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High-Degeneracy Ordering of Polyampholyte Gels from a Random-Field Model

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Experiments have yielded multiple coexistence loops for gels with random positive and negative ionic groups, exhibiting the existence of up to seven distinct macroscopic phases distinguished by volume discontinuities. We introduce for this system a model composed of local degrees of freedom for ionization and for ionized cross-binding which are spatially arrayed with random connectivity. This model yields the multiple coexistence of phases, as well as volume versus excess charge curves, similar to the experimental results.

Keywords: Gels, polyampholytes, phase coexistence.

1. Introduction

Gels have been known to undergo a phase transition between a swollen and a collapsed phase [1]. More recently, many additional phases have been discovered by Annaka and Tanaka [2] in gels with random positive and negative ionic monomer groups. These phases are distinguished from each other and from the usual swollen and collapsed phases by density and local environment [2-4]. At the same final pH and temperature, depending on the path taken to that point in thermodynamic phase space, a multiplicity of phases is observed. In this paper, we develop for this phenomenon a model composed of local degrees of freedom for ionization and, if ionized, cross-binding, spatially arrayed in a random connectivity. This physical picture of the system directly leads to a spin model with two types of local degrees of freedom, coupled by competing quenched random interactions due to random fields. This spin model yields the multiple coexistence phenomena. The many phases can be understood as randomly coordinated phases. The model also yields volume versus charge curves in qualitative agreement with experiment [5] and another type of theory [6-8].

2. Experimental Systems

The measurements of diameter versus pH on gels with different ratios of acrylic acid (the anionic group) and MAPTAC (methyl-amido-propyl-trimethyl ammonium chloride, the cationic group) share a general feature [2]: As pH is changed from either extreme toward neutral, a large jump occurs from the swollen phase to the collapsed phase; as the pH is changed from neutral toward either extreme, many smaller jumps occur as the gel expands.

The microscopic picture of these systems is as follows. The gel is composed of crosslinked polymer chains that contain random sequences of ionic groups. In a very acidic (basic) solution, the anionic (cationic) groups are neutralized and the cationic (anionic) groups are ionized; therefore, the gel swells from self-repulsion [6,7], although this repulsion is somewhat screened by the excess opposite charge in the solvent. As the pH is brought toward neutrality, both groups become partially ionized. Opposite charges can bind randomly across the gel [9], which lowers the energy and the entropy; the reduction of entropy arises from restricting the self-avoiding random walk of polymers.

3. Microscopic Model

We now build a model for these systems. The gel is modelled by volume elements i arranged as a simple cubic lattice. Each volume element, referred to as a site from here on, is randomly assigned a net cationic or anionic character. For a

cationic (anionic) site i, the local variable $q_i = +1$ (-1) or 0 denotes, respectively, ionized or neutralized states. This amounts to a spin-1 Ising model under a strong random field that suppresses randomly one of the magnetized states at each site. The relative abundance of ionized or neutralized states is controlled by the pH, which equals the ionization reaction constant pK_a (pK_b) of an acid (base) when half the substance is ionized and half is neutral in the absence of other interactions. This contribution to the Hamiltonian can be expressed as

$$-\beta H_{pH} = \sum_i \Delta_i q_i, \tag{1}$$

$\Delta_i = (T_o/T)(pH - pK_a)$ and

$$\Delta_i = (T_o/T)(pK_b - pH), \tag{2}$$

for cationic or anionic components, respectively, where $T_o = 298K$ is the standard temperature and T is the actual temperature.

In the gel, charges interact via the Coulomb potential. In this model, the first way in which the Coulomb interaction manifests itself is that oppositely ionized neighboring sites can bind. The local variable $b_i = 1(0)$ denotes, respectively, that the site i is bound (unbound) to another nearby site. When a bond forms, the charges involved offset each other, thereby neutralizing their interactions with other charges. Thus, each site can participate in only one bond, so that the $b_i = 1$ states occur in pairs. We take a bond to be possible between a site and its six nearest neighbors, twelve second neighbors, and eight third neighbors. In other words, all of the sites within a 2x2x2 unit cube mutually interact and each site participates in eight unit cells. This contribution to the Hamiltonian can be expressed as

$$-\beta H_{bind} = \sum_i J_B b_i, \tag{3}$$

where $2J_B > 0$ is the binding energy. Since binding contracts the gel, a normalized measure of volume is

$$v = 1 - < b_i > . \tag{4}$$

Another way in which the Coulomb potential manifests itself is by the interaction of nearby but unbound charges. Such a contribution to the Hamiltonian can be expressed as

$$-\beta H_{Coul} = \sum_\mu \sum_{ij}^{\mu} (J_0 - J_1 b_\mu) q_i q_j (1 - b_i)(1 - b_j), \tag{5}$$

where the first sum is over the unit cubes μ, the second sum is over the sites of each unit cube, and b_μ is the number of bound pairs within cube μ. The occurrence of two opposing terms, with interaction constants J_0 and J_1, allows for the drastically different local environments of expansion and contraction. (i) In the absence of bound pairs ($b_\mu = 0$), the local gel is expanded and envelopes counterions from the solution. If the unit cube is populated by like charges, it will admit counterions of the opposite sign and be in an energetically favorable state. If the unit cube is populated by unlike charges, the counterions will interact with their like charges on the gel and cause an energetically unfavorable state. This effective attraction between separated like charges just reflects the attraction of each charge to an intermediary unlike charge, which of course also is the basis of ionic solid formation.[10] It is also known to occur quite generally [11], in ion agglomerates [11,12] and in living polymers [11,13-17], as confirmed through studies of conductances and reaction kinetics. In a study of another system closely related to the gel system of this paper, the properties of linear polyelectrolytes can be explained again by the effective attraction between like charges on the polymer due to the intermediary of the oppositely charged ions in the surrounding solution [18]. In our system, the connectivity imposed by the gel frustrates the full realization of this effect, in the cubes populated by unlike charges, as mentioned above. (ii) In the presence of bound pairs ($b_\mu > 0$), the local gel is contracted and its charges interact directly, energetically favorably for unlike charges and vice versa. The higher the number of bound pairs b_μ, the more contracted is the gel, with the interaction getting stronger as $J_1 b_\mu$.

Thus, the complete Hamiltonian containing the Coulomb, binding, and pH effects is

$$-\beta H = \sum_\mu \sum_{ij}^{\mu} (J_0 - J_1 b_\mu) q_i q_j (1 - b_i)(1 - b_j) + \sum_i (\Delta_i q_i + J_B b_i). \tag{6}$$

In the determination of b_μ, the contribution of a bound pair belonging to several unit cubes is shared by the latter, so that edge, face-diagonal, and body-diagonal pairs respectively contribute 1/4, 1/2, and 1 to each μ.

4. Results

We have studied the model defined by the Hamiltonian of Eq.(6) using Monte Carlo simulation and have found that the distinctive qualitative features of the polyampholyte gel experiments are reproduced. Data is shown below at 33% MAPTAC concentration, with which the largest number of distinct phases was observed experimentally [2,3]. An 8x8x8 system of volume elements with open boundary conditions was simulated, with $J_B = 2(T_o/T)$, $J_o = 0.2(T_o/T)$, and $J_1 = 1.6(T_o/T)$. The results were robust with respect to varying the choices of interaction constants.

To demonstrate the multiplicity of collapsed phases, the system at a given pH was annealed (heated and cooled) repeatedly. The systems at extremal pH are in the maximally expanded phase at lower temperatures, as seen for $pH = 2.0$ in Fig.1(a) and $pH = 15.0$ in Fig.1(e). The system at neutral $pH = 7.0$ is in the maximally collapsed phase at lower temperatures, as seen in Fig.1(c). By contrast, the systems at intermediate pH indeed access, at lower temperatures, multiple phases with distinct partial collapses, when they are cycled up and down the temperature scale, as seen for $pH = 2.4$ in Fig.1(b) and $pH = 13.25$ in Fig.1(d).

Fig.2(a) shows the volume of the gel as a function of the excess charge in the gel, $Q = (1/N)\sum_i q_i$, where N is the number of volume elements in the model. The characteristic flat bottom, sandwiched between the sharp rises, seen experimentally (Figs.2(b,c) from Ref.[5]), is thus obtained from the model. This result is also in qualitative agreement with the more macroscopic theoretical approach of Refs.[6-8].

We have thus constructed a model Hamiltonian of coupled charge and binding degrees of freedom, based on microscopic phenomenology, that captures the qualitative behavior observed by Annaka and Tanaka in their experiments [2,3] on polyampholyte gels. The model can be discussed in spin language: A random field on an $s = 1$ model induces a quenched random spatial distri-

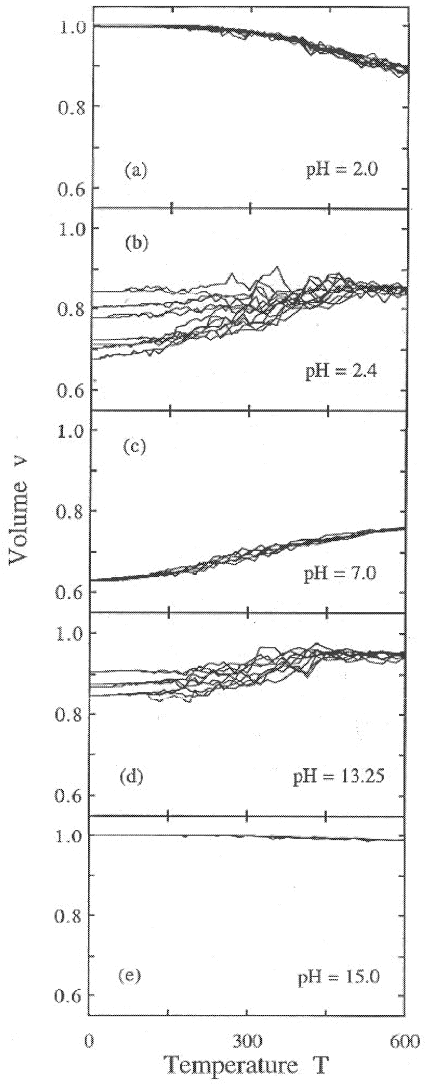

Figure 1. Gel volume as a function of temperature. For each pH, the system is repeatedly annealed (heated and cooled) in search of multiple phase coexistence, using $T/(T_o + T)$ steps of 0.01 and, at each temperature, 200 (after discarding 100) Monte Carlo steps per spin. At intermediate pH (b,d), it is seen that multiple phase coexistence indeed occurs, with distinct partial collapses. For extremal pH (a,e) and neutral pH (c), the gel is in the totally expanded and collapsed phases respectively.

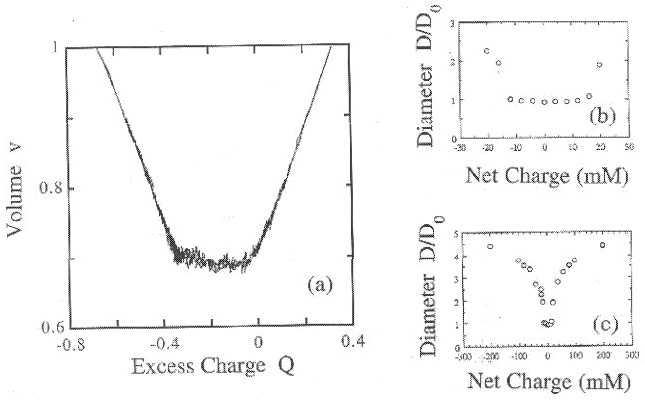

Figure 2. (a) Calculated volume as a function of net charge on the gel. (b,c) Experimental swelling degree of AMPS/MAPTAC copolymer gel as a function of net charge concentration from Ref.[5].

bution of possible opposite spin states that equilibrate with zero-spin states via the pH. The nonzero spins represent the ionized monomers and have alternate local binding configurations bringing together opposite pairs. As the occurrence of the up and down spins is changed via the pH, the system moves from maximal binding (collapsed gel) to non-binding (expanded gel). In between, in the partial binding regimes, the multiplicity of local binding configurations gives rise to a macroscopic diversity, namely the coexistence of multiple phases with distinct partial collapses.

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References

[1] T. Tanaka, D. Fillmore, S.-T. Sun, I. Nishio, G. Swislow, and A. Shah, Phys. Rev. Lett. **45**, 1636 (1980).

[2] M. Annaka and T. Tanaka, Nature **355**, 430 (1992).

[3] M. Annaka and T. Tanaka, Phase Transition **47**, 143 (1994).

[4] Refs.[2,3] appear to be the first observations of a gel phase transition driven by electrostatic interactions.

[5] X. Yu, Ph.D. thesis, MIT (1993).

[6] Y. Kantor, M. Kardar, and H. Li, Phys. Rev. Lett. **69**, 61 (1992).

[7] Y. Kantor, M. Kardar, and H. Li, Phys. Rev. E **49**, 1383 (1994).

[8] Y. Kantor and M. Kardar, Europhys. Lett. **27**, 643 (1994).

[9] Hydrogen bonding, weaker than Coulomb binding, can pair anionic groups, but is not strong enough to drive the phase transitions considered here, as discussed in F. Ilmain, T. Tanaka, and E. Kokufuta, Nature **349**, 400 (1991).

[10] N.W. Ashcroft and N.D. Mermin, Solid State Physics (Holt, Rinehart, and Winston, New York, 1976).

[11] M. Szwarc, Carbonions, Living Polymers, and Electron Transfer Processes (Wiley, New York, 1968).

[12] R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. **55**, 21, 476, 1019, 2387 (1933).

[13] D. N. Bhattacharya, J. Smid, and M. Szwarc, J. Am. Chem. Soc. **86**, 5024 (1964).

[14] D. N. Bhattacharya, C. L. Lee, J. Smid, and M. Szwarc, J. Phys. Chem. **69**, 612 (1965).

[15] S. C. Greer, Comp. Mat. Science **4**, 334 (1995). See, for example, Fig.3 in this reference.

[16] S. C. Greer, Adv. Chem. Phys. **94**, 261 (1996).

[17] S. Kara, C. Tamerler, H. Bermek and Ö. Pekcan, Int. J. Bio. Macromolecules **31**, 177 (2003).

[18] M. J. Stevens and K. Kremer, J. Chem. Phys. **103**, 1669 (1995).