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Effect of low-molecular-weight salt on the nematic ordering in solutions of rodlike polyelectrolytes

Igor I. Potemkin,[1,2,*] Nikolay N. Oskolkov,[1,2] Alexei R. Khokhlov,[1,2] and Peter Reineker[3]
[1]*Physics Department, Moscow State University, Moscow 119992, Russia*
[2]*Department of Polymer Science, University of Ulm, 89069 Ulm, Germany*
[3]*Department of Theoretical Physics, University of Ulm, 89069 Ulm, Germany*

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Nematic ordering is studied in solutions of rodlike macroions in the presence of monovalent salt ions. The correlation free energy of electrostatic interactions is calculated within the framework of the Debye-Hückel approach. The phase diagram of the system is obtained. We have shown that the addition of salt destroys the weakly ordered nematic phase which is stable at small polymer concentrations. On the other hand, the salt widens the region of the phase separation between the isotropic (or weakly ordered nematic) and the highly ordered nematic phases at high polymer concentrations. An explanation of these effects is proposed.

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I. INTRODUCTION

When macroions are immersed in a medium of low-molecular-weight ions (counter- and salt ions) we deal with the screened electrostatic interactions between the macroions if the distance between them is larger than the electrostatic screening length. The screening length depends on the state of the ions (freely moving or condensed) and on their concentration. In the case of freely moving ions (high dielectric constant or temperature) it is assumed that the macroions interact with each other via the screened Debye-Hückel potential. In particular, this approach is widely used for the derivation of the energy of electrostatic interactions in liquid-crystalline polyelectrolyte solutions [1–10]. Despite a well-defined interaction potential between the macroions, the ultimate theoretical results depend on the way how the system is treated. As far as the second virial coefficient $B=1/2\int d^3r[1-\exp(-U(r)/k_BT)]$ with the Debye-Hückel potential energy $U(r)/k_BT=l_BZ^2\exp(-r/r_D)/r$ is convergent at large length scales, the electrostatic interaction between the macroions can be treated as pairwise interactions of similarly charged monopoles (mean-field treatment). In this case B is always positive which means that the electrostatic forces between the macroions are repulsive. Approaches of this kind were used in Refs. [1–5] for the analysis of nematic ordering in rodlike polyelectrolyte solutions. The main prediction of these theories is that the Coulomb repulsion between two similarly charged rods favors perpendicular orientation between them, i.e., prevents liquid-crystalline ordering.

An alternative approach is based on the treatment of the system of macroions with low-molecular-weight ions as a Debye-Hückel plasma. It is well known that the correlation electrostatic energy (per unit volume) of the ideal gas of Z and monovalent ions takes the form [11]

$$\frac{\mathcal{F}_{DH}}{k_BT}=-\frac{2\pi^{1/2}}{3}[l_B(nZ^2+c)]^{3/2}, \tag{1}$$

where $l_B=e^2/(\epsilon k_BT)$ is the Bjerrum length, and n and c are the concentrations of Z and monovalent ions, respectively. If the concentration of Z ions is small, $nZ^2\ll c$, $\mathcal{F}_{DH}$ can be expanded into a series in powers of n:

$$\frac{\mathcal{F}_{DH}}{k_BT}=-\frac{2\pi^{1/2}}{3}[l_Bc]^{3/2}-\frac{l_BZ^2}{2r_D}n-\frac{\pi}{2}l_B^2Z^4r_Dn^2+\cdots, \tag{2}$$

where $r_D=1/(4\pi l_Bc)^{1/2}$ is the Debye screening length of monovalent ions. In Eq. (2) the first term corresponds to the correlation energy of monovalent ions. The second term describes the attraction of each macroion to Z oppositely charged monovalent ions via an unscreened Coulomb potential at length scales smaller than the Debye screening length. The third term in Eq. (2) corresponds to the pair-wise interactions between the macroions. However in contrast to the mean-field treatment, the second virial coefficient of the correlation interactions between the macroions is negative, $B_{corr}=-\pi l_B^2Z^4r_D/2$. It means that these interactions are attractive. The correlated attraction has a transparent physics which can be explained on the mean-field level. Two dipoles of the moments $\mathbf{d}_1$ and $\mathbf{d}_2$, $|\mathbf{d}_1|=|\mathbf{d}_2|=d$ separated by a distance r have the electrostatic potential energy $U(r,\mathbf{n})=[\mathbf{d}_1\cdot\mathbf{d}_2-3(\mathbf{d}_1\cdot\mathbf{n})(\mathbf{d}_2\cdot\mathbf{n})]/r^3$, $\mathbf{n}=\mathbf{r}/r$. Weak electrostatic interactions $[|U(r,\mathbf{n})|/k_BT\ll 1]$ in a disperse gas of particles of radius r_0 possessing dipole moment can be calculated in the second virial approximation. The second virial coefficient is $B_{dip}=\int d^3r d\Omega_{\mathbf{d}_1,\mathbf{d}_2}[1-\exp(-U(r,\mathbf{n})/k_BT)]/(8\pi)\approx\int d^3r d\Omega_{\mathbf{d}_1,\mathbf{d}_2}(U(r,\mathbf{n})/k_BT-[U(r,\mathbf{n})/k_BT]^2/2+\cdots)/(8\pi)$, where $d\Omega_{\mathbf{d}_1,\mathbf{d}_2}$ means integration with respect to the relative orientation of the dipoles [11]. Integration of the first term in the expansion gives zero and $B_{dip}\approx -2\pi d^4/[9r_0^3(k_BT)^2]$. Therefore, if we treat each macroion in the Debye-Hückel gas as a virtual dipole (a monopole surrounded by a cloud of counterions) with a moment $d\sim eZr_D$ and a radius $r_0\sim r_D$, we obtain $B_{corr}=B_{dip}$. Thus, the electrostatic interactions of the small fraction of macroions in the Debye-Hückel gas are pair-wise but with completely different second virial coeffi-

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[*] Author to whom correspondence should be addressed. Electronic address: igor@polly.phys.msu.ru

cient of even opposite sign compared to the one in the mean-field theory.

The mentioned simple example demonstrates that the consideration of the correlation effects is very important for a proper description of polyelectrolyte systems. In particular, our recent studies of salt-free solutions of rodlike polyelectrolytes [9,10] within a Debye-Hückel-like theory predicted a quite different behavior of the solution compared with the mean-field theories. Namely, it was shown that the electrostatic interactions favor nematic ordering [9] and stabilize the weakly ordered nematic phase already at very small polymer concentrations, which are even smaller then the overlap concentration of the rods [10].

The aim of the present paper is to study the role of low-molecular-weight salt ions on the nematic ordering in rodlike polyelectrolyte solutions, taking into account the correlation electrostatic energy. The phase diagram of the solution will be constructed.

II. MODEL

Let us consider a solution of N charged rodlike macromolecules (chains) surrounded by their counterions and low-molecular-weight salt ions in the volume V. Each chain consists of $m \gg 1$ monomer units and has the length L, $L=am$, where a is the linear size of a monomer unit. The degree of ionization of the chain (the fraction of charged units) is τ, $0 \leqslant \tau \leqslant 1$; each charged unit has an elementary charge e. The average concentrations of monomer units of the rods, monovalent counter- and salt ions are $\rho = mN/V$, $\tau\rho$ and $2c$, respectively (the average concentration of positive (negative) ions of the salt is equal to c). Following the formalism of the Debye-Hückel theory, let us consider an "ideal gas" of macro-, counter- and salt ions (four-component system), where the corresponding concentrations weakly fluctuate around their average values, $\rho(\mathbf{x}) = \rho + \psi(\mathbf{x})$, $\rho_c(\mathbf{x}) = \tau\rho + \xi(\mathbf{x})$, $c^{\pm}(\mathbf{x}) = c + \nu^{\pm}(\mathbf{x})$; $\psi(\mathbf{x})$, $\xi(\mathbf{x})$ and $\nu^{\pm}(\mathbf{x})$ are the amplitudes of the density fluctuations with $\rho \gg \psi(\mathbf{x})$, $\tau\rho \gg \xi(\mathbf{x})$, $c \gg \nu^{\pm}(\mathbf{x})$; $\mathbf{x}$ is the spatial coordinate. In the Gaussian approximation the density fluctuations contribute to the free energy functional according to

$$\frac{\delta F(\psi,\xi,\nu^+,\nu^-)}{k_BT} = \frac{1}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\left[\frac{|\xi_{\mathbf{q}}|^2}{\tau\rho} + \frac{|\nu^+_{\mathbf{q}}|^2}{c} + \frac{|\nu^-_{\mathbf{q}}|^2}{c} + \frac{|\psi_{\mathbf{q}}|^2}{m\rho t_{\mathbf{q}}} + \frac{l}{q^2}|\tau\psi_{\mathbf{q}} - \xi_{\mathbf{q}} + \nu^+_{\mathbf{q}} - \nu^-_{\mathbf{q}}|^2\right], \tag{3}$$

where we used Fourier transformed amplitudes; $\mathbf{q}$ is the wave vector and $|\xi_{\mathbf{q}}|^2 \equiv \xi_{\mathbf{q}}\xi_{-\mathbf{q}}$, etc. The first three terms in Eq. (3) come from the translational entropy of counter- and salt ions. The fourth, anisotropic term corresponds to the structural contribution of the rods (for the detailed derivation of this term, see Ref. [9]); $t_{\mathbf{q}}$ in its denominator is the structural function

$$t_{\mathbf{q}} = \int d\mathbf{n} f(\mathbf{u},\mathbf{n}) \frac{4\sin^2(\mathbf{q}\cdot\mathbf{n}L/2)}{(\mathbf{q}\cdot\mathbf{n})^2 L^2}. \tag{4}$$

Here $f(\mathbf{u},\mathbf{n})$ is the orientational distribution function, $\int d\mathbf{n} f(\mathbf{u},\mathbf{n}) = 1$; $\mathbf{u}$ is the unit vector of the preferred orientation of the rods (director) and $\mathbf{n}$ is the unit vector directed along the axis of the chain. At large length scales, $qL \ll 1$, the structural function tends to unity, $t_{\mathbf{q}} \to 1$, and the corresponding contribution to the free energy functional 3 describes translational motion of the rods. At small length scales, $qL \gg 1$, this contribution shows that the spatially inhomogeneous distribution of overlapping rods is entropically unfavorable. For example, in the isotropic phase, $f(\mathbf{u},\mathbf{n}) = 1/(4\pi)$, this term is proportional to $q\psi_{\mathbf{q}}\psi_{-\mathbf{q}}$. The last term in Eq. (3) is the Coulomb interaction contribution of all components of the system. Here the parameter l is proportional to the Bjerrum length, $l = 4\pi l_B$. This term vanishes in the limit $q \to 0$ because of macroscopic electric neutrality of the system.

The contribution of the fluctuating charges to the total free energy of the spatially homogeneous solution, F_{DH}, can be found following a standard procedure:

$$F_{DH} = -k_BT\left(\ln \int \mathcal{D}\psi\mathcal{D}\xi\mathcal{D}\nu^{\pm} \exp\left\{-\frac{\delta F(\psi,\xi,\nu^+,\nu^-)}{k_BT}\right\} - \ln \int \mathcal{D}\psi\mathcal{D}\xi\mathcal{D}\nu^{\pm} \exp\left\{-\left.\frac{\delta F(\psi,\xi,\nu^+,\nu^-)}{k_BT}\right|_{l=0}\right\}\right) - F_0, \tag{5}$$

where $\mathcal{D}\psi\mathcal{D}\xi\mathcal{D}\nu^{\pm} \equiv \Pi_{\mathbf{q}} d\psi_{\mathbf{q}} d\xi_{\mathbf{q}} d\nu^+_{\mathbf{q}} d\nu^-_{\mathbf{q}}$ is a product of differentials; F_0 is the self-energy of macro-, counter- and salt ions. The calculation of the Gaussian integrals in Eq. (5) is done in the Appendix. The result is

$$\mathcal{F}_{DH} = \frac{F_{DH}}{Vk_BT} = \frac{1}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\left[\ln\left(1 + \tau\rho l \frac{1 + m\tau t_{\mathbf{q}} + 2c/(\tau\rho)}{q^2}\right) - \tau\rho l \frac{1 + m\tau t_{\mathbf{q}} + 2c/(\tau\rho)}{q^2}\right]. \tag{6}$$

This expression is negative independent of polymer and salt concentration as well as of the orientation of the chains. $\mathcal{F}_{DH}$ decreases with the increase of polymer concentration.

The total free energy of isotropic and nematic phases takes the following form:

$$\mathcal{F}_{i,n} = \frac{\rho}{m}\int d\mathbf{n} f(\mathbf{u},\mathbf{n}) \ln(4\pi f(\mathbf{u},\mathbf{n})) + \frac{\rho^2}{2m^2}\int d\mathbf{n}_1 d\mathbf{n}_2 f(\mathbf{u},\mathbf{n}_1) \times f(\mathbf{u},\mathbf{n}_2) B(\gamma) + \frac{\rho}{m}\ln\left(\frac{\rho}{m}\right) + c\ln(c) + (\tau\rho + c) \times \ln(\tau\rho + c) + \frac{1}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\left[\ln\left(1 + \tau\rho l \frac{1 + m\tau t_{\mathbf{q}} + \frac{2c}{\tau\rho}}{q^2}\right) - \tau\rho l \frac{1 + m\tau t_{\mathbf{q}} + \frac{2c}{\tau\rho}}{q^2}\right]. \tag{7}$$

The first two terms in Eq. (7) come from the Onsager theory for neutral rods [1]. Here $B = 2aL^2 \sin\gamma$ is the second virial coefficient of rods whose axes form an angle γ. The next three terms are the contributions of translational motion of rods and low-molecular-weight ions. Counterions and salt ions of the same sign are assumed to be indistinguishable from each other.

III. VALIDITY OF THE DEBYE-HÜCKEL APPROACH

The content of the Debye-Hückel theory is an assumption of small density fluctuations of charged units of the system, i.e., effects such as Manning condensation of low-molecular-weight ions and fluctuation-driven aggregation of macroions are excluded from the consideration. To ensure this restriction, we have to take into account that the electrostatic interaction energies of various units should be smaller than the corresponding entropic contributions. The salt-free regimes in semidilute and dilute solutions were analyzed in Refs. [9,10]. Here we examine the regime of high salt concentration, $\tau^2\rho \ll al^{1/2}c^{3/2}$ [at $\tau \gg a(lc)^{1/2}$] or $\tau\rho \ll c$ [at $\tau \ll a(lc)^{1/2}$], and of long rods, $clL^2 \gg 1$, in the semidilute solution. For simplicity we consider the isotropic phase of the solution, $f(\mathbf{u},\mathbf{n})=1/4\pi$, and the conditions of applicability of the Debye-Hückel theory for the isotropic phase will be valid also for the nematic phase. In this regime the electrostatic free energy 6 can be expanded into a powers series in ρ:

$$\begin{aligned}\mathcal{F}_{DH} = {} & \frac{1}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\left[\ln\left(1+\frac{2cl}{q^2}\right)-\frac{2cl}{q^2}\right] \\ & - \int \frac{d\mathbf{q}}{(2\pi)^3}\frac{\tau\rho c l^2(1+m\pi t_{\mathbf{q}}^{(0)})}{q^2(q^2+2cl)} \\ & - \frac{1}{4}\int \frac{d\mathbf{q}}{(2\pi)^3}\frac{(\tau l\rho)^2(1+m\pi t_{\mathbf{q}}^{(0)})^2}{(q^2+2cl)^2} - \cdots,\end{aligned}$$

$$t_{\mathbf{q}}^{(0)} = \frac{1}{qL}\int_{-qL/2}^{qL/2} dx \frac{\sin^2(x)}{x^2}. \tag{8}$$

Here the first term corresponds to the electrostatic interactions between the salt ions. The second and third terms are the energy of interactions between counterions (or salt ions of the same sign) and rods, and the energy of pairwise interactions of the rods, respectively. In the considered limit Eq. (8) can be calculated as

$$\mathcal{F}_{DH} \approx \begin{cases} -\dfrac{(2cl)^{3/2}}{12\pi} - \dfrac{\rho\tau^2 l}{8\pi a}\ln(2clL^2) - \dfrac{\pi l^{1/2}\tau^4\rho^2}{32(2c)^{3/2}a^2} - \cdots, \\ \tau \gg a(lc)^{1/2}, \\ -\dfrac{(2cl)^{3/2}}{12\pi} - \dfrac{\rho\tau l(2cl)^{1/2}}{8\pi} - \dfrac{l^{3/2}\tau^2\rho^2}{32\pi(2c)^{1/2}} - \cdots, \\ \tau \ll a(lc)^{1/2}. \end{cases} \tag{9}$$

The limits $\tau \gg a(lc)^{1/2}$ and $\tau \ll a(lc)^{1/2}$ get transparent physical meanings, if we introduce a characteristic distance between charged groups in the rod, $\Delta = a/\tau$, and the Debye screening length $r_D = 1/(2cl)^{1/2}$. Then these limits take the form, $r_D \gg \Delta$ and $r_D \ll \Delta$, respectively. The expansion of $\mathcal{F}_{DH}$ in the limit $\tau \gg a(lc)^{1/2}$ [Eq. (9)] is obtained, if we use the condition $2clL^2 \gg 1$ in the second term of Eq. (8) and take $t_{\mathbf{q}}^{(0)} \approx \pi/(qL)$ at $qL \gg 1$ (semidilute solution) in the third term.

The first and the second terms of the expansion (9) have to be smaller than the contributions of translational entropy of the salt ions, $\sim c$, and of counterions, $\sim \tau\rho$, respectively (the logarithmic factors are omitted). In the dilute solution the entropic contribution of rods, $\mathcal{F}_{ent}$, is proportional to ρ/m. It describes translational motion of the rods. To estimate the entropic contribution in the semidilute regime we use scaling arguments. Taking into account that $\mathcal{F}_{ent}$ cannot depend on m in this regime, we assume $\mathcal{F}_{ent} \sim \rho(\rho a^3)^{\beta}$. This term should cross over to the entropy of translational motion, ρ/m, at the overlap concentration $\rho^* \sim 1/(a^3m^2)$, i.e., $\beta = 1/2$. The physical meaning of $\mathcal{F}_{ent} \sim (\rho a)^{3/2}$ is the entropic penalty because of the density inhomogeneities: $\mathcal{F}_{ent} \sim a\psi(\mathbf{x})\nabla\psi(\mathbf{x})/\rho \sim a\rho/\xi \sim (\rho a)^{3/2}$, where the density fluctuations are strong, $\psi(\mathbf{x}) \sim \rho$, at length scales smaller than the correlation radius $\xi \sim 1/(\rho a)^{1/2}$. Therefore, the third term of the expansion (9) has to be smaller than $\mathcal{F}_{ent} \sim (a\rho)^{3/2}$. Collecting all the conditions, which must be fulfilled simultaneously, we get the following criteria of applicability of the Debye-Hückel theory:

$$(a)\Delta \ll r_D: \quad a(cl)^{1/2} \ll \tau \ll a/l, \quad cl^3 \ll 1, \quad l\rho\tau^8 \ll a^7c^3,$$

$$\rho\tau^2 \ll al^{1/2}c^{3/2},$$

$$(b)\ \Delta \gg r_D: \quad \tau \ll a(cl)^{1/2}, \quad cl^3 \ll 1, \quad \tau\rho \ll c. \tag{10}$$

IV. SPINODAL OF THE NEMATIC ORDERING

To demonstrate the orientational action of the Coulomb interactions and the influence of the low-molecular-weight ions on the nematic ordering, let us calculate the spinodal of the isotropic phase of the solution toward nematic ordering. It can be performed by expanding the distribution function into a series of Legendre polynomials

$$f(\mathbf{u},\mathbf{n}) \approx \frac{1}{4\pi}\left(1+\frac{5S}{2}[3(\mathbf{u}\cdot\mathbf{n})^2-1]+\cdots\right),$$

$$S = \int d\mathbf{n} f(\mathbf{u},\mathbf{n})\frac{3(\mathbf{u}\cdot\mathbf{n})^2-1}{2}, \tag{11}$$

and equating to zero the coefficient λ in the square term of the expansion

$$\mathcal{F}_n = \mathcal{F}_i + \lambda S^2 + \cdots,$$

$$\begin{aligned}\lambda = {} & \frac{5\rho}{2m} - \frac{5\pi\rho^2a^3}{32} \\ & - \frac{1}{4(2\pi)^3}\int d\mathbf{u}\int_0^{\infty} dq q^2 \frac{(l\rho m)^2\tau^4(\delta t_{\mathbf{q}})^2}{\left[q^2+l\rho\tau\left(1+m\pi t_{\mathbf{q}}^{(0)}+\dfrac{2c}{\tau\rho}\right)\right]^2},\end{aligned}$$

$$\delta t_{\mathbf{q}} = \frac{15}{2}\left(3\frac{(\mathbf{u}\cdot\mathbf{q})^2}{q^2}-1\right)\left[\frac{1}{(qL)^2}\left(1-\frac{\sin qL}{qL}\right)-\frac{t_{\mathbf{q}}^{(0)}}{6}\right],$$

$$t_{\mathbf{q}}^{(0)} = \frac{1}{qL}\int_{-qL/2}^{qL/2} dx \frac{\sin^2(x)}{x^2}, \tag{12}$$

where S is the order parameter of the nematic phase. The first term in λ comes from the first term of the total free energy, Eq. (7). It is positive and responsible for the entropic penalty of the chains because of their orientation. The next two terms in λ describe the orientational effect of the excluded volume and of the Coulomb interactions, respectively. Let us examine analytically the regime of high salt concentration, $\tau^2\rho \ll al^{1/2}c^{3/2}$, $clL^2 \gg 1$. In this regime the values of the wave vector $q \sim (lc)^{1/2}$ give the main contribution to the third term of λ. Therefore, we should consider the limit $qL \gg 1$ in $\delta t_{\mathbf{q}}$ (semidilute regime) and neglect the terms $1 + m\tau t_{\mathbf{q}}^{(0)}$ compared with $2c/(\tau\rho)$ in the denominator. In this limit the solution of the equation $\lambda = 0$ takes the form

$$\rho = \frac{16}{\pi a^3 m}\frac{(2c)^{3/2}}{(2c)^{3/2} + \tau^4 l^{1/2}/(4a^5)}. \tag{13}$$

It is clearly seen that the increase of the salt concentration, c, requires an increase of the polymer concentration, ρ, to form the nematic phase. In other words, the salt addition reduces the orientational effect of the Coulomb forces due to the screening of charges on the chains.

The value of ρ in the spinodal has to be subjected to the criteria of applicability of the Debye-Hückel theory, Eq. (10). For the most interesting limit $\tau \gg c^{3/8}a^{5/4}/l^{1/8}$, which belongs to the case (a) of Eq. (10), $\rho \approx 64a^2(2c)^{3/2}/(\pi m\tau^4 l^{1/2})$ and this value is valid at the conditions

$$c^{3/8}a^{5/4}/l^{1/8} \ll \tau \ll a/l,$$

$$(a/lm)^{1/2} \ll \tau \ll m^{1/4}c^{3/8}a^{5/4}/l^{1/8}, \quad cl^3 \ll 1, \tag{14}$$

which are consistent in a very wide range of the values of τ.

The numerical solution of the equation $\lambda = 0$ for arbitrary values of c is plotted in the variables τ and ϕm, $\phi = \rho a^3$ in Fig. 1. It is seen that the addition of salt gradually shifts the spinodal towards higher values of the fraction of charged groups and of the polymer concentration. These curves are in the range of the applicability of the Debye-Hückel theory except for the case $\tau \approx 1$ at small salt fraction. In this regime orientation of the rods occurs at polymer concentration smaller than the overlap concentration and is accompanied by the formation of a Wigner crystal [10]. The expression obtained for the spinodal is only qualitatively correct for this regime [10].

V. PHASE DIAGRAM

The phase diagram of the solution is calculated with the total free energy given by Eq. (7). On this way two simplifications are used. First, the trial function for the orientational distribution function is chosen in the Onsager form:

$$f(\mathbf{u},\mathbf{n}) = \frac{\alpha\cosh(\alpha\mathbf{u}\cdot\mathbf{n})}{4\pi\sinh(\alpha)}, \tag{15}$$

where α is the variation parameter, $0 \leq \alpha < \infty$; $\alpha = 0$ and $\alpha > 0$ correspond to the isotropic and nematic phases of the solution, respectively. Complete orientation (parallel rods) is attained in the limit $\alpha \to \infty$ when $f(\mathbf{u},\mathbf{n}) \to \delta(\mathbf{u}-\mathbf{n})$. Second, our numerical calculations of $\mathcal{F}_{DH}$ with the Onsager function for $f(\mathbf{u},\mathbf{n})$ have shown that it can be approximated by a simple interpolation form

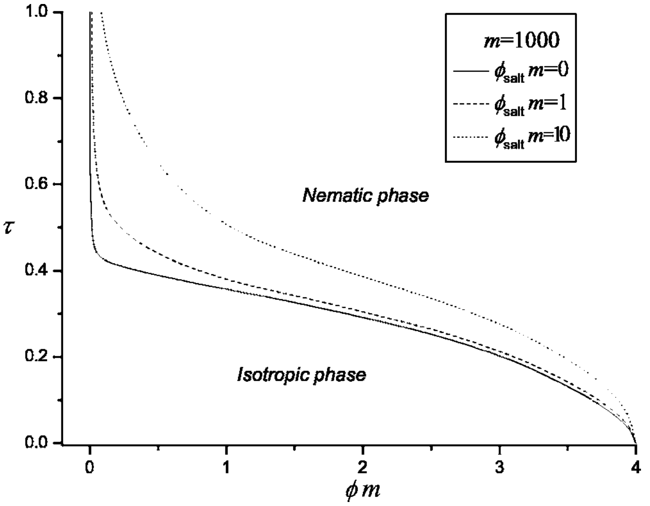

FIG. 1. Spinodal in variables: fraction of charged groups on the chain, τ, and polymer volume fraction multiplied by the number of monomer units in the charged rod, $\phi m \equiv \rho a^3 m$, for various values of the salt concentration; $\phi_{salt}m \equiv ca^3 m = 0$ (solid), 1 (dashed), and 10 (dotted).

$$\mathcal{F}_{DH}(\alpha) = \mathcal{F}_{ord} + (\mathcal{F}_{dis} - \mathcal{F}_{ord})\exp(-\alpha^4) \tag{16}$$

with an accuracy of not less than 10%. Here $\mathcal{F}_{dis}$ and $\mathcal{F}_{ord}$ are exact correlation free energies calculated with $f(\mathbf{u},\mathbf{n}) = 1/(4\pi)$ and $f(\mathbf{u},\mathbf{n}) = \delta(\mathbf{u}-\mathbf{n})$, respectively. It is this form for $\mathcal{F}_{DH}$ that is used in the calculation of the phase diagram.

The chemical potentials and the osmotic pressure are calculated following a standard way:

$$\mu_{i,n} = \frac{\partial\mathcal{F}_{i,n}}{\partial\rho}, \quad \mu_{i,n}^{salt} = \frac{\partial\mathcal{F}_{i,n}}{\partial c}, \quad \pi_{i,n} = \mu_{i,n}\rho + \mu_{i,n}^{salt}c - \mathcal{F}_{i,n}. \tag{17}$$

The analysis of the total free energy of the nematic phase as a function of the parameter α shows that the free energy may have two minima at finite values of α. It means that two nematic phases (I and II) differing in the value of the order parameter can be stable. Phase equilibrium between various phases is found by solving the following equations:

$$\mu_i(\rho_0,c_0) = \mu_n(\rho_1,c_1),$$

$$\mu_i^{salt}(\rho_0,c_0) = \mu_n^{salt}(\rho_1,c_1),$$

$$\pi_i(\rho_0,c_0) = \pi_n(\rho_1,c_1),$$

$$\frac{\partial\mathcal{F}_n}{\partial\alpha_1} = 0, \quad \text{isotropic} - \text{nematic } I,$$

$$\mu_i(\rho_0,c_0) = \mu_n(\rho_2,c_2),$$

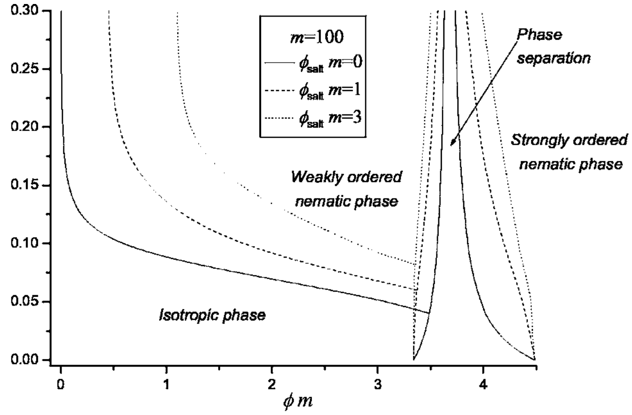

FIG. 2. Phase diagram of the solution of charged rods at various values of the salt volume fraction: $\phi_{salt}m=0$ (solid), 1 (dashed), and 3 (dotted).

$$\mu_i^{salt}(\rho_0,c_0)=\mu_n^{salt}(\rho_2,c_2),$$

$$\pi_i(\rho_0,c_0)=\pi_n(\rho_2,c_2),$$

$$\frac{\partial\mathcal{F}_n}{\partial\alpha_2}=0,\quad \text{isotropic}-\text{nematic } II,$$

$$\mu_n(\rho_1,c_1)=\mu_n(\rho_2,c_2),$$

$$\mu_n^{salt}(\rho_1,c_1)=\mu_n^{salt}(\rho_2,c_2),$$

$$\pi_n(\rho_1,c_1)=\pi_n(\rho_2,c_2),$$

$$\frac{\partial\mathcal{F}_n}{\partial\alpha_1}=0,$$

$$\frac{\partial\mathcal{F}_n}{\partial\alpha_2}=0,\quad \text{nematic } I-\text{nematic } II. \tag{18}$$

Here the conditions of fixed numbers of salt ions and rods in the system have to be taken into account. For example, in the case of coexisting nematic phases it can be written as $cV=c_1V_1+c_2V_2$ and $\rho V=\rho_1V_1+\rho_2V_2$, where V_1 and V_2 are the volumes of the phases, $V_1+V_2=V$. Combining these conditions we get the following relation between c_1, c_2, ρ_1 and ρ_2:

$$c=c_1\frac{\rho_2-\rho}{\rho_2-\rho_1}+c_2\frac{\rho-\rho_1}{\rho_2-\rho_1}. \tag{19}$$

The resulting phase diagram of the solution is presented in Fig. 2. The orientational effect of Coulomb interactions becomes detectable already in the range of small polymer concentrations (salt-free regime) where the weakly ordered nematic phase *I* is stabilized (solid curve). The width of the phase separation region between the isotropic and the nematic phase is very small and cannot be represented at the length scale of the diagram. In contrast, the width of the phase separation region between the isotropic phase and the highly ordered nematic phase *II* is significant. It narrows with the increase of τ from the maximum value at $\tau=0$ corresponding to the neutral rod chains. In the salt-free solution (solid curves) this behavior is caused by the increase of the number of counterions with τ: the contribution of the translational motion of counterions, which is proportional to τ, dominates over the Coulomb term $\sim\tau^2$ [10]. The phase separation is always accompanied by entropy losses of those counterions, which are localized in a denser phase to compensate its macroscopic charge. Therefore, the larger is the number of counterions, the smaller is the concentration jump at the phase separation. The coexistence of two nematic phases at certain intermediate values of the fraction of ionized groups is the result of two stabilizing factors: weakly and highly ordered nematic phases are stabilized by Coulomb and excluded volume interactions, respectively.

The effect of the low-molecular-weight salt is demonstrated by dashed and dotted curves in Fig. 2. We can distinguish two qualitatively different effects of the salt on the phase behavior. The addition of salt prevents nematic ordering at small polymer concentration because of the screening of electrostatic interactions between macroions which are responsible for the stabilization of the weakly ordered phase. On the other hand, the coexistence of the isotropic (weakly ordered nematic) and highly ordered nematic phases occurs at smaller values of the polymer concentration in the presence of the salt ions compared to the salt-free solution, see Fig. 2. This effect has an entropic reason. In the salt-free regime counterions hinder phase separation: the maximum of the translational entropy of counterions is achieved in the spatially-homogeneous state of the system, rather than in the phase separated state where counterions have to be distributed inhomogeneously between the phases. In other words, phase separation is impeded when the rods of the rare phase cannot "draw" their counterions into the denser phase. In the presence of salt (delivering additional ions of the same sign as that of the counterions), their entropy markedly increases and the loss in entropy as a result of phase separation decreases: it is no longer significant for the chains whose ions (host or guest) will be drawn inside the denser phase.

The order parameter $S=1-3[\alpha\cosh(\alpha)/\sinh(\alpha)-1]/\alpha^2$ as a function of the polymer volume fraction ϕ at different values of the salt volume fraction is plotted in Fig. 3. The horizontal lines correspond to the order parameters of the coexisting nematic phases. The effect of the salt on the value of S is significant for the nematic phase *I*: the increase of ϕ_{salt} decreases the order parameter. In contrast, the order parameter of the nematic phase *II* is practically not changed with ϕ_{salt}. This effect is connected with the dominance of the excluded volume interactions over the electrostatic interactions at high polymer concentrations. Therefore, the screening by the salt ions does not play a role.

Our theoretical predictions are qualitatively consistent with experimental data obtained for various polyelectrolyte systems. Orienting action of electrostatic interactions was detected in aqueous solutions of tobacco mosaic virus (TMV) [12] and of rodlike micelles which are formed by aggregation of synthetic polyelectrolytes poly(p-phenylene)sulfonates (PPPs) [13]. In the case of nonaggregated TMV particles (length, $L=300$ nm; diameter, $a=18$ nm), the onset of phase separation of the isotropic, salt-free solution occurs at virus concentration $\phi_i\approx 2.3\%$ [12].

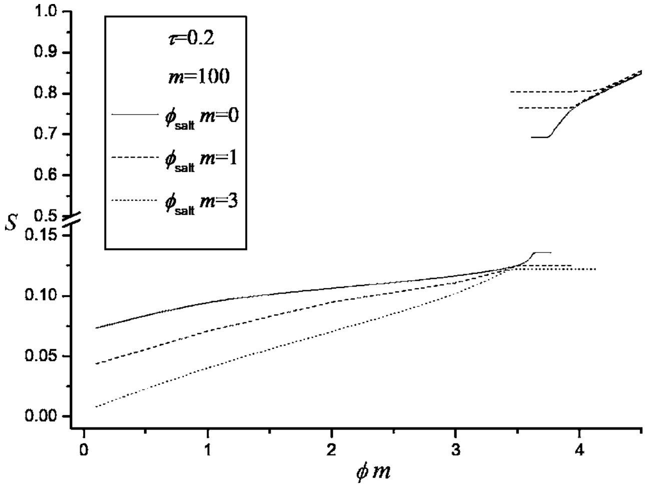

FIG. 3. Order parameter of the nematic phase S as a function of the polymer volume fraction multiplied by the number of monomer units in the rod, ϕm, at various values of the salt volume fraction: $\phi_{salt} m=0$ (solid), 1 (dashed), and 3 (dotted). The fraction of charged groups in the chain is chosen to be $\tau=0.2$.

Taking the overlap concentration $\phi^{*}=3a^2/(2L^2)\times 100\% \approx 0.54\%$ and the value of ϕ_i for neutral rods, $\phi_i^{Ons}=3.34a/L\times 100\% \approx 20\%$ [1] as checkpoints, we can conclude that the nematic phase of TMV solution is formed at concentration, which corresponds to the semidilute regime but is considerably smaller than that of the neutral rods. Addition of low-molecular-weight salt (NaCl) destroys the nematic phase which can be restored by the increase of TMV concentration [12]. Such behavior is consistent with our predictions for nematic phase I which is stabilized by electrostatic interactions (see Fig. 2). In the case of PPPs micelles, which are cylinders of the length $L=500$ nm and diameter $a=3.4$ nm, the nematic phase of the salt-free solution appears at $\rho_i=1.1$ g/L [13] whereas $\rho^{*}=0.037$ g/L and $\rho_i^{Ons}=12$ g/L. Therefore, we also can attribute the nematic ordering of PPPs micelles to the electrostatic interactions because the steric repulsion of the rods can not cause orientation at $\rho<\rho_i^{Ons}$.

VI. CONCLUSIONS

A theory of nematic ordering in solutions of rodlike polyelectrolyte chains in the presence of low-molecular-weight salt is developed. The system is treated similarly to the Debye-Hückel plasma. We have shown that the many-body Coulomb interactions favor nematic ordering. The addition of salt prevents the formation of the weakly ordered nematic phase at small values of polymer concentration and widens the coexistence region of the isotropic (or weakly ordered) and the highly ordered nematic phases at high values of polymer concentration.

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APPENDIX: CORRELATION FREE ENERGY

One of the possible ways to calculate the Gaussian integrals in Eq. (5) is the replacement of the continuous integration over the wave vector $\mathbf{q}$, Eq. (3), by a discrete summation over the wave numbers $\mathbf{k}$, $\mathbf{q}=2\pi\{k_x/\mathcal{L}_x, k_y/\mathcal{L}_y, k_z/\mathcal{L}_z\}$, $k_x, k_y, k_z=0, \pm 1, \pm 2, \ldots$, where $\mathcal{L}_{x,y,z}$ are the linear dimensions of the system, $\mathcal{L}_x\mathcal{L}_y\mathcal{L}_z=V$

$$\frac{\delta F(\psi,\xi,\nu^+,\nu^-)}{k_BT} = \frac{1}{2V}\sum_{\mathbf{k}}\left[\frac{|\xi_{\mathbf{k}}|^2}{\tau\rho} + \frac{|\nu_{\mathbf{k}}^+|^2}{c} + \frac{|\nu_{\mathbf{k}}^-|^2}{c} + \frac{|\psi_{\mathbf{k}}|^2}{m\rho t_{\mathbf{k}}} + \frac{l}{q_{\mathbf{k}}^2}|\tau\psi_{\mathbf{k}} - \xi_{\mathbf{k}} + \nu_{\mathbf{k}}^+ - \nu_{\mathbf{k}}^-|^2\right],$$

$$q_{\mathbf{k}}^2 \equiv (2\pi)^2\left(\frac{k_x^2}{\mathcal{L}_x^2} + \frac{k_y^2}{\mathcal{L}_y^2} + \frac{k_z^2}{\mathcal{L}_z^2}\right). \tag{A1}$$

Then the expressions in the logarithms of Eq. (5) are infinite products of integrals over variables $\psi_{\mathbf{k}}$, $\xi_{\mathbf{k}}$, $\nu_{\mathbf{k}}^+$ and $\nu_{\mathbf{k}}^-$. Diagonalization of the square form, Eq. (A1), can be done via the following variable substitution

$$\xi_{\mathbf{k}} = \bar{\xi}_{\mathbf{k}} + (\tau\psi_{\mathbf{k}} + \nu_{\mathbf{k}}^+ - \nu_{\mathbf{k}}^-)\frac{\tau\rho l}{\tau\rho l + q_{\mathbf{k}}^2},$$

$$\nu_{\mathbf{k}}^+ = \overline{\nu_{\mathbf{k}}^+} - (\tau\psi_{\mathbf{k}} - \nu_{\mathbf{k}}^-)\frac{cl}{(\tau\rho + c)l + q_{\mathbf{k}}^2},$$

$$\nu_{\mathbf{k}}^- = \overline{\nu_{\mathbf{k}}^-} + \tau\psi_{\mathbf{k}}\frac{cl}{(\tau\rho + 2c)l + q_{\mathbf{k}}^2},$$

$$\frac{\delta F(\psi,\bar{\xi},\overline{\nu^+},\overline{\nu^-})}{k_BT} = \frac{1}{2V}\sum_{\mathbf{k}}\left[|\bar{\xi}_{\mathbf{k}}|^2\left(\frac{1}{\tau\rho} + \frac{l}{q_{\mathbf{k}}^2}\right) + |\overline{\nu_{\mathbf{k}}^+}|^2\left(\frac{1}{c} + \frac{l}{\tau\rho l + q_{\mathbf{k}}^2}\right) + |\overline{\nu_{\mathbf{k}}^-}|^2\left(\frac{1}{c} + \frac{l}{(\tau\rho + c)l + q_{\mathbf{k}}^2}\right) + |\psi_{\mathbf{k}}|^2\left(\frac{1}{m\rho t_{\mathbf{k}}} + \frac{\tau^2 l}{(\tau\rho + 2c)l + q_{\mathbf{k}}^2}\right)\right]. \tag{A2}$$

Using the well-known result for the Gaussian integral

$$\int_{-\infty}^{\infty} dx\, \exp(-\beta x^2) = \sqrt{\frac{\pi}{\beta}}, \tag{A3}$$

and integrating the exponents over $\bar{\xi}_{\mathbf{k}}$, $\overline{\nu_{\mathbf{k}}^+}$, $\overline{\nu_{\mathbf{k}}^-}$ and $\psi_{\mathbf{k}}$, we obtain

$$\begin{aligned}\frac{\Delta F_{el}}{k_B T} &= -\ln \prod_{\mathbf{k}} \sqrt{\frac{\frac{1}{\tau\rho}\frac{1}{c^2}\frac{1}{m\rho t_{\mathbf{k}}}}{\left(\frac{1}{\tau\rho}+\frac{l}{q_{\mathbf{k}}^2}\right)\left(\frac{1}{c}+\frac{l}{\tau\rho l+q_{\mathbf{k}}^2}\right)\left(\frac{1}{c}+\frac{l}{(\tau\rho+c)l+q_{\mathbf{k}}^2}\right)\left(\frac{1}{m\rho t_{\mathbf{k}}}+\frac{\tau^2 l}{(\tau\rho+2c)l+q_{\mathbf{k}}^2}\right)}} \\ &= \frac{1}{2}\sum_{\mathbf{k}} \ln\left(1+\tau\rho l\frac{1+2c/(\tau\rho)+m\tau t_{\mathbf{k}}}{q_{\mathbf{k}}^2}\right) = \frac{V}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\ln\left(1+\tau\rho l\frac{1+2c/(\tau\rho)+m\tau t_{\mathbf{q}}}{q^2}\right), \qquad \text{(A4)}\end{aligned}$$

where we have returned from summation to integration.

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