

Anisotropic scattering profiles of charged gels in a deformed state

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The structure factor of weakly charged polymer gels under external mechanical strain is calculated considering both thermal and frozen concentration fluctuations as well as the screening of ionic interactions. The butterfly patterns are discussed based on our result. [S1063-651X(99)14105-9]

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It is now a well-known fact that the frozen inhomogeneity of the crosslink density results in a large-scale density variation when gels are swollen [1]. Furthermore, when the swollen gels are uniaxially elongated, these density variations have an extended correlation length in the stretched direction longer than in the perpendicular direction [2-4]. On the other hand, the thermal density fluctuations are suppressed in the stretched direction. This is responsible for the formation of the so-called anomalous butterfly patterns of the scattering intensity. It is characterized by the unusual orientation of iso-intensity lines along the direction of maximum dilation at small scattering vectors.

When charges are introduced into a neutral polymer gel, electrostatic (Coulomb) interactions modify the behavior of polymer gels significantly. To give a notable example, such a system undergoes a microphase separation transition when the solvent becomes poorer with respect to the network polymer [5,6]. This is because a macroscopic phase separation would lead to a great loss in the translational entropy for counterions which are compelled to follow the polymer chains in the polymer rich domains due to the overall electric neutrality requirement. In view of the intricate interplay between the long range nature of ionic interactions and the nonionic interactions inherent in the network structure, a study of the butterfly patterns of charged gels is of great interest. However, only a few experimental [7,8] and theoretical [9] works are available in the literature.

Recently one of the present authors [10] presented a phenomenological model of charged polymer gels based on the classical elasticity theory. Our formulation accounts for the thermal and the frozen concentration fluctuations as well as for the screening of Coulomb interactions. The structure factor that we obtained reproduces all the qualitative features of the scattering experiment. Since the fluctuations treated there were those around isotropic states, we extend our method to fluctuations around anisotropically swollen states in the present paper. To this end we consider a weakly charged gel in θ or poor solvent. Figure 1 shows the normal and the abnormal butterfly patterns for the charged gel that are calculated from our theory presented below.

In a previous paper [10], we proposed a free energy functional of the gel, which consists of the mixing free energy F_{mix} , the gradient free energy F_{inh} , the elastic free energy F_{el} , and the electrostatic free energy F_{ch} . The first two parts

can be expressed in terms of the local polymer volume fraction $\phi(\mathbf{x})$ at the spatial position \mathbf{x} as

$$F_{\text{mix}} = v_1^{-1} k_B T \int d\mathbf{x} [(1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi)], \quad (1)$$

$$F_{\text{inh}} = \frac{1}{2} \int d\mathbf{x} C(\phi) |\nabla \phi|^2, \quad (2)$$

with $v_1 = a^3$, a being the monomer size and $C(\phi) = k_B T / (12a\phi)$; χ is the polymer-solvent interaction parameter, k_B is the Boltzmann constant, and T is the temperature of the system. The elastic part is given by

$$F_{\text{el}} = \frac{k_B T}{2} \int d\mathbf{x}_0 \nu(\mathbf{x}_0) \left(\frac{\partial x_i}{\partial x_j^0} \right)^2, \quad (3)$$

where the integration region is limited to the region occupied by the initial relaxed state, $\mathbf{x}_0 = \{x_j^0\}$ ($j=1,2,3$) being the Cartesian coordinates of the original position while $\mathbf{x} = \{x_j\}$ is the real position in the deformed gel. The ν is the local crosslink number density. The ionic part is taken to be of the form

$$F_{\text{ch}} = k_B T \int d\mathbf{x} \left[\frac{\epsilon_s}{2k_B T} |\mathbf{E}|^2 + \rho_i \ln \left(\frac{\rho_i}{e} \right) + c_i \ln \left(\frac{c_i}{e} \right) + c_s \ln \left(\frac{c_s}{e} \right) \right]. \quad (4)$$

Here the local counterion densities due to chains and salt counterions are denoted by $\rho_i(\mathbf{x})$ and $c_i(\mathbf{x})$, respectively, and the concentration of salt co-ions by $c_s(\mathbf{x})$. The local electric field $\mathbf{E}(\mathbf{x})$ is related to the local monomer density $\rho(\mathbf{x})$ via

$$\nabla \cdot \mathbf{E}(\mathbf{x}) = e [f \rho(\mathbf{x}) + c_s(\mathbf{x}) - \rho_i(\mathbf{x}) - c_i(\mathbf{x})] / \epsilon_s, \quad (5)$$

where e is the elementary charge, ϵ_s being the dielectric constant of the solvent, and f is the degree of ionization. It can be shown that at the level of the Debye-Hückel approximation the only effect of the electrostatic interactions (4) is to replace the second virial coefficient $w \equiv v_1(1 - 2\chi)$ by the effective [wave-vector (\mathbf{q}) dependent] one

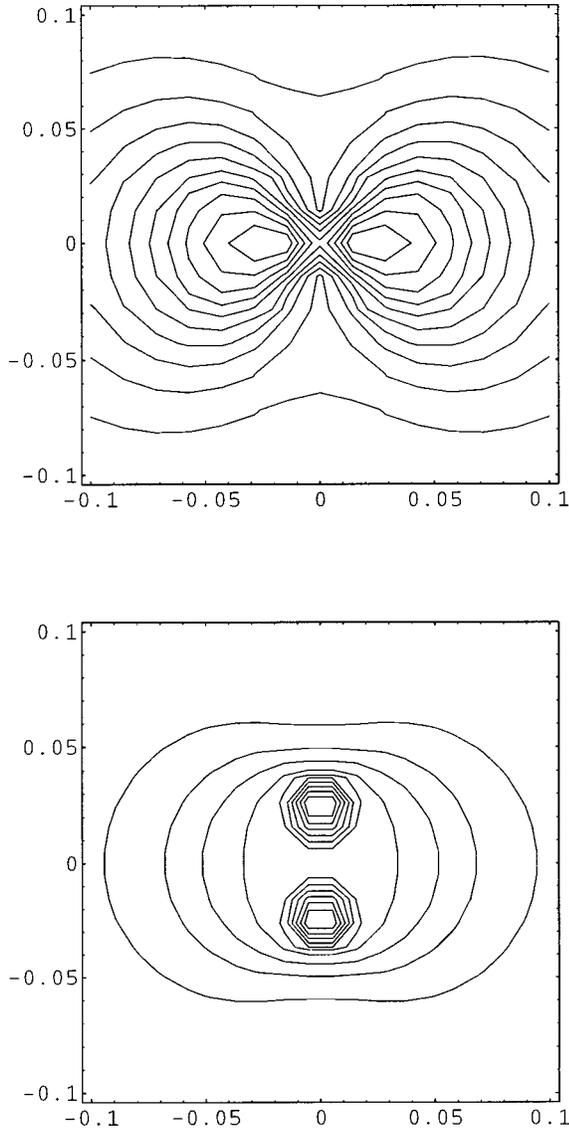


FIG. 1. Theoretical isointensity curves for a charged gel stretched uniaxially (in the horizontal direction); the upper one (abnormal butterfly) represents the gel with $\chi=0.5$ while the lower normal pattern corresponds to the gel with $\chi=0.64$. The scales of parallel and perpendicular scattering vectors are in units of \AA^{-1} . The plot is obtained from Eq. (8) with $N=50$, $\Lambda=2$, and $p^*=5$; other parameters used are $\phi_0=0.07$, $\phi=0.1$, $f=0.0457$, $a=8.12$ (\AA), $\hat{l}_B=10.8$, and $\hat{c}_s=0.04$ as in Ref. [10].

$$\tilde{w}_{\mathbf{q}} = w + \frac{4\pi l_B f^2}{q^2 + \kappa^2}, \quad (6)$$

with $l_B \equiv e^2 / (4\pi\epsilon_s k_B T)$ being the Bjerrum length; κ^{-1} is the Debye screening length given by

$$\kappa^2 = 4\pi l_B (f\bar{\rho} + 2\bar{c}_s), \quad (7)$$

where $\bar{\rho}$ and \bar{c}_s are average densities of monomers and salt cations.

The other things being the same, we can readily examine small fluctuations around anisotropic, homogeneous states, just as Onuki did for neutral gels in Ref. [3]. Thus the scattering function (normalized by ϕ) in the anisotropically deformed charged gels becomes

$$S(\mathbf{q}) = \frac{1}{H(\mathbf{Q})} + \frac{\hat{p}(\hat{\mathbf{q}})}{H^2(\mathbf{Q})}, \quad (8)$$

where

$$H(\mathbf{Q}) = 12\phi \left(1 - 2\chi + \phi + \frac{f^2}{Q^2 / (\hat{l}_B N) + \hat{c}_t \phi} \right) + \frac{Q^2}{N} + \frac{6}{N} \left(\frac{\phi_0}{\phi} \right)^{2/3} J(\hat{\mathbf{q}}), \quad (9)$$

with $\mathbf{Q} = aN^{1/2}\mathbf{q}$, $\hat{l}_B = 4\pi l_B / a$, $\hat{c}_t = f + 2\hat{c}_s$, $\hat{c}_t = \bar{c}_s / \bar{\rho}$, and

$$\hat{p}(\mathbf{q}) = p^* \frac{6}{N} \left(\frac{\phi_0}{\phi} \right)^{2/3} J^2(\hat{\mathbf{q}}). \quad (10)$$

Here N is the average number of chain monomers between neighboring crosslinks, and ϕ_0 is the average polymer volume fraction in the relaxed state; in Eqs. (9) and (10) and hereafter the average volume fraction is simply written as ϕ (or ϕ_0). The dimensionless parameter p^* represents the degree of frozen inhomogeneities, and $J(\hat{\mathbf{q}})$ depends on the direction $\hat{\mathbf{q}} \equiv \mathbf{q}/q$ of the wave vector \mathbf{q} as

$$J(\hat{\mathbf{q}}) = (\phi/\phi_0)^{2/3} A_{im} A_{jm} \hat{q}_i \hat{q}_j, \quad (11)$$

where $\{A_{ij}\}$ is the average strain tensor.

The scattering function (8) shows a rich variety of possible behavior, which depends on the values of many thermodynamic parameters. Let us specifically examine $S(\mathbf{q})$ of the uniaxially deformed gels as a function of the solvent quality. [In passing, we emphasize that the result (8) is obtained by the mean-field approach. Therefore the applicability of our result to gels in good solvents is very limited; in an athermal solvent we expect that the strong fluctuation effect leads to the breakdown of the mean-field approach. See also the remark given in [11].] For uniaxially stretched gels, $\{A_{ij}\}$ is diagonal and $A_{xx} = (\phi_0/\phi)^{1/3}\Lambda$, $A_{yy} = A_{zz} = (\phi_0/\phi)^{1/3}\Lambda^{-1/2}$, so that

$$J(\hat{\mathbf{q}}) = \left(\Lambda^2 - \frac{1}{\Lambda} \right) \cos^2 \theta + \frac{1}{\Lambda}. \quad (12)$$

The Λ is the elongation ratio ($\Lambda > 1$) with respect to the isotropically swollen state, and $\cos \theta = q_x/q$. The divergence of $S(q=0)$ which signals the macrophase separation takes place at $\chi = \chi_{\text{ma}}$ where

$$\chi_{\text{ma}} = \frac{1}{2} \left(1 + \phi + \frac{f^2}{(f+2\hat{c}_s)\phi} \right) + \frac{(\phi_0/\phi)^{2/3}}{4\phi N \Lambda}, \quad (13)$$

while the microphase separation point at which $S(\mathbf{q})$ diverges at a finite \mathbf{q} is reached at $\chi = \chi_{\text{mi}}$,

$$\chi_{\text{mi}} = \frac{1}{2} (1 + \phi) + \left(\frac{\hat{l}_B}{12\phi} \right)^{1/2} f - \frac{f+2\hat{c}_s}{24} \hat{l}_B + \frac{(\phi_0/\phi)^{2/3}}{4\phi N \Lambda}. \quad (14)$$

As may be easily proved, the inequality $\chi_{\text{ma}} \geq \chi_{\text{mi}}$ holds (the equality applying to the Lifshitz point). It then implies that one will observe only the microphase separation upon de-

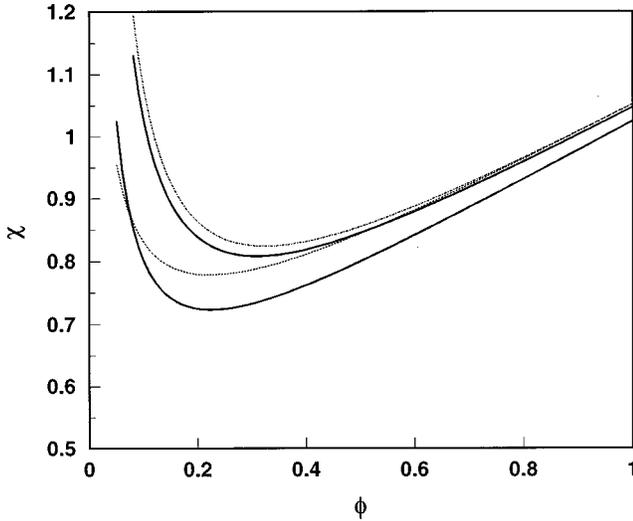


FIG. 2. The abnormal to normal crossover threshold (χ_c) vs polymer volume fraction (ϕ) for charged gels at $f=0.1$ in the reactor batch ($\phi = \phi_0$) with no added salt. The upper curve corresponds to the gel with $p^*=2$, the lower to the $p^*=1.1$ gel; the other parameters used are $N=50$ and $\Lambda=2$. In each case we observe the normal (abnormal) butterfly pattern for $\chi > (<) \chi_c$. The dotted curve represents the microphase separation instability (χ_{mi}), while the macrophase separation threshold (χ_{ma}) is drawn by the dash-dotted curve.

crease of the solvent quality, irrespective of the deformation. The new feature characteristic of polyelectrolyte gels can be seen by studying the crossover from the abnormal to the normal butterfly pattern. The crossover condition depends sensitively on the strength of neutralization degree and salt concentration. We define this abnormal to normal ($A \rightarrow N$) crossover point by the condition that $\partial_\theta^2 S(0)|_{\theta=\pi/2} = 0$. This condition becomes $\chi = \chi_c$ where

$$\chi_c = \frac{1}{2} \left(1 + \phi + \frac{f^2}{(f + 2\hat{c}_s)\phi} \right) - \frac{(\phi_0/\phi)^{2/3}}{8\phi N(p^* - \Lambda/2)}, \quad (15)$$

with $p^* > \Lambda/2$, and the abnormal butterfly pattern will appear at $\chi < \chi_c$.

Inspection of expressions (14) and (15) shows that for fixed p^* , the microphase separation instability precludes the $A \rightarrow N$ crossover in the dilute concentration ($\phi \ll 1$) regime [11]. By decreasing degrees of ionization, however, we predict the appearance of the crossover as the scattered intensity increases. For fixed f , on the other hand, the magnitude of anomalous angular anisotropy of $S(\mathbf{q})$ increases dramatically by the increase of the degree of inhomogeneity p^* , similarly to the case of neutral gels. As shown in Fig. 2, the $A \rightarrow N$ crossover threshold is pushed down by decreasing p^* .

The scattering profiles measured by the small-angle neutron scattering (SANS) experiment on two different poly-

(acrylic acid) gels under almost the same conditions were reported in Ref. [7]. For a weakly charged sample (with $f=0.1$) synthesized by adding the neutralizer (NaOH) before crosslinking, the anisotropy is normal, whereas it is abnormal for the sample (with $f=0.1$) synthesized with NaOH added after crosslinking. The observation of both types of butterfly shapes can be attributed to the different degrees of inhomogeneities in the two samples. Another observation of a dramatic increase of the scattered intensity with decreasing the ionization degree or with increasing the salt concentration is also in accord with our result; as naturally expressed by Eq. (14), the presence of salt (or equivalently, the weakening of the repulsive electrostatic interaction) reduces the stability of the gel against microphase separation. However, the concomitant experimental result that the normal butterfly pattern for a gel with no added salt turned into the abnormal one with added salt at small q is in conflict with our result (15); according to our theory, increasing \bar{c}_s lowers the threshold value of χ_c , disfavoring an abnormal shape. We notice that an alternative theoretical approach to charged gels, developed recently in Ref. [9], suffers from the same difficulty. At present we cannot explain the experimental salt dependence of the scattering at low q .

In this connection we note that a weakly charged poly(*N*-isopropylacrylamide-*co*-acrylic acid) (*N*IPA-*co*-AAc) gel was investigated in Ref. [8] under uniaxial deformation at various temperatures. Due to the strong hydrophobicity of poly-MIPA, the SANS pattern showed an abnormal butterfly pattern in spite of the presence of charges. The gel was prepared when the acrylic acid was ionized. Hence, this result should be compared with the normal pattern reported in Ref. [7] for the ionized gel in the presence of NaOH. The contradiction between two results may result from the difference in the degree of hydrophobicity and the degree of ionization between the two systems. In order to resolve these discrepancies we clearly need more scattering experiments which probe the wider range of thermodynamic parameters. At the same time a more quantitative comparison between theory and experiment, as is done in Ref. [8], should be very informative.

In summary, the previous phenomenological model of charged gels has been extended to treat the anisotropically deformed states. The crossover between abnormal and normal butterfly patterns is discussed in comparison with available, albeit scanty, experimental observations. The problem cannot be resolved completely.

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