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On the scattering properties of a weakly charged polymer gel

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Abstract. A phenomenological model is presented to describe weakly charged polymer gels based on the classical elasticity theory. The structure factor of the gel is calculated considering both thermal and frozen concentration fluctuations as well as the screened Coulomb interaction. In agreement with the recent experimental finding the result shows anomalous crosslink-density dependence of the scattering profiles.

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1 Introduction

A polymer gel (or network) consists of a number of chain macromolecules joined together by chemical covalent bonds, resulting in a highly elastic body. A rich variety of unique phenomena has been disclosed due to this soft network structure [1,2]. Thus polymer gels have found a wealth of practical application in nutritious and cosmetic industries, petrochemistry, biotechnology, *etc.*

An interesting class of polymer gels is provided by the charged polymer gel (polyelectrolyte network). Since a gel contains topologically frozen structures, the complete description of the structure of gels requires information not only about the parameters of the state of observation but also about those in the state of preparation; the latter determines the statistical properties of crosslink inhomogeneities in the network. Furthermore, the presence of even a small fraction of charges on the network chains modifies strongly the physical and chemical properties of gels [3]. This is due to the intricate interplay between ionic (Coulomb) interactions of charged units and non-ionic interactions inherent in the network structure. In particular, the long range nature of the Coulomb interaction and the role of small counter-ions that ensures the electrical neutrality render the theoretical analysis [4] of those charged systems most difficult contrary to the case of neutral polymer systems.

In this paper we report on our theoretical attempt to investigate the scattering properties of polyelectrolyte gels. We are motivated to attack this problem because at present extensive scattering experimental data on polyelectrolyte *networks in a solvent* [5,6] are compared with theoretical predictions as to polyelectrolyte *solutions* [7] for lack of a quantitative theoretical description of polyelectrolyte gels. We restrict ourselves in what follows to the weak screening limit in which the fraction of charged links is small, and neglect the excluded-volume effect supposing theta or poor solvents. In order to treat effects induced by the presence of crosslinks, we have employed an elasticity-type calculation which was used earlier by Onuki [8] in predicting many features of neutral gels. For thermal fluctuations, the Onuki theory uses, in effect, a classical expression of the scattering of a semidilute solution of neutral polymers, which is here replaced by the one for semidilute solutions of weakly charged polyelectrolytes. The electrostatic interaction is taken into account in the present formulation at the level of the Debye-Hückel theory.

The correlation function of density fluctuations that we have obtained reproduces the well-known features of scattering experiments. Namely, the structure factor exhibits a peak at a non-zero wavevector. This maximum diverges at a microphase separation transition.

Onuki's model for non-ionic polymer gels, which lays the foundation of our formulation, is first described in Section 2. We then develop the approach to charged gels, and the screening of Coulomb interactions by counter-ions and salt ions is discussed in Section 3. In Section 4 we generalize the theory to incorporate a possible effect which is incurred when a sufficient density of crosslinks are introduced in the gels. The final section contains details of our results pertinent to the scattering properties. At the same time a very recent theory of charged gels by Rabin and Panyukov [9] is critically compared with our theory.

2 Theoretical background: Onuki's model of neutral gels

Onuki [8,2] developed a theory of deformed swollen gels based on the elasticity theory formalism. In this theory both thermal density fluctuations and density variations due to the frozen heterogeneities in the elastic medium

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are taken into account. Here we briefly describe Onuki's approach for purposes of the later use in our formulation of charged gels.

Let us consider a gel swollen by solvent. Let $\phi(\mathbf{x})$ be the local polymer volume fraction at the spatial position $\mathbf{x}$. The free energy of the gel is assumed to be the sum of an elastic term and a contribution from mixing with the solvent, which is assumed to be a theta or poor solvent. Thus the free energy change F_N after mixing of solvent and initially unstrained gel is given by

$$F_N = F_{\mathrm{mix}} + F_{\mathrm{inh}} + F_{\mathrm{el}}, \qquad (1)$$

where F_{mix} is the (Flory-Huggins) mixing free energy:

$$\begin{aligned} F_{\mathrm{mix}} &= v_1^{-1} k_{\mathrm{B}} T \int \mathrm{d}\mathbf{x}\, [(1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)] \\ &\equiv \int \mathrm{d}\mathbf{x}\, f(\phi), \end{aligned} \qquad (2)$$

with $v_1 \equiv a^3$, a being the monomer size; χ is the polymer-solvent interaction parameter, k_{B} is the Boltzmann constant ant T is the temperature of the system. The F_{inh} is the gradient free energy:

$$F_{\mathrm{inh}} = \frac{1}{2} \int \mathrm{d}\mathbf{x}\, C\, |\nabla\phi|^2, \qquad (3)$$

where the coefficient C is an unknown function of ϕ in Onuki's model. (We remark, however, that this parameter can be determined from the thermal scattering for neutral polyelectrolyte solutions. See Eq. (28) *ff.* below.) The elastic free energy F_{el} is taken to be of the form [10]

$$F_{\mathrm{el}} = \frac{k_{\mathrm{B}} T}{2} \int \mathrm{d}\mathbf{x}_0\, \nu(\mathbf{x}_0) \left[\left(\frac{\partial x_{\mathrm{i}}}{\partial x_j^0} \right)^2 + 2B \ln \frac{\phi}{\phi_0} \right], \qquad (4)$$

where the integration region is limited to the region occupied by the initial relaxed state (usually identified with the state of preparation), and x_j^0 $(j = 1, 2, 3)$ is the Cartesian coordinates of the original position $\mathbf{x}_0$ of the relaxed gel before deformation; we have thus distinguished $\mathbf{x}_0$ from the position of the deformed gel $\mathbf{x}$, and $\phi_0(\mathbf{x}_0)$ is the local volume fraction in the relaxed state. The ν is the local crosslink number density[1], and we do not fix the controversial coefficient B at a particular value [11] for the moment.

With the free energy (1) we can study thermal fluctuations as well as frozen concentration fluctuations. In order to study the thermal fluctuations of ϕ in homogeneous gels, we consider the displacement $\mathbf{u}$ from the average position of isotropically deformed gels:

$$\mathbf{x} = \lambda \mathbf{x}_0 + \mathbf{u} \qquad (5)$$

where $\lambda \equiv (\phi_0/\phi)^{1/3}$ is the elongation ratio. Here and hereafter the mean value of ϕ (or ϕ_0) is simply written as ϕ (ϕ_0). To second order in $\mathbf{u}$, the deviation δF_N^{th} of F_N is given by

$$\delta F_N^{\mathrm{th}} = \frac{1}{2} \int_{\mathbf{q}} \left[(K + \mu/3 + C\phi^2 q^2)\, |\mathbf{q}\cdot\mathbf{u}_{\mathbf{q}}|^2 + \mu q^2\, |\mathbf{u}_{\mathbf{q}}|^2 \right], \qquad (6)$$

where $\mathbf{u}_{\mathbf{q}}$ is the Fourier transform of $\mathbf{u}$, and $\int_{\mathbf{q}} \equiv \int \mathrm{d}\mathbf{q}/(2\pi)^3$. The K and μ are the mean osmotic bulk modulus and the mean shear modulus, respectively, and are given by

$$K = \phi^2 \frac{\partial^2 f}{\partial \phi^2} + k_{\mathrm{B}} T \bar{\nu} \left[B\frac{\phi}{\phi_0} - \frac{1}{3} \left(\frac{\phi}{\phi_0} \right)^{1/3} \right], \qquad (7)$$

$$\mu = k_{\mathrm{B}} T \bar{\nu} (\phi/\phi_0)^{1/3}, \qquad (8)$$

where $\bar{\nu}$ is the average crosslink density. The first term on the right of equation (7) is the classical osmotic modulus (K_{FH}) of polymer solutions. In the semidilute region it may be approximated by

$$K_{\mathrm{FH}} = v_1^{-1} k_{\mathrm{B}} T \phi^2 (1 - 2\chi + \phi), \qquad (9)$$

where a ϕ^3-term is retained for stability against collapse in poor solvents.

In addition to the contribution of the thermal concentration fluctuations, we consider the contribution due to frozen fluctuations around heterogeneities; they are formed by the introduction of crosslinks in the system. We assume that the deviation of the crosslink density, $\delta\nu(\mathbf{x}_0) = \nu(\mathbf{x}_0) - \bar{\nu}$, is of short-ranged[2] as

$$\langle \delta\nu(\mathbf{x}_0) \delta\nu(\mathbf{x}_0 + \mathbf{x}_0') \rangle = \bar{\nu} p \delta(\mathbf{x}_0'), \qquad (10)$$

the parameter p representing the degree of inhomogeneity. Assuming the linear response of the heterogeneities to a deformation (which restricts the range of the parameter p to $p \ll 1$ [8]), we then find that the deviation $\delta F_{\mathrm{N}}^{\mathrm{f}}$ of F_{N} due to the frozen density variations is written as

$$\delta F_{\mathrm{N}}^{\mathrm{f}} = -\frac{\mu}{2} \int_{\mathbf{q}} \left\{ \tilde{p}^{-1} + \left[\epsilon + 1 + (C\phi^2/\mu) q^2 \right]^{-1} \right\}^{-1} |\mathbf{q}\cdot\mathbf{u}_{\mathbf{q}}|^2 \qquad (11)$$

with $\tilde{p} \equiv p(\lambda - B\lambda^{-1})^2$ and $\epsilon \equiv K/\mu + 1/3$.

One could obtain [8] the structure factor for the density fluctuations from the combination of equations (6, 11). Here, however, we move on to consider the structure factor for the charged polymer gels.

3 Extension to a weakly charged gel

If gels contain charged ions, fluctuations of the charge densities induce the monomer density fluctuations. Let us

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[1] In the definition of ν, we have absorbed the so-called (and disputable) front factor to the first term of the integrand in equation (4).

[2] In terms of the Fourier transform $\nu_{\mathbf{q}}$ of $\delta\nu(\mathbf{x}_0)$, equation (10) is rewritten as $\langle |\nu_{\mathbf{q}}|^2 \rangle = (\phi_0/\phi)\bar{\nu}p$. Thus this assumption amounts to neglecting a possible wave-vector dependence of the frozen heterogeneities fluctuations.

denote by $\rho_\mathrm{i}(\mathbf{x})$ and $c_\mathrm{i}(\mathbf{x})$ the local counter-ion densities due to chain and salt counter-ions, respectively, and by $c_\mathrm{s}(\mathbf{x})$ the concentration of salt co-ions. In order to derive the (effective) electrostatic free energy functional of the monomer density $\rho(\mathbf{x})$, we start with the following free energy:

$$F_\mathrm{ch} = k_\mathrm{B}T\int \mathrm{d}\mathbf{x}\left[\frac{\epsilon_\mathrm{s}}{2k_\mathrm{B}T}\,|\mathbf{E}|^2 + \rho_\mathrm{i}\ln\left(\frac{\rho_\mathrm{i}}{\mathrm{e}}\right) + c_\mathrm{i}\ln\left(\frac{c_\mathrm{i}}{\mathrm{e}}\right) + c_\mathrm{s}\ln\left(\frac{c_\mathrm{s}}{\mathrm{e}}\right)\right]. \tag{12}$$

The first term in the integrand is the electrostatic energy of Coulombic interactions, ϵ_s being the dielectric constant of the solvent, and the other terms represent the free ion entropies. The local electric field $\mathbf{E}(\mathbf{x})$ is related to the local charge density *via*

$$\nabla\cdot\mathbf{E}(\mathbf{x}) = e\left[f\rho(\mathbf{x}) + c_\mathrm{s}(\mathbf{x}) - \rho_\mathrm{i}(\mathbf{x}) - c_\mathrm{i}(\mathbf{x})\right]/\epsilon_\mathrm{s}. \tag{13}$$

Here e is the elementary charge, and f is the fraction of charged monomers (*i.e.*, the degree of ionization). For simplicity, the counter-ions of the polyion and of the salt molecule are assumed to be monovalent. Let $\delta\rho$, δc_s, $\delta\rho_\mathrm{i}$ and δc_i be the small deviations of the corresponding densities from the average values $\bar\rho$, $\bar c_\mathrm{s}$, $\bar\rho_\mathrm{i}$ and $\bar c_\mathrm{i}$; owing to the electroneutrality we have $\bar\rho_\mathrm{i} + \bar c_\mathrm{i} = f\bar\rho + \bar c_\mathrm{s}$ with $\bar c_\mathrm{i} = \bar c_\mathrm{s}$. We denote Fourier transforms of $\delta\rho$, δc_s, $\delta\rho_\mathrm{i}$ and δc_i by $\rho(\mathbf{q})$, $c_\mathrm{s}(\mathbf{q})$, $\rho_\mathrm{i}(\mathbf{q})$ and $c_\mathrm{i}(\mathbf{q})$, respectively.

Expanding the right-hand side of equation (12) in powers of these deviations, and ignoring the cubic and higher order terms (the Debye-Hückel (DH) approximation [12]) yield

$$F_\mathrm{ch} = Vk_\mathrm{B}T\bar f_\mathrm{ch} + \delta F_\mathrm{ch}\left[\rho_\mathrm{i}, c_\mathrm{i}, c_\mathrm{s}, \rho\right], \tag{14}$$

where V is the volume of the system, and

$$\bar f_\mathrm{ch} = \bar\rho_\mathrm{i}\ln\frac{\bar\rho_\mathrm{i}}{\mathrm{e}} + 2\bar c_\mathrm{s}\ln\frac{\bar c_\mathrm{s}}{\mathrm{e}}, \tag{15}$$

$$\delta F_\mathrm{ch}\left[\rho_\mathrm{i}, c_\mathrm{i}, c_\mathrm{s}, \rho\right] = \frac{k_\mathrm{B}T}{2}\int_\mathbf{q}\left[\frac{|\rho_\mathrm{i}(\mathbf{q})|^2}{\bar\rho_\mathrm{i}} + \frac{|c_\mathrm{i}(\mathbf{q})|^2 + |c_\mathrm{s}(\mathbf{q})|^2}{\bar c_\mathrm{s}} + \frac{4\pi l_\mathrm{B}}{q^2}\,|f\rho(\mathbf{q}) + c_\mathrm{s}(\mathbf{q}) - \rho_\mathrm{i}(\mathbf{q}) - c_\mathrm{i}(\mathbf{q})|^2\right], \tag{16}$$

with $l_\mathrm{B} \equiv e^2/(4\pi\epsilon_\mathrm{s}k_\mathrm{B}T)$ being the Bjerrum length. The effective free energy of the monomer density, $\delta F_\mathrm{DH}[\rho]$, can be obtained by integrating over the ionic degrees of freedom:

$$\delta F_\mathrm{DH}[\rho] = -k_\mathrm{B}T \times \ln\iiint \mathcal{D}\rho_\mathrm{i}\mathcal{D}c_\mathrm{i}\mathcal{D}c_\mathrm{s}\exp(-\delta F_\mathrm{ch}\left[\rho_\mathrm{i}, c_\mathrm{i}, c_\mathrm{s}, \rho\right]/k_\mathrm{B}T). \tag{17}$$

We find

$$\delta F_\mathrm{DH} = \frac{k_\mathrm{B}T}{2}\int_\mathbf{q}\frac{4\pi l_\mathrm{B}f^2}{q^2+\kappa^2}\,|\rho(\mathbf{q})|^2, \tag{18}$$

which is of the form of screened Coulomb interactions; the screening length κ^{-1} is given by

$$\kappa^2 = 4\pi l_\mathrm{B}\bar c_\mathrm{t}, \tag{19}$$

with $\bar c_\mathrm{t} \equiv f\bar\rho + 2\bar c_\mathrm{s}$ being the total density of ions. In equation (18) the constant term proportional to $V\kappa^3$ has been ignored in comparison with $V\bar f_\mathrm{ch}$ of (14) since the DH approximation is valid for $\bar c_\mathrm{t}\kappa^{-3} \gg 1$.

Consequently, in order to describe the (weakly) charged gel system, we must add to the previous free energy, $F_\mathrm{N} + \delta F_\mathrm{N}^\mathrm{th} + \delta F_\mathrm{N}^\mathrm{f}$, an electrostatic contribution F_ion:

$$F_\mathrm{ion} = F_\mathrm{DH} + \delta F_\mathrm{DH} \tag{20}$$

where

$$F_\mathrm{DH} = k_\mathrm{B}TV\bar c_\mathrm{t}(\phi/\phi_0)\ln(\phi/\phi_0), \tag{21}$$

and δF_DH is given by equation (18). Hence we find that the only effect of the electrostatic contribution F_ion on the free energy cost of fluctuations of polymer concentration is to replace the bulk modulus K of (7) by the 'dressed' one, $\tilde K_q$:

$$\tilde K_q = k_\mathrm{B}Tv_1^{-1}\phi^2(1 - 2\chi + \phi + v_1^{-1}\frac{4\pi l_\mathrm{B}f^2}{q^2+\kappa^2}) + k_\mathrm{B}T\bar\nu\left[B\frac{\phi}{\phi_0} - \frac{1}{3}\left(\frac{\phi}{\phi_0}\right)^{1/3}\right]. \tag{22}$$

The result that the electrostatic interactions replace the second virial coefficient $w \equiv v_1(1-2\chi)$ by the effective one $\tilde w_q$ where

$$\tilde w_q = w + \frac{4\pi l_\mathrm{B}f^2}{q^2+\kappa^2}, \tag{23}$$

has also been obtained, for polyelectrolyte gels, by Rabin and Panyukov [9].

The conclusion of our analysis above is that the structure factor $I(q) \equiv \langle|\rho(\mathbf{q})|^2\rangle$ for the density fluctuations of weakly-charged polymer gels in the isotropically swollen state is given by the following expression

$$I(q) = \frac{\phi^2}{\nu_\mathrm{s}\lambda^2}\left\{\frac{1}{\tilde\epsilon_q + (C\phi^2/\mu)q^2} + p^*\left[\frac{1 - B\lambda^{-2}}{\tilde\epsilon_q + (C\phi^2/\mu)q^2}\right]^2\right\}, \tag{24}$$

where

$$\nu_\mathrm{s} = \bar\nu/\lambda^3, \qquad \tilde\epsilon_q = \tilde K_q/\mu + 4/3, \qquad p^* = p\lambda^2. \tag{25}$$

Equivalently, using the dimensionless variables

$$\mathbf{Q} = a\mathbf{q}N^{1/2}, \qquad \hat l_\mathrm{B} = 4\pi l_\mathrm{B}/a, \qquad \hat c_\mathrm{t} = \bar c_\mathrm{t}/\bar\rho = f + 2\hat c_\mathrm{s}, \qquad \hat c_\mathrm{s} = \bar c_\mathrm{s}/\bar\rho \tag{26}$$

where N is the average number of chain monomers between neighboring crosslinks:

$$N = \phi_0/(2v_1\bar\nu), \tag{27}$$

we can rewrite equation (24) as

$$I(q) = 2v_1\phi N\left(\frac{\phi}{\phi_0}\right)^{2/3}\left\{\frac{1}{\tilde{\epsilon}_q + \tilde{C}Q^2(\phi/\phi_0)^{2/3}} + p^*\left[\frac{1-B(\phi/\phi_0)^{2/3}}{\tilde{\epsilon}_q + \tilde{C}Q^2(\phi/\phi_0)^{2/3}}\right]^2\right\}. \qquad (28)$$

Here, knowing that $C \sim k_{\mathrm{B}}T/(a\phi)$ from the scaling theory for θ solvents [13], we have set $\tilde{C} \equiv 2a\phi C/(k_{\mathrm{B}}T)$, which is assumed to be a constant hereafter.

In order to fix the as yet unknown constant $\tilde{C}$, we shall make contact with a statistical theory of weakly charged polyelectrolytes of Borue and Erukhimovich (BE) [7]. They calculated the density correlation function of the polyelectrolyte solution in the DH approximation. It turns out that with $\tilde{C} = 1/6$ our structure factor in the limit $N \to \infty$ (which corresponds to considering polyelectrolyte solutions) coincides with the BE's [3]. Using the variables of BE's theory, we then find that our structure factor can be written as

$$S(q) \equiv (12v_1\phi)^{-1}I(q) = \frac{1}{F(x)} + \frac{\hat{p}}{F^2(x)}, \qquad (29)$$

where

$$F(x) = \frac{a^2}{r_0^2}\left(x^2+t+\frac{1}{x^2+s}\right)+\frac{6}{\mathrm{N}}\left[B+\left(\frac{\phi_0}{\phi}\right)^{2/3}\right], \qquad (30)$$

$$\hat{p} = \frac{6}{N}p^*\left(\frac{\phi_0}{\phi}\right)^{2/3}\left[1-B\left(\frac{\phi}{\phi_0}\right)^{2/3}\right]^2, \qquad (31)$$

and

$$r_0^4 = a^4/(12\hat{l}_{\mathrm{B}}f^2\phi), \qquad x = r_0 q, \qquad s = r_0^2\kappa^2,$$
$$t = -12(r_0/a)^2 h\phi/v_1, \qquad h = -v_1(1-2\chi+\phi). \qquad (32)$$

We remark that the scattering function $S(q)$ is the scattering intensity normalized by ϕ, as usually done for solutions. Alternatively, in our original notations,

$$S(q) = \frac{1}{H(Q)} + \frac{\hat{p}}{H^2(Q)}, \qquad (33)$$

with

$$H(Q) = 12\phi\left[1-2\chi+\phi+\frac{f^2}{Q^2/(\hat{l}_{\mathrm{B}}N)+\hat{c}_{\mathrm{t}}\phi}\right] + \frac{Q^2}{N} + \frac{6}{N}\left[B+\left(\frac{\phi_0}{\phi}\right)^{2/3}\right]. \qquad (34)$$

4 Incorporation of crosslink-induced transition

Each crosslink forces two chains to come in close contact, so that the structural units engaged in crosslinkages do not contribute to excluded-volume repulsions. In other words, crosslinks promote an effective attraction between chains. The increase of the degree of crosslinking is then expected to induce a local collapse and favors a clustering of polymers. In fact, it has been pointed out [14,13] that we may reach a collapse transition or the border of spinodal decomposition [4]. The possibility that at a new *critical* threshold the gel undergoes a phase separation triggered by increased crosslink density is confirmed theoretically [15,16] and experimentally [17], albeit the exact nature of the state beyond the transition is not well understood yet.

The above fact suggests that our preceding approach to the properties of frozen inhomogeneities may be improved by inclusion of critical (enhanced) fluctuations of the transition. To this end, we take into account the coupling between the frozen (quasi-static) heterogeneity and the concentration fluctuations as follows. The correlation of the crosslink-density fluctuations $\delta\nu$ is expressed in Fourier transform as

$$\langle|\nu_{\mathbf{q}}|^2\rangle = \frac{1}{V}\int\!\!\int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\langle\exp\left[i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')\right]\delta\nu(\mathbf{x}_0)\delta\nu(\mathbf{x}'_0)\rangle, \qquad (35)$$

with $\mathbf{x} = \lambda\mathbf{x}_0 + \mathbf{u}$ (see Eq. (5)). Introducing the decoupling approximation in the spirit of the mode-coupling theory, we rewrite equation (35) as

$$\langle|\nu_{\mathbf{q}}|^2\rangle = \frac{1}{V}\int\!\!\int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\langle\exp\left[i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')\right]\rangle\langle\delta\nu(\mathbf{x}_0)\delta\nu(\mathbf{x}'_0)\rangle. \qquad (36)$$

Since the correlation of frozen heterogeneities decays on length scales (of the order of mesh size, $R \sim aN^{1/2}$) which are much larger than the correlation length of the thermal (density) fluctuations, the quenched fluctuations are very likely to predominantly show up in the small-q ($q \ll R^{-1}$) scattering. Hence $\langle\exp[i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')]\rangle$ may be taken at $q \to 0$ to yield

$$\langle|\nu_{\mathbf{q}}|^2\rangle = \frac{1}{V}\int\!\!\int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\langle\delta\nu(\mathbf{x}_0)\delta\nu(\mathbf{x}'_0)\rangle. \qquad (37)$$

The $\langle\delta\nu\delta\nu\rangle$ is now calculated. We assume that all crosslinks are established in a solution of linear polymers instantaneously. Polymers that happen to be close immediately prior to the crosslinking process are linked with a certain probability. Therefore the $\langle\delta\nu\delta\nu\rangle$ correlator should reflect the density correlation in the initial preparation state. We may thus postulate that $\delta\nu$ is related to $\delta\rho^{(0)}$, the density fluctuations in the initial system, by the following linear relation:

$$\delta\nu = \delta\tilde{\nu} + \alpha\delta\rho^{(0)}. \qquad (38)$$

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[3] Let us recall that in the BE theory the structure factor for the Gaussian chain ($S_0(q)$) given by the Debye function is approximated by its asymptotic ($qR_{\mathrm{G}} \gg 1$) form: $S_0(q) \simeq 12/q^2a^2$, where R_{G} is the gyration radius of the chain. The value $\tilde{C} = 1/6$ essentially comes from this fact.

[4] In crosslinking polymerization the effect of increasing crosslink density is well established experimentally and always favors phase separation irrespective of the solvent power [14].

The coefficient α will be assumed to be simply a constant. The components of the random part, $\delta\tilde{\nu}$, obey the short-ranged correlation as in the original Onuki's theory:

$$\langle \delta\tilde{\nu}(\mathbf{x}_0)\delta\tilde{\nu}(\mathbf{x}'_0)\rangle = \bar{\nu}p\delta(\mathbf{x}_0 - \mathbf{x}'_0) = \bar{\nu}p\frac{\phi_0}{\phi}\delta(\mathbf{x} - \mathbf{x}'). \quad (39)$$

It then follows that

$$\langle |\nu_{\mathbf{q}}|^2\rangle = \frac{\phi_0}{\phi}[\bar{\nu}p + \alpha^2 S^{(0)}(q=0)], \quad (40)$$

where $S^{(0)}(q) \equiv \langle |\rho^{(0)}_{\mathbf{q}}|^2\rangle$, $\rho^{(0)}_{\mathbf{q}}$ being the Fourier transform of $\delta\rho^{(0)}$, is the density correlation function in the preparation state. Finally, let $\bar{\nu}_{\mathrm{c}}$ be the critical crosslink density, at which a continuous transition is assumed to occur. Then, taking the Curie-Weiss form [5] for the static susceptibility $S^{(0)}(q=0)$, we find

$$\langle |\nu_{\mathbf{q}}|^2\rangle = \frac{\phi_0}{\phi}\bar{\nu}p\left(1 + \frac{\gamma}{\bar{\nu}/\bar{\nu}_{\mathrm{c}} - 1}\right), \quad (41)$$

where γ is a phenomenological constant. This implies that the amplitude p of the crosslink density fluctuations in equation (10) is replaced by

$$p\left(1 + \frac{\gamma}{N/N_{\mathrm{c}} - 1}\right), \quad (42)$$

reflecting the distance from the transition point, $N_{\mathrm{c}} \equiv \phi_0/(2v_1\bar{\nu}_{\mathrm{c}})$.

To summarize, equations (33, 34) with (instead of (31))

$$\hat{p} = \frac{6}{\mathrm{N}}\left(1 + \frac{\gamma}{N/N_{\mathrm{c}} - 1}\right)p^*\left(\frac{\phi_0}{\phi}\right)^{2/3}\left[1 - B\left(\frac{\phi}{\phi_0}\right)^{2/3}\right]^2 \quad (43)$$

constitute our main result for the structure factor of weakly charged gels as a function of various parameters and experimental variables.

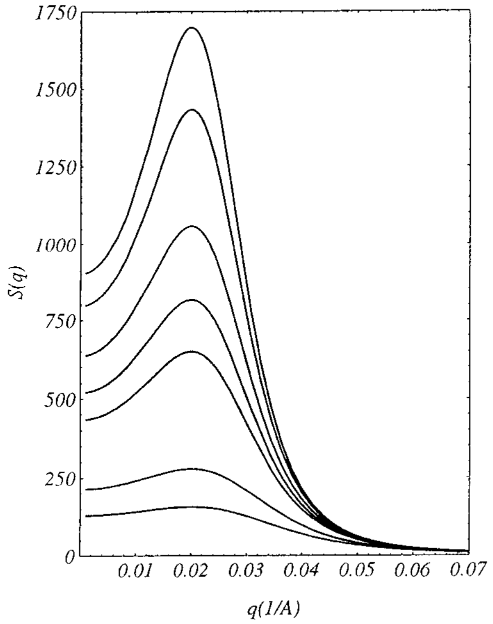

Fig. 1. Variation of the structure factor $S(q)$ with the interaction parameter: $\chi = 0.650$, 0.655, 0.660, 0.661, 0.662, 0.663 and 0.6635 from lowest to uppermost. The scale of the vertical axis is in arbitrary units. The parameters used are $p^* = 2$, $N = 50$, $N_{\mathrm{c}} = 12$, $\gamma = 1.5$, $B = 0$ and $\hat{c}_{\mathrm{s}} = 0.04$. Other parameters are representative of the experiment of reference [6]: $a = 8.12$ (Å), $\phi = 0.1$, $\phi_0 = 0.07$, $f = 0.0457$ and $\hat{l}_{\mathrm{B}} = 10.8$.

5 Discussion

By employing the generalized elastic free energy, we have derived an explicit expression for the shape of the structure factor of a weakly charged polyelectrolyte gel. The scattered intensity is given by a competition between thermal concentration fluctuations and frozen heterogeneity fluctuations. In order to consider the latter, the crosslink density is assumed to fluctuate in space with amplitude $\hat{p}$ given by equation (43). The screening of the Coulomb interaction between charged segments of polyelectrolyte chains at nonzero concentrations is taken into account in the Debye-Hückel approximation. In the absence of crosslinks, our result reduces to the form of the Borue and Erukhimovich theory for polyelectrolyte solutions. In the case of nonionic gels, our formula coincides with Onuki's result with one modification. Namely, we have allowed for the instability of a liquid-like state of polymers for larger crosslink densities. As it turns out, a nonuniform dependence on the crosslink density of the scattering intensity that emerges (see below) is a direct consequence of this effect.

Figure 1 shows the dependence of $S(q)$ on temperature in terms of the interaction parameter χ. Two typical features that have been observed in the small-angle neutron scattering experiment [5,6] are reproduced; the scattering peak at a finite wavevector, and the enhanced peak upon increasing the value of χ (*i.e.*, decreasing the quality of the solvent). The dependence of the scattering intensity on the crosslink density is plotted in Figure 2 in the intermediate density regime. The behavior that the intensity increases as the crosslink density is decreased (or N is increased) is characteristic of the classical picture, and is also contained in Onuki's theory for neutral gels. We note, however, that the prediction has not yet been borne out by experiment. (See, for instance, Ref. [18]; for a partial

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[5] Although the detailed form of $S^{(0)}(q)$ is outside of the scope of the present phenomenological treatment, it should be noted that the RPA calculation in reference [16] yields the Ornstein-Zernike form for $S^{(0)}(q)$ of neutral gels as

$$S^{(0)}(q) = \frac{1}{N\phi_0(1 - 2\chi + \phi_0) - 1 + Q^2/2}.$$

The assumed Curie-Weiss form is consistent with this result. It is a well-known feature of critical phenomena that the (linear) susceptibility exhibits the divergence at the transition.

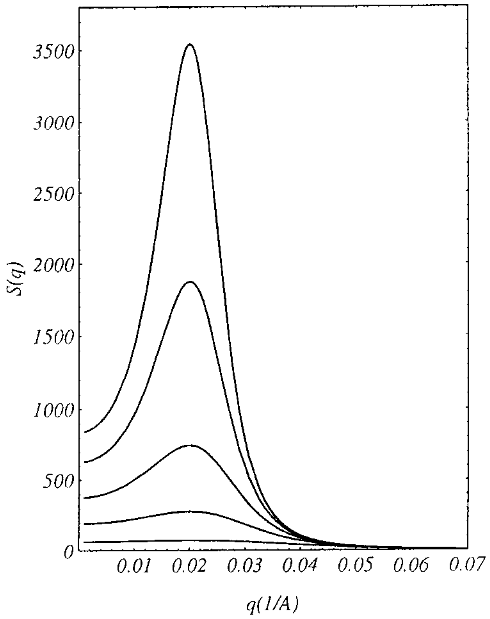

Fig. 2. Variation of the structure factor $S(q)$ at $\chi = 0.64$ with the average number of chain monomers between neighboring crosslinks: $N = 50$, 100, 130, 150 and 160 from lowest to uppermost. All other parameters are the same as in Figure 1. The scale of the vertical axis is in arbitrary units.

support, however, see Ref. [19].) The influence of the presence of the critical crosslink density $(1/N_\mathrm{c})$ is most clearly seen by looking at the scattering intensity as a function of N. As shown in Figure 3, a simple extention of the Onuki model without the N_c-term could not describe the crosslink-induced transition and it fails to yield a strong increase of the scattering intensity near the transition.

Quite recently Rabin and Panyukov (RP) extended their theory of neutral gels [15,16] to charged gels [9]. They considered the charged gel prepared in a good solvent and studied in a poor or θ solvent. They used the replica field theory to take into account the frozen inhomogeneity of networks of Gaussian chains. They then generalized the theory to the case of gels in good solvents using a scaling method [6]. In this way they calculated the structure factor for the charged gels. With the units in which their structure factor $(S^{\mathrm{RP}}(q))$ of neutral gels becomes equal to ours in the limit $q \to 0$, $N \to \infty$, it is given by

$$S^{\mathrm{RP}}(q) = \frac{\mathrm{N}}{12}\left\{\frac{\hat{g}_q}{\Gamma_q} + \frac{3}{\Gamma_q^2(1+Q^2)^2}\left[2 + \frac{3}{\hat{w}_q^{(0)} - 1 + Q^2 t_\phi/2}\right]\right\}, \tag{44}$$

where

$$\Gamma_q = 1 + \hat{w}_q \hat{g}_q, \tag{45}$$

$$\begin{aligned}\hat{g}_q &= \frac{1}{Q^2/2 + 1/(4Q^2) + 1} + \frac{2/t_\phi}{(1+Q^2)^2},\\ \hat{w}_q &= \phi N\left[1 - 2\chi + \phi + \frac{f^2}{Q^2/(\hat{l}_\mathrm{B}N) + \hat{c}_\mathrm{t}\phi}\right],\\ \hat{w}_q^{(0)} &= \phi_0 N\left[\phi_0^{1/4} + \frac{(f^{(0)})^2}{Q^2 t_\phi/(\hat{l}_\mathrm{B}N) + f^{(0)}\phi_0}\right]\end{aligned} \tag{46}$$

and $t_\phi \equiv (\phi_0/\phi)^{2/3}\phi_0^{-1/4}$, $f^{(0)}$ being the ionization degree in the state of preparation.

The two theoretical models (*i.e.*, RP's and ours) analyse the effects of the network heterogeneity and elasticity in quite a different manner. In the following we therefore list the contrarieties and similarities of predictions by these models.

The distinctive difference already exists in the prediction as to the properties of neutral gels. Let us look at the longitudinal modulus defined by

$$E_\mathrm{L} = \phi^2/\left[12\phi v_1 k_\mathrm{B} T S(q \to 0)\right]^{-1}. \tag{47}$$

Firstly to compare the two theories on an equal footing, we consider the RP model in which both the initial and final states of the network are under a poor or θ condition (see [15]). For gels at the reaction bath (*i.e.*, at $\phi = \phi_0$), we then find

$$E_\mathrm{L}(\mathrm{RP}) = v_1^{-1}\phi\left[(1 - 2\chi + \phi)\phi - 1/N\right] \tag{48}$$

for the RP theory. Thus, in the RP theory, $S(q = 0)$ increases monotonically on increasing the crosslink density.

In marked contrast to this, our theory predicts that a different variation of $S(q = 0)$ with the crosslink density is possible depending on the degree of frozen heterogeneities. This can be seen most easily by looking at the large-N formula for E_L given from equation (33):

$$E_\mathrm{L}(\mathrm{present}) = v_1^{-1}\phi\left[\phi(1 - 2\chi + \phi) - \frac{(1-B)^2}{2N}(p^* - p_\mathrm{c}^*)\right],$$
$$N/N_\mathrm{c} \gg 1, \tag{49}$$

thus showing that the sign of the combination $p^* - p_\mathrm{c}^*$ matters where $p_\mathrm{c}^* \equiv (1+B)/(1-B)^2$. In fact, for $p^* \gg p_\mathrm{c}^*$, $S(0)$ increases on increasing the crosslink density as in the RP theory. For $p^* < p_\mathrm{c}^*$, however, a minimum of $S(0)$ develops, as shown in Figure 3. We note that this effect is indifferent to the precise value of the disputable parameter B (although the absolute value of $S(0)$ itself depends on B).

In this connection we remark that in the case of gels prepared and studied both in the good-solvent limit, the RP theory predicts that

$$E_\mathrm{L}(\mathrm{RP}) = v_1^{-1}\phi(\phi^{5/4} - 1/N). \tag{50}$$

Therefore, no qualitative change is incurred in this case as to the crosslink density dependence of $S(0)$. Only when the gels are prepared in the good solvent and studied in a poor or θ solvent this theory predicts such a minimum.

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[6] It should be noted that our theory is a mean field theory so that the results given in this paper do not describe the gels in the good solvent limit.

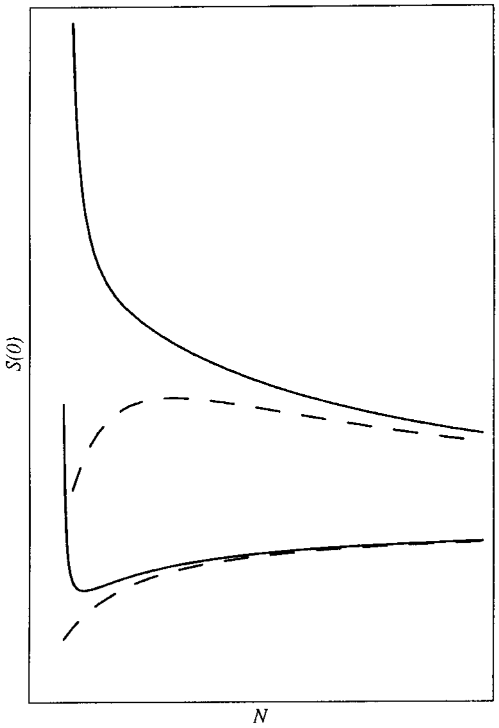

Fig. 3. Schematic drawing of the scattering intensity at zero wavevector, $S(0)$, as a function of the average number of chain monomers between neighboring crosslinks. The upper curve corresponds to a relatively high degree of frozen heterogeneity (p^*), the lower curve being for a small p^*. The dashed curves represent the respective cases with $N_c = 0$.

(The last point is discussed in detail in a separate paper [21].)

The third important point of our remarks is concerned with the argument first proposed by Bastide and Leibler [22]. It is argues that the small-scale heterogeneities in the crosslink density of unswollen gels result in large-scale density fluctuations only when the gels are swollen. In the RP theory (and in our theory as well[7]), on the other hand, the large-scale inhomogeneities are detectable already in the reaction bath; this can be seen by putting $\phi = \phi_0$ in equation (44) to find the nonvanishing contribution from the second term, which represents fluctuations of static density inhomogeneities. Recall that in their argument for the occurrence of the large-scale heterogeneities, Bastide and Leibler assumed the instantaneous crosslinking of a semidilute polymer solution to prepare the gel. In view of the fact that RP also assumed the preparation with the instantaneous cross linking in order to employ the replica method in the calculation of the structure factor, the above-mentioned contrast is puzzling.

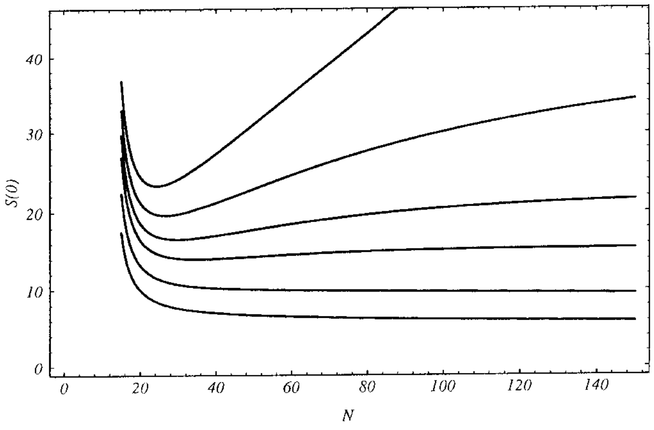

Fig. 4. The scattering intensity $S(0)$ *versus* the average number N of chain monomers between neighboring crosslinks for gels at $\phi = \phi_0 = 0.1$ with the interaction parameter $\chi = 0.55$, 0.58, 0.60, 0.61, 0.62 and 0.63 from lowest to uppermost. All other parameters are the same as in Figure 1. The scale of vertical axis is in arbitrary units.

It should be added in this connection that in the RP theory there is no parameter such as p (p^*) of our theory which represents the degree of irregularity of the crosslinking. This is because the crosslinking can occur with equal probability at any location along the chain in the case of the instantaneous crosslinking. As a consequence, some topological disorder which is present already when making a network results in the spatial fluctuations of the crosslinking density.

The fourth point concerns the charged-gel case and is related to the first point mentioned above. It has been demonstrated elsewhere [21] that in the RP model the crosslink-density dependence of the scattered intensity from the gels prepared in the good solvent and studied in a poor or θ solvent is not monotonous; with regard to the N-dependence of the peak intensity $S(q^*)$ (and $S(q = 0)$ as well) there occurs the minimum (inflection) under appropriate conditions. The present theory shows that this inflection behavior should be true also in the case of a poor or θ solvent, as illustrated in Figure 4.

The last remark is now in order. Some time ago de Gennes [23] argued, utilizing an analogy with dielectric media, that in crosslinked polymer *mixtures* the scattering maximum at a non-zero q should occur by lowering the temperature. The appearance of the maximum at a finite q is a consequence of the competition between two opposing forces: attractive polymer-polymer interactions when the blend attempts to phase separate and the elastic restoring force because of the crosslinks. In the ionic polymer networks in a *solution*, the scattering intensity exhibits a similar maximum. In this case of charged gels, however, it is the repulsive Coulombic interaction between charged groups that gives rise to the scattering peak at a finite q. The elastic force of the network is not strong enough in the presence of solvent and plays a subdominant role in opposing the attractive polymer-polymer interaction. (The full extreme of this situation is polyelectrolyte solutions. In the absence of networks, there appears the scattering maximum at a finite q in that case [7]). In fact,

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[7] The following contrast against the Bastide-Leibler picture would be absent in our theory if Onuki's assertion [8] (see also [11]) regarding the constant B were valid, according to which $B = 1$.

some calculations show that in our model the peak position q^* is finite only for a non-zero degree of ionization, f. (However, we must keep in mind that our model does not consider a possible wavevector dependence of the crosslink density fluctuations (Sect. 4). It could well be that in a more elaborate treatment of this effect the finite $q^* \sim 1/(aN^{1/2})$ is possible even in the neutral gels, and indeed this is what the RP theory predicts.)

In closing it must be stressed that experimental results [5,6,20] are in strong qualitative agreement with the analytical expression given in the present paper. In particular, one of our theoretical predictions that by increasing the interaction parameter (χ) one can pass from a region in which the scattering intensity is a monotonically increasing function of the crosslink density, to one in which a minimum in the crosslink density dependence exists (as given in Fig. 4) has been verified by the recent light scattering experiment [20]. More acute quantitative comparison with the experimental data will be given in a separate paper, and the dynamic properties of polyelectrolyte gels will also be considered.

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