Scattering Properties of Dipolar Gels

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ABSTRACT: We study the effects of dipolar interactions of polymer chains where the dipolar moments are aligned along the polymer segments on the scattering properties of dipolar gels made by randomly cross-linking dipolar chains in polar solvent. Using the field-theoretical approach, the dipolar interactions of polar solvent and dipolar polymer segments are decomposed into Cartesian components which enables the use of collective density variables. After integrating out the degree of freedoms due to dipolar interactions of polymer segments, it is found the effective interactions between monomer density fields are increased, and the net increase in the effective interactions due to dipolar interactions of polymer segments increases with wavenumber and the magnitude of dipolar moment of polymer segments. Because of the increase of effective virial coefficients of dipolar gels, both the thermal fluctuations and static density inhomogeneities of such gels are suppressed compared to its neutral counterparts. Similar to uniaxially stretched neutral gels, the scattering intensity is enhanced in the direction along the stretching axis for dipolar gels. Also in the direction parallel to the stretching direction, it is found there is enhanced orientational ordering of dipolar density field in Θ solvent.

I. Introduction

Polymer gel synthesized by cross-linking a polymer solution or a melt is a solid permeated by solvent. Thus, polymer gels combine both the properties of solid and liquid. Charged polymer gels, i.e., cross-linked polyelectrolyte chains, are capable of swelling to much greater extents than their uncharged counterparts due to the main entropic contribution from counterion release in solvents (the most common one is water) and electrostatic repulsion between charged momoners. Our understanding of the statistical mechanics of polymer gels including charged gels has been hindered by the quenched noise nature of permanent cross-linkings. The long-range nature of Coulomb interaction and strong correlation in charged gels further complicate the theoretical study of charged gels.[1–10] Nonetheless, since the 1990s, great progress has been achieved in the theoretical understanding of polymer gels including charged gels.[3,5,8–10] For neutral gels, Panyukov and Rabin have presented a comprehensive statistical mechanical analysis of randomly cross-linked polymer networks using replica field theory.[8] They also developed a phenomenological theory of density fluctuations and static inhomogeneities guided by insights provided by their replica field-theoretical results.[9] Rabin and Panyukov further extended their phenomenological theory to weakly charged gels.[10] In the random phase approximation, the Debye−Hückel free energy is added to the free energy for neutral polymer gels, resulting in the simple replacement of the second virial coefficients in the state of preparation and in the final observed state by effective interaction coefficients containing sreened Coulomb interactions.

Dipolar interaction in polymer gels is an important issue which needs special attention. For example, the dielectric properties of the solvents are crucial to the proper functionings of charged gels.[11–15] In polar solvents, the polyions and counterions can easily dissociate from each other and associate with solvent molecules—thereby becoming solvated, which can lead to very high degree of swelling of charged gels in polar solvents. On the contrary, in nonpolar solvents, charged gels simply collapse. Ion association and dipolar interaction become important in mixture of water with organic solvent where the dielectric permittivity becomes lower than that of pure water, leading to formations of ion pairs and multiplets which can act as additional cross-links, as well as the decrease of the degree of swelling due to the decrease in the amount of mobile counterions.[16] A supercollapsed state of poly(diallyldimethylammonium chloride) gel is found in an aqueous solution of sodium iodide other than sodium chloride or bromide.[17] Iodide ions possess higher polarizability compared to chloride or bromide, so they can form a larger number of ion pairs. Ion pairs involving iodide have a higher dipolar moment, which, in turn, can further promote their association to form multiplets. Another example involving dipolar interactions is ferrogels where magnetic particles with typical size of about 10 nm are the carriers of magnetic moments. These magnetic particles are embedded in a flexible polymeric network and eventually attached to the polymer chains. Jarkova and Vilgis[18] proprosed a primitive model where the magnetic moments are assumed to align along the polymer chains for the studying of the scattering properties of ferrogels. In ref 18, the dipolar interaction is only treated approximately.

In this paper, as the first step toward to the understanding of the electrostatics of ion pairs and multiplets in charged gels, we intend to study the statistical mechanics and scattering properties of dipolar gels permeated with dipolar solvent where the dipolar moments are assumed to align along the polymer segments. Such model system is schematically shown in Figure 1. Our therotical formalism is based on field-theoretical approach and random phase approximation (RPA), we explicitly and accurately take into account the interactions involving dipolar moments by decomposing dipolar interactions into Cartesian components. The rest of the paper is organized as follows. In the next section, we study the effects of dipolar solvent on the electrostatics of semidilute polyelectrolyte solution, and calculate the mean-field Hamiltonian including dipole−dipole and dipole-ion interactions from which the effect of dipolar solvent on the electrostatics of polyelectrolyte solutions can be deduced. Also in this section, we compare our results with those from a recently proposed dipolar Poisson−Boltzmann model.[19,20] In section III, we study the statistical mechanics of dipolar chains in dipolar solvent and derive the effective Hamiltonian. In this section, the effect of dipolar solvent deduced from section II has been taken into account implicitly, which simplifies the mathematical manipulations in the field-theory analysis. In section IV, we study the scattering properties of dipolar gels permeated by

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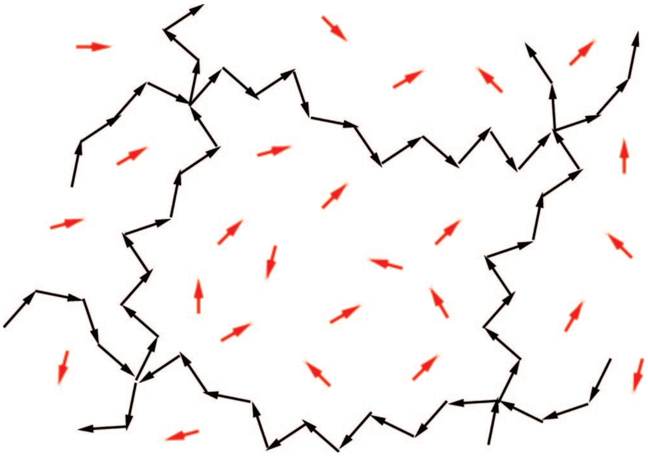

Figure 1. Schematic representation of dipolar gel where dipolar moments are aligned along the polymer segments in a dipolar solvent.

dipolar solvent and the orientational ordering of dipolar moments on the polymer chains under uniaxial stretching. Finally, in section V, we draw the main conclusions of this paper.

II. Mean-Field Theory and Electrostatics of Semidilute Polyelectrolyte Solution with Dipolar Solvent

A. Dipolar Interactions. The polyelectrolyte solution basically consists of three components, i.e., polyions with volume fraction $\bar{\phi}_p$, the counterions with number density $\bar{\phi}_i$, and generally the water as solvent with number density C_d. If the salt is added, there will be one component more with number density $\bar{\phi}_s$. The free energy of the solution consists of two parts: the entropic contribution and the contribution due to monomer fluctuations and Coulomb interactions. The Hamiltonian of the system can be written as

$$\beta H = \sum_{\alpha=1}^{n_p} \frac{3}{2a^2} \int_0^N \mathrm{d}s \left(\frac{\partial \vec{R}_\alpha(s)}{\partial s} \right)^2 + v_2 + v_3 + v_E \tag{1}$$

where n_p is the total number of chains, a is the monomer size, N is the degree of polymerization of chain, $\vec{R}_\alpha(s)$ denotes the position vector of the s monomer of the αth chain, and $\beta = 1/(k_BT)$. In the above equation, the first term on the right-hand side is the Wiener measure that models the connectivity of Gaussian chain; v_2 is the two-body interaction of polymer chains, i.e., excluded volume interaction, which can be modeled as $v/2\sum_{\alpha=1}^{n_p}\sum_{\beta=1}^{n_p}\int_0^N \mathrm{d}s \int_0^N \mathrm{d}s'\ \delta(\vec{R}_\alpha(s) - \vec{R}_\beta(s'))$ using the Dirac δ-function with v the second virial coefficient; v_3 denotes the three-body interaction of polymer chains which can be modeled in a similar fashion as v_2, i.e., invoking two Dirac δ-functions and three integrations over arc length from 0 to N; and last v_E describes the Coulomb interactions. The Coulomb potential includes interactions between polyion−polyion v_{pp}, polyion−counterion v_{pi}, and counterion−counterion v_{ii}, all of which are interacting through $1/r$ potential with r the distance between two point charges. The way how these Coulomb interactions yield (in Gaussian approximation, random phase approximation) the effective (mean-field) potentials, such as e.g. the Debye−Hückel screening, has been shown explicitly in ref 21, so for brevity, they will not be given here. Because the primary focus of this section is on the effect of dipolar solvent on the electrostatics of polyelectrolyte solution, in the Coulomb potential v_E, there are additional terms due to interactions involving dipolar solvent molecules. The first term involving dipolar solvent is dipolar−dipolar interaction

$$v_{dd} = \sum_{i=1}^{n_d}\sum_{j=1}^{n_d} \frac{1}{4\pi\epsilon_0 r_{ij}^{\ 3}} \left[\vec{\mu}_i \cdot \vec{\mu}_j - \frac{3(\vec{r}_{ij}\cdot\vec{\mu}_i)(\vec{r}_{ij}\cdot\vec{\mu}_j)}{r_{ij}^{\ 2}} \right] \tag{2}$$

where n_d is the total number of dipolar solvent molecules, ϵ_0 is the dielectric permittivity of the medium, $r_{ij} = |\vec{r}_i - \vec{r}_j|$, and $\vec{\mu}_i$ is the dipolar moment of ith dipolar solvent molecule. It should be noted that the dielectric permittivity should be set as vacuum permittivity instead of that of the dipolar solvent in order to avoid double counting the effect of dipolar solvent. In the rest of the paper, ϵ_0 is reserved to vacuum permittivity. The second interaction term involving diplar solvent is dipolar−polyion interaction

$$v_{dp} = \sum_{\alpha=1}^{n_p}\sum_{i=1}^{n_d} \int_0^N \mathrm{d}s\ \frac{ef\vec{\mu}_i\cdot(\vec{r}_i - \vec{R}_\alpha(s))}{4\pi\varepsilon_0|\vec{r}_i - \vec{R}_\alpha(s)|^3} \tag{3}$$

where e is the elementary charge and f is the fraction of charge on each monomer unit. The last one involving dipolar solvent molecules is dipolar−counterion interaction

$$v_{di} = \sum_{i=1}^{n_i}\sum_{j=1}^{n_d} \frac{e\vec{\mu}_j\cdot(\vec{r}_j - \vec{r}_i)}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|^3} \tag{4}$$

The dipolar−dipolar interaction can be rewritten in terms of Cartesian components of distance vectors and dipolar moment vectors. In tensor notation, it is

$$v_{dd} = \sum_{i=1}^{n_d}\sum_{j=1}^{n_d} \frac{1}{4\pi\epsilon_0 r_{ij}^{\ 5}} [(r_{ij}^\gamma r_{ij}^\gamma \delta_{\alpha\beta} - 3r_{ij}^\alpha r_{ij}^\beta)\mu_i^\alpha \mu_j^\beta] \tag{5}$$

where $\alpha = x$, or y, or z, the same is true for β and γ, and Einstein summation for repeated index is implied. Define microscopic density operator for dipolar molecules

$$\hat{\phi}_\mu^\alpha(\vec{r}) = \sum_{i=1}^{n_d} \delta(\vec{r} - \vec{r}_i)\mu_i^\alpha \tag{6}$$

which in Fourier space is

$$\hat{\phi}_\mu^\alpha(\vec{q}) = \sum_{i=1}^{n_d} \mu_i^\alpha \mathrm{e}^{i\vec{q}\cdot\vec{r}_i} \tag{7}$$

the dipolar−dipolar interaction can be expressed in the following form

$$\frac{v_{dd}}{k_BT} = \left(\frac{4\pi\lambda_B}{e^2}\right)\left(\frac{q_\alpha q_\beta}{q^2}\right)\hat{\phi}_\mu^\alpha(\vec{q})\hat{\phi}_\mu^\beta(-\vec{q}) \tag{8}$$

where $\lambda_B = e^2/(4\pi\epsilon_0 k_BT)$ is the Bjerrum length; q_α and q_β are the αth and βth Cartesian component of wave vector $\vec{q}$, respectively. Invoking microscopic density operators for monomers and counterions

$$\hat{\phi}^p(\vec{q}) = \sum_{\alpha=1}^{n_p} \int_0^N \mathrm{d}s\ \mathrm{e}^{i\vec{q}\cdot\vec{R}_\alpha(s)}, \quad \hat{\phi}^i(\vec{q}) = \sum_j^{n_i} \mathrm{e}^{i\vec{q}\cdot\vec{r}_j} \tag{9}$$

the dipolar−polyion and dipolar−counterion interactions can be rewritten as

$$\frac{v_{pd}}{k_BT} = -\left(\frac{4\pi f\lambda_B}{e}\right)\left(\frac{iq_\alpha}{q^2}\right)\hat{\phi}_\mu^\alpha(\vec{q})\hat{\phi}^p(-\vec{q}) \tag{10}$$

and

$$\frac{v_{id}}{k_BT} = \left(\frac{4\pi\lambda_B}{e}\right)\left(\frac{iq_\alpha}{q^2}\right)\hat{\phi}_\mu^\alpha(\vec{q})\ \hat{\phi}^i(-\vec{q}) \tag{11}$$

where we have assumed that counterions are positively charged, which is the case for sodium polystyrenesulfonate. In the spirit of field theory, we introduce collective density fields $\phi^p(\vec{r})$, $\phi^i(\vec{r})$, and $\phi_\mu^\alpha(\vec{r})$ for polyions, counterions, and dipolar moments, respectively.

B. Effect of Dipolar Solvent. After the application of the standard Hubbard−Stratonovich transformation to the canonical partition function, the free energy of the system can be written as

$$\mathrm{e}^{-\beta F} = \mathrm{e}^{-\beta F_0} \int \prod_{\vec{q}\neq 0} \prod_{\alpha} D\phi^p(\vec{q})\, D\phi^i(\vec{q})\, D\phi_\mu^\alpha(\vec{q}) \mathrm{e}^{-\beta H[\phi^p(\vec{q}),\phi^i(\vec{q}),\phi_\mu^\alpha(\vec{q})]} \tag{12}$$

where F_0 is the macroscopic free energy ($\vec{q} = \vec{0}$) and the Hamiltonian due to Gaussian fluctuations is given by

$$\begin{aligned}\beta H[\phi^{\mathrm{p}}(\vec{q}), \phi^i(\vec{q}), \phi_\mu^\alpha(\vec{q})] = {} & \frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{1}{S_{\mathrm{p}}^0(\vec{q})} + \upsilon + \bar{\phi}_{\mathrm{p}}\omega + \frac{4\pi\lambda_{\mathrm{B}} f^2}{q^2}\right]\phi^{\mathrm{p}}(\vec{q})\, \phi^{\mathrm{p}}(-\vec{q}) + \frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{1}{\bar{\phi}_i} + \frac{4\pi\lambda_{\mathrm{B}}}{q^2}\right]\phi^i(\vec{q})\phi^i(-\vec{q}) - {}\\ & \sum_{\vec{q}\neq 0}\left(\frac{4\pi\lambda_{\mathrm{B}} f}{q^2}\right)\phi^{\mathrm{p}}(\vec{q})\phi^i(-\vec{q}) + \frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{\delta_{\alpha\beta}}{S_{\alpha\beta}^0} + \left(\frac{4\pi\lambda_{\mathrm{B}}}{e^2}\right)\left(\frac{q_\alpha q_\beta}{q^2}\right)\right] \times {}\\ & \phi_\mu^\alpha(\vec{q})\phi_\mu^\beta(-\vec{q}) + \sum_{\vec{q}\neq 0}\left(\frac{4\pi\lambda_{\mathrm{B}}}{e}\right)\left(\frac{iq_\alpha}{q^2}\right)\phi_\mu^\alpha(\vec{q})\, \phi^i(-\vec{q}) - {}\\ & \sum_{\vec{q}\neq 0}\left(\frac{4\pi\lambda_{\mathrm{B}} f}{e}\right)\left(\frac{iq_\alpha}{q^2}\right)\phi_\mu^\alpha(\vec{q})\, \phi^{\mathrm{p}}(-\vec{q})\end{aligned} \tag{13}$$

where υ and ω are the second and third virial coefficients, respectively, $S_{\mathrm{p}}^0(\vec{q})$ is the bare structure factor of the polyions which is of Gaussian type for weakly charged polyelectrolytes, $\bar{\phi}_i$ is the bare structure factor of pointlike counterions, and $S_{\alpha\beta}^0$ is the bare structure factor for dipolar solvent molecules without external interactions, which can be obtained from the Jacobian

$$J = \int \prod_{i=1}^{n_{\mathrm{d}}} D\vec{r}_i \prod_{\alpha} \delta[\phi_\mu^\alpha(\vec{q}) - \sum_{i=1}^{n_d} \mu_i^\alpha \mathrm{e}^{i\vec{q}\vec{r}_i}] \tag{14}$$

in a similar way for the polymers in ref 22. Because dipolar solvent molecules are isotropic under no external potential, there should be no cross-coupling of the different components of the dipolar moments, which simplifies the derivation of bare structure factors from the Jacobian. After straightforward calculation, the bare structure factors for dipolar moments are

$$S_{\alpha\alpha}^0 = \left(\sum_{i=1}^{n_{\mathrm{d}}} \mu_i^\alpha \mu_i^\alpha\right)/V = \frac{1}{3} C_{\mathrm{d}} \mu^2 \tag{15}$$

where V is the total volume of the system, μ is the magnitude of the dipolar moment, and C_{d} is the number density of dipolar solvent. It should be noted that in eq 15 no summation over α is assumed.

The free energy within Gaussian approximation is given by $\beta F = -\ln Z$, i.e.

$$\beta F = \beta F_0 - \ln \int \prod_{\vec{q}\neq 0} \prod_{\alpha} D\phi^{\mathrm{p}}(\vec{q}) D\phi^i(\vec{q}) D\phi_\mu^\alpha \mathrm{e}^{-\beta H[\phi^p(\vec{q}),\phi^i(\vec{q}),\phi_\mu^\alpha(\vec{q})]} \tag{16}$$

The functional integral over density fields ϕ_μ^α can be carried out simply in this Gaussian approximation. Carrying out the triple Gaussian integrals over ϕ_μ^α, we are left with

$$\begin{aligned}\int \prod_{\vec{q}\neq 0} D\phi^{\mathrm{p}}(\vec{q}) D\phi^i(\vec{q}) \exp\Bigg[& -\frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{1}{S_{\mathrm{p}}^0(\vec{q})} + \upsilon + \bar{\phi}_{\mathrm{p}}\omega + \left(\frac{4\pi\lambda_{\mathrm{B}} f^2}{q^2}\right)(1 - S_{\mathrm{d}})\right]\phi^{\mathrm{p}}(\vec{q})\, \phi^{\mathrm{p}}(-\vec{q}) - \frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{1}{\bar{\phi}_i} + \left(\frac{4\pi\lambda_{\mathrm{B}}}{q^2}\right) \times \right.\\ & \left.(1 - S_{\mathrm{d}})\right]\phi^i(\vec{q})\phi^i(-\vec{q}) + \sum_{\vec{q}\neq 0}\left(\frac{4\pi\lambda_{\mathrm{B}} f}{q^2}\right)(1 - S_{\mathrm{d}})\phi^p(\vec{q})\phi^i(-\vec{q})\Bigg]\end{aligned} \tag{17}$$

where

$$S_{\mathrm{d}} \equiv \frac{(4\pi\lambda_{\mathrm{B}}/e^2/q^2)S_{\alpha\beta}^0 q_\alpha q_\beta}{1 + (4\pi\lambda_{\mathrm{B}}/e^2/q^2)S_{\alpha\beta}^0 q_\alpha q_\beta} = \frac{(4\pi\lambda_{\mathrm{B}}/e^2)S_{xx}^0}{1 + (4\pi\lambda_{\mathrm{B}}/e^2)S_{xx}^0} \tag{18}$$

It is clear from eq 17, after integrating out the degree of freedom of dipolar solvent molecules, the electrostatic interactions among polyions and counterions are decreased by a fraction of S_{d}. To make the effect of dipolar solvent more transparent, let us rewrite the electrostic interaction term for polyion−polyion as follows:

$$\left(\frac{4\pi\lambda_{\mathrm{B}} f^2}{q^2}\right)(1 - S_{\mathrm{d}}) = \left(\frac{e^2 f^2}{\epsilon_0 q^2 k_{\mathrm{B}} T}\right)\frac{1}{1 + (1/(\varepsilon_0 k_{\mathrm{B}} T))S_{xx}^0} = \frac{e^2 f^2}{q^2 k_{\mathrm{B}} T[\epsilon_0 + S_{xx}^0/(k_{\mathrm{B}} T)]} \tag{19}$$

From the above equation, it is clear that the dipolar interactions from diplar solvent result in renormalization of dielectric permittivity of the medium, i.e., $\epsilon_0 \to \epsilon_0 + S_{xx}^0/(k_{\mathrm{B}}T)$, which is consistent with the analysis of a recently proposed Dipolar Poisson−Boltzmann equation involving dipolar solvent.[20] The so-called dipolar Poisson−Boltzmann equation is obtained from field-theoretical approach on mean-field level. The dipolar Poisson−Boltzmann equation is shown below for the case of 1:1 salt in a dipolar solvent

$$-\epsilon\nabla^2\psi = -2C_s e \sinh(\beta e\psi) + C_{\mathrm{d}}\mu\vec{\nabla}\cdot\left[\left(\frac{\vec{\nabla}\psi}{|\vec{\nabla}\psi|}\right)\boldsymbol{G}(\beta\mu|\vec{\nabla}\psi|)\right] \tag{20}$$

where ψ is the electric potential, C_s is the salt concentration, $\mathbf{G}(u) = \cosh(u)/u - \sinh(u)/u^2$. For weak electric potential, one can expand the function $\mathbf{G}$ to first order and obtain

$$(\epsilon + \beta S_{xx}^0)\nabla^2\psi = 2C_S e \sinh(\beta e\psi) \tag{21}$$

where $\beta = 1/(k_{\mathrm{B}}T)$. It becomes obvious from the above equation that the effect of dipolar interactions on the electrostatics is the renormalization of dielectric constant. This renormalization of dielectric permittivity is exactly the linear response theory of dipoles related to fluctuations of the dipole moments.[13,14]

The effective interaction between polyions derived above using Gaussian approximation is equivalent to polar solvent-mediated interaction in electrolyte solution. Such a mean-field approximation is applicable to semidilute polyelectrolyte solution because, apart from the interactions being long ranged, the density fluctuations of monomers are also small, especially for large concentrations and gels. In such mean-field approximation, the charge correlation is neglected as usual. Furthermore, the local dielectric heterogeneity near the polymer segments is neglected.

The charge density created by a point dipole $\vec{\mu}$ at point $\vec{r}_0$ is given by $\hat{\rho}_{\mathrm{d}}(\vec{r}) = -\vec{\mu}\cdot\vec{\nabla}\delta(\vec{r} - \vec{r}_0)$.[20] Then the microscopic density operators for dipoles can be defined as

$$\hat{\rho}(\vec{r}) = -\sum_{i=1}^{n_{\mathrm{d}}} \mu_i^\alpha \nabla_\alpha \delta(\vec{r} - \vec{r}_i) \tag{22}$$

which in Fourier space is directly related to our density operators for dipolar moments

$$\hat{\rho}(\vec{q}) = -\sum_{i=1}^{n_d} \mu_i^{\alpha}(iq_{\alpha})e^{i\vec{q}\cdot\vec{r}_i} = -iq_{\alpha}\phi_{\mu}^{\alpha}(\vec{q}) \qquad (23)$$

III. Effective Hamiltonian of Dipolar Chains in Dipolar Solvent

In this section, we derive the effective Hamiltonian of dipolar chains in dipolar solvent. Using the similar approach as shown in ref 23, for dipolar chains, we can invoke the following density operators with $\hat{\rho}(\vec{q})$ for monomer and $\hat{u}_{\alpha}(\vec{q})$ for dipolar moments along the bond vector $\vec{b}_s^m$ of the segment s of mth polymer chain:

$$\hat{\rho}(\vec{q}) = \sum_{m=1}^{n_p}\sum_{s=1}^{N} e^{i\vec{q}\cdot\vec{R}_s^m}, \quad \hat{u}_{\alpha}(\vec{q}) = \sum_{m=1}^{n_p}\sum_{s=1}^{N} \frac{(b_s^m)_{\alpha}}{b} e^{i\vec{q}\cdot\vec{R}_s^m} \qquad (24)$$

where b is the bond length and α corresponds to either x, y, or z. Then the dipolar–dipolar interaction between the directed bond vectors can be expressed in following collective variables:

$$\frac{V_{dd}}{k_BT} = \left(\frac{4\pi\lambda_B\mu^2}{e^2}\right)\left(\frac{q_{\alpha}q_{\beta}}{q^2}\right)\hat{u}_{\alpha}(\vec{q})\ \hat{u}_{\beta}(-\vec{q}) \qquad (25)$$

where μ is the magnitude of dipolar moment along the monomer segment and λ_B is defined in terms of the effective permittivity of the system composed of dipolar chains and dipolar solvent. In section II, we have explicitly demonstrated the effect of dipolar solvent amounts to renormalization of dielectric permittivity of the medium. In this section, we would like to treat dipolar chains implicitly using the effective permittivity of the medium, without invoking the dipolar interactions of dipolar solvent molecules explicitly in the partition function and Hamiltonian. In doing so, the mathematical manipulations in deriving the effective Hamiltonian of dipolar chains in dipolar solvent is simplified. Nevertheless, the physics of dipolar solvent should be unalterred from that shown in section II.

Similar to the derivations in ref 23, the Jacobian can be expressed as follows:

$$J = \int \prod_{\vec{q}\neq 0}\prod_{\alpha} D\phi(\vec{q})D\eta^{\alpha}(\vec{q})\ \exp[i\sum_{\vec{q}\neq 0}\phi(\vec{q})\rho(-\vec{q}) + i\sum_{\vec{q}\neq 0}\eta^{\alpha}(\vec{q})u_{\alpha}(-\vec{q})]\ \exp\left[-\frac{1}{2}\sum_{\vec{q}\neq 0}S^0(\vec{q})\phi(\vec{q})\phi(-\vec{q}) - \frac{1}{2}\sum_{\vec{q}\neq 0}G_{\alpha\beta}^0(\vec{q})\eta^{\alpha}(\vec{q})\eta^{\beta}(-\vec{q}) - \sum_{\vec{q}\neq 0}P_{\alpha}^0(\vec{q})\phi(\vec{q})\eta^{\alpha}(-\vec{q})\right] \qquad (26)$$

with

$$G_{\alpha\beta}^0 = \delta_{\alpha\beta}\left(\frac{n_pN}{3V}\right), \quad S^{\circ}(\vec{q}) = \left(\frac{n_p}{V}\right)\sum_{m,n}\exp[-b^2q^2(m-n)/6] \qquad (27)$$

and

$$P_{\alpha}^0 = iq_{\alpha}D^0(\vec{q}), \quad D^0(\vec{q}) = \left(\frac{n_pb}{3V}\right)\sum_{m>n}\exp[-b^2q^2(m-n)/6] \qquad (28)$$

In eq 26, the fields $\phi(\vec{q})$ and $\eta^{\alpha}(\vec{q})$ are conjugate to the density fields $\rho(\vec{q})$ and $u_{\alpha}(\vec{q})$, respectively. After performing multiple Gaussian integrals, the Jacobian can be simplified as

$$J = \exp\left[-\frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{G^0(\vec{q})}{\Delta S^0(\vec{q})}\right]\rho(\vec{q})\rho(-\vec{q}) - \frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{\delta_{\alpha\beta}}{G^0(\vec{q})} + \frac{q_{\alpha}q_{\beta}(D^0(\vec{q}))^2}{G^{\circ}(\vec{q})\Delta S^{\circ}(\vec{q})}\right]u_{\alpha}(\vec{q})u_{\beta}(-\vec{q}) + \sum_{\vec{q}\neq 0}\left[\frac{iD^0(\vec{q})q_{\alpha}}{\Delta S^{\circ}(\vec{q})}\right]u_{\alpha}(\vec{q})\rho(-\vec{q})\right] \qquad (29)$$

with

$$G^0(\vec{q}) = \frac{n_pN}{3V}, \quad \Delta S^0(\vec{q}) = S^0(\vec{q})G^0(\vec{q}) - q^2[D^0(\vec{q})]^2 \qquad (30)$$

Then the total effective Hamiltonian after plugging in the contribution from the Jacobian becomes

$$\frac{H}{k_BT} = \frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{G^0(\vec{q})}{\Delta S^0(\vec{q})} + v\right]\rho(\vec{q})\rho(-\vec{q}) + \frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{\delta_{\alpha\beta}}{G^0(\vec{q})} + \frac{(D^0(\vec{q}))^2q_{\alpha}q_{\beta}}{G^0(\vec{q})\Delta S^0(\vec{q})} + \left(\frac{4\pi\lambda_B\mu^2}{e^2q^2}\right)q_{\alpha}q_{\beta}\right]u_{\alpha}(\vec{q})u_{\beta}(-\vec{q}) - \sum_{\vec{q}\neq 0}\left[\frac{iD^0(\vec{q})q_{\alpha}}{\Delta S^0(\vec{q})}\right]u_{\alpha}(\vec{q})\rho(-\vec{q}) \qquad (31)$$

where v is the second virial coefficient. The degree of freedoms due to diplar interactions can be integrated out by performing triple Gaussian integrals for the partition function, resulting in the following effective Hamiltonian in terms of monomer density field $\rho(\vec{q})$ only:

$$\frac{H}{k_BT} = \frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{G^0(\vec{q})}{\Delta S^0(\vec{q})} + v - \frac{(D^0(\vec{q}))^2q^2}{\Delta S^0(\vec{q})[S^0(\vec{q}) + (4\pi\lambda_B\mu^2/e^2)\Delta S^0(\vec{q})]}\right]\rho(\vec{q})\rho(-\vec{q}) \qquad (32)$$

The effective Hamiltonian shown in the above equation is identical to that shown in eq 3.22 of ref 23, except that G^0 in the present study which explicitly takes into account the dipolar–dipolar interactions between dipolar moments along the polymer chains is one-third of that in ref 23 and the interaction term $4\pi\lambda_B\mu^2/e^2$ replaces $J(\vec{q})$ in ref 23. It is of interest to examine the net effect from dipolar interactions by comparing the effective Hamiltonian with the bare Hamiltonian:

$$\frac{H_0}{k_BT} = \frac{1}{2}\sum_{\vec{q}\neq 0}\left[\frac{1}{S^0(\vec{q})} + v\right]\rho(\vec{q})\rho(-\vec{q}) \qquad (33)$$

The net effect can be easily obtained as follows:

$$\frac{\Delta H}{k_BT} = \frac{H - H_0}{k_BT} = \frac{1}{2}\sum_{\vec{q}\neq 0} \times \left[\frac{[D^0(\vec{q})]^2q^2}{[S^0(\vec{q})]^2}\ \frac{[4\pi\lambda_B\mu^2/e^2]}{1 + [4\pi\lambda_B\mu^2/e^2][\Delta S^0(\vec{q})/S^0(\vec{q})]}\right]\rho(\vec{q})\rho(-\vec{q}) \qquad (34)$$

Using the fact $D^0(\vec{q}) = (n_pN/V)bNf_D(qR_g)/6$, where $f_D(qR_g)$ is the Debye function with R_g the radius of gyration, the term $\Delta S^0(\vec{q})/S^0(\vec{q})$ inside the denominator of the second term in the above equation can be explicitly written as

$$\frac{\Delta S^0(\vec{q})}{S^0(\vec{q})} = \left(\frac{n_pN}{3V}\right)\left[1 - \frac{q^2b^2Nf_D(qR_g)}{12}\right] \approx \left(\frac{n_pN}{3V}\right)f_D(qR_g) \qquad (35)$$

where $f_D(qR_g)$ is assumed to be of the simple form of $1/(1 + q^2R_g^2/2)$. Then eq 34 can be simplified as

$$\frac{\Delta H}{k_BT} = \frac{1}{2}\sum_{\vec{q}\neq 0}\left[\left(\frac{q^2b^2}{36}\right)\frac{4\pi\lambda_B\mu^2/e^2}{1 + [4\pi\lambda_B\mu^2/e^2](\rho_m/3)f_D(qR_g)}\right]\rho(\vec{q})\rho(-\vec{q}) \qquad (36)$$

where we have defined $\rho_m = (n_pN)/V$, which is the momoner density of the system. Therefore, the net effect due to dipolar interactions along the chains amounts to $\Delta H > 0$. It can be easily seen from the above equation that, in the limit of $\vec{q} \to 0$, $\Delta H \to 0$. Also, note, as $\mu \to 0$, $\Delta H \to 0$.

It is obvious, compared to concentrated neutral polymer solution, the scattering intensity of dipolar chains in concentrated dipolar solvent is reduced due to the increase of effective interactions from the contribution of dipolar moments along the chains. Similar to neutral chains in solution, the scattering intensity of dipolar chains in dipolar solvent decreases monotonically with the increase of wavenumber q.

IV. Scattering Properties of Dipolar Gels

Rabin and Panyukov have developed a phenomenological theory for neutral gels and also extended it to weakly charged gels, where the second virial coefficients in both the state of preparation and the final state are replaced by effective virial coefficients which include the electrostatic contributions.[9,10] In the study of the scattering properties of gels made by randomly cross-linking dipolar chains with dipolar moments along the polymer backbones, we can also make such replacement of the second virial coefficients by effective virial coefficients including the net contribution of dipolar chains shown in eq 36.

The structure factor consists of two parts: one due to thermal fluctuations and the other due to static density inhomogeneities

$$S(\vec{q}) = \overline{\langle \rho(\vec{q})\ \rho(-\vec{q}) \rangle} = G(\vec{q}) + C(\vec{q}) \tag{37}$$

where $\rho(\vec{q}) = \rho^{\mathrm{eq}}(\vec{q}) + \rho^{\mathrm{th}}(\vec{q})$ and

$$G(\vec{q}) = \langle \rho(\vec{q})\ \rho(-\vec{q}) \rangle = \langle \rho^{\mathrm{th}}(\vec{q})\ \rho^{\mathrm{th}}(-\vec{q}) \rangle, \quad C(\vec{q}) = \overline{\rho^{\mathrm{eq}}(\vec{q})\ \rho^{\mathrm{eq}}(-\vec{q})} \tag{38}$$

where $\rho^{\mathrm{eq}}(\vec{q})$, $\rho^{\mathrm{th}}(\vec{q})$, and $\rho(\vec{q})$ are the Fourier components of the equilibrium monomer density fluctuations, of the thermal density fluctuations, and of the total density fluctuations. In the above equations, overbar denotes structure (ensemble) average, and bracket denotes thermal average. Please note $\langle \rho^{\mathrm{eq}}(\vec{q}) \rangle \neq 0$ and $\overline{\rho^{\mathrm{eq}}(\vec{q})} = 0$. For neutral gels,the thermal correlator and static correlator are defined as

$$G(\vec{q}) = \frac{a^{-3}\phi\overline{N}g(\vec{q})}{1 + w(\vec{q})\ g(\vec{q})} \tag{39}$$

$$C(\vec{q}) = \frac{a^{-3}\phi\overline{N}}{[1 + w(\vec{q})\ g(\vec{q})]^2(1+Q^2)^2} \times \left[6 + \frac{9}{w^{(0)}_{\lambda*\vec{q}} - 1 + ({Q_{\|}}^2\lambda^2 + {Q_{\perp}}^2/\lambda)(\phi_{\mathrm{prep}}/\phi)^{2/3}{\phi_{\mathrm{prep}}}^{-1/4}/2}\right] \tag{40}$$

where $\bar{N}$ denotes average degree of polymerization between cross-link points; ϕ_{prep} and ϕ denote the monomer volume fractions in the state of preparation and the final state, respectively; $Q = a\bar{N}^{1/2}q$ is the dimensionless wave vector (a is the monomer size); $Q_{\|}$ and $Q_{\perp}$ denote the projections of the wave vector along and normal to the stretching direction, respectively; λ is the stretching ratio; the function $g(\vec{q})$ for gels in Θ or poor solvents is

$$g(\vec{q}) = \frac{1}{Q^2/2 + (4Q^2)^{-1} + 1} + \frac{2Q^2\phi^{2/3}{\phi_{\mathrm{prep}}}^{-5/12}}{(1+Q^2)^2({Q_{\|}}^2\lambda^2 + {Q_{\perp}}^2/\lambda)} \tag{41}$$

As in refs 9 and 10, we consider dipolar gels prepared in a good solvent and studied in a Θ or poor solvent. From eq 36, the dimensionless interaction parameters including dipolar interactions from dipolar polymer segments in the state of preparation and in the final state respectively can be easily obtained as

$$w^{(0)}_{\lambda*\vec{q}} = {\phi_{\mathrm{prep}}}^{5/4}\overline{N} + \left[\frac{({Q_{\|}}^2\lambda^2 + {Q_{\perp}}^2/\lambda)(\phi_{\mathrm{prep}}/\phi)^{5/12}}{36}\right] \times \frac{4\pi\lambda^0_{\mathrm{B}}\mu^2\phi_{\mathrm{prep}}/a^3/e^2}{1 + [4\pi\lambda^0_{\mathrm{B}}\mu^2\phi_{\mathrm{prep}}/a^3/e^2]/[1 + ({Q_{\|}}^2\lambda^2 + {Q_{\perp}}^2/\lambda)(\phi_{\mathrm{prep}}/\phi)^{5/12}/12]/3} \tag{42}$$

$$w(\vec{q}) = (1 - 2\chi + \phi)\phi\overline{N} + \left(\frac{Q^2}{36}\right)\frac{4\pi\lambda_{\mathrm{B}}\mu^2\phi/a^3/e^2}{1 + [4\pi\lambda_{\mathrm{B}}\mu^2\phi/a^3/e^2]/[1 + Q^2/12]/3} \tag{43}$$

where χ is the Flory−Huggins interaction parameters. Note in the above two equations the Bjerrum lengths λ^0_{B} and λ_{B} are defined in terms of the effective dielectric permittivities of the dipolar solvents in the state of preparation and the final observation state, respectively. Please further note in the above two equations the dimensionless interaction parameters are obtained by nondimensionalization of the interaction parameters with $\bar{\rho}^{(0)}\bar{N}$ and $\bar{\rho}\bar{N}$, respectively, where $\bar{\rho}^{(0)} = \phi_{\mathrm{prep}}a^{-3}$ and $\bar{\rho} = \phi a^{-3}$. As elaborated in refs 8 and 9 in good solvent, where strong thermal fluctuations lead to the breakdown of the mean field, the well-known de Gennes blob picture of semidilute solutions and renormalization group are adopted. On length scales smaller than the correlation length (i.e., blob size), density flucutations are large and the gel behaves as a polymer solution. On scales larger than the blob size, density fluctuations are smaller, and the mean-field description can be used with appropriately renormalized parameters. In Θ and poor solvents, there is no renormalization of monomer size, and the third virial coefficient $\bar{\rho}a^6$ is introduced.

It can be easily seen that the modified interactions parameters in eqs 42 and 43 are both larger than their respective counterparts for neutral gels. From eqs 39 and 40, it is obvious that the contributions to scattering intensities from both thermal fluctuations and static density inhomogeneities in dipolar gels are reduced compared to neutral gels. Furthermore, the static correlation is suppressed more than thermal correlation because of the quadratic form involving $w(\vec{q})$ in the denominator in eq 40 as opposed to the linear form involving $w(\vec{q})$ in the denominator in eq 39. It should also be noted, similar to the behavior of neutral gels, the scattering intensities for both thermal fluctuations and static inhomogeneities in dipolar gels decrease monotonically with increasing wavenumber q. In Figure 2, a comparison of correlators for neutral gels and dipolar gels is displayed, with the lowest two broken curves corresponding to thermal correlators, the two middle broken curves corresponding to static correlators, and the uppermost two solid lines for total structure factors, among which the lower ones in each of these three sets of curves are for dipolar gels. As expected, from Figure 2 it can be easily seen that both thermal and static correlations for dipolar gels are suppressed compared to those for neutral gels, and static correlation is suppressed

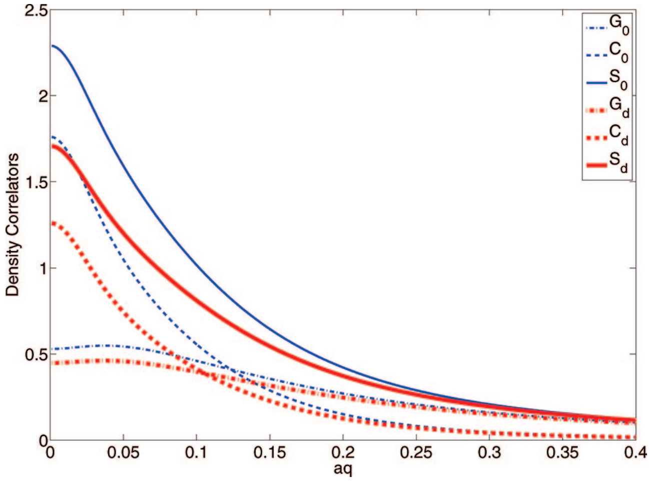

Figure 2. Comparison of correlators for neutral gels (thin blue) and dipolar gels (thick red) prepared in a good solvent and observed in a Θ solvent. $\phi_{\mathrm{prep}} = \phi = 0.1$, $\lambda = 1$, $\bar{N} = 100$, $\mu = 1.85D$, $a = 3A$, $\epsilon = 10\epsilon_0$ in both initial and final states.

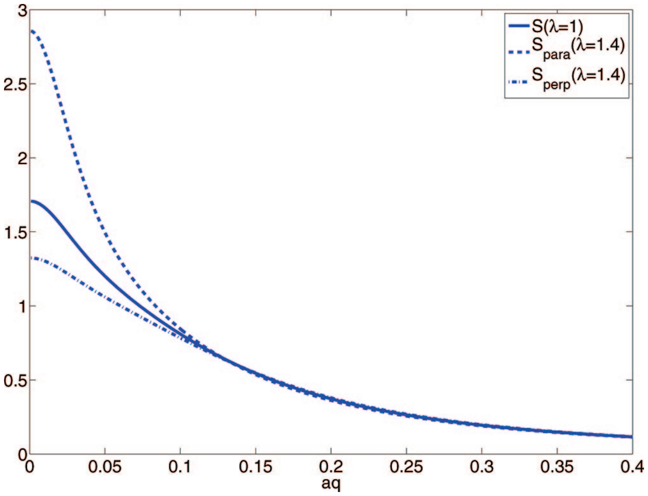

Figure 3. Angular-dependent structural factors of a uniaxially deformed gels ($\lambda = 1.4$), along (S_{para}) and normal to (S_{perp}) the stretching axis. The structure factor of the corresponding unstretched dipolar gel (solid line) is shown for comparison. Other parameters are the same as those in the previous figure.

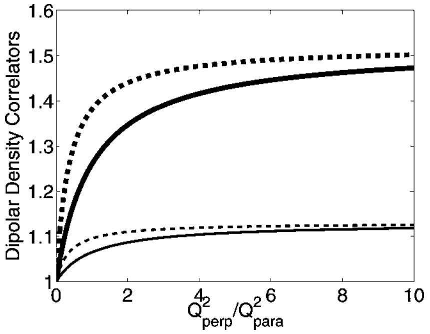

Figure 4. Plots of dipolar density correlators along the stretching direction $O_{||}$ of an uniaxially deformed gels ($\lambda = 1.4$) vs $Q_{\perp}^2/Q_{||}^2$. The thinner lines correspond to the same parameters as in Figure 2 with solid thinner line corresponding to unstretched state and broken thinner line corresponding to stretched state. The thicker lines correspond to larger volume fraction and smaller dielectric permittivity with $\phi = 0.2$ and $\epsilon = 5\epsilon_0$. The solid thicker line is for the unstretched state.

more than its thermal counterpart. Furthermore, at large wave-number, the various correlators for dipolar gel approach their neutral gel counterparts. In Figure 3, the total structure factors are plotted for a uniaxially stretched dipolar gel with stretching ratio of 1.4. At small q, the scattering intensity parallel to the stretching direction becomes larger than that for an undeformed dipolar gel, and the situation is reversed in the direction normal to the stretching axis. At large q limit, all the curves coincide with each other. The scattering properties for uniaxially stretched dipolar gel shown in Figure 3 are similar to those for neutral gels.

The orientational ordering of dipolar moments on the polymer chains under uniaxial stretching is of particular interest. This can be studied through the analysis of the effective screened potential $\langle \eta^{\alpha}(\vec{q})\eta^{\beta}(\vec{q})\rangle$ or the dipolar density correlator $\langle u_{\alpha}(\vec{q})u_{\beta}(-\vec{q})\rangle$, where the bracket denotes thermal average using Hamiltonian $H[\eta^{\alpha}(\vec{q})]$ and $H[u_{\alpha}(\vec{q})]$, respectively. Because the coefficient matrix $\mathbf{M}$ of $\mathbf{u}^{\mathrm{T}}\cdot\mathbf{M}\cdot\mathbf{u}$ is singular as can be seen from eq 25, where $\mathbf{u}$ is the vector representation of the dipolar density field, it is more appropriate to investigate the behaviors of dipolar density correlator $\langle u_{\alpha}(\vec{q})u_{\beta}(-\vec{q})\rangle$. The Hamiltonian involving dipolar density field $u_{\alpha}(\vec{q})$ only can be easily obtained by integrating out the monomer density field $\rho(\vec{q})$ in eq 31. The matrix element of the coefficient matrix $\mathbf{A}$ in the resulting Hamiltonian is shown below:

$$\mathbf{A}_{\alpha\beta} = \frac{\delta_{\alpha\beta}}{G^0(\vec{q})} + \frac{(D^0(\vec{q}))^2 \upsilon q_{\alpha} q_{\beta}}{G^0(\vec{q})[G^0(\vec{q}) + \upsilon \Delta S^0(\vec{q})]} + \left(\frac{4\pi\lambda_{\mathrm{B}}\mu^2}{e^2 q^2}\right) q_{\alpha} q_{\beta} \tag{44}$$

Then the dipolar density correlators can be easily obtained as the matrix elements of the inverse matrix of $\mathbf{A}$. For example

$$\langle u_z(\vec{q})\, u_z(-\vec{q})\,\rangle = G^0(\vec{q})\left[\frac{1/G^0(\vec{q}) + D({q_x}^2 + {q_y}^2)}{1/G^0(\vec{q}) + D({q_x}^2 + {q_y}^2 + {q_z}^2)}\right] \tag{45}$$

and

$$\langle u_y(\vec{q})\, u_z(-\vec{q})\,\rangle = -G^0(\vec{q})\left[\frac{D q_y q_z}{1/G^0(\vec{q}) + D({q_x}^2 + {q_y}^2 + {q_z}^2)}\right] \tag{46}$$

with

$$D = \frac{\upsilon \overline{N}^2 a^2}{4[(1 + \overline{N} q^2 a^2/12)^2 + \upsilon(\phi/a^3)\overline{N}]} + \frac{4\pi\lambda_{\mathrm{B}}\mu^2}{e^2 q^2} \tag{47}$$

Other matrix elements can be obtained by permutation of indices. Assuming the dipolar gel is studied under uniaxial stretching in Θ solvent (setting $\upsilon = 0$), the dipolar density correlator for the dipolar density component along the stretching direction $O_{||}$ before stretching can be easily obtained as

$$O_{||} = \left[\frac{\phi/a^3}{3 + (4\pi\lambda_{\mathrm{B}}\mu^2\phi/a^3/e^2)}\right]\left[1 + \left(\frac{4\pi\lambda_{\mathrm{B}}\mu^2\phi}{3a^3e^2}\right)\frac{{Q_{\perp}}^2}{{Q_{\perp}}^2 + {Q_{||}}^2}\right] \tag{48}$$

After stretching with stretching ratio of $\lambda > 1$, the dipolar density correlator $O_{||}$ changes to

$$O_{||}^{\lambda} = \left[\frac{\phi/a^3}{3 + (4\pi\lambda_{\mathrm{B}}\mu^2\phi/a^3/e^2)}\right]\left[1 + \left(\frac{4\pi\lambda_{\mathrm{B}}\mu^2\phi}{3a^3e^2}\right)\frac{{Q_{\perp}}^2\lambda}{{Q_{\perp}}^2\lambda + {Q_{||}}^2/\lambda^2}\right] \tag{49}$$

It is obvious that $O_{||}^{\lambda}$ is larger than $O_{||}$, indicating enhanced orientational ordering of dipolar moments on the polymer chains along the stretching direction. In Figure 4, a comparison of the dipolar density correlator $O_{||}$ before and after uniaxial stretching is displayed. It can be seen from the figure, after uniaxial stretching, the intensities of dipolar density correlation along the stretching direction are enhanced at nonzero $Q_{\perp}^2/Q_{||}^2$. In the large $Q_{\perp}^2/Q_{||}^2$ limit, the effect of orientational ordering of dipolar density field diminishes. Furthermore, as the dipolar effect gets stronger (i.e., larger μ, ϕ, λ_{B} and smaller a), the increase of orientational ordering of dipolar density field becomes larger as can be seen from the thicker lines in the figure.

The situation at other solvent quality (i.e., $\upsilon \neq 0$) is more complicated. We can study the orientational ordering of dipolar moments on polymer chains upon uniaxial stretching by checking the change of dipolar density correlator $O_{||}$ after infinitely small stretching with $\lambda = 1 + \delta\lambda$. Using Taylor expansion, after some algebra, the change of dipolar density correlator is found to be $\delta O_{||} \cong B\delta\lambda$ with the sign determining part of B:

$$\begin{aligned} B \propto \upsilon\overline{N}\left[\left(\frac{\phi}{a^3}\right)\upsilon\overline{N}{Q_{\perp}}^2 + 4(1 + Q^2/12)({Q_{\perp}}^2 - 2{Q_{||}}^2)\right]Q^4 + \\ 8\upsilon\overline{N}\left[(1+Q^2/12)^2 + \left(\frac{\phi}{a^3}\right)\upsilon\overline{N}\right]\left[\left(\frac{4\pi\lambda_{\mathrm{B}}\mu^2\phi}{a^3e^2}\right){Q_{\perp}}^2 - Q^2\right]Q^2 + \\ 48\left(\frac{4\pi\lambda_{\mathrm{B}}\mu^2}{e^2}\right)\left[(1+Q^2/12)^2 + \left(\frac{\phi}{a^3}\right)\upsilon\overline{N}\right]2\left[\left(\frac{4\pi\lambda_{\mathrm{B}}\mu^2\phi}{3a^3e^2}\right) + 1\right]{Q_{\perp}}^2 \end{aligned} \tag{50}$$

Because there are quite a few parameters involved in the above expression, we do not further pursue the details governing the sign of the above expression. Nonetheless, from the two terms involving minus sign in the first and second lines of eq 50, it is obvious that, for relatively large dipolar effect, in the region with $Q_\perp^2$ comparable to or larger than $Q_\parallel^2$, there is enhanced orientational ordering of dipolar density field along the stretching direction.

The scattering properties of dipolar gels elucidated in the present study can be compared with those for ferrogels studied by Jarkova,[18] where it is assumed the polymer segments interact with each other via dipolar interactions, same as the dipolar interactions in the present study. For the ferrogels, in the case of $J < 0$ corresponding to repulsive interactions between polymer segments, the scattering intensity decreases monotonically with the increase of wavenumber q, which is exactly the same as that in the present study. Note that the interaction parameter $4\pi\lambda_B\mu^2/e^2$ in the present study corresponds to $-J(\vec{q})$ in ref 18. Then, the case $J > 0$ in ref 18 without external magnetic field becomes unphysical because both studies adopt the same kind of field-theoretical approach and random phase approximation (RPA), except that how the statistical mechanics of cross-linking is handled differs in the present study and in ref 18. For both un-cross-linked dipolar melt and ferromelt, the scattering intensity decreases monotonically with increasing of wavenumber q. Also, the case $J > 0$ for the ferromelt in ref 18 in no external magnetic field is unphysical. In the absence of external electric field for dipolar gels or magnetic field for ferrogels, on large length scale (globally), the dipolar interaction is much weaker than thermal energy k_BT as can be seen by comparing dipolar energy $n\cdot(\vec{E}\cdot\vec{\mu})$ vs k_BT, where n is the number of dipolar moments of one dipolar chain (same as degree of polymerization N, assuming $N \approx 10^3$). For polymer segment with the same magnitude of dipolar moment as that of water, the electric field needs to be as high as 10^6 V/m in order for dipolar energy to become roughly the same as thermal energy at room temperature. Therefore, the anticipated preferred alignment of dipolar moments in the absence of external magnetic field in ref 18 cannot be realized globally, although some local preferred alignment of dipolar moments is possible.

V. Conclusions

In this work, the scattering properties of dipolar gels made by randomly cross-linking dipolar chains with dipolar moments aligned along the polymer segments in dipolar solvent is studied using combined field-theoretical and phenomenological approaches. First, we use field-theoretical approach to study the effect of dipolar solvent on the electrostatics of semidilute polyelectrolyte solutions. By decomposing the dipole moments into Cartesian components, the Edwards Hamiltonian is obtained on the basis of collective density variables. For semidilute polyelectrolyte solution, after integrating out the degree of freedom from dipolar solvent molecules, it is found the Coulomb interactions among polyions and mobile ions are reduced, resulting in the renormalization of dielectric constant for the medium. This result regarding the electrostatic effect of dipolar solvent is consistent with a newly proposed dipolar Poisson–Boltzmann equation, which is also obtained using field-theoretical approach. Because our field-theoretical approach uses Gaussian fields, the nonlinearity of the electrostatics is lost.

Second, we use field-theoretical approach and bond vector representation of dipolar chain to derive the effective Hamiltonian of dipolar chains in dipolar solvent. The effect of dipolar solvent is taken into account implicitly here using the effective permittivity of the medium as elucidated in the study of the effect of dipolar solvent in semidilute polyelectrolyte solution, which simplifies the mathematical manipulations. After integrating out the degree of freedoms due to dipolar moments along the polymer backbones, it is found the effective interaction is increased compared to ordinary neutral chains. The net contribution from the dipolar moments along the chains $\Delta H \rightarrow 0$ as the magnitude of dipolar moment along polymer segment $\mu \rightarrow 0$. Also, as wavenumber $q \rightarrow 0$, $\Delta H \rightarrow 0$. Compared to concentrated neutral polymer solution, the scattering intensity of dipolar chains in dipolar solvent is reduced due to the increase of effective interactions from the contribution of dipolar moments along the chains. Similar to neutral chains in solution, the scattering intensity of dipolar chains in dipolar solvent decreases monotonically with the increase of wavenumber q, in contrast to the behavior of polyelectrolyte chains in dipolar solvent where there is a maximum of intensity at finite wavenumber q.

Finally, the scattering properties of dipolar gels permeated with dipolar solvent is studied using the phenomenological theory developed in ref 9. In the scattering functions for neutral gels, the second virial coefficient can be replaced by the sum of second virial coefficient and the net contribution to interaction potential due to dipolar moments along polymer segments, leading to the scattering functions for dipolar gels. The increase of the effective second virial coefficients in the state of preparation and the state of observation in dipolar gels leads to suppression of both thermal density fluctuations and static density inhomogeneities. Also similar to neutral gels, the scattering intensity of dipolar gels decreases monotonically with the increase of wavenumber q. For uniaxially stretched dipolar gels, similar to neutral gels, the scattering intensity is enhanced along the direction of stretching. Furthermore, in the direction parallel to the stretching direction, it is found there is enhanced orientational ordering of dipolar density field in Θ solvent. As the dipolar effect gets stronger, the enhancement of orientational ordering gets bigger.

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