Semiflexible Polyelectrolytes at the Liquid-Crystal Phase Transition

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ABSTRACT: The statistical properties of semiflexible polyelectrolytes at the isotropic–nematic phase transition are studied by including the twisting term originating from the electrostatic interaction between polymer segments in the free energy. Since the twisting effect is very small, we perform a perturbation calculation that can be used to determine the linear corrections to the isotropic and nematic densities at the phase transition. We also estimate the higher-order corrections using a numerical approach.

1. Introduction

Semiflexible polyelectrolytes are charged polymer chains that interact with each other through the repulsive electrostatic interaction in addition to other types of interactions existing between their neutral, uncharged counterparts. It has been observed experimentally that the solutions of polyelectrolytes, such as the aqueous solutions of DNA molecules and xanthan molecules and colloidal suspensions of filamentous bacteriophage, undergo an isotropic–cholesteric phase transition to form an orientationally ordered phase at high densities; a few examples of recent experiments are given in refs 1–14. The properties of the isotropic–cholesteric phase transition should be similar to those of the isotropic–nematic phase transition in more conventional polymer systems. To understand the phase transition occurring in these systems, theoretical models[15-23] have been developed to account for both the electrostatic and excluded-volume interactions. The latter is thought to be the main mechanism that causes neutral lyotropic polymers to form a liquid crystal phase.[15,24-30]

Theoretical calculations predict[15-23] that the electrostatic interaction may affect the thermodynamic properties of the phase transition in three respects. First, because of the repulsive nature of the interaction, the diameter D of the semiflexible filaments, used to characterize the strength of the excluded-volume interaction, must be effectively enlarged. This implies that in writing down a statistical model that only contains the excluded-volume interaction, D should be replaced by an effective diameter D_{eff}, to account for the electrostatic interaction effectively. The expression for D_{eff} in terms of D, κ^{-1} (the Debye–Hückel screening length for a polyelectrolyte in a solution with added salt), and ν (the linear charge density of the polyelectrolyte) was first calculated by Onsager[15] and later examined by Stroobants et al.[18] Although the original derivation was intended for polyelectrolyte rods, the generalization is simple to model semiflexible polyelectrolyte chains. The most significant electrostatic effect is the decreasing of the transition density ρ_{nem} because it is expected that the rescaled transition density $\rho_{\mathrm{nem}}L^2D_{\mathrm{eff}}$ has a universal value for polymers with $L \gg D_{\mathrm{eff}}$. Here, L is the total contour length of the polymer chains. Several experiments in different systems have verified this expectation.

Second, accurate to the second virial coefficient approximation, the effect of charge produces a twisting term in the free energy that favors a perpendicular rather than parallel relative orientation between two polyelectrolyte segments. This term can be written in terms of the relative angle between the two segments and a twisting coefficient $h = (\kappa D_{\mathrm{eff}})^{-1}$. The twisting effect on the phase transition, however, is theoretically estimated to be a weaker one. For the twisting parameter h ranging between [0, 0.5], Stroobants et al.[18] have obtained numerical solutions of the Onsager model for rigid polyelectrolyte rods, revised to include the twisting term. Furthermore, they have also devised a perturbation theory using Onsager's trial-function approximation,[15] to verify the initial slopes of the determined quantities as functions of h. The numerical solutions[31] as well as the perturbation results[19] were also obtained for flexible chains modeled by including the twisting term in the Khokhlov–Semenov free energy.[32,33] Here, the flexible-chain limit is defined as the limit when the total contour length L is much greater than the Kuhn length l: $L \gg l$. For most real systems, however, the polymer chains are semiflexible; i.e., L is comparable with l.[34,35] In this paper, we generalize our previous numerical approach[36] to solve the mean-field model of the isotropic–nematic phase transition for semiflexible neutral chains to find the numerical solution of the model including the twisting term. A perturbation theory is also developed to solve the phase-equilibrium and free-energy-minimization condition for a weak h.

Third, it has been shown that the repulsion between segments of the same polyelectrolyte chain enhances the persistence length. For a semiflexible polyelectrolyte chain, the problem can be quite complex: we can show that the enhancement is actually path-dependent by generalizing the Skolnick–Fixman calculation[17] for a flexible chain to the semiflexible case. Fortunately, this effect is expected to be quite weak in the systems that interest us here and thus can be neglected.

Finally, because of the redistribution of mobile ions, the electrostatic potential in solution depends on the polyelectrolyte concentration through the Debye–Hückel screening length κ^{-1}. Therefore, κ^{-1} is different for the

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isotropic and liquid crystal phases.[7,22] This dependence is not considered in this paper.

2. Free Energy

Let $f(\Omega)$ be the orientational distribution function of the polymer segment, averaged with respect to the contour coordinate along the chain, where Ω is the solid angle specifying the direction at which the segment points in a three-dimensional space. The free energy of the generalized Onsager model as a functional of $f(\Omega)$ is assumed to be[24]

$$\frac{\beta F}{N} = \ln \frac{4\pi C}{Q} - \int \mathrm{d}\Omega\, \omega(\Omega) f(\Omega) + C\rho[f] + hC\eta[f] \quad (1)$$

where the excluded-volume interaction is represented by

$$\rho[f] = \int\int \mathrm{d}\Omega\, \mathrm{d}\Omega' \,|\sin \gamma| f(\Omega) f(\Omega') \quad (2)$$

and the twisting effect is represented by the last term

$$\eta[f] = \int\int \mathrm{d}\Omega\, \mathrm{d}\Omega' \,[-|\sin \gamma| \ln|\sin \gamma| - |\sin \gamma|(\ln 2 - 1/2)] f(\Omega) f(\Omega') \quad (3)$$

In eq 1, the dimensionless effective number density

$$C = L^2 D_{\mathrm{eff}} N/V \quad (4)$$

is introduced, where N/V is the number of polymer chains per unit volume. The angle between the two unit vectors pointing at the directions specified by the solid angles Ω and Ω' is denoted by γ. Note that the scaling factor $4/\pi$ is absent in our notation compared with that of refs 18, 19, and 31. The total partition function Q of a single polymer chain and the distribution function $f(\Omega)$ can be written as[32,33]

$$Q = \int \mathrm{d}\Omega\, q(t = 1,\Omega) \quad (5)$$

$$f(\Omega) = \frac{1}{Q}\int_0^1 \mathrm{d}t\, q(1 - t,\Omega) q(t,\Omega) \quad (6)$$

where $q(t,\Omega)$ satisfies

$$\frac{\partial q(t,\Omega)}{\partial t} = [\alpha \nabla^2 - \omega(\Omega)] q(t,\Omega) \quad (7)$$

with an initial condition $q(t = 0,\Omega) = 1$. In the above equations, the contour variable t $(0 \le t \le 1)$ denotes the contour coordinate along the chain and the points $t = 0$ and 1 are the two ends of the chain. The quantity $q(t,\Omega)$ is the distribution function of a partial chain of length tL that has the final end (coordinate t) pointing at the direction specified by the solid angle Ω. The flexibility constant α is defined as[36,37]

$$\alpha = L/l \quad (8)$$

with l being the Kuhn statistical segment length. The function $\omega(\Omega)$, representing the mean-field effect of the neighboring chains acting on the chain under consideration, can be obtained self-consistently by minimizing the free energy with respect to the distribution function $f(\Omega)$.[19,32,36] This procedure leads to

$$\omega(\Omega) = \lambda + 2C\int \mathrm{d}\Omega' \,|\sin \gamma| f(\Omega') + 2hC\int \mathrm{d}\Omega' \,[-|\sin \gamma| \ln|\sin \gamma| - |\sin \gamma|(\ln 2 - 1/2)] f(\Omega') \quad (9)$$

where λ corresponds to the Lagrange multiplier associated with the normalization condition

$$\int \mathrm{d}\Omega\, f(\Omega) = 1 \quad (10)$$

Table 1. Coefficients in Eq 14 for C_{I0}, W_0, S_0, C_{I1}, C_{N1}, and S_1

	a_0	a_1	a_2	a_3	b_1	b_2	b_3
C_{I0}	4.1895	26.1020	66.0026	117.846	3.4806	9.0331	0.0000
W_0	0.2737	3.0357	3.0666	10.7859	26.8263	86.7892	143.145
S_0	0.7922	8.8479	11.8593	32.7591	15.6956	34.2650	70.9379
C_{I1}	0.7032	18.25	4.945	38.21	23.89	6.966	50.23
C_{N1}	0.6789	41.16	343.9	336.9	65.95	475.7	485.5
S_1	0.1900	−1.383	2.252	−1.655	15.73	−30.88	29.20

For the isotropic phase, the rescaled pressure can be written as

$$\beta L^2 D_{\mathrm{eff}} P_I(C_I) = C_I + \frac{\pi}{4} C_I^2 \quad (11a)$$

and the rescaled chemical potential

$$\beta \mu_I(C_I) = 1 + \ln C_I + \frac{\pi}{2} C_I \quad (11b)$$

For the nematic phase, the rescaled pressure can be written as

$$\beta L^2 D_{\mathrm{eff}} P_N(C_N) = C_N[1 + (\lambda - \int \mathrm{d}\Omega\, \omega(\Omega) f(\Omega))/2] \quad (12a)$$

and the rescaled chemical potential

$$\beta \mu_N(C_N) = 1 + \ln \frac{4\pi C_N}{Q} - \lambda \quad (12b)$$

where f, ω, and λ are the solutions to eqs 6, 7, 9, and 10 when C_N and α are given. To measure the degree of the orientational order at C_N we define the order parameter to be

$$S = \int \mathrm{d}\Omega\, P_2(\Omega) f(\Omega) \quad (13)$$

Equating the pressure and the chemical potential of the isotropic phase to those of the nematic phase yields the coexistence densities at the phase transition.

For neutral semiflexible polymer chains at the phase transition, $h = 0$, the isotropic density $C_{I0}(\alpha)$, the relative number density difference $W \equiv C_{N0}(\alpha)/C_{I0}(\alpha) - 1$, and the order parameter $S_0(\alpha)$, can be accurately represented by the empirical formula[36]

$$\frac{a_0 + a_1\alpha + a_2\alpha^2 + a_3\alpha^3}{1 + b_1\alpha + b_2\alpha^2 + b_3\alpha^3} \quad (14)$$

where the corresponding numerical coefficients a_i and b_i can be found in Table 1. Here in this paper we use the subscript 0 to denote the physical quantities of the neutral semiflexible polymer chains with effective diameter D_{eff}. They are treated in the next section as the unperturbed, zeroth order approximation in h. Since they were already calculated in ref 36, these zeroth order quantities are assumed to be known throughout this paper.

3. The Linear Correction

If the twisting effect is weak, we can expand the physical properties near $h = 0$ in their Taylor expansions such as

$$C_I(\alpha) = C_{I0}(\alpha)[1 + C_{I1}(\alpha)h + C_{I2}(\alpha)h^2 + C_{I3}(\alpha)h^3 + ...] \quad (15a)$$

$$C_N(\alpha) = C_{N0}(\alpha)[1 + C_{N1}(\alpha)h + C_{N2}(\alpha)h^2 + C_{N3}(\alpha)h^3 + ...] \quad (15b)$$

and

$$S(\alpha) = S_0(\alpha)[1 + S_1(\alpha)h + S_2(\alpha)h^2 + S_3(\alpha)h^3 + ...] \quad (16)$$

In this section, we shall determine the coefficients $C_{I1}(\alpha)$, $C_{N1}(\alpha)$, and $S_1(\alpha)$ using a perturbation scheme.

To the first order in h, we write

$$f(\Omega) = f_0(\Omega) + [f_c(\Omega)C_{N1} + f_h(\Omega)]h \quad (17)$$

$$q(t,\Omega) = q_0(t,\Omega) + [q_c(t,\Omega)C_{N1} + q_h(t,\Omega)]h \quad (18)$$

$$\omega(\Omega) = \omega_0(\Omega) + [\omega_c(\Omega)C_{N1} + \omega_h(\Omega)]h \quad (19)$$

In writing down eqs 17–19, we have further separated the linear term into two terms, one corresponding to the change caused by the change in C_I and C_N from C_{I0} and C_{N0} while the twisting term is formally kept zero, and another corresponding to the change caused by the twisting term while the densities C_I and C_N are forced to their zeroth order values. This separation is not a necessary step in the perturbation calculation, but it has several advantages in carrying out the actual calculation. The correction terms, $f_\kappa(\Omega)$, $\omega_\kappa(\Omega)$, and $q_\kappa(t,\Omega)$, where $\kappa = c, h$, are related self-consistently by

$$f_\kappa(\Omega) = g_\kappa(\Omega) - f_0(\Omega)\int \mathrm{d}\Omega\, g_\kappa(\Omega) \qquad (\kappa = c, h) \quad (20)$$

$$g_\kappa(\Omega) = \frac{2}{Q_0}\int_0^1 \mathrm{d}t\, q_0(1-t,\Omega)q_\kappa(t,\Omega) \qquad (\kappa = c, h) \quad (21)$$

and

$$\frac{\partial q_\kappa(t,\Omega)}{\partial t} = [\alpha\nabla^2 - \omega_0(\Omega)]q_\kappa(t,\Omega) - \omega_\kappa(\Omega)q_0(t,\Omega) \qquad (\kappa = c, h) \quad (22)$$

where $\omega_c(\Omega)$ and $\omega_h(\Omega)$ are given by

$$\omega_c(\Omega) = 2C_{N0}\int \mathrm{d}\Omega'\, |\sin\gamma|[f_0(\Omega') + f_c(\Omega')] \quad (23a)$$

$$\omega_h(\Omega) = 2C_{N0}\int \mathrm{d}\Omega'\, |\sin\gamma|[(-\ln|\sin\gamma| - \ln 2 + 1/2)f_0(\Omega') + f_h(\Omega')] \quad (23b)$$

These equations result from a perturbation expansion of eqs 5–7 and 9. Once $f_c(\Omega)$ and $f_h(\Omega)$ become available by solving eqs 20–23, from the equilibrium conditions we can easily obtain C_{I1} and C_{N1},

$$C_{I1} = \frac{C_{N0}^2\eta_h}{(C_{N0} - C_{I0})(1 + \pi C_{I0}/2)} \quad (24a)$$

$$C_{N1} = \frac{C_{N0}}{1 + 2C_{N0}(\eta_c + \rho_c)}\left[\frac{(2C_{I0} - C_{N0})\eta_h}{(C_{N0} - C_{I0})} - 2\rho_h\right] \quad (24b)$$

where

$$\eta_c = \int\int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, |\sin\gamma| f_0(\Omega)f_0(\Omega') \quad (25a)$$

$$\eta_h = \int\int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, [-|\sin\gamma|\ln|\sin\gamma| - |\sin\gamma|(\ln 2 - 1/2)]f_0(\Omega)f_0(\Omega') \quad (25b)$$

and

$$\rho_\kappa = \int\int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, |\sin\gamma| f_0(\Omega)f_\kappa(\Omega') \qquad (\kappa = c, h) \quad (26)$$

Note the calculation of C_{I1} does not involve f_κ. Thus, any numerical error introduced when eqs 20–23 are solved for f_κ will not contribute to C_{I1}.

For a system of rodlike polymers ($\alpha = 0$), the relationship between $f_\kappa(\Omega)$ and $\omega_\kappa(\Omega)$ becomes simple. From eqs 20–22 we have

$$f_\kappa(\Omega) = -\omega_\kappa(\Omega) + f_0(\Omega)\int \mathrm{d}\Omega\, \omega_\kappa(\Omega) \qquad (\kappa = c, h) \quad (27)$$

Solving the linear equation set, eqs 27 and 23, we obtain from eqs 24–26

$$C_{I1}(\alpha = 0) = 0.7032 \qquad C_{N1}(\alpha = 0) = 0.6789 \quad (28)$$

and

$$S_1(\alpha = 0) = 0.1900 \quad (29)$$

The numerical procedure used to calculate eqs 27 and 23 is explained in Appendix A. Our perturbation scheme is different from that of Stroobants et al.[18] who used the Onsager variational method[15] instead of the exact treatment of the distribution function. The results found by Stroobants et al.[18] are $C_{I1} = 0.675$ and $C_{N1} = 0.730$, close to our exact solution in eq 28.

For a system of infinite wormlike chains ($\alpha \gg 1$), the conformation entropy can be rewritten in terms of f. We can show that f_c and f_h satisfy

$$\nabla^2\left(\frac{f_\kappa}{f_0}\right) + \frac{\nabla f_0}{f_0}\cdot\nabla\left(\frac{f_\kappa}{f_0}\right) = \frac{2}{\alpha}\omega_\kappa(\Omega) - \frac{2}{\alpha}\int \mathrm{d}\Omega\, \omega_\kappa(\Omega)f_0(\Omega) \qquad (\kappa = c, h) \quad (30)$$

Equation 24 now becomes

$$C_{I1}(\alpha \gg 1) = \frac{2C_{N0}^2\eta_h}{\pi C_{I0}(C_{N0} - C_{I0})} \quad (31a)$$

$$C_{N1}(\alpha \gg 1) = \frac{(2C_{I0} - C_{N0})\eta_h}{2(C_{N0} - C_{I0})(\eta_c + \rho_c)} - \frac{\rho_h}{\eta_c + \rho_c} \quad (31b)$$

Again, using the numerical analysis explained in Appendix A, we obtain

$$C_{I1}(\alpha \gg 1) = 0.7606 \qquad C_{N1}(\alpha \gg 1) = 0.694 \quad (32)$$

and

$$S_1(\alpha \gg 1) = -0.0567 \quad (33)$$

These results can be compared with Odijk's estimation[19] of $C_{I1} = 0.872$, $C_{N1} = 0.802$ and are more close to Vroege's[20] $C_{I1} = 0.775$, $C_{N1} = 0.662$. The last two sets of results come from a variational perturbation method similar to that of Stroobants et al.[18] for $\alpha = 0$.

For an arbitrary α, the numerical calculation becomes more involved. The numerical approach in Appendix A

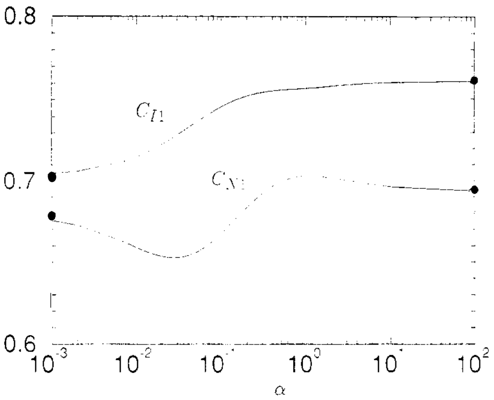

Figure 1. Coefficients of the linear corrections to the phase boundary number densities, C_{I1} and C_{N1}, vs the flexibility α. The asymptotic limits are $C_{I1}(\alpha = 0) = 0.7032$, $C_{N1}(\alpha = 0) = 0.6789$, and $C_{I1}(\alpha \gg 1) = 0.7606$, $C_{N1}(\alpha \gg 1) = 0.694$.

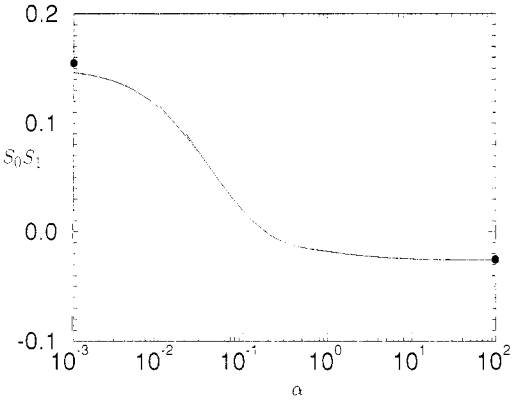

Figure 2. Coefficients of the linear correction to the order parameter, S_1S_0, at C_N vs the flexibility α.

is still used here. Figures 1 and 2 show C_{I1} and C_{N1}, and S_1 as functions of the flexibility α at the isotropic–nematic phase equilibrium, respectively. The relative errors of these numerical results are estimated to be smaller than 0.5%.

4. Discussion

As illustrated in Figures 1 and 2, from $\alpha = 0$ to $\alpha \gg 1$, C_{I1} monototically increases while S_1 monotonically decreases. The location of the crossover from the rodlike to flexible-chain-like behavior takes place near $\alpha_c \simeq 0.02$, which is much smaller than $\alpha_c \simeq 1$ for the crossover in C_{I0}, C_{N0}, and S_0.[36]

In Figure 1 we can also observe that C_{N1} first decreases when α starts to increase from the rod limit. This indicates a possible narrowing of the biphasic gap in semiflexible polyelectrolytes. At $\alpha \simeq 0.2$, C_{N1} begins to approach its $\alpha \gg 1$ limit. An interesting weak maximum exists near $\alpha = 1$, which is approximately the location for the crossover from the rodlike to flexible-chain-like behavior in C_{I0} and C_{N0}; however the connection is unclear. Comparing C_{I1} and C_{N1} with C_{I0} and C_{N0}, we may conclude that near $\alpha = 0$, polyelectrolyte polymers are more sensible to the rod flexibility than neutral ones. The numerical results in Figures 1 and 2 can be represented by the empirical formula in the same form as eq 14. The corresponding numerical coefficients a_i and b_i are listed in Table 1.

The twisting coefficient h is generally expected to be weak, ranging from $h = 0$ to $h = 0.25$.[18] For the latter, the linear correction terms to C_I and C_N calculated in the previous section may no longer be accurate, as shown by Stroobants et al.[18] and Vroege[20] for the $\alpha = 0$ and $\alpha \gg 1$ limits. In order to obtain an accurate description of the twisting effect in the whole range of h, we have solved the phase equilibrium conditions using the numerical algorithm described in ref 36 for h = 0, 0.1, 0.2, 0.3, 0.4, and 0.5 for each given α. The numerical results for the relative differences $C_I(\alpha)/C_{I0}(\alpha) - 1$, $C_N(\alpha)/C_{N0}(\alpha) - 1$, and $S(\alpha)/S_0(\alpha) - 1$ are then fitted to the empirical formula

Table 2. Coefficients in Eqs 34 and 35 for $C_I/C_{I0} - 1$

	P_1	P_2	P_3	P_4
A_0	0.7032	−0.6822	−1.553	0.715
A_1	18.25	0	−1.325	0.4478
A_2	4.945	0	0	0
A_3	38.21	0	−2.422	1.235
A_4	23.89	0	−0.5879	0
A_5	6.966	0	0.7130	0
A_6	50.23	0	−1.693	0

Table 3. Coefficients in Eqs 34 and 35 for $C_N/C_{N0} - 1$

	P_1	P_2	P_3	P_4
A_0	0.6789	−1.084	−2.572	1.578
A_1	41.16	0	−2.042	0.9932
A_2	343.9	0	−1.862	0.8214
A_3	336.9	0	−2.323	1.188
A_4	65.95	0	−1.277	0
A_5	475.7	0	−1.120	0
A_6	485.5	0	−1.567	0

Table 4. Coefficients in Eqs 34 and 35 for $S/S_0 - 1$

	P_1	P_2	P_3	P_4
A_0	0.1900	−0.02192	−2.090	2.003
A_1	−1.383	3.464	−3.305	3.815
A_2	2.252	−4.368	−2.775	1.558
A_3	−1.655	3.793	−4.112	4.304
A_4	15.73	0	−0.3011	0
A_5	−30.88	0	0	0
A_6	29.20	0	−3.479	3.024

$$\frac{A_0(h) + A_1(h)\alpha + A_2(h)\alpha^2 + A_3(h)\alpha^3}{1 + A_4(h)\alpha + A_5(h)\alpha^2 + A_6(h)\alpha^3} \tag{34}$$

where

$$A_n(h) = \frac{P_1 h + P_2 h^2}{1 + P_3 h + P_4 h^2} \qquad n = 0, 1, ..., 6 \tag{35}$$

The corresponding numerical coefficients P_1, P_2, P_3, and P_4 in these equations for $C_I/C_{I0} - 1$, $C_N/C_{N0} - 1$, and $S/S_0 - 1$ are listed in Tables 2–4, respectively.

The Padé approximation of the form in eq 14 to represent an α-dependent quantity, however, lacks any theoretical justification. In fact, as demonstrated by the Kratky–Porod expression for $\langle R^2 \rangle$ and $\langle R^4 \rangle$,[38,39] such a quantity depends on the combinations of $1/\alpha^n$ and $e^{-l(l+1)\alpha}$, where n and l are integers. Because of this reason, the large α behavior, in particular the derivatives of eq 14 at large α, might be inaccurate.

Experimentally, several groups have investigated extensively the phase behavior of polyelectrolytes.[1-14] In a recent publication, Tang and Fraden reported[14] that the phase boundary concentrations of colloidal suspensions of filamentous bacteriophage basically agree with our previous numerical result for $\alpha = 0.2$, if the twisting effect is ignored. This is a critical test of the theoretical values for C_{I0} and C_{N0}. The ratio $W = C_N/C_I - 1$, however, displays a weak, yet interesting, variation as a function of the ionic strength.[14] Using eqs 15a and 15b, we can write

$$W = \left[\frac{C_{N0}(\alpha)}{C_{I0}(\alpha)} - 1\right]\left[1 + \frac{C_{N1}(\alpha) - C_{I1}(\alpha)}{C_{N0}(\alpha) - C_{I0}(\alpha)}C_{N0}(\alpha)h + \mathcal{O}(h^2)\right] \quad (36)$$

Since $C_{N1}(\alpha) < C_{I1}(\alpha)$ for any given α (see Figure 1), we conclude that the relative density W of polyelectrolytes is always smaller than that of their neutral counterparts. The parameter W measured by Tang and Fraden tends to increase as h decreases, a behavior that is qualitatively consistent with eq 36. However, their W disagrees with our calculations in the entire range of h, which rules out the possibility that the variation in W is caused by the twisting effect. The variation may be attributed to the concentration dependence of the electrostatic potential,[7,22] the influence of the polydispersity,[40,41] and the end effect originating from the truncation of the virial series.

In conclusion, we have generalized the mean-field theory of the isotropic–nematic phase transition for neutral semiflexible chains to polyelectrolyte semiflexible chains. The twisting effect on the isotropic–nematic phase transition of semiflexible polymers is studied by the perturbation analysis and numerical calculations within the second virial coefficient approximation.

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Appendix A: Procedure for the Numerical Calculation

In all three calculations presented in section 3, the numerical analysis is based on the same scheme. We formally write

$$G[f_\kappa(\theta)] = \hat{O}_1 f_\kappa(\theta) - \hat{O}_2 f_\kappa(\theta) \qquad (\kappa = c, h) \qquad \text{(A1)}$$

where $\hat{O}_1$ and $\hat{O}_2$ are linear operators on $f_\kappa(\theta)$. For $\alpha = 0$, $\hat{O}_1 = 1$, and $\hat{O}_2$ represents the procedure of evaluating the right-hand side of eq 27 when $f_\kappa(\theta)$ is given for eq 23. For $\alpha \gg 1$, $\hat{O}_1$ represents the derivative operators on the left-hand side of eq 30, and $\hat{O}_2$ the procedure of calculating the right-hand side of eq 30. For a general α, $\hat{O}_1 = 1$, and $\hat{O}_2$ represents the procedure of calculating the right-hand side of eq 20, through solving eqs 21 and 22 when ω_κ is written in terms of f_κ as in eq 23.

The numerical procedure proceeds as follows. The interval $[0, \pi]$ for the variable is divided into $n_\theta = 200$ equal segments, and at each of the $n_\theta + 1$ grid points, the value of $f_\kappa(\theta)$ is specified. Using the appropriate basis vectors in the $n_\theta + 1$ dimensional space, we represent the operators $\hat{O}_1$ and $\hat{O}_2$ by two $(n_\theta + 1) \times (n_\theta + 1)$ matrices. Letting $G[f] = 0$ in eq A1 is now equivalent to the problem of solving $n_\theta + 1$ linear equations of $n_\theta + 1$ unknown $f_\kappa(\theta_i)$, $i = 1, 2, ..., n_\theta + 1$, which can be done easily. In practice, the symmetry $f_\kappa(\theta) = f_\kappa(\pi - \theta)$ is considered, so that we only need to deal with the matrices of $(n_\theta/2 + 1) \times (n_\theta/2 + 1)$ dimensions.

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