = 1$.

Iteration Method

- Set the random initial values for W_p, W_M and pressure ξ.
- Solve modified diffusion equations Eq.13 and Eq.14 numerically to calculate propagator $q(\mathbf{r})$ and reverse propagator $q^+(\mathbf{r})$.
- Update density $\rho_p^n(\mathbf{r})$ and $\rho_M^n(\mathbf{r})$ by using Eq.10 and Eq.11.
- Update external field at the nth step iteration W^n to get value at the $(n+1)$ iteration W^{n+1}:

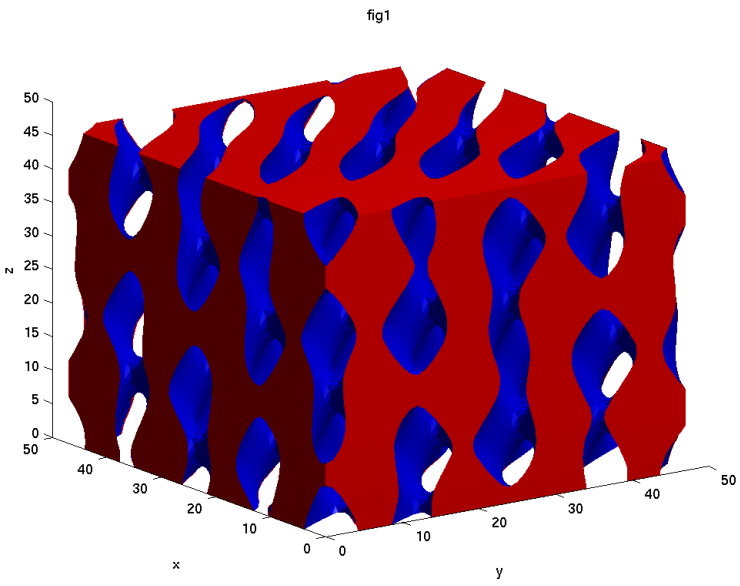
$$\begin{aligned} W_m^{n+1} - W_m^n &= \lambda' \frac{\delta H}{\delta \rho_p^n} + \lambda \frac{\delta H}{\delta \rho_m^n}, \\ W_p^{n+1} - W_p^n &= \lambda' \frac{\delta H}{\delta \rho_m^n} + \lambda \frac{\delta H}{\delta \rho_p^n}, \end{aligned} \tag{17}$$

  where λ' and λ are relaxation parameters, subjected to $\lambda' < \lambda$ and $\lambda > 0$.
- Update the pressure field via

$$\xi^{n+1}(\mathbf{r}) = (w_p^{n+1} + w_m^{n+1})/2; \tag{18}$$

- Go to step 2 until convergence, ie $|H - H_0| < 10^{-6}$.

Outline



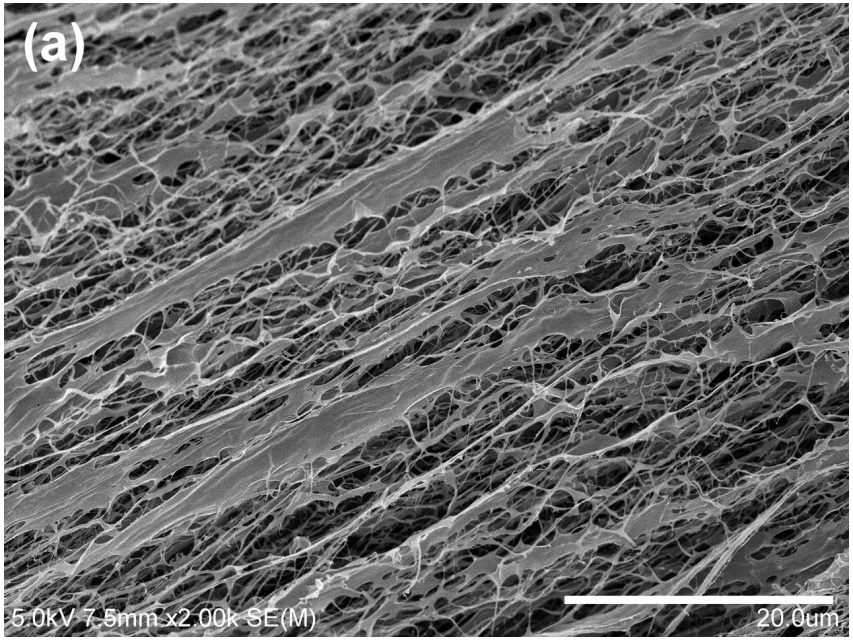
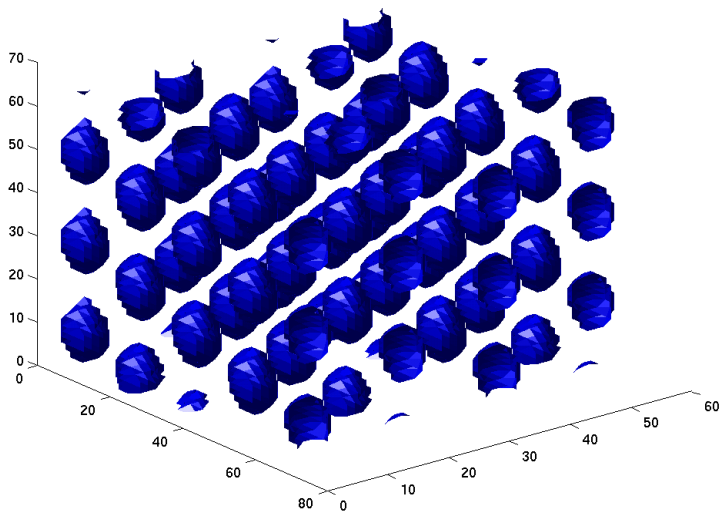


Figure: The one on the left is three-dimensional density plot of a morphological phase at volume fraction of MMSs f_m is 0.15, and $\chi N = 10.4$. The color red indicate MMSs. We can call this phase state the **strip state**. The one on the right is a snapshot extracted from experiment.



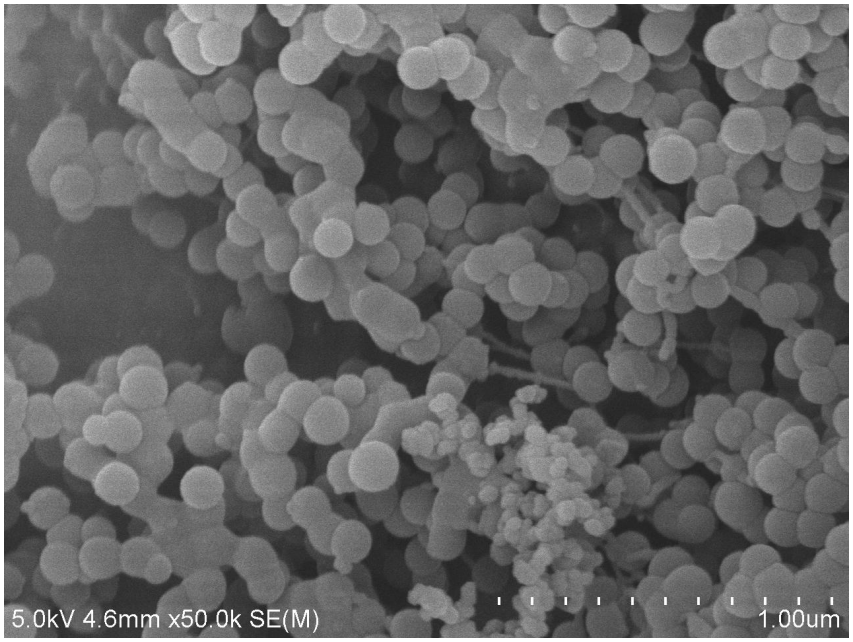
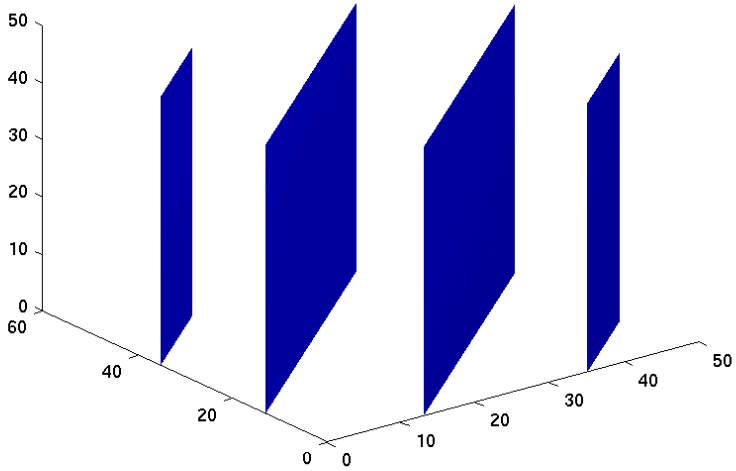


Figure: The one on the left is the density profile of MMMS with volume fraction is 0.35. We call this phase state the **sphere state**.The one on the right is a snapshot from experiment.



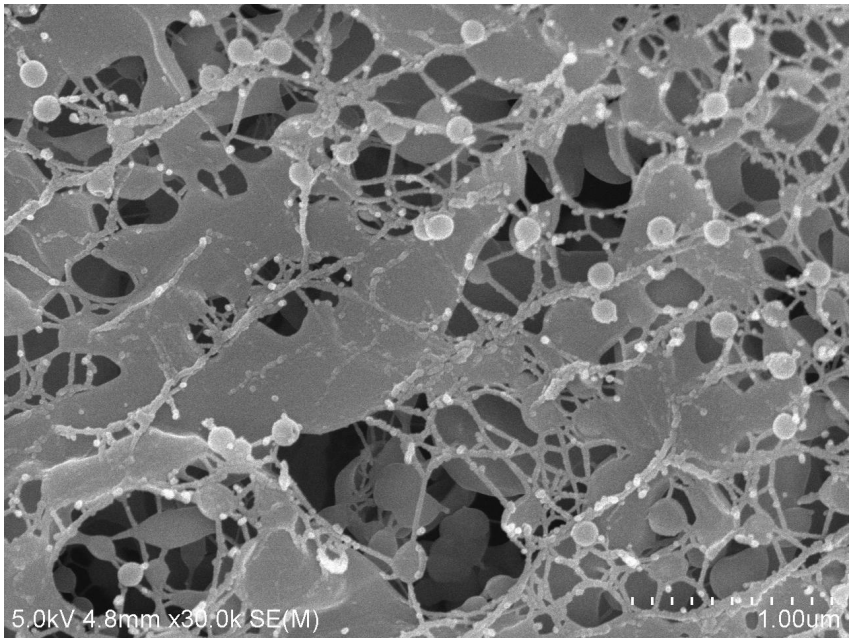


Figure: The one on the left is the density profile of polymer chains with the density is $f_p = 0.75$. We call the **lamella state**. The one on the right is a snapshot from experiment.

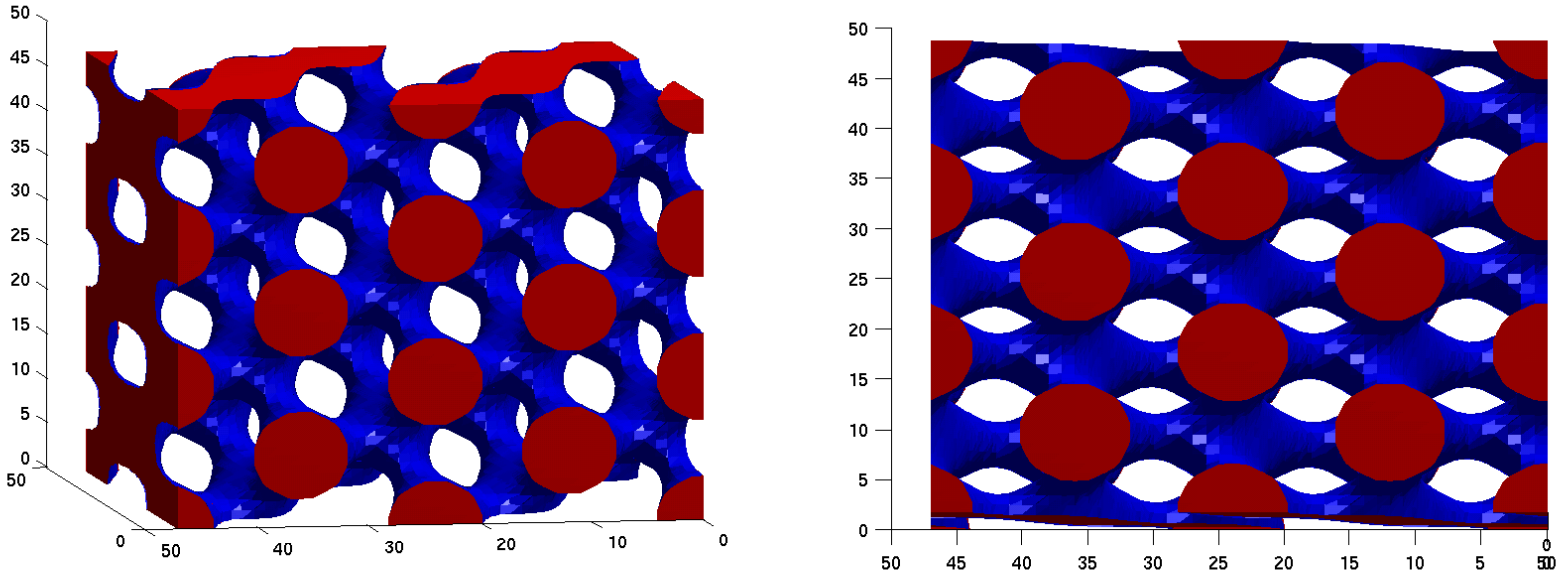


Figure: New Morphological Structure. We can call the **sphere perforate cylinder state**.

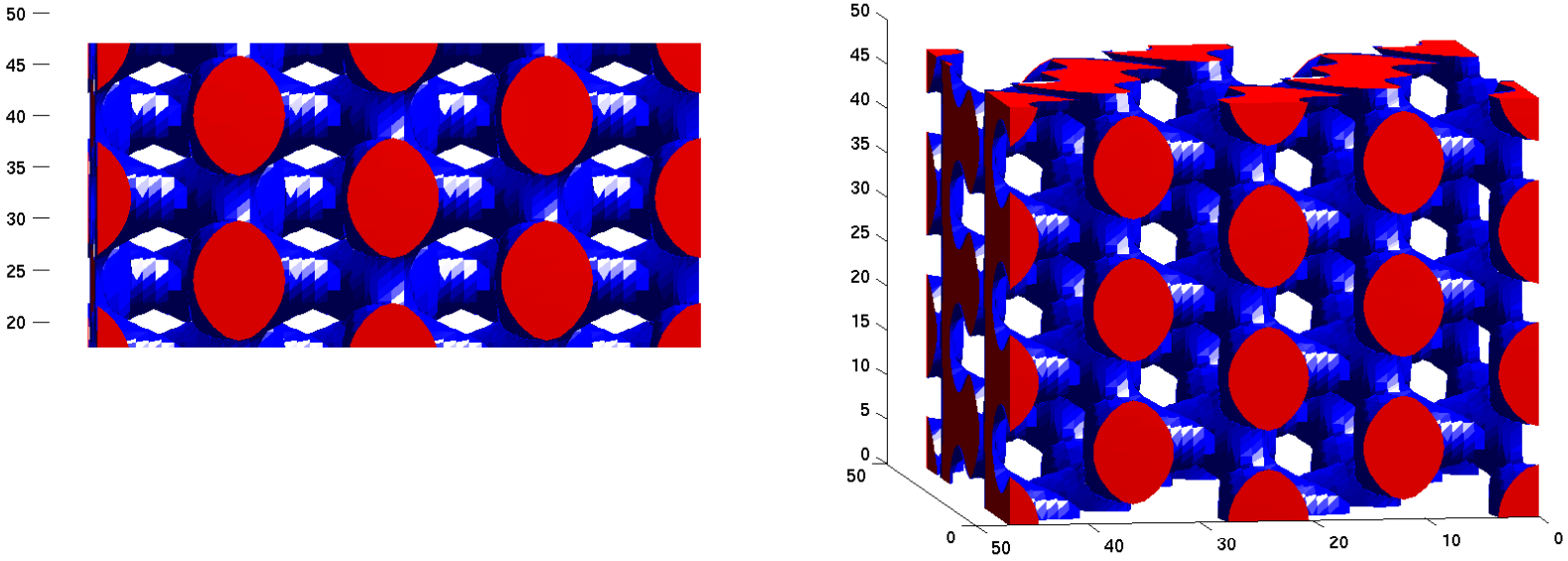


Figure: New Morphological Structure. We can call the **sphere perforate cylinder state**.

Phase diagram

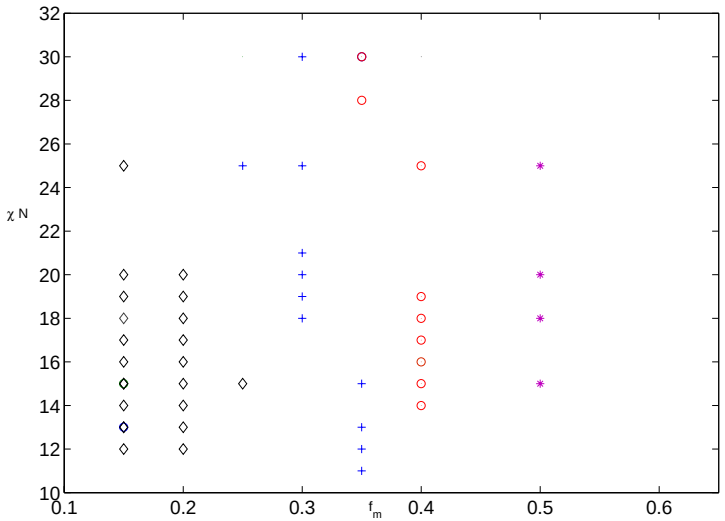


Figure: Phase diagram of MMC hydrogel as a function of interaction force χN and total fraction of MMSs f_m. The polymer chain length is $N = 80$. Circle denotes the **sphere** state, $'+'$ denotes **strip** state, diamond denotes the **lamella** state and $'*'$ denotes **disorder** state.

Ratio of sphere

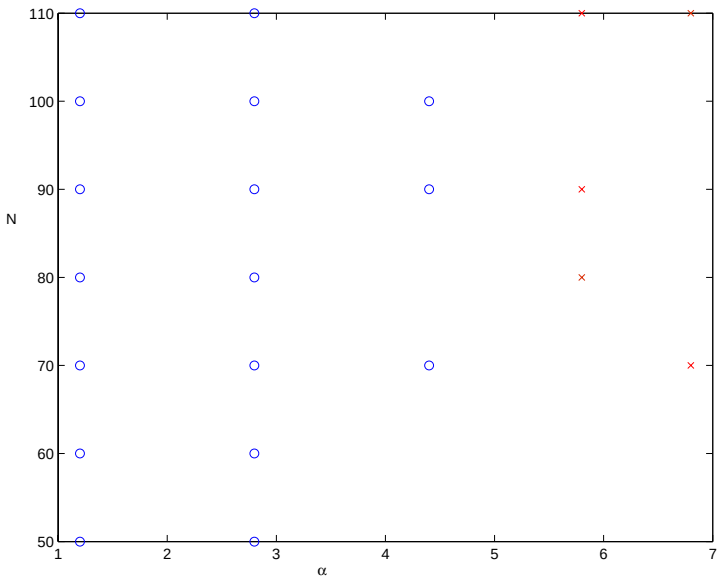


Figure: Phase diagram of MMC hydrogel as a function of parameter α, which denotes the ratio of the radius of MMS sphere and the volume of each segment of a grained polymer chain, and the parameter of polymer chain length. Circle means the **ordered** and **lamella** phases (including that **sphere** state, **strip** state and **sphere perforate cylinder** state) while '+' means **disorder** phase.

Journal of Theoretical and Computational Chemistry, 2013, DOI: 10.1142/S021963361350048X.

Outline

TDGL equation for traditional hydrogels

The time dependent Ginzburg-Landau(TDGL) mesoscopic simulation method is a microscale method to simulate the structural evolution of phase-separation in polymer blends and block copolymers.

$$\frac{\partial \phi(\mathbf{r},t)}{\partial t} = \nabla \cdot M_0 \nabla \frac{\delta U[\phi(\mathbf{r},t)]}{\delta \phi(\mathbf{r},t)} + \zeta(\mathbf{r},t). \tag{19}$$

U: the free energy

M_0: the mobility may depend on the order parameter ϕ.

$\zeta(r,t)$: a thermal noise term with zero mean. It satisfies

$$< \zeta(\mathbf{r},t)\zeta(\mathbf{r}',t') >= -2k_B T M_0 \nabla^2 \delta(\mathbf{r}-\mathbf{r}')\delta(t-t').$$

k_B: the Boltzmann constant.

TDGL equation for traditional hydrogels

The Flory-Huggins-de Gennes free energy functional U can be expressed as:

$$\frac{U[\phi(\mathbf{r})]}{k_B T} = \int \left[\frac{U_{FH}[\phi(\mathbf{r})]}{k_B T} + \kappa(\phi) |\nabla \phi(\mathbf{r})|^2 \right] d\mathbf{r}, \tag{20}$$

$\kappa(\phi) = \sigma^2/36\phi(1-\phi)$, σ is the Huhn length of the polymer.

$U_{FH}(\phi)$ is the Flory-Huggins free energy concentration of mixing, given by

$$\frac{U_{FH}(\phi)}{k_B T} = \frac{\phi}{N_A} \ln \phi + \frac{(1-\phi)}{N_B} \ln(1-\phi) + \chi\phi(1-\phi).$$

χ: the enthalpic interaction parameter.

N_A and N_B are the number of segments in polymer A and polymer B respectively.

Boltzmann Entropy Theorem

S:entropy, Ω:the total microscopic state number of the system. The entropy of a system is a function of the number of microscopic states, given by

$$S = k_B \ln \Omega.$$

The MMC gel has a well-defined reticular structure, so the Flory-Huggins free energy is not applicable anymore.

We introduce reticular free energy based on Boltzmann Entropy Theorem. It contains three main parts: **model assumption, variable definition and model deduction**.

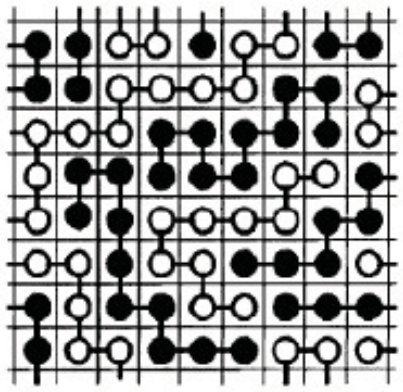


Figure: Black bead chains represent the polymer A, white bead chains represent the polymer B.

Model assumptions

- Each solvent molecule occupies a lattice. Each polymer chain occupies N connected lattices. Each macromolecular occupies M lattices.
- The polymer chain is completely flexible, and all conformational entropies are equivalent.
- The polymerization degrees of all the polymer chains are equal.
- Large balls and polymer chains share the same properties and are independent of each other.
- All polymer chains distribute among large balls.
- The number of the graft chain around a large ball is proportional to the perimeter. Without loss of generality, we assume the proportional valve is one.

Variable definition

Variables	Definition
n_r	the number of water molecules
n_s	the number of segments in polymer
n_L	the number of MMs
M	the number of lattices occupied by MMs
N	polymerization degree
ϕ_r	$\frac{n_r}{n_r+n_s+Mn_L}$
ϕ_s	$\frac{n_s}{n_r+n_s+Mn_L}$
ϕ_L	$\frac{Mn_L}{n_r+n_s+Mn_L}$
R	the number of MMs around a MMs
L	the number of chain between MMs

the relationship between the two variables as follows

$$\frac{\phi_s}{N} = \frac{\phi_L \times R \times L}{2}, \tag{21}$$

that is

$$\phi_s = \phi_L \cdot \frac{R \times L \times N}{2}, \quad n_s = n_L \cdot \frac{R \times L \times N}{2}.$$

Model deduction

We take the total volume of the system as $n_r + n_s + Mn_L$. the change of entropy:

$$\Delta S = k_B \left[\ln \left(\frac{n_r + n_s + Mn_L}{\pi \left(\frac{\sqrt{M}}{\sqrt{\pi}} + \frac{N}{2} \right)^2 n_L} \right)^{n_L} + \ln \left(\frac{n_r + n_s + Mn_L}{\pi \left(\frac{\sqrt{M}}{\sqrt{\pi}} + \frac{N}{2} \right)^2 n_L} \times \frac{R \times L}{2} \right)^{\frac{n_s}{N}} \right]. \tag{22}$$

the entropy can be rewritten as:

$$\Delta S = -k_B V \left[\frac{\phi_s}{\tau} \ln \left(\frac{\phi_s \alpha}{\tau} \right) + \frac{\phi_s}{N} \ln \left(\frac{\phi_s \beta}{\tau} \right) \right].$$

$V = n_r + n_s + Mn_L,$
$\alpha = \pi \left(\frac{\sqrt{M}}{\sqrt{\pi}} + \frac{N}{2} \right)^2,$
$\beta = \pi \left(\frac{\sqrt{M}}{\sqrt{\pi}} + \frac{N}{2} \right)^2 \frac{2}{RL}.$
$\tau = \frac{R \times L \times N}{2}$

Model deduction

the interaction term:

$$Interaction\ energy = \chi(\phi_s + \phi_L)(1 - \phi_s - \phi_L) = \chi\phi_s\rho\left[1 - \phi_s\rho\right].,$$

$\phi_L = \frac{\phi_s M}{\tau}$.
$\rho = 1 + M/\tau$,
Similarly, we get the solvent entropy,

$$solvent\ entropy = (1 - \phi_s\rho)\ln(1 - \phi_s\rho).$$

According to the relationship between entropy S and energy F, $dS = \frac{dF}{T}$, the reticular free energy is

$$\begin{aligned} F = k_B T \Bigg[& \frac{\phi_s}{\tau}\ln\left(\frac{\phi_s\alpha}{\tau}\right) + \frac{\phi_s}{N}\ln\left(\frac{\phi_s\beta}{\tau}\right) \\ & + (1 - \phi_s\rho)\ln(1 - \phi_s\rho) + \chi\phi_s\rho(1 - \phi_s\rho)\Bigg]. \end{aligned} \tag{23}$$

Outline

MMC-TDGL equation

Set $\phi = \phi_s$ the volume fraction of polymer

$g = \frac{\delta F(\phi)}{\delta \phi}$ denotes the variation F with respective to ϕ.

the dimensionless form of the MMC-TDGL equation Eq. (19) with the reticular free energy

$$\frac{\partial \phi(\mathbf{r}, t)}{\partial t} = \nabla \cdot M_0 \nabla \left(g - \frac{1}{18\phi(1-\phi)} \nabla^2 \phi \right) + \nabla \cdot \zeta,$$

with $< \zeta(\mathbf{r}, t) >= 0$, and $< \zeta(\mathbf{r}, t)\zeta(\mathbf{r}', t') >= \varepsilon M_0 \nabla^2 \delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$, where ε is the magnitude of the fluctuation.

The spectral methods

$\Delta x = \frac{2\pi}{128}$, $\Delta t = 0.001$. $M = 0.2, \chi = 0.4, T = 300, N = 400$.

Numerical results

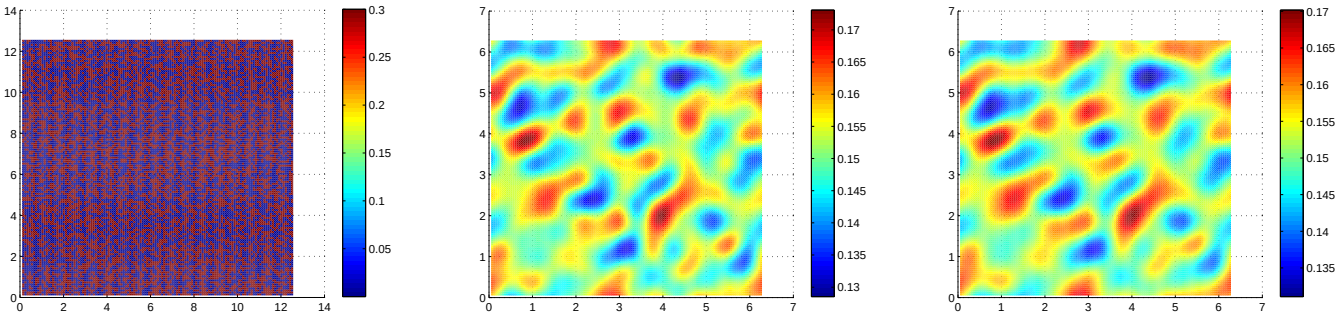


Figure: Temporal evolution of patterns for the initial volume fraction of polymer $\phi = 0.3$ at time tmax=0, 0.6, 1.

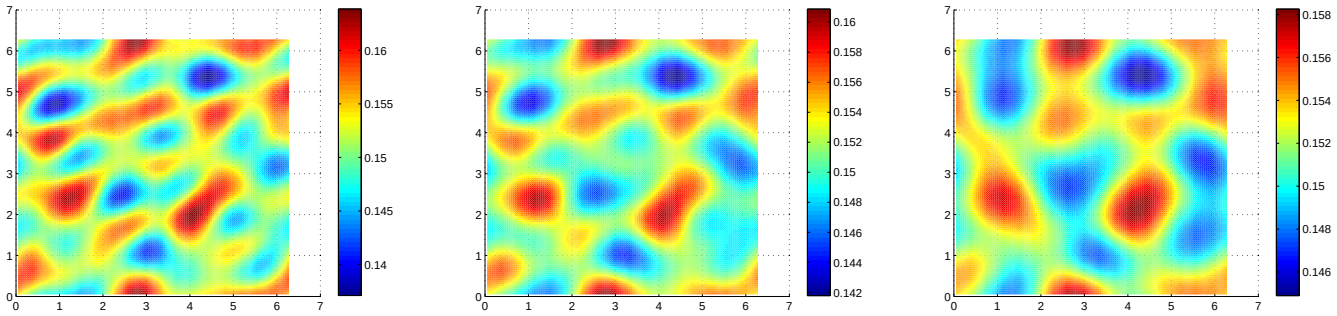


Figure: Temporal evolution of patterns for the initial volume fraction of polymer $\phi = 0.3$ at time tmax=3, 8, 20.

Numerical results

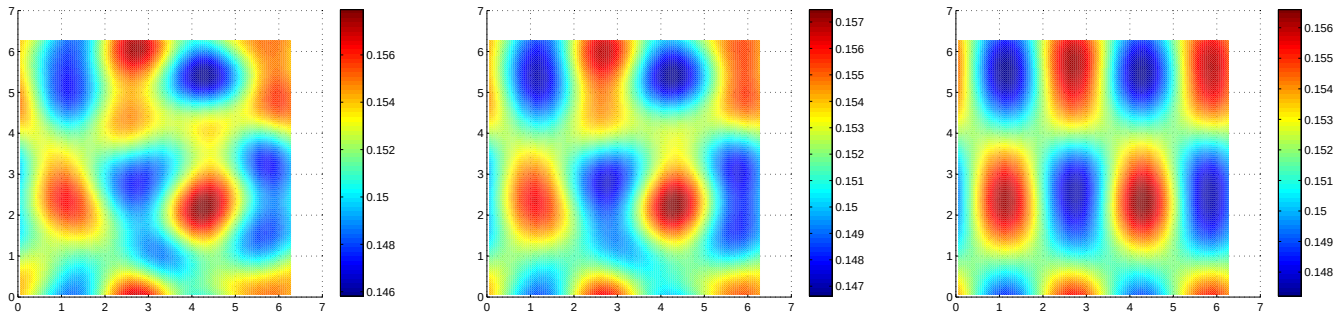


Figure: Temporal evolution of patterns for the initial volume fraction of polymer $\phi = 0.3$ at time tmax=30, 50, 120.

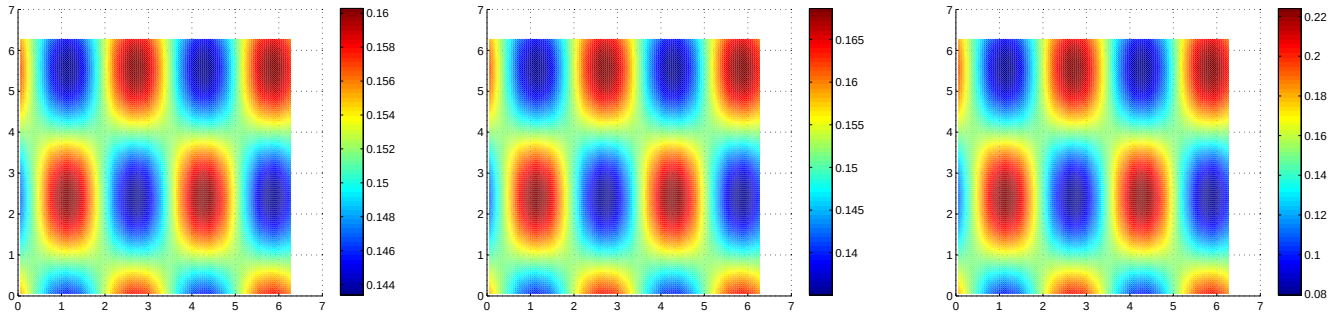


Figure: Temporal evolution of patterns for the initial volume fraction of polymer $\phi = 0.3$ at time tmax=4000,8000,10000.

Comparison with Experimental Results

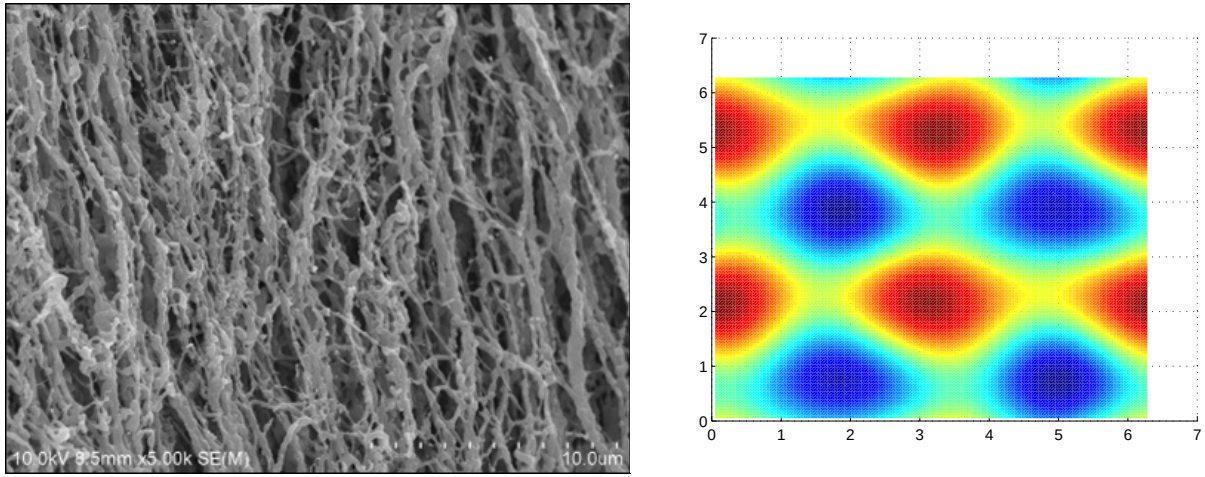


Figure: Comparison between the experimental results(left) and numerical results(right).

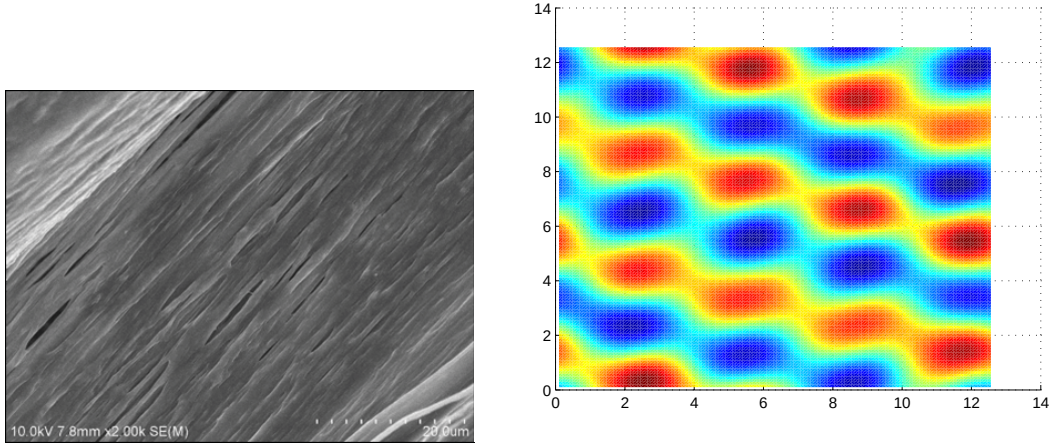


Figure: Comparison between the experimental results(left) and numerical results(right).

Comparison with Experimental Results

Now we expect to choose information entropy as an index to measure the overall state. It defines as

$$H(\phi) = E\left[log\frac{1}{p_i}\right] = -\sum_{i=1}^{n} p_i \log p_i,$$

where p_i is the occurrence probability of the $\phi = i$ constituent in the total area. In information entropy of phase separation, p_i is defined as the probability of concentration.

Comparison with Experimental Results

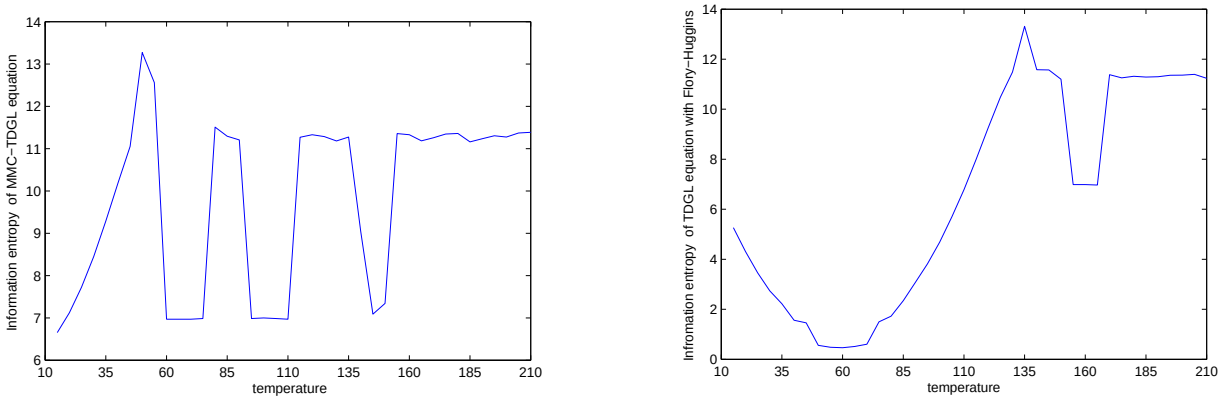


Figure: Information entropy varies with the reticular free energy (left) and the Flory-Huggins free energy(right), respectively. Temperature is from 10^oC to 210^oC, horizontal axis indicate the number of steps with the temperature growth as 5^oC per step, N=400.

Comparison with Experimental Results

- Chemical experiments show that the optimum reaction conditions are that irradiation of the MMS emulsion in oxygen for 2h at room temperature, polymerization for 6h, and a reaction temperature of 40^oC. At high temperatures (50^oC, 60^oC, and 65^oC), gel-like materials are also obtained, but they are partly or completely dissolved in water, indicating that there is no strong interaction between the MMSs for a few reasons.
- T $\uparrow \rightarrow$ **polymerize**
  T $\uparrow \rightarrow$ **thermal movement** $\rightarrow$ **dissolve**
  So the competition of them will lead to polymerize and dissolve alternately.

Zhai D., Zhang, H. Investigation on the application of the TDGL equation in macromolecular microsphere composite hydrogel, *Soft Matter*, 2013, 820-825.

Outline

Conclusion

- Structure SCMFT model for MMC hydrogel and obtain the micro-structures.
- Structure-Property relationship? Structural factors: nanoparticle size, grafting density, polymer chain length, chain conformation, entanglement?
- Introduce the reticular free energy, and obtain the phase transition.
- What effect the phase transition? Structural factors: nanoparticle size, grafting density, polymer chain length, chain conformation, entanglement,$\cdots$
- Stochastic links?
- Mathematical problems? DFT and SCMFT? How many micro-structures? Computational methods? $\cdots$

All models are wrong,

but some are useful!

–George Box