Nanopatterns in Tethered Membranes of Weakly Charged Chains with Hydrophobic Backbones

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Networks of weakly charged chains with self-attracting interactions such as those due to hydrophobic backbones form stable, locally segregated patterns in aqueous solutions.[1−3] The nanophase (termed microphase) segregated patterns are induced by external stimuli, which include changes in temperature, pH, salt concentration, osmotic pressure,[4−6] or the electric field.[7] Since the nanophase-segregation transition is accompanied by fast large volume changes, these hydrogels have generated great technological interest for microactuator applications.[8]

Here we analyze, by computer simulations, charged thin gels or tethered membranes for potential applications as actuators, sensors, and delivery vehicles of charged nanoparticles. We model weakly charged telechelic chains with hydrophobic groups in the presence of oppositely charged nanoparticles. We find stable nanopatterns of hydrophobic−hydrophilic domains in a broad range of external parameters. The hydrophobic domains of collapsed charged chains in the gels are separated by polar (hydrophilic) regions rich in water where the nonattractive nanoparticles are dissolved. The equilibrium structure of the thin gel or tethered membrane depends on the salt concentration. The nanopattern melts into a macroscopic segregated structure when $\kappa L^* > 1$, where κ is the inverse screening length and L^* is the size of the nanophase domain.[9,10] When the nanopattern melts, the nanoparticles are released from the gel, and the system's size is strongly reduced. The large size contraction and effective release of nanoparticles provide evidence that tethered membranes are ideal for sensing and delivery applications.

We model the charged tethered membrane or two-dimensional (2D) gel with a bead−spring model, where each bead is a coarse-grained unit (CGU). The hydrophobic beads or CGUs are physically adsorbed onto a surface. Each CGU is connected to four neighbors by a spring (except for corners and edges, which are connected to two and three CGUs, respectively). The adsorbed gel is surrounded by oppositely charged monovalent nanoparticles with the same size of the CGUs, which neutralize the systems in the salt-free case. Our simulations show that these nanoparticles (or cargo for delivery) can be transferred reversibly from the inside to the outside of the thin gel by changing the salt concentration and/or the solvent quality. We analyze the distribution of particles in the different states using a canonical ensemble, which implies that the number of particles, the area of box, and the temperature are constant. The unit of length is σ, which is the Lennard-Jones (LJ) interaction parameter between CGUs. The unit of energy is k_BT, where k_B is the Boltzmann factor and T is temperature. The spring constant k between CGUs is $0.1k_BT/\sigma^2$, which corresponds to the elastic constant of a Gaussian chain with length of 30 monomers. The charge q of a CGU is 0.3 e, which implies that the backbone charge fraction f is 0.01 for monovalent monomers. All excluded-volume interactions between particles are LJ potential types, which are cut and shifted at a cutoff distance r^c.

$$U_{ij}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \quad (1)$$

where i and j denote particle types. $i = 1$ represents a CGU, and $i = 2$ represents a nanoparticle. In this study, we set $\sigma_{11} = \sigma_{12} = \sigma_{22} = \sigma$, $\epsilon_{12} = \epsilon_{22} = k_BT$, $r^c_{11} = 2.5\sigma$, and $r^c_{12} = r^c_{22} = 2^{1/6}\sigma$. We use screened Coulomb interactions between the charged components

$$U_{lm}(r) = \frac{l_B q_l q_m}{r} e^{-\kappa r} \quad (2)$$

where q_l and q_m are the charges of the particles l and m, respectively. The Bjerrum length $l_B = 5\sigma$. These Coulomb interactions are vanished at the cutoff distance 25σ.[11] Since the simulation box is $140\sigma \times 140\sigma$, there are no Coulomb interactions between gels when the gel is in the nanophase and macrophase segregated states.

The LAMMPS package[12] is used in this study. There are 1600 CGUs and 408 nanoparticles in a box of size $140\sigma \times 140\sigma$ with periodic boundary conditions. While the electrostatic repulsions between CGUs cause the gel to swell, the LJ attractions between CGUs contract the gel. The equilibrium structure of the gel depends on the competition between these two interactions. There are three possible states shown in Figure 1. When the attraction is weak ($\epsilon_{11} = 1k_BT$), the electrostatic

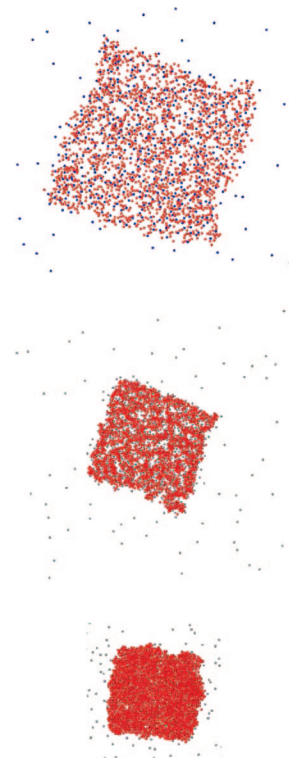

Figure 1. Snapshots from MD simulations for the system at different strengths of attraction between CGUs. Top is for $\epsilon_{11} = 1k_BT$ and $\kappa = 0$, middle is for $\epsilon_{11} = 3k_BT$, and $\kappa = 0$ and lower is for $\epsilon_{11} = 3k_BT$ and $\kappa = 0.9\sigma^{-1}$. The dark (red) particles represent CGUs while the light (silver) ones represent the nanoparticles. Some nanoparticles ourside the gel are removed for clarity.

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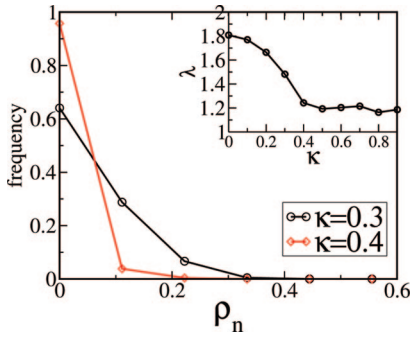

Figure 2. Nanoparticle density distribution (frequency) versus density ρ_n for grid size $3\sigma \times 3\sigma$ and $\epsilon_{11} = 3k_BT$ at different salt concentrations; when $\kappa \geq 4$, the curves nearly superimpose on the top of the curve $\kappa = 4$. The inset shows the degree of swelling (λ) as a function of κ.

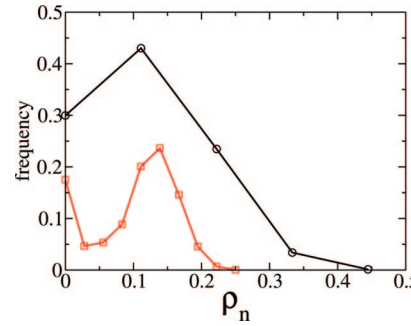

Figure 3. Nanoparticle density distribution (frequency) versus density ρ_n for different grid sizes: The circles (black curve) are for grid size of $3\sigma \times 3\sigma$, and the squares (red curve) are for grid size of $6\sigma \times 6\sigma$. For salt-free case and $\epsilon_{11} = 3k_BT$.

repulsion dominates, and the gel swells homogeneously and the nanoparticles penetrate the gel due to the electrostatic attraction between nanoparticles and CGUs. When the attraction increases ($\epsilon_{11} = 3k_BT$), percolated nanoclusters of CGUs form. The nanopattern size is determined by the balance between the electrostatic repulsions and LJ attractions between CGUs. When the salt concentration is high, the nanophase will collapse into a dense macrophase segregated structure.

The strength of electrostatic interactions can be tuned by the salt concentration. We study here the effect of salt concentration by introducing the inverse Debye screening length κ. Nanopatterns occur at salt-free or low salt concentration with most nanoparticles absorbed in the hydrophilic nanodomains. As the salt concentration increases, the electrostatic interactions become weaker. At a critical salt concentration, the gel collapses and almost all nanoparticles are expelled to the surrounding medium, as shown in the bottom of Figure 1. The inset of Figure 2 shows the degree of swelling by plotting the swollen area ratio λ of the gel at different salt concentrations: $\lambda = A(\kappa_i)/A_{min}$, where $A(\kappa_i)$ is the area of the membrane at κ_i and A_{min} is the closest packed membrane area, which is $40\sigma \times 40\sigma$. Since the shape of the gel is not regular, it is impossible to get the exact area of the gel. We have estimated this quantity by the finite difference Newton's forward method. We slice the box along x-axis with a constant width of 1σ. For each slice we find the maximum and minimum values of the y coordinates of CGUs inside that slice and calculate the difference between these two extremes. The total area of the gel is the sum of the area in that slice between these two extremes. The size of the gel changes sharply when it macroscopically segregates. Figure 2 shows that macrophase separation occurs between $\kappa = 0.3$ and $\kappa = 0.4$. According to the theory,[10] the nanophase domain melts when $\kappa L^* \approx 1$. Therefore, the domain size L^* is about 3σ, which is consistent with the middle snapshot in Figure 1.

A recent study of three-dimensional thermoreversible polyelectrolyte gel shows that disordered nanophase segregated structures might be more stable than periodic structures due to the resulting charge heterogeneities.[13] We find here that percolated nanodomains are also preferred in 2D homogeneous gels, contrary to ionic pattern with self-attractive interactions between equal charged components in 2D.[14] In order to find the fluctuation in the number of nanoparticles in the hydrophilic domains, we compute the density distribution of nanoparticles by dividing the gel into grids of size $L^* \times L^* \simeq 3\sigma \times 3\sigma$ and calculate the resulting ensemble average of density of nanoparticle for each grid site which is inside the membrane.[15] Figure 2 shows the density distributions of nanoparticles at different salt concentrations for $\epsilon_{11} = 3k_BT$. In the nanophase segregated state, when $\kappa \leq 0.3$, some nanoparticles are inside the membrane. In the macrophase segregated state, where $\kappa \geq 0.4$, nearly all nanoparticles are pushed outside the membrane. This shows that we can deliver the nanoparticles by changing the salt concentration.

The distributions of nanoparticles in the nanodomains shown in Figure 2 are very broad due to fluctuations when $\kappa \leq 3$, as in random copolymers.[15−17] We test this analogy by obtaining the density distributions of nanoparticles in salt-free gel for box grids of sizes $L \approx L^*$ and $L > L^*$. As shown in Figure 3 for $\epsilon_{11} = 3k_BT$, which gives $L^* \simeq 3\sigma$, the nanoparticles are broadly distributed when the grids are of size $L \leq L^*$. This type of distribution is called multifractal because it cannot be described by a single mean value and the second moment or width of the fluctuations (like a Gaussian type distribution). Instead, since the fluctuations are broad, all the moments of the multifractal distribution are required. When $L > L^*$, one obtains the standard distribution with a mean value and narrow fluctuations of nanoparticles inside the gel, as expected.

The heterogeneous density distribution for $L \leq L^*$ is indeed characteristic of percolated nanodomains with broad interfaces, as in random copolymer microphases.[15−17] This distribution maximizes the entropy of the system, in comparison with narrow distributions in strongly segregated stripe nanophases obtained if the nanoparticles are self-attracting (that is, if the nanoparticles have hydrophobic groups)[10,14] or in tethered charged hydrophobic chains to surfaces.[18] Disordered nanophases are also expected in three dimensions (3D),[13] provided that the cross-link density is high to avoid the formation of pearl-like (necklaces) conformations.[19] Though necklaces cannot be obtained with our model, they are expected in adsorbed membranes with large number of monomers per cross-links.[20] We cannot study membranes with low cross-link densities with our model because we are neglecting the excluded volume of the chain backbone. In our model the chains are phantom because they are not adsorbed. Instead, they are assumed to be off the 2D surface, embedded in the third dimension, in the hydrophobic regions of collapsed chains. The extension of our results to chains with adsorbed backbones with excluded volume, however, is straightforward.

Figure 4 shows the average density distributions of CGUs at the different salt concentrations for $\epsilon_{11} = 3k_BT$. It clearly indicates two behaviors for the CGU density distribution (the grid size is 3σ) as a function of the inverse screening length κ. One corresponds to nanophase segregation, and the other one corresponds to macrophase separation. From the width of the

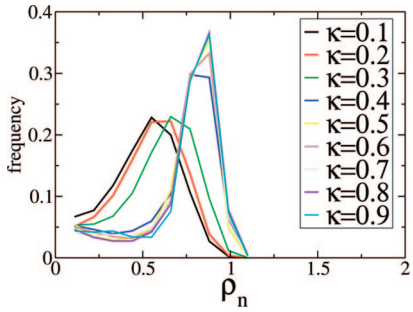

Figure 4. Local density distribution of CGUs (frequency) versus density ρ_n at different salt concentrations and grid size $3\sigma \times 3\sigma$ for $\epsilon_{11} = 3k_BT$.

peak, we can see that the density fluctuation in the nanophase segregation is larger than that in the macrophase separation.

In summary, our simple model shows that weakly charged tethered membranes or thin gels adsorbed on surfaces with hydrophobic backbone can undergo transitions from a swollen state to a nanophase segregated state as the strength of the backbone attraction increases. Furthermore, as the concentration of salt increases, the nanophase segregated system undergoes a transition to a macrophase segregated state. All these transitions are accompanied by large changes in the dimensions of the system, a characteristic of charged gels.[1,21] In the nanophase segregated state, we find that the local ionic density fluctuations are large. These fluctuations might account for the formation of percolated nanodomains rather than periodic nanophases. The release of nanoparticles (or molecules) from the polymer gel at different external conditions makes these systems ideal vehicles for delivery of charged nanoparticles.

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