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Citation: *The Journal of Chemical Physics* **104**, 4309 (1996); doi: 10.1063/1.471240

View online: <http://dx.doi.org/10.1063/1.471240>

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# Microscopic simulation of phase transition in interacting ionic gels

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(Received 27 September 1995; accepted 13 December 1995)

Ionic polymer networks are studied using the bond fluctuation method. Gels are known to exist in expanded or collapsed phases as demonstrated by Tanaka *et al.*'s experiments on ionic gels. Two interactions—the quality of the solvent and the work done by a gas of counterions—suffice to characterize the first-order phase transition indicated in these two-dimensional simulations. A technique is introduced which prevents local attractive interactions from hindering global relaxation. © 1996 American Institute of Physics. [S0021-9606(96)50411-5]

First-order phase transitions in ionic gels have been observed experimentally by Tanaka *et al.*<sup>1</sup> Unfortunately, until recently, effective microscopic studies of gels (cross-linked polymer networks) were limited since efficient numerical techniques had only been developed to simulate the polymer chains. Additional constraints prevent cross-links from diffusing under the local symmetry operations of many Monte Carlo (MC) techniques, namely, the kink-jump, crankshaft, and reptation algorithms.<sup>2</sup> Approaches which capably generate statistical fluctuations of the positions of volume-excluding chains are therefore not necessarily suitable for simulating gels. However, branched polymers can be naturally included in a recent MC algorithm, the bond fluctuation method (BFM);<sup>3</sup> this affords an opportunity to conduct simulations of gels.

In this paper, I use the BFM to study phase transitions of ionic gels. I also introduce a method which prevents attractive interactions from inhibiting the global relaxation of the gel. Gels are an interesting class of materials used commercially for many applications from delivering drugs to making cement. There are also biological gels in our eyes and joints. Mean-field theories for gels were developed by Flory and Huggins<sup>4</sup> but microscopic simulations of gels have not been attempted<sup>5–7</sup> until recently, and never before to study phase transitions. The simulation techniques developed here may also help to provide understanding of, for example, the complicated local behavior of novel gels with competing ionic interactions.<sup>8</sup>

The BFM models a polymer as a bead necklace. Simulating physical chains requires that the separation  $r_{ij}$  between beads  $i$  and  $j$  satisfy (i) a hard-core repulsion between beads and (ii) a tethering constraint for neighboring beads,

$$r_{ij} \geq \rho_{\min}, \text{ for all pairs } ij, \quad (1)$$

$$r_{ij} \geq \rho_{\max}, \text{ when } ij \text{ are chain neighbors.} \quad (2)$$

Chain crossings are prohibited with a proper choice of the maximum separation of connected beads  $\rho_{\max}$  for a given hard-core bead size  $\rho_{\min}$ .<sup>3,7</sup> The positions of the beads are discretized to a lattice in real space for computational

efficiency;<sup>3</sup> for example, the hard-core condition may be calculated rapidly by storing bead positions in a logical array. BFM studies have been performed for polymer chains in two dimensions<sup>3,9</sup> and in three dimensions<sup>3,10–13</sup> and for gels in two and three dimensions.<sup>5–7</sup>

A convenient mental picture of the two-dimensional gel is that of a fishnet; the segments of rope (the polymer chains) can wriggle around but the knots (the cross-links) maintain a global topological order. The networks considered (shown in Fig. 1) were composed of  $(L+1)^2$  cross-links in a spatially fluctuating array topologically equivalent to a square lattice, connected by chains with  $(n-1)$  beads between cross-links.

Assuming no interactions between the chains in the network, the Rouse model<sup>14</sup> estimate of the relaxation time, in Monte Carlo steps (MCS), is

$$\tau_0 = (bnL)^2. \quad (3)$$

With  $\rho_{\min}=2$  and  $\rho_{\max} = \sqrt{13}$ , the characteristic distance between neighboring beads is taken to be  $b=3$ . Statistical averages are computed after every  $\tau_0$  MCS.

In every MCS, a move for each bead is attempted once. Two moves are attempted per MCS for cross-links to improve the diffusivity of these more highly constrained beads. In each move, the bead and the direction of a move of unit length are randomly selected. Tests are made that, in the proposed position, the bead neither overlaps with any other bead nor violates the tethered-bead constraint. If these constraints [Eqs. (1)–(2)] are satisfied, then the interaction energies are calculated and standard Metropolis sampling<sup>2</sup> determines whether the move is accepted.

Two interactions are considered. The first measures the relative affinity of a chain to be surrounded by solvent as opposed to by other polymers and is called the polymer–polymer interaction. The second is the work done to confine the gas of counterions to the volume of the gel and is called the hydrogen ion pressure.

Experimentally,<sup>1</sup> the quality of the solvent is varied by altering the relative composition of water and acetone (the vertical axis of Fig. 2). Acetone is a less polar solvent and increases the polymer–polymer affinity in polyacrylamide/polyacrylic acid gels. The polymer–polymer interaction measures the relative preference for a bead to sit next to solvent vs some other bead. In the simulation, other beads  $j$  within a thin shell around the bead  $i$ , such that

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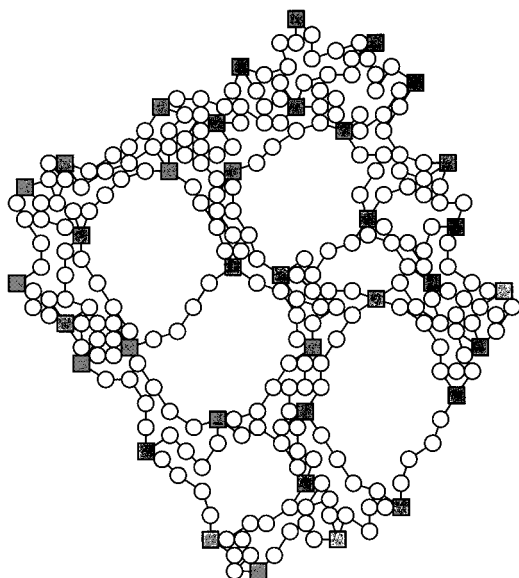


FIG. 1. Configuration for an interacting gel in two dimensions.  $n-1=4$  is the number of beads in a chain.  $L=5$  is the number of unit cells on a side. Polymer-polymer coupling  $J_P=-2$  and hydrogen ion coupling  $J_H=5$  are used. Cross-links are depicted with shaded squares.

$$r_{ij} \leq \rho_P, \quad (4)$$

contribute a factor  $\exp\{-J_P\}$  to the Boltzmann weight. Thus the local interaction is modeled by a finite square-well potential. The radius of the shell is taken to be the tethering radius,

$$\rho_P = \rho_{\max}, \quad (5)$$

so chain neighbors are always within the well; thus, tethered beads do not alter the dynamics of the solution since their interaction energy is the same for all allowed positions.

The second interaction is from the hydrogen ion pressure. This pressure is proportional to the degree of acidity of the gel prepared. For the experiments of Tanaka *et al.*, acrylamide gels were made and then, by base-catalyzed hydrolysis, monomers of acrylamide were slowly converted to monomers of acrylic acid ( $-\text{CONH}_2$  to  $-\text{COOH}$ ).<sup>1</sup> The phase transition's dependence on hydrolysis is shown by the sequence of graphs in Fig. 2. The experiments were carried out at  $\text{pH}=7$ , where acrylic acid is generally ionized ( $\text{A}^-$  plus free  $\text{H}^+$  ions) while acrylamide is generally neutral ( $\text{AH}$ ).

The degree of ionization influences the dynamics of the gel because the counterions ( $\text{H}^+$ ) are confined by Coulomb interactions to the volume occupied by the gel. Inside that volume, the positive charge of the hydrogen ions is compensated by the background of negative charge of the ionized acrylic acid monomer  $\text{A}^-$ . When an  $\text{H}^+$  tries to leave the volume of the gel, the Coulomb force pulls it back inside. This force tends to expand the surface of the gel and is known as the hydrogen ion pressure.

To a first approximation, the  $N_+$  hydrogen ions behave like an ideal gas confined to a volume  $V$  or, for the two-

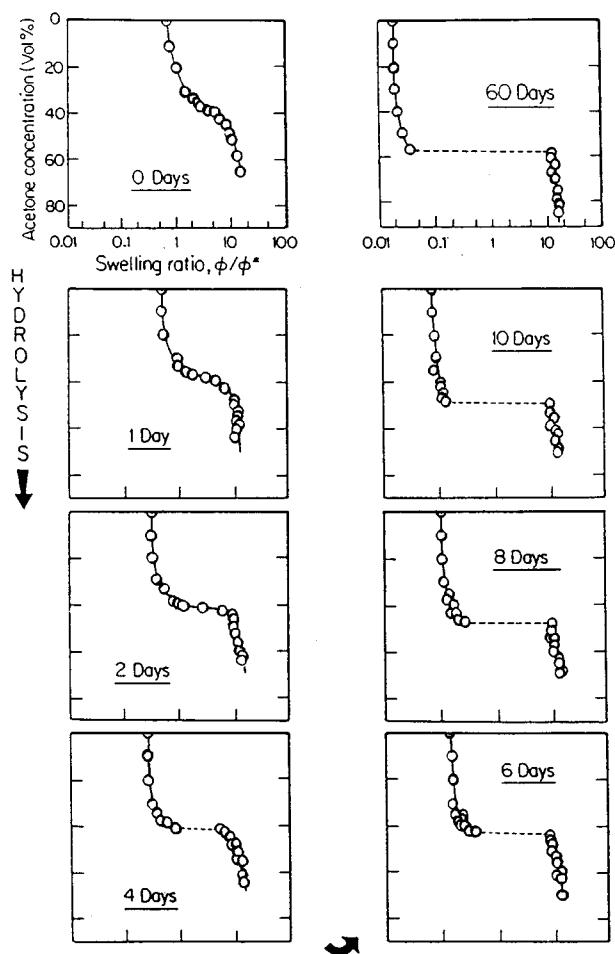


FIG. 2. Experimental data from Ref. 1. The acetone concentration dependence of the swelling ratio,  $\phi/\phi^* \sim (\text{volume})^{-1}$ , for increasing periods of hydrolyzation (1 day, 2 days,...) of the gel network, with accompanying increase in the acidity of the gel. The gel shrinks with higher acetone concentration due to the increase in polymer-polymer affinity.

dimensional case considered here, an area  $A$ . The work  $\Delta W$  done against this pressure contributes the hydrogen ion part of the Boltzmann energy factor

$$\Delta W = \frac{-N_+ k_B T}{A} \Delta A, \quad (6)$$

$$\Delta(-\beta \mathcal{H}_H) = J_H C_0 \frac{\Delta A}{A}, \quad (7)$$

where  $\beta^{-1} = k_B T$  and the normalization factor

$$C_0 = \frac{4N_{\text{beads}}}{2n} \quad (8)$$

is constructed, for  $\rho_{\min}=2$ , to be the minimum area the gel can occupy divided by the largest  $\Delta A$  for  $N_{\text{beads}}$  close-packed beads.

In this study, the energy change from the hydrogen ion pressure [Eq. (7)] is calculated whenever a surface cross-link move is attempted. This approach is used, even though in  $d=2$  the chains themselves compose a well-defined surface,

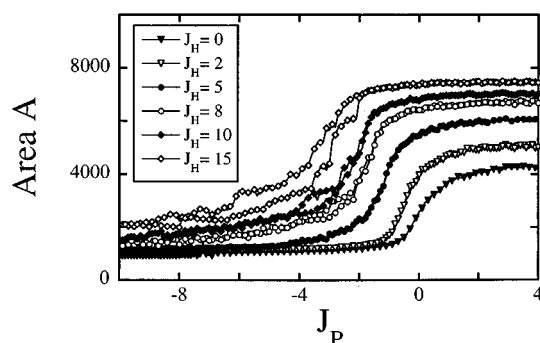


FIG. 3. The dependence of the area, varying the polymer–polymer interaction strength  $J_P$  at fixed hydrogen ion pressure  $J_H$  for  $L=5$ ,  $n=5$  gels in two dimensions. The hysteresis loops indicate a discontinuous (first-order) phase transition for  $J_H \geq 8$ . Points are generated with  $10\tau_0$  MCS, after discarding  $5\tau_0$  MCS, sampling every  $\tau_0=5625$  MCS.

because it may be generalized to  $d=3$ . In three dimensions, the holes between the chains mean the surface of the gel is ill defined; however, the cross-links do form a topologically simply-connected surface—one without holes. Thus it is preferable to use surface cross-links to define the volume.

With an attractive polymer–polymer interaction,  $J_P < J_P^{\text{crit}}$ , the system separates into two phases, one dense, the other dilute. This state turns out to be nonergodic and an effort must be made to ensure that the equilibrium ensemble is adequately sampled; fully stretched chains are nondiffusive because beads are far from the square-well potential of another bead [Eq. (4)] while close-packed tightly-bound states are nondiffusive because an activation energy is required to separate beads before dense clusters can move. The latter is in part because the bead positions have been discretized to a lattice. Physically, there should be no impediment for large clusters to move. One way to overcome this obstacle would have been to introduce cluster moves; however, global connectivity constraints complicate implementing that approach in the simulation.

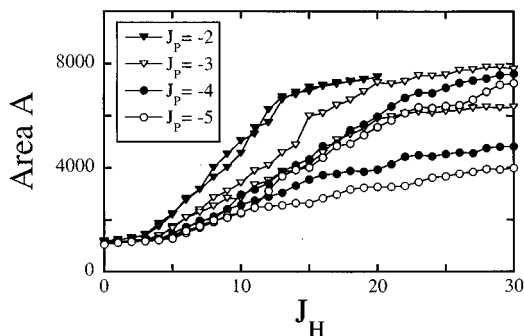


FIG. 4. The area is plotted varying the hydrogen ion pressure at fixed polymer–polymer interaction strength for  $L=5$ ,  $n=5$  gels in two dimensions. Data are plotted in the phase separation region. There is no phase separation for  $J_P = -2$ , indicating this is above the critical point. Phase separation increases as binding becomes stronger ( $J_P < -2$ ). Points are generated with  $10\tau_0$  MCS, after discarding  $5\tau_0$  MCS, sampling every  $\tau_0=5625$  MCS.

Instead, these problems are solved by building some degeneracy into the dense phase. To ensure diffusion, the number of beads benefitting from the local interaction energy  $J_P$  is capped at six. The polymer–polymer interaction Hamiltonian becomes

$$-\beta\mathcal{H}_P = -J_P \sum_i \min(6, \mathcal{N}_i), \quad (9)$$

where  $\mathcal{N}_i$  is the number of beads within a distance  $\rho_P$  of bead  $i$ . The cap on the number interacting is chosen from physical grounds, six is the number of nearest-neighbors in close-packed systems in two dimensions. Without this cap, further-neighbors would profit from the short-range benefit of excluding solvent molecules. In the revised simulation,  $\mathcal{N}_i$  may be seven or more, but without additional energetic benefit. With the cap, beads tend to be spaced further apart and diffusivity improves dramatically; thus, the modified simulation technique yields ergodic sampling.

The area in the  $xy$ -plane is calculated using the relation

$$A = \sum_s \frac{1}{2} [(\mathbf{R}_s - \mathbf{R}_{\text{COM}}) \times (\mathbf{R}_{s+1} - \mathbf{R}_s)] \cdot \hat{z}, \quad (10)$$

where the vector  $\mathbf{R}_s$  labels the sequence of points on the gel's surface with  $s$  increasing counterclockwise around the perimeter, where  $\mathbf{R}_{\text{COM}}$  is the position of the gel's center of mass, and where  $\hat{z}$  is a unit vector perpendicular to the  $xy$ -plane.

The results of the gel simulations for  $L=5$  and  $n=5$  are given in Figs. 3 and 4. In Fig. 3, the polymer–polymer interaction  $J_P$  is scanned for various fixed hydrogen ion coupling  $J_H$ . Hysteresis loops indicating first-order transitions are observed for  $J_H \geq 8$ . In Fig. 4,  $J_P$  is held fixed while  $J_H$  is varied: Phase separation is evident for  $J_P \leq -2$ . Quantitative agreement between values for the area obtained by scanning in each direction confirms that thermodynamic minima have been found. While the finite size of the simulation is evident in the  $J_H=0$  scan of Fig. 3—the competition between repulsion of the hard cores and the attraction of  $J_P$  leads to what is known as the  $\theta$ -transition between compact and self-avoiding scaling regimes in very long polymer chains<sup>15</sup>—it should be noted that the  $\theta$ -transition is experimentally also not sharp (see Fig. 2).

This work is the first use of the BFM to study phase transitions in cross-linked material. A method was introduced for interactions of a bead with its surroundings which prevents the system from getting “stuck” and allows it to find the global minima. To generalize these studies to three dimensions, it will likely be important to use  $\rho_{\text{min}} \geq 3$  in order to allow for “inchworm” diffusion of beads to speed global relaxation.<sup>7</sup>

I thank A. Nihat Berker for suggesting this problem and for critical reading of the manuscript. I am also grateful to Yacov Kantor and Toyochi Tanaka for helpful discussions. This work is supported by the U.S. National Science Foundation Grant Nos. DMR-90-22933 and DMR-94-00334.

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