

## Presence of Electrostatic Potential Wells in the Ionic Polymer Network

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The electrostatic potential distribution of cross-linked polyelectrolyte gels has been numerically calculated on the base of Poisson-Boltzmann equation using a three dimensional network geometry. The simulational result revealed that besides potential energy valleys around the polymer chains, there should exist deep electrostatic potential energy wells at every cross-linking point.

Polyelectrolyte gel consists of a charged network and a fluid filling the interstitial space of the network. Different from the polyelectrolyte solution, the charged polymer gel exhibits a variety of unique behaviors such as phase-transition,<sup>1</sup> specific adsorption equilibrium,<sup>2</sup> presence of unfrozen water<sup>3</sup> and chemomechanical behavior.<sup>4</sup> The unique properties and behaviors observed in the polyelectrolyte gel should well be characterized by the nature of cross-linked charged network, together with those of their counter ions and the solvents.

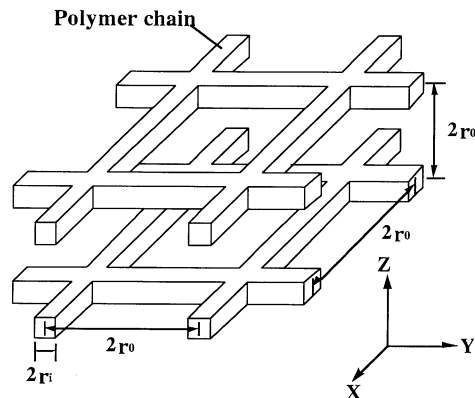
The polyelectrolyte is a wide field to which a large number of researcher groups have made contribution on evaluating the electrostatic potential in polyelectrolyte solutions.<sup>5-8</sup> The earliest theoretical studies of which involved the application of the Poisson-Boltzmann to this problem in which the polyion was taken to be a hard cylindrical rod.<sup>5</sup> Oosawa and Manning's counterion condensation theory postulated that sufficient numbers of counterions condense on the polyion so as to reduce the effective value of  $\xi$  to unity, thereby removing the instability of the system.<sup>6,7</sup> Recently the hypernetted chain(HNC) integral equation has been applied to a cell model of a dilute polyelectrolyte solution.<sup>8</sup> The principal advantage of this approach is that it provides a better treatment of the ion-ion correlations that is possible with the Poisson-Boltzmann equation.

However, so far as authors know, no attempt has been made to evaluate the electrostatic potential distribution of a polyelectrolyte gel because of the experimental as well as theoretical difficulties of the analysis. We have paid a special interest in the electrostatic field formed at the cross-linking points(knots) because of specific features observed in the gel should largely be associated with the presence of these knots.

We have previously attempted to describe the electroconstrative behavior of polyelectrolyte gels with a one-dimensional capillary model in which Katchalsky's rod-like model have been used to evaluate the electrostatic potential of the polyelectrolyte gel.<sup>5,9</sup>

However, this one-dimensional model is not appropriately enough to evaluate the electrostatic potential of the gel because the contribution of cross-linking point to the electric field have not been taken into consideration. We present here a three-dimensional simulation for a polyelectrolyte network made of stacking of two dimensional mesh-like networks in parallel one after another. The simulational results may make it possible to elucidate specific features observed in the polyelectrolyte gel such as the presence of bound and unfrozen water.

We supposed that cross-linking points of the gel is periodically distributed on the chain segments and the macro charges are evenly distributed(Figure 1) on the chain. We assume that the polymer network is made from the periodical stacking of the square-shaped meshes, each  $2r_0$  distance apart. Assumption was also made that the ionic chain has a square cross-section with a length of  $2r_1$ , and the distance between two adjacently parallel chains is  $2r_0$ . The coordinate is chosen as that the x-y plane is parallel to mesh plates and the origin is located in the center of a square mesh with  $z=0$  in the midway of two adjacent meshes.



**Figure 1.** Network structure used for three-dimensional simulation of the electrostatic potential for a cross-linked polyelectrolyte gel.

The electrostatic potential  $\psi(x,y,z)$  among the polymer chains is given by Poisson-Boltzmann equation:

$$\Delta\psi(x,y,z) = -\frac{\rho_0}{\epsilon} \exp\left\{-\frac{e\psi(x,y,z)}{kT}\right\} \quad (1)$$

Where  $\epsilon$  is the dielectric constant,  $e$  the charge of a elementary electron,  $k$  the Boltzmann constant,  $T$  the temperature, and  $\rho_0$  the average counter ion density which can be expressed by

$$\rho_0 = \frac{e}{2b(r_0^2 - 2r_1^2)} \quad (2)$$

where  $b$  is the distance between two ionizable groups on the polymer chain. Here, we confine to univalent counter ions of a polyanionic gel. The normal derivative of potential on the surface of polymer chains should be:

$$\frac{\partial\psi(x,y,z)}{\partial n} = -\sigma/\epsilon \quad (n=x,y,z) \quad (3)$$

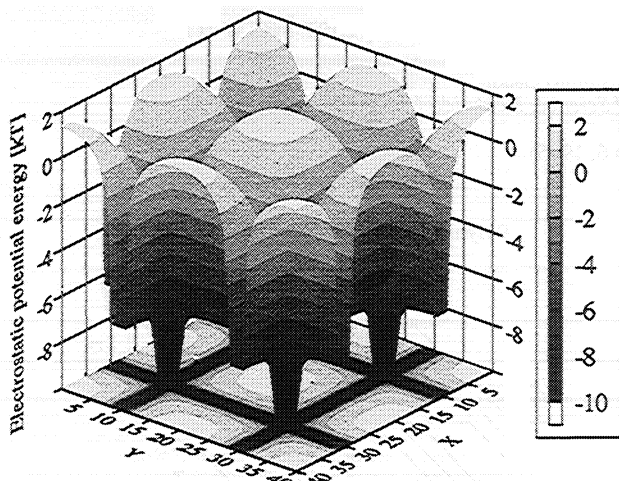
where  $\sigma$  is the surface charge density of the chains, which is given by  $\sigma = e/4 r_1 b$

The charge density of counter ions  $\rho(x,y,z)$  is determined by Boltzmann distribution

$$\rho(x,y,z) = \rho_0 \exp\left\{-\frac{e\psi(x,y,z)}{kT}\right\} \quad (4)$$

The simulation was carried out on a cubic box with a side length of  $r_0$  ( $1/2^3$  of a periodical unit cell) and then copied to the whole periodical unit according to the symmetry. The simulation box was divided into  $10 \times 10 \times 10$  lattice cells. To make the surface of polyions on lattice points,  $r_0 = 10r_1$  was used. Equation 1 was expressed by Poisson's difference equations and the electrostatic potential on lattice points were calculated by Liebmann's method. A relaxation parameter of 0.5 has been used to accelerate the calculation. An iterative difference value of  $\epsilon = 10^{-7} kT$  was used to determine the accuracy of the calculation. Symmetric conditions have been used on walls of the simulation box, i.e., the normal derivatives of potential on walls are zero.

The simulation has been carried out for a poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) gel which is a fully ionized polyelectrolyte having sulfonic groups as macro-ions and  $H^+$  as counter-ions. The radius of the polymer chain  $r_1$  of the PAMPS is  $r_1 = 6.08 \times 10^{-10}$  m. Although a square-shaped cross-



**Figure 2.** Spatial profile of the electrostatic potential energy for the plane of  $z=r_0$ , which represents the plane within the mesh-like network. X and Y axes are in unit of  $r_1$  ( $=60.8$  nm).

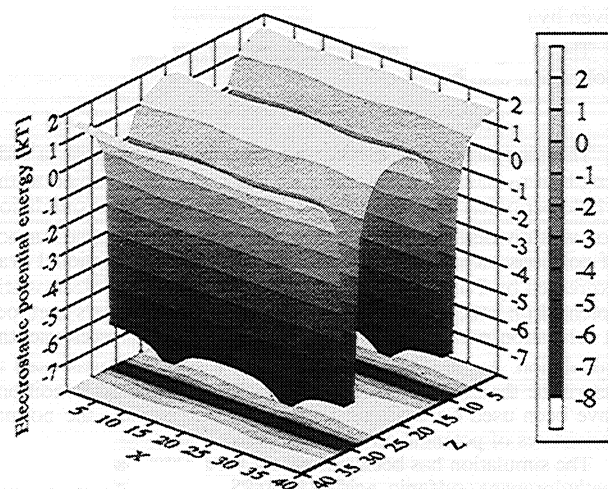
section, instead of circular-shaped cross-section, was used for the simulation, the surface area as well as the surface charge density was kept constant as  $2\pi r_1=8a$ . The other constants used are  $b=2.55 \times 10^{-10}$  m,  $\epsilon_r=78$  ( $\epsilon=\epsilon_r \epsilon_0$ ,  $\epsilon_0$  is the dielectric constant in vacuum),  $T=300$  K.

Figure 2 shows a spatial profile of electrostatic potential energy  $e\psi(x,y,z)$  in the unit of kT on  $z=r_0$ , which represents the planes of mesh-like networks. The potential energy distribution is almost homogenous in the plane of  $z=0$ , which is located in the midway of two mesh-like networks.

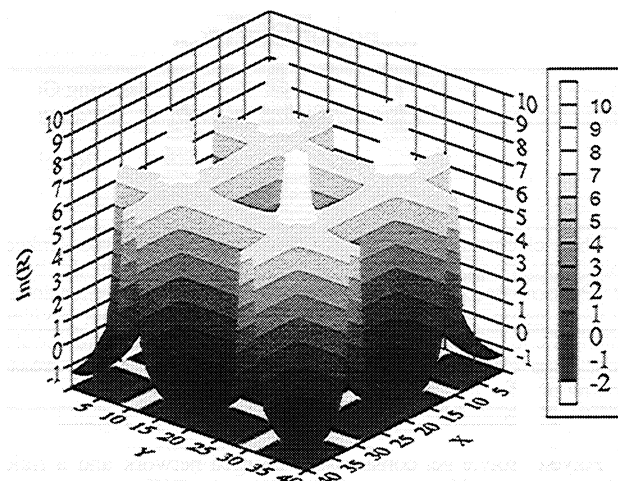
Figure 3 shows the electrostatic potential energy distribution on the plane of  $y=r_0$ , which is the plane perpendicular to the mesh-like network and with cross-linking points located in the plane.

The figures show that there exist potential energy wells at every cross-linking points and valleys along the polymer chain. The steep potential well and valley accordingly introduce electric fields as high as  $10^8$  V/m near the network knots and chains.

Figure 4 shows the spatial profile of the relative charge density  $\rho(x,y,z)/\rho_0$  of the counter ions on  $z=r_0$ . It indicates that counter ions are mostly localized around the network knots as well as the



**Figure 3.** Spatial profile of the electrostatic potential energy for the plane of  $y=r_0$ , which represents the plane perpendicular to the mesh-like network and with cross-linking points lie in the plane. X and Z axes are in unit of  $r_1$  ( $=60.8$  nm).



**Figure 4.** Spatial profile of the relative charge density of the counter ions on  $z=r_0$ .  $R=\rho(x,y,z)/\rho_0$  X and Y axes are in unit of  $r_1$  ( $=60.8$  nm).

polymer chains. The charge density of counter ions decreased very sharply with an increase in the distance from the polymer chain. Counter ions located in the deep potential valley ( $\gg kT$ ) should strongly be bound to the polyion. The amount of these bound counter ions would increase with the increase in the cross-linking density.

The deep potential wells and high counterion densities at crosslinking points might bring about an instability and results in the counterion condensation as predicted by Oosawa and Manning for the polyelectrolyte solution.<sup>6,7</sup>

The presence of deep electrostatic potential valley should strongly confine the motion of water molecules and restricts the configuration favorable to form crystal structure.<sup>11</sup> This might bring about decreased entropy and enthalpy changes of solvent molecules at crystallization, due to enhanced polarization and should decrease the melting temperature. The enhanced electric conductivity of the charged gel swollen in DMSO below the melting point is explained in terms of presence of unfrozen carrier ions near the polymer chains and knots.<sup>12</sup>

The treatment of a crosslinked polyelectrolyte gel with a rigid periodical structure and the interaction between small ions with a mean field might oversimplified the problem. The presence of deep potential wells at crosslinking points could come from this simplification, it would be informative to understand the potential distribution of the polyelectrolyte gels, especially in the case of without the presence of simple salts. Therefore, this work could be a first step towards developing more accurate theory and understanding the specific nature of polyelectrolyte gels.

#### References and Notes

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