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Rodlike polyelectrolyte solutions: Effect of the many-body Coulomb attraction of similarly charged molecules favoring weak nematic ordering at very small polymer concentration

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The correlation free energy of the many-body Coulomb interactions in the solution of rodlike polyelectrolytes with counterions is calculated. For this purpose a theory of the Debye-Hückel type, based on the density functional approach, is developed. We have shown that for all the analyzed regimes electrostatic interactions of similarly charged rods are attractive independent of their mutual orientation. Coexistence of weakly and highly ordered nematic phases at intermediate degrees of ionization of the molecules is predicted. It is shown that the electrostatic attractive forces favor liquid-crystalline ordering and stabilize a weakly ordered nematic phase at very small polymer concentrations. In other words, isotropic solutions of charged rods are in many cases intrinsically unstable with respect to orientational ordering.

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I. INTRODUCTION

The basic principle, which underlies liquid-crystalline ordering in solutions of neutral rodlike molecules, was expounded by Onsager more than half a century ago [1]. Since that time deep understanding of the liquid-crystalline phase in the solutions of rodlike polymers [2–4] and of molecules with various flexibility mechanisms [5–8] has been achieved. Studies of nematic ordering in the solutions of rigid-rod polyelectrolytes (including biological objects, such as DNA, tobacco mosaic viruses, etc.) have been started more than two decades ago [9–20]. However, in contrast to neutral solutions, in the field of polyelectrolytes there is a very wide spectrum of theoretical models and predictions. Most of the approaches were based on the consideration of only pairwise Coulomb interactions of the chains in the second virial approximation [10,11,13,18]. It is well known [21], that the integrals in the two-ion term in the second virial expansion for the unscreened interactions are divergent. Therefore, this approximation can be applicable if at least two conditions are assumed: (*i*) two macroions interact via the screened Debye-Hückel potential [10,11,13,18] and (*ii*) the screening radius (the Debye radius of low-molecular ions) is smaller than the distance between the macroions. The latter condition can be achieved at high salt concentrations (compared to the concentration of counterions) [10,18]. The choice of the virial approach excludes correlation attraction of low-molecular ions from consideration and postulates electrostatic repulsion between two similarly charged macroions. One of the main predictions of the virial theories is the increase of the net second virial coefficient due to electrostatic interactions. This can result in the narrowing of the phase separation region and the second orientational transition to a highly ordered nematic phase [10,18].

Another model, based on the bare potential energy constructed from the Debye-Hückel potential, was proposed in Ref. [20]. Here the effective potential energy between two segments of different polyelectrolyte rods was calculated in the Maier-Saupe approximation [22]. This energy was shown to be also repulsive and anisotropic, favoring perpendicular orientation between the rods.

A recent attempt to account for the effect of the many-body correlations of charged rods on the isotropic-nematic transition was undertaken in Ref. [17]. The model of weakly interacting rods immersed in oppositely charged nonfluctuating medium was developed. The interaction potential between the rods was chosen in the Debye-Hückel form. The resulting correlation free energy was found to be positive and reducible to the virial electrostatic energy under certain conditions.

The goal of this paper is to develop the consistent theory of liquid-crystalline ordering in solutions of rodlike polyelectrolytes which properly considers the many-body Coulomb interactions of charged groups (both macro and counterions), as well as the effect of the translational motion of counterions. We will consider the polyelectrolyte regime of the *salt-free* solution with *freely floating monovalent* counterions at the high temperature (or high dielectric constant), i.e., the counterion condensation due to the Manning mechanism [23,24] and ion pair formation [25–27] will not be taken into account in the present theory. The main difference of our model is that *unscreened* Coulomb interactions among the macro and counterions will be considered as a starting point of the theory. It means that this approximation cannot be reduced to the virial expansion (as in the consideration with the screened potential [17]). Assuming that charge fluctuations in the solution are small, we will elaborate a Debye-Hückel-like theory on the basis of the Gaussian approximation for the density functional. Charge fluctuations of both rods and counterions will be taken into account. The general expression for the electrostatic correlation energy of the solution with the arbitrary orientational distribution function of rods will be derived via integration of the statistical weight over the density fluctuations. The explicit forms of this energy will be obtained for the two limiting states of the solu-

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tion: the isotropic (disordered) and completely ordered (parallel orientation of the molecules) states. Various phase diagrams for liquid-crystalline ordering will be constructed.

The most important predictions of our model can be summarized as follows.

(1) The many-body Coulomb interactions of similarly charged rods are *attractive* independently of the mutual orientation of rods. This effect is valid for semidilute and dilute regimes.

(2) Electrostatic attraction favors liquid-crystalline ordering. It stabilizes a weakly ordered nematic phase at very small polymer concentrations. Coexistence of weakly and highly ordered nematic phases is possible.

(3) Translational motion of counterions narrows the phase separation region of the coexisting isotropic and ordered nematic phases.

II. ELECTROSTATIC INTERACTIONS IN THE SOLUTIONS OF RODLIKE MOLECULES

Let us consider a solution of charged rodlike molecules and their low-molecular mobile counterions. Let us denote as L and m the length and the number of monomer units for each molecule, respectively, $L=am$ where a is linear size of monomer units. Monomer unit density in a solution of N rods can be written as

$$\rho(\mathbf{x})=m\sum_{i=1}^{N}\int_{-L/2}^{L/2}\frac{ds_i}{L}\,\delta(\mathbf{x}-\hat{\mathbf{n}}_i s_i-\mathbf{R}_i), \tag{1}$$

where $\mathbf{x}$ is the current spatial coordinate; s_i and $\hat{\mathbf{n}}_i$ are the current longitudinal length and the unit vector directed along the axis of i^{th} cylinder, respectively; $\mathbf{R}_i$ is the coordinate of its center. The total number of monomer units in the system can be found by integration of $\rho(\mathbf{x})$ over the whole volume of the system, V,

$$\int_V d^3x\,\rho(\mathbf{x})=mN. \tag{2}$$

Fourier component for the density (1) takes the form

$$\begin{aligned}\rho_{\mathbf{q}}&=m\sum_{i=1}^{N}\int_{-L/2}^{L/2}\frac{ds_i}{L}\exp[-i\mathbf{q}\cdot(\hat{\mathbf{n}}_i s_i+\mathbf{R}_i)]\\&=2m\sum_{i=1}^{N}\frac{\sin(\mathbf{q}\cdot\hat{\mathbf{n}}_i L/2)}{\mathbf{q}\cdot\hat{\mathbf{n}}_i L}\exp(-i\mathbf{q}\cdot\mathbf{R}_i),\end{aligned} \tag{3}$$

where $\mathbf{q}$ is the wave vector. Let us denote as $f(\hat{\mathbf{u}},\hat{\mathbf{n}}_i)$ an orientational distribution function of the molecules. Here $\hat{\mathbf{u}}$ is unit vector of preferential orientation of the molecules (director) and the function f is normalized as follows: $\int d\hat{\mathbf{n}}_i f(\hat{\mathbf{u}},\hat{\mathbf{n}}_i)=1$. The contribution to the partition function of the solution coming from the density fluctuations of the monomer units of rods $\psi_{\mathbf{q}}=\rho_{\mathbf{q}}-(2\pi)^3\rho\,\delta(\mathbf{q})$ with respect to the average value $\rho=mN/V$ can be written as follows:

$$\begin{aligned}Z_{str}(\psi)=\frac{1}{N!}\int\prod_{i=1}^{N}d\mathbf{R}_i d\hat{\mathbf{n}}_i f(\hat{\mathbf{u}},\hat{\mathbf{n}}_i)&\\\times\delta\Biggl(\psi_{\mathbf{q}}-2m\sum_{i=1}^{N}\frac{\sin(\mathbf{q}\cdot\hat{\mathbf{n}}_i L/2)}{\mathbf{q}\cdot\hat{\mathbf{n}}_i L}\exp(-i\mathbf{q}\cdot\mathbf{R}_i)&\\+(2\pi)^3\rho\,\delta(\mathbf{q})\Biggr).&\end{aligned} \tag{4}$$

Introducing the conjugate field φ, the partition function (4) can be presented as

$$\begin{aligned}Z_{str}(\psi)=\frac{1}{N!}\int\prod_{i=1}^{N}d\mathbf{R}_i d\hat{\mathbf{n}}_i f(\hat{\mathbf{u}},\hat{\mathbf{n}}_i)&\\\times\int\mathcal{D}\varphi\times\exp\Biggl\{i\int\frac{d\mathbf{q}}{(2\pi)^3}\varphi_{-\mathbf{q}}\psi_{\mathbf{q}}-i&\\\times\int\frac{d\mathbf{q}}{(2\pi)^3}\varphi_{-\mathbf{q}}\Biggl(2m\sum_{i=1}^{N}\frac{\sin(\mathbf{q}\cdot\hat{\mathbf{n}}_i L/2)}{\mathbf{q}\cdot\hat{\mathbf{n}}_i L}&\\\times\exp(-i\mathbf{q}\cdot\mathbf{R}_i)-(2\pi)^3\rho\,\delta(\mathbf{q})\Biggr)\Biggr\},&\end{aligned} \tag{5}$$

where $\mathcal{D}\varphi\equiv\Pi_{\mathbf{q}}d\varphi_{\mathbf{q}}$ is the product of differentials. Expanding the exponent in Eq. (5) into the series in powers of the small density fluctuations, $\rho_{\mathbf{q}}-(2\pi)^3\rho\,\delta(\mathbf{q})$, up to square terms and integrating over the coordinates $\mathbf{R}_i$ and the orientation vectors $\hat{\mathbf{n}}_i$, one can obtain

$$\begin{aligned}Z_{str}(\psi)=\frac{V^N}{N!}\int\mathcal{D}\varphi\exp\Biggl(i\int\frac{d\mathbf{q}}{(2\pi)^3}\psi_{\mathbf{q}}\varphi_{-\mathbf{q}}\Biggr)&\\\times\Biggl\{1-\frac{m\rho}{2}\int\frac{d\mathbf{q}}{(2\pi)^3}t_{\mathbf{q}}\varphi_{\mathbf{q}}\varphi_{-\mathbf{q}}+\ \dots\Biggr\},&\\t_{\mathbf{q}}=\int d\hat{\mathbf{n}}f(\hat{\mathbf{u}},\hat{\mathbf{n}})\frac{4\sin^2(\mathbf{q}\cdot\hat{\mathbf{n}}L/2)}{(\mathbf{q}\cdot\hat{\mathbf{n}})^2L^2}.&\end{aligned} \tag{6}$$

Reconstructing exponent in Eq. (6) using Gaussian approximation, $1-\varphi^2\approx\exp(-\varphi^2)$, we find

$$Z_{str}(\psi)=\mathrm{const}\frac{V^N}{N!}\exp\Biggl(-\frac{1}{2m\rho}\int\frac{d\mathbf{q}}{(2\pi)^3}t_{\mathbf{q}}^{-1}\psi_{\mathbf{q}}\psi_{-\mathbf{q}}\Biggr) \tag{7}$$

after integration over the field φ. Here the constant const is independent of the density fluctuations ψ.

Let us consider the case of monovalent charged groups of the rods and their mobile counterions (possessing elementary charges $+e$ and $-e$, respectively) without salt: counterions are the only mobile low-molecular ions in the solution. Let us denote as Δ the distance between charged groups of the rod; then $\tau=a/\Delta$, $0<\tau<1$, is the fraction of the charged groups and their density is defined as $\tau\rho(\mathbf{x})$. Counterions provide macroscopic electrical neutrality of the solution and their density $c(\mathbf{x})$ is subjected to the condition $c_{\mathbf{q}=0} = \int d\mathbf{x} c(\mathbf{x}) = \tau \int d\mathbf{x} \rho(\mathbf{x}) = \tau\rho_{\mathbf{q}=0}$.

Local violation of electrical neutrality in the solution contributes to the Coulomb energy as

$$\frac{\delta F_{Coul}(\psi,\xi)}{k_BT} = \frac{l}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\frac{(\tau\psi_{\mathbf{q}}-\xi_{\mathbf{q}})(\tau\psi_{-\mathbf{q}}-\xi_{-\mathbf{q}})}{q^2}, \tag{8}$$

where the parameter $l = 4\pi l_B$ is proportional to the Bjerrum length $l_B = e^2/(\epsilon k_BT)$; ϵ is the dielectric constant of the solution; and $\xi_{\mathbf{q}}$ is the Fourier component of the density fluctuations of counterions $\xi_{\mathbf{q}} = c_{\mathbf{q}} - (2\pi)^3\delta(\mathbf{q})\tau\rho$, $\xi_{\mathbf{q}=0} = 0$.

To calculate the contribution of electrostatic interactions to the free energy of the solution we follow the Debye-Hückel theory [21] and consider small density fluctuations in "ideal gas" of rod molecules with counterions. Free energy functional of such a system can be written as a sum of three terms

$$F(\psi,\xi) = k_BT\int d\mathbf{x} c(\mathbf{x}) \ln[c(\mathbf{x})] - k_BT \ln Z_{str}(\psi) + \delta F_{Coul}(\psi,\xi), \tag{9}$$

where the first term is the energy of translational motion of counterions, the second term is the structural contribution of rodlike molecules, see Eq. (7), and the third term is the Coulomb energy, Eq. (8). Expansion of the first term in Eq. (9) into the series in powers of the variable ξ up to the quadratic term enables us to write Eq. (9) in the following form:

$$F(\psi,\xi) = k_BT\tau m N \ln(\tau\rho) + k_BTN \ln(\rho/m) + \delta F(\psi,\xi),$$

$$\frac{\delta F(\psi,\xi)}{k_BT} = \frac{1}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\left[\frac{\xi_{\mathbf{q}}\xi_{-\mathbf{q}}}{\tau\rho} + \frac{\psi_{\mathbf{q}}\psi_{-\mathbf{q}}}{m\rho t_{\mathbf{q}}} + \frac{l}{q^2}|\tau\psi_{\mathbf{q}}-\xi_{\mathbf{q}}|^2\right]. \tag{10}$$

The first two terms in F correspond to the energies of translational motion of counterions and rod molecules, respectively, in spatially homogeneous solution while δF describes small density fluctuations. The contribution of fluctuating charges to the total free energy of the solution ΔF_{el} can be found following a standard way:

$$\Delta F_{el} = -k_BT\left(\ln \int \mathcal{D}\psi\mathcal{D}\xi \exp\left\{-\frac{\delta F(\psi,\xi)}{k_BT}\right\} - \ln \int \mathcal{D}\psi\mathcal{D}\xi \exp\left\{-\frac{\delta F(\psi,\xi)}{k_BT}\bigg|_{l=0}\right\}\right), \tag{11}$$

where $\mathcal{D}\psi\mathcal{D}\xi \equiv \Pi_{\mathbf{q}} d\psi_{\mathbf{q}} d\xi_{\mathbf{q}}$ is a product of differentials. Calculation of Gaussian integrals in Eq. (11) is done in Appendix A. The result is

$$\Delta F_{el} = k_BT\frac{V}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\ln\left(1+\tau\rho l\frac{1+m\tau t_{\mathbf{q}}}{q^2}\right). \tag{12}$$

This expression diverges at $q\to\infty$ because self-energies of counterions and rodlike molecules contribute to ΔF_{el} according to the form of the Coulomb energy, Eq. (8). Therefore, to derive the electrostatic energy of interactions of the macromolecules with each other and the counterions we have to subtract the corresponding self-energies from Eq. (12). The total self-energy of the rodlike molecules ΔF_{el}^{sr} is the sum of the energies of each molecule,

$$\Delta F_{el}^{sr} = k_BT\sum_{i=1}^{N}\int d\hat{\mathbf{n}}_i f(\hat{\mathbf{u}},\hat{\mathbf{n}}_i) \times \frac{l}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\frac{\tau^2 v_{\mathbf{q}}(\hat{\mathbf{n}}_i) v_{-\mathbf{q}}(\hat{\mathbf{n}}_i)}{q^2},$$

$$v_{\mathbf{q}}(\mathbf{n}_i) = 2m\frac{\sin(\mathbf{q}\cdot\hat{\mathbf{n}}_i L/2)}{\mathbf{q}\cdot\hat{\mathbf{n}}_i L}\exp(-i\mathbf{q}\cdot\mathbf{R}_i), \tag{13}$$

where $v_{\mathbf{q}}(\hat{\mathbf{n}}_i)$ is the Fourier component of the density of i^{th} molecule [see Eq. (3), where $\rho_{\mathbf{q}} = \Sigma_i v_{\mathbf{q}}(\hat{\mathbf{n}}_i)$]. The result of calculations in Eq. (13) can be written as

$$\Delta F_{el}^{sr} = k_BT\frac{Nm^2\tau^2 l}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\frac{t_{\mathbf{q}}}{q^2}. \tag{14}$$

Correspondingly, the self-energy of $Nm\tau$ counterions has the form

$$\Delta F_{el}^{sc} = k_BT\frac{Nm\tau l}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\frac{1}{q^2}. \tag{15}$$

Correlation electrostatic energy of fluctuating charges, i.e., the energy of rods-rods, rods-counterions, and counterions-counterions many-body Coulomb interactions, takes the form

$$\Delta F_{corr} = \Delta F_{el} - \Delta F_{el}^{sr} - \Delta F_{el}^{sc} = k_BT\frac{V}{2}\int \frac{d\mathbf{q}}{(2\pi)^3}\left[\ln\left(1+\tau\rho l\frac{1+m\tau t_{\mathbf{q}}}{q^2}\right) - \tau\rho l\frac{1+m\tau t_{\mathbf{q}}}{q^2}\right]. \tag{16}$$

To check the validity of our approach let us reproduce first the classical result of the Debye-Hückel theory for ideal plasma with pointlike positive and negative charges having valency $z_1 = \tau m$ and $z_2 = 1$, respectively. For this purpose we have to consider the limit $L\to 0$ in Eq. (6) leading to $t_{\mathbf{q}} = 1$. For this limit the integral (16) is calculated exactly and has the form

$$\frac{\Delta F_{corr}}{V} = -\frac{k_BT}{12\pi}[l\tau\rho(1+\tau m)]^{3/2} = -k_BT\frac{2\pi^{1/2}}{3}\left[\frac{e^2}{\epsilon k_BT}(c_1z_1^2+c_2z_2^2)\right]^{3/2},$$

$$c_1=\frac{\rho}{m}, \quad c_2=\rho\tau, \tag{17}$$

which coincides with the classical result [21].

The opposite limit of rods with well defined shape can be obtained at $L\to\infty$. We will analyze two important cases: (i) disordered state of the solution when all orientations of the molecules are equally probable and (ii) completely ordered state when all molecules are oriented in parallel to each other.

A. Disordered state

In disordered state of the solution the distribution function $f(\hat{\mathbf{u}},\hat{\mathbf{n}})$ in Eq. (6) is constant, namely $f(\hat{\mathbf{u}},\hat{\mathbf{n}})=1/(4\pi)$, thus the structural function takes the form

$$t_{\mathbf{q}}=\frac{1}{qL}\int_{-qL/2}^{qL/2}dx\frac{\sin^2(x)}{x^2}. \tag{18}$$

The calculation of the free energy (16) with the structural function (18) as well as the corresponding contributions to the osmotic pressure and the chemical potential of the solution is presented in Appendix B [see Eqs. (B9), (B10)]. Interpolation form of the contribution of Coulomb interactions to the osmotic pressure can be written as

$$\Delta p_{dis}\approx-\frac{l\tau^2\rho}{12\pi a}-\frac{(l\rho\tau)^{3/2}}{24\pi}. \tag{19}$$

One can see that electrostatic interactions give a negative contribution to the osmotic pressure of the solution for all analyzed regimes [see Eqs. (B7), (B8)]. It means that the many-body Coulomb interaction of fluctuating charges favors the attraction of the molecules: Δp_{dis} decreases with the increase of polymer concentration.

Let us estimate the range of applicability of the derived expression. The main limitation of our approach is the assumption of small density fluctuations: electrostatic interactions only weakly perturb the homogeneous densities of rods and counterions. It means that the correlation free energy should be smaller than the energy of translational motion of rods and counterions which results in

$$l\tau/a<1 \quad \text{at} \quad l\rho a^2/\tau\ll 1 \quad (m\tau\gg 1),$$

$$\tau\rho l^3<1 \quad \text{at} \quad l\rho a^2/\tau\gg 1 \quad (m\tau\gg 1),$$

$$\tau(m\tau)^2\rho l^3<1 \quad \text{at} \quad m\tau\ll 1.$$

In the considered polyelectrolyte regime, $l\leqslant a$, these inequalities are always valid ($\tau\leqslant 1$).

B. Completely ordered state

In the completely ordered state of the solution, when all molecules are oriented in parallel to each other, the distribution function $f(\hat{\mathbf{u}},\hat{\mathbf{n}})$ in Eq. (6) has the form $f(\hat{\mathbf{u}},\hat{\mathbf{n}})=\delta(\hat{\mathbf{n}}-\hat{\mathbf{u}})$ and

$$t_{\mathbf{q}}=4\frac{\sin^2(\mathbf{q}\cdot\hat{\mathbf{u}}L/2)}{(\mathbf{q}\cdot\hat{\mathbf{u}}L)^2}. \tag{20}$$

The calculation of the correlation free energy with this function as well as the corresponding chemical potential and the osmotic pressure is presented in Appendix C. The pressure takes the form

$$\Delta p_{ord}\approx-\frac{l\tau^2\rho}{8\pi a}-\frac{(l\rho\tau)^{3/2}}{24\pi}. \tag{21}$$

This contribution is also negative for all analyzed regimes. This means that independently of the molecule orientation many-body charge interactions stimulate attraction of similarly charged molecules. The free energy of the completely ordered state, Eq. (C8), is smaller than the free energy of the disordered state, Eq. (B10): the larger the argument of logarithm (length of rods), the larger the difference between the energies. If we assume that the free energy as a function of molecular orientation is monotonous, we can conclude that Coulomb attraction *favors ordering* of the molecules.

The physical reason of Coulomb attraction of the molecules in the completely ordered state at small polymer concentrations is the following. A system of infinitely long parallel rods has cylindrical symmetry and symmetry of electric field of each individual molecule is close to cylindrical one if their volume fraction ϕ is small, $\phi\ll 1$. Then the total Coulomb energy of N rods is approximately equal to the sum of energies of individual molecules. It is well known that the energy of a cylinder logarithmically diverges and depends on the outer radius R, which is determined by the volume fraction ϕ, $R=a/\phi^{1/2}$. Neglecting charge fluctuations, the Coulomb energy in main approximation (with respect to small volume fraction ϕ) takes the form

$$\frac{U_{cyl}}{k_BT}=N\frac{(em\tau)^2}{k_BTL}\ln(R/a)=Nm\frac{l\tau^2}{8\pi a}\ln(1/\phi). \tag{22}$$

The calculation of the osmotic pressure with this formula gives exactly the same expression as the first term in Eq. (21). Therefore, the driving force of Coulomb attraction at small concentrations is the tendency to reduce the energy of the cylinder by decreasing the volume fraction. Note that the alternative decrease of the Coulomb energy of the cylinder via the Manning mechanism of counterion condensation [23,24] becomes possible only at $l>a$.

III. FREE ENERGIES OF ISOTROPIC AND NEMATIC PHASES

To describe nonCoulomb interactions at liquid-crystalline ordering in the solution of rodlike molecules let us use the Onsager approach [1] with the orientational distribution function

$$f(\hat{\mathbf{u}},\hat{\mathbf{n}})=\frac{\alpha}{4\pi\sinh(\alpha)}\cosh(\alpha\hat{\mathbf{u}}\cdot\hat{\mathbf{n}}), \quad \int d\hat{\mathbf{n}}f(\hat{\mathbf{u}},\hat{\mathbf{n}})=1, \tag{23}$$

where α is the variation parameter, $0 \leqslant \alpha < \infty$; $\alpha = 0$ and $\alpha > 0$ correspond to isotropic (disordered) and nematic phases of the solution, respectively. Complete nematic ordering is attained in the limit $\alpha \to \infty$ when $f(\hat{\mathbf{u}},\hat{\mathbf{n}}) \to \delta(\hat{\mathbf{u}} - \hat{\mathbf{n}})$. The Onsager approach, developed initially for neutral rodlike molecules, is based on the consideration of the two contributions to the free energy characterizing different phases: entropic losses of rods because of their orientation and pairwise excluded volume repulsion of the molecules which is orientation-dependent,

$$\begin{aligned}\mathcal{F}_{Onsager}(\alpha) &= \frac{\rho}{m}\int d\hat{\mathbf{n}} f(\hat{\mathbf{u}},\hat{\mathbf{n}}) \ln[4\pi f(\hat{\mathbf{u}},\hat{\mathbf{n}})] \\ &\quad + \frac{\rho^2}{2m^2}\int d\hat{\mathbf{n}}_1 d\hat{\mathbf{n}}_2 f(\hat{\mathbf{u}},\hat{\mathbf{n}}_1) f(\hat{\mathbf{u}},\hat{\mathbf{n}}_2) B(\gamma) \\ &= \frac{\rho}{m}\left\{ \ln[\alpha \coth(\alpha)] - 1 + \frac{\arcsin[\tanh(\alpha)]}{\sinh(\alpha)} \right\} \\ &\quad + 2\rho^2 a^3 \frac{I_2(2\alpha)}{\sinh(\alpha)^2}, \mathcal{F}_{Onsager}(0) = \rho^2 a^3,\end{aligned} \tag{24}$$

where $B(\gamma) = 2L^2 a \sin(\gamma)$ is the second virial coefficient of rods making an angle γ with respect to each other; I_2 is the Bessel function.

To describe Coulomb interactions of the molecules in the nematic phase, where the order parameter

$$S = \int d\hat{\mathbf{n}} f(\hat{\mathbf{n}},\hat{\mathbf{u}}) \frac{3(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}})^2 - 1}{2} = 1 - \frac{3}{\alpha^2}\left(\frac{\alpha \cosh(\alpha)}{\sinh(\alpha)} - 1 \right) \tag{25}$$

can be less than unity (parameter α has some finite value), we have to calculate the correlation free energy, Eq. (16), with the orientational distribution function, Eq. (23).

A. Instability of disordered state toward nematic ordering at small polymer concentrations

In this section we will show that already at small polymer concentrations the isotropic phase becomes unstable with respect to weak orientation of the molecules. For this purpose let us calculate the spinodal of isotropic-nematic ordering. It can be done using general approach [independently of particular choice of the trial function, Eq. (23)] which is based on the expansion of the distribution function $f(\hat{\mathbf{u}},\hat{\mathbf{n}})$ of the weakly ordered state into the series of Legendre polynomials,

$$f(\hat{\mathbf{u}},\hat{\mathbf{n}}) \approx \frac{1}{4\pi}\left(1 + \frac{5S}{2}[3(\hat{\mathbf{u}} \cdot \hat{\mathbf{n}})^2 - 1] + \dots \right), \quad S \ll 1. \tag{26}$$

We will consider in Eq. (26) the first two terms of the series due to weak orientation of the molecules. Then the structural function can be presented in the following form:

$$t_{\mathbf{q}}^{wo} = t_{\mathbf{q}} + \delta t_{\mathbf{q}}, \tag{27}$$

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

where $t_{\mathbf{q}}$ is the structural function of the disordered state, Eq. (18). Expansion of the correlation free energy (16) with the structural function of weakly ordered molecules, $t_{\mathbf{q}}^{wo}$, into the series in powers of $\delta t_{\mathbf{q}}$ results in

$$\mathcal{F}_{wo} = \mathcal{F}_{dis} + \delta\mathcal{F}, \tag{28}$$

$$\delta\mathcal{F} = -\frac{1}{4(2\pi)^3}\int d\hat{\mathbf{u}} \int_0^\infty dq q^2 \frac{(l\rho m)^2 \tau^4 \delta t_{\mathbf{q}}^2}{[q^2 + l\rho\tau(1 + m\tau t_{\mathbf{q}})]^2}.$$

For the most interesting case of the large number of charged units on the chain, $m\tau \gg 1$, we can use asymptotic forms of the functions $t_{\mathbf{q}}$ and $\delta t_{\mathbf{q}}$ at $qL \gg 1$ (see Appendix B). In this limit the integral in Eq. (28) takes the form

$$\delta\mathcal{F} = -\frac{5}{24\pi}\frac{l\rho\tau^2}{a}S^2. \tag{29}$$

Similarly, calculation of the orientational entropy of rod molecules [first term in Eq. (24)] with distribution function (26) gives

$$\delta\mathcal{F}_{orient} = \frac{5\rho}{2m}S^2. \tag{30}$$

Neglecting the contribution of excluded volume repulsion of rods at small polymer concentrations, which is proportional to ρ^2, we can write the excess energy of the weakly ordered state in the following form:

$$\delta\mathcal{F}_{tot} = \delta\mathcal{F}_{orient} + \delta\mathcal{F} = \frac{5}{2}\rho\left(\frac{1}{m} - \frac{l\tau^2}{12\pi a} \right) S^2. \tag{31}$$

Therefore, if the fraction of charged groups of rod molecules τ exceeds some certain value, $\tau > \sqrt{12\pi a/(lm)}$, the isotropic state of the solution becomes unstable even at very small polymer concentrations: the longer the polymer chain, the smaller the threshold value of τ.

B. Approximation for anisotropic Coulomb free energy

The calculation of the correlation free energy of Coulomb interactions for arbitrary values of the order parameter S (α) can be given only numerically. To overcome computational difficulties and to get qualitatively correct results we use simple interpolation form assuming monotonous dependence of the correlation free energy on α,

$$\mathcal{F}_{corr}(\alpha) = \frac{1}{1+\alpha}\mathcal{F}_{dis} + \frac{\alpha}{1+\alpha}\mathcal{F}_{ord}. \tag{32}$$

It decreases from $\mathcal{F}_{dis}$ at $\alpha = 0$ up to the value $\mathcal{F}_{ord}$ at $\alpha = \infty$.

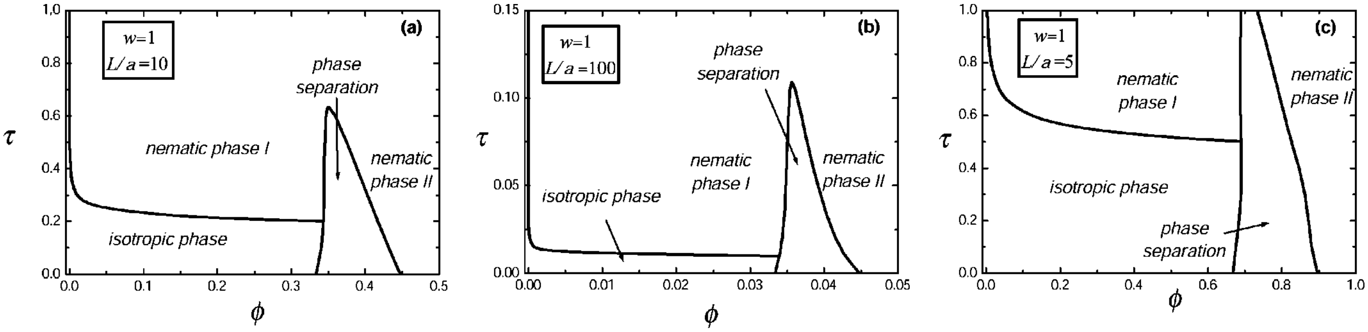

FIG. 1. Phase diagrams of the solution of the rigid-rod polyelectrolyte in variables: polymer volume fraction ϕ and the fraction of charged groups of the rods τ for different values of the aspect ratio of the molecules; $L/a=10$ (a), $L/a=100$ (b), and $L/a=5$ (c); $w=1$.

The resulting free energies of the isotropic ($\mathcal{F}_i$) and nematic ($\mathcal{F}_n$) phases of the solution have the form

$$\mathcal{F}_i=\mathcal{F}_{corr}(0)+\mathcal{F}_{Onsager}(0)+\mathcal{F}_{tr},$$

$$\mathcal{F}_n=\mathcal{F}_{corr}(\alpha)+\mathcal{F}_{Onsager}(\alpha)+\mathcal{F}_{tr}, \tag{33}$$

$$\mathcal{F}_{tr}=\tau\rho\ln(\tau\rho a^3)+\frac{\rho}{m}\ln\left(\frac{\rho a^3}{m}\right),$$

where $\mathcal{F}_{tr}$ is the energy of the translational motion of counterions and rods. The chemical potentials ($\mu_{i,n}$) and osmotic pressures ($\pi_{i,n}$) of various phases of the solution are derived following a standard way:

$$\mu_{i,n}=\frac{\partial\mathcal{F}_{i,n}}{\partial\rho},\qquad \pi_{i,n}=\rho^2\frac{\partial}{\partial\rho}\left(\frac{\mathcal{F}_{i,n}}{\rho}\right). \tag{34}$$

Thus, the system described by the free energies (33) favors liquid-crystalline ordering due to excluded volume repulsion of the molecules and their Coulomb attraction while losses in orientational entropy of the molecules counteract this ordering.

IV. RESULTS AND DISCUSSIONS

The analysis of the free energy (33) of nematic phase as a function of the parameter α shows that at certain conditions this function may reveal 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. To construct the phase diagram of such a solution we have to solve the set of the following equations:

$$\begin{aligned}&\mu_i(\rho_0)=\mu_n(\rho_1), &&\mu_i(\rho_0)=\mu_n(\rho_2),\\ &\pi_i(\rho_0)=\pi_n(\rho_1), &&\pi_i(\rho_0)=\pi_n(\rho_2),\\ &\frac{\partial\mathcal{F}_n(\rho_1)}{\partial\alpha_1}=0, &&\frac{\partial\mathcal{F}_n(\rho_2)}{\partial\alpha_2}=0,\end{aligned}$$

$$\begin{aligned}&\mu_n(\rho_1)=\mu_n(\rho_2),\\ &\pi_n(\rho_1)=\pi_n(\rho_2),\\ &\frac{\partial\mathcal{F}_n(\rho_1)}{\partial\alpha_1}=0,\quad \frac{\partial\mathcal{F}_n(\rho_2)}{\partial\alpha_2}=0,\end{aligned} \tag{35}$$

giving the binodals for isotropic/nematic I, isotropic/nematic II, and nematic I/nematic II phases, respectively.

Phase diagrams of the solution in variables: polymer volume fraction $\phi=\rho a^3$ and the fraction of charged groups of the rod τ are presented in Fig. 1 at various values of aspect ratio of rodlike molecule, $L/a=m$. Figure 1 depicts the diagram at $L/a=10$. In accordance with the analysis of the spinodal of the order-disorder transition, the isotropic phase remains stable only below a certain value of τ. Above this value weakly ordered nematic phase I appears already at very small polymer concentrations. The width of the phase separation region between these phases is very small and is not distinguishable at the length scale of the diagram. In contrast, the width of the phase separation region between the isotropic and highly ordered nematic phase II is significant. It narrows with the increase of τ from the maximum value at $\tau=0$ corresponding to neutral rod chains. Such behavior is caused by the increase of a number of counterions with τ: the contribution of translational motion of counterions, which is proportional to τ, dominates over the Coulomb term $\sim\tau^2$ at small values of τ. Phase separation is always accompanied by entropy losses of those counterions, which are localized in denser phase to compensate its macroscopic charge. Therefore, the larger the number of counterions, the smaller should be the concentration jump at the phase separation.

Coexistence of two nematic phases at certain intermediate values of the degree of ionization of rod molecules τ is the result of two stabilizing factors: weakly ordered nematic phase I and highly ordered nematic phase II are stabilized by Coulomb and excluded volume interactions, respectively. When these two kinds of interactions become comparable (with the increase of τ) the difference between the nematic phases vanishes at the critical point.

The influence of the aspect ratio of rodlike molecules on phase behavior of the solution is demonstrated in Figs. 1(b) and 1(c). These figures correspond to $L/a=100$ and $L/a=5$, respectively. The increase of the length of the molecules leads to expansion of the stability region of the nematic phase in both directions: its boundaries are shifted toward smaller polymer volume fractions ϕ (as for the case of neutral solutions) and smaller values of τ [compare Figs. 1(a) and 1(b)]. Formation of weakly ordered nematic phase I at smaller values of τ (weaker Coulomb attraction), Fig. 1(b), is

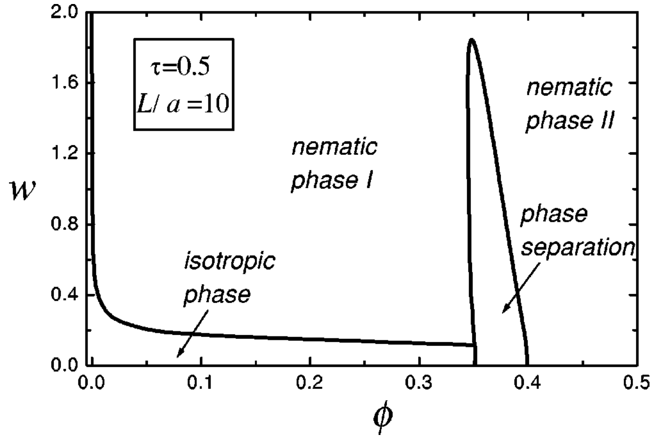

FIG. 2. Phase diagram of the solution of rodlike molecules in variables: polymer volume fraction ϕ and the parameter $w = 4\pi e^2/(a\epsilon k_B T)$ at a fixed fraction of charged groups τ.

caused by smaller losses of orientational entropy of longer rods which is in accordance with the condition for the spinodal; at the spinodal there should be $\tau \sim 1/m^{1/2}$. The phase diagram for short enough rod molecules can exhibit phase separation and two different nematic phases within the whole range of values of τ, Fig. 1(c).

The parameter $w = 4\pi e^2/(a\epsilon k_B T)$ strongly depends on the dielectric constant of the solution and the variation of ϵ can induce phase transitions. The phase diagram in variables $\phi - w$ at fixed values of the degree of ionization τ and aspect ratio L/a is presented in Fig. 2. One can see that there is a wide enough range of polymer volume fractions ϕ where the order-disorder transition occurs at the increase of the dielectric constant (decrease of w).

In contrast to athermal and lyotropic liquid-crystalline solutions [6,8], where both concentration and temperature variation can result in phase separation with the abrupt jump of the order parameter, for polyelectrolyte solution the variation of the order parameter can be continuous, starting from a very small value. In Fig. 3 the order parameter S, Eq. (25), is plotted as a function of polymer volume fraction ϕ, at different fractions of charged groups τ and fixed values of the aspect ratio and of parameter w. At small values of τ, where only the isotropic and highly ordered nematic phase *II* are stable, the order parameter is constant in the coexistence region; then it grows with ϕ, Fig. 3(a). In weakly ordered nematic phase *I*, which is stable at intermediate values of τ, the order parameter can vary within a small enough interval, Fig. 3(b). Gradual variation of the order parameter becomes possible at high fractions of charged groups, exceeding the critical value, Fig. 3(c) and 3(d).

V. CONCLUSIONS

In the present paper the theory of liquid-crystalline ordering in the solution of charged rodlike molecules is proposed. We studied polyelectrolyte regime of the solution, i.e., when the parameter w is small enough, $e^2/(a\epsilon k_B T) < 1$. Assuming that in this regime counterion condensation does not occur and that charge fluctuations are small, we developed a theory of the Debye-Hückel type to take into account rods-rods, rods-counterions, and counterions-counterions many-body Coulomb interactions. The energy of such interactions was calculated for two states of the solution: (i) disordered and (ii) completely ordered (the order parameter is equal to unity). We found that for all the analyzed regimes the many-body Coulomb interactions of similarly charged rods are *attractive* independent of their mutual orientation. The Coulomb energy of the completely ordered state was shown to be lower than the Coulomb energy of the disordered state. It means that electrostatic attraction of the molecules promotes liquid-crystalline ordering in addition to the usual excluded volume driven mechanism. As a result, the existence of two nematic phases differing in the value of the order parameter is predicted. We found that the weaker ordered nematic

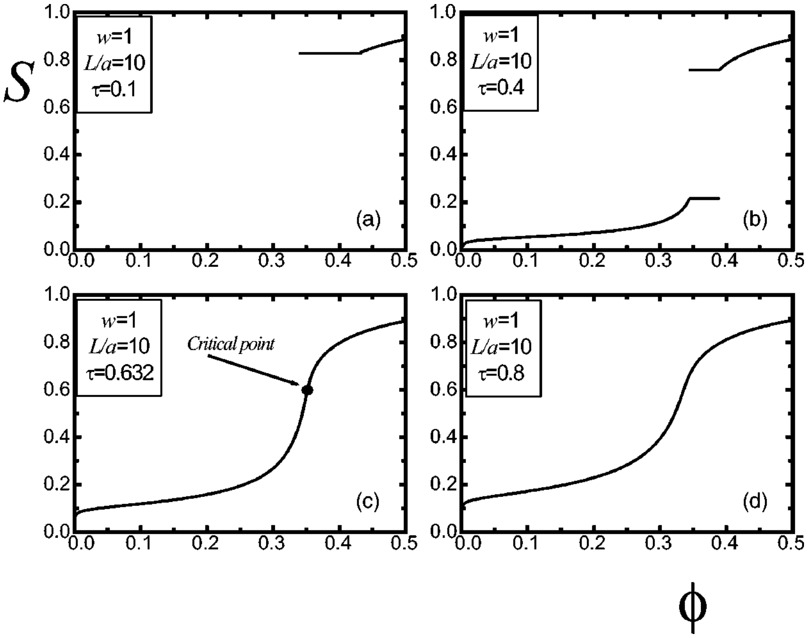

FIG. 3. Order parameter of the nematic phase S as a function of polymer volume fraction ϕ at different values of the volume fraction of charges τ: $\tau = 0.1$ (a), 0.4 (b), 0.632 (c), 0.8 (d). The horizontal lines in (a) and (b) correspond to coexistence regions.

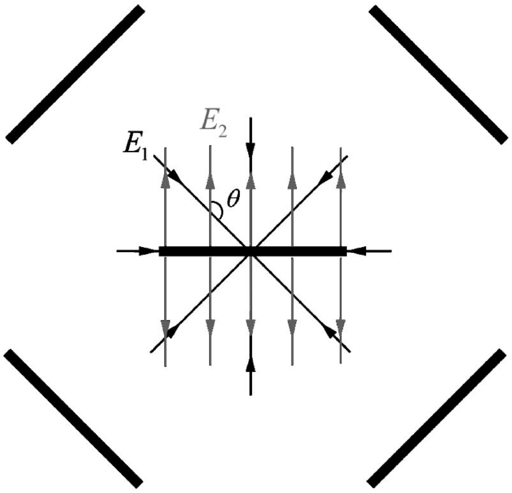

FIG. 4. Schematic representation of the force lines of the electric field in the isotropic state of the solution of rodlike molecules. The gray lines depict the electric field of the selected molecule. This field has cylindrical symmetry. The superposition of the electric fields of all the rod molecules and counterions, except the field of the selected molecule, is depicted by the black lines. It has spherical symmetry. E_1 and E_2 are the intensities of the fields making the angle θ with respect to each other.

phase is stabilized by Coulomb interactions already at very small polymer concentrations. This effect is not connected with the fluctuation mechanism (at least for small concentrations). It is a consequence of the ‘‘competition’’ between (i) intrinsic cylindrical symmetry of electric field of single rodlike molecules and (ii) spherical symmetry of electric fields of all rod molecules and counterions (except the field of the selected molecule) in isotropic phase of the solution, Fig. 4. In dilute solutions the Debye screening length of counterions, $r_D=1/\sqrt{l\tau\rho}$, is large and interactions between rod molecules are long range. Let us select one molecule in the solution, Fig. 4. The force lines of the electric field, obtained by superposition of the electric fields of all rods and counterions except for the selected molecule, are drawn in black. This field has spherical symmetry because all rod molecules in isotropic phase of the solution are oriented in an arbitrary way. Gray lines depict the cylindrical field of the selected molecule. It is well known [28], that the energy of the electric field per unit of volume is proportional to the square of the total intensity of the field, $U_{el}\sim(\mathbf{E}_1+\mathbf{E}_2)^2$. Therefore, this energy depends on the mutual orientation of the force lines, $U_{el}\sim E_1^2+E_2^2+2E_1E_2\cos\theta$, and the minimum of the energy can be attained at the antiparallel orientation of the lines (at $\theta=\pi$). Because charges of rigid rod molecule cannot change configuration, the orientation of the molecules is the only way to minimize the free energy.

Therefore, we arrive at a fundamental conclusion: long-range electrostatic interactions in very dilute solutions of rigid rods should induce a very weakly ordered nematic phase. In other words, isotropic solutions of this type are intrinsically unstable with respect to orientational ordering.

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APPENDIX A: CORRELATION FREE ENERGY

One of the possible ways to calculate the Gaussian integrals in Eq. (11) is substitution of continual integration over the wave vector $\mathbf{q}$ in the fluctuating free energy δF, Eq. (10), by discrete summation over wave numbers $\mathbf{k}$, $\mathbf{q}=2\pi\{k_x/\mathcal{L}_x,k_y/\mathcal{L}_y,k_z/\mathcal{L}_z\}$, $k_x,k_y,k_z=0,\pm1,\pm2,\ldots,$ where $\mathcal{L}_{x,y,z}$ are linear dimensions of the system, $\mathcal{L}_x\mathcal{L}_y\mathcal{L}_z=V$:

$$\frac{\delta F(\psi,\xi)}{k_BT}=\frac{1}{2V}\sum_{\mathbf{k}}\left[\frac{\xi_{\mathbf{k}}\xi_{-\mathbf{k}}}{\tau\rho}+\frac{\psi_{\mathbf{k}}\psi_{-\mathbf{k}}}{m\rho t_{\mathbf{k}}}+\frac{l}{q_{\mathbf{k}}^2}|\tau\psi_{\mathbf{k}}-\xi_{\mathbf{k}}|^2\right], \tag{A1}$$

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

Then the expressions in logarithms of Eq. (11) are infinite products of integrals over variables $\psi_{\mathbf{k}}$ and $\xi_{\mathbf{k}}$. Diagonalization of the square form, Eq. (A1), can be done via the following variable substitution:

$$\xi_{\mathbf{k}}=\overline{\xi_{\mathbf{k}}}+\psi_{\mathbf{k}}\frac{\tau^2\rho l}{\tau\rho l+q_{\mathbf{k}}^2},$$

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

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 $\psi_{\mathbf{k}}$ and $\overline{\xi_{\mathbf{k}}}$, we obtain

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

where in the last equality we have returned from summation to integration.

APPENDIX B: DISORDERED STATE

The calculation of the correlation free energy, Eq. (16), in the disordered state [with structural function (18)] can be performed via integration by parts over the dimensionless variable $y=qL$, $0<y<\infty$, $d\mathbf{q}=4\pi q^2dq=4\pi y^2dy/L^3$,

$$\mathcal{F}_{dis}=\frac{\Delta F_{corr}}{k_BTV}=\frac{1}{(2\pi)^2L^3}\left[\frac{y^3}{3}\ln\left(1+\tau\rho lL^2\frac{1+m\tau t_y}{y^2}\right)\Bigg|_0^\infty-\frac{\tau\rho lL^2}{3}\int_0^\infty dy\frac{m\tau y^3t_y'-2y^2(1+m\tau t_y)}{y^2+\tau\rho lL^2(1+m\tau t_y)}-\tau\rho lL^2\int_0^\infty dy(1+m\tau t_y)\right], \tag{B1}$$

$$t_y=\frac{2}{y}\int_0^{y/2}dz\frac{\sin^2(z)}{z^2},$$

where t_y' is the derivative of the function t_y. Using the relation

$$t_y'=-\frac{t_y}{y}+\frac{4\sin^2(y/2)}{y^3}, \tag{B2}$$

we represent Eq. (B1) as

$$\mathcal{F}_{dis}=\frac{\tau\rho l}{(2\pi)^2L}\left[\frac{\pi m\tau}{3}-\frac{1}{3}\int_0^\infty dy\times\frac{4m\tau\sin^2(y/2)+\tau\rho lL^2(1+m\tau t_y)(2+3m\tau t_y)}{y^2+\tau\rho lL^2(1+m\tau t_y)}\right]. \tag{B3}$$

The contribution of electrostatic interactions to the chemical potential of the solution can be found from Eq. (16),

$$\Delta\mu_{dis}=\frac{\partial\mathcal{F}_{dis}}{\partial\rho}=-\frac{\rho\tau^2l^2L}{(2\pi)^2}\int_0^\infty dy\frac{(1+m\tau t_y)^2}{y^2+\tau\rho lL^2(1+m\tau t_y)}. \tag{B4}$$

Combining Eqs. (B3) and (B4) one can obtain the corresponding contribution to the osmotic pressure of the solution in the following form:

$$\begin{aligned}\Delta p_{dis}&=\Delta\mu_{dis}\rho-\mathcal{F}_{dis}\\&=-\frac{l\tau^2\rho}{12\pi a}+\frac{l\tau^2\rho}{3\pi^2a}\int_0^\infty dy\frac{\sin^2(y/2)}{y^2+\tau\rho lL^2(1+m\tau t_y)}\\&\quad-\frac{l^2\tau^2\rho^2L}{3(2\pi)^2}\int_0^\infty dy\frac{(1+m\tau t_y)}{y^2+\tau\rho lL^2(1+m\tau t_y)}.\end{aligned} \tag{B5}$$

Now let us consider two limiting cases.

1. Large number of charged units per chain, $m\tau\gg1$

In this case the second term in Eq. (B5) is small and can be neglected. Also, the asymptotic form of the function t_y at $y\gg1$, $t_y\approx\pi/y$, can be used

$$\Delta p_{dis}\approx-\frac{l\tau^2\rho}{12\pi a}-\frac{l^2\rho^2\tau a}{3(2\pi)^2}\int_0^\infty dz\frac{z+\pi}{z^3+\dfrac{l\rho a^2}{\tau}(z+\pi)}. \tag{B6}$$

One can distinguish two regimes depending on $l\rho a^2/\tau$:

$$\Delta p_{dis}\approx-\frac{l\tau^2\rho}{12\pi a}-\begin{cases}\dfrac{\sqrt{3}}{54\pi^{2/3}}\dfrac{(l\rho)^{4/3}\tau^{5/3}}{a^{1/3}} & \text{at}\quad \dfrac{l\rho a^2}{\tau}\ll1\\[2ex] \dfrac{1}{24\pi}(l\rho\tau)^{3/2} & \text{at}\quad \dfrac{l\rho a^2}{\tau}\gg1.\end{cases} \tag{B7}$$

The first regime corresponds to the case when the distance between charged groups of the molecule, $\Delta=a/\tau$, is smaller than the Debye screening length of counterions, $r_D=1/\sqrt{l\tau\rho}$, $\Delta^2/r_D^2=l\rho a^2/\tau\ll1$. In the considered limit of the large number of charged groups, $m\tau\gg1$, and $l\sim a$ this regime is realized at small enough polymer volume fractions, $a^3\rho\ll\tau$. The linear term in Eq. (B7) gives main contribution to pressure at $l\rho a^2/\tau\ll1$ in comparison with the upper term in the curly bracket. From physical viewpoint it means that interchain attraction dominates over the chains-counterions attraction and the structure of the molecule determines the interaction law.

The second regime in Eq. (B7) corresponds to small Debye screening length r_D, $r_D\ll\Delta$, at high concentrations, $\tau\ll a^3\rho<1$. In this case the structure of interpenetrating chains does not play a role and the main contribution to the osmotic pressure has the same form as for pointlike molecules (lower term in the curly bracket).

2. Small number of charged units per chain, $m\tau\ll1$

For the considered rodlike chains with well defined shape, $m\gg1$, the condition $\tau\ll1/m$ means vanishing values of τ, $\tau\to0$. In this limit the third term in Eq. (B5) gives the dominant contribution to the pressure at finite values of the polymer concentration ρ:

$$\Delta p_{dis}\approx-\frac{1}{24\pi}(l\rho\tau)^{3/2}. \tag{B8}$$

Obviously, this result coincides with the corresponding pressure of pointlike charges of density $\tau\rho$ because the molecular structure does not play a role in this limit.

Comparison of Eqs. (B7) and (B8) enables us to choose the contribution of charge interactions to pressure in the following form:

$$\Delta p_{dis}\approx-\frac{l\tau^2\rho}{12\pi a}-\frac{(l\rho\tau)^{3/2}}{24\pi}, \tag{B9}$$

which unifies both limits of τ and ρ. We will use in the following this interpolation form for the description of liquid-crystalline transitions. The corresponding free energy and chemical potential in this approximation take the form

$$\mathcal{F}_{dis} \approx -\frac{l\tau^2\rho}{12\pi a}[\ln(\rho l a^2\tau^2 m^3) - C_1] - \frac{(l\rho\tau)^{3/2}}{12\pi},$$

$$C_1 = \frac{12}{\pi}\int_0^\infty dy\,\ln(y)\,\frac{\sin^2(y/2)}{y^2} - \ln(\pi) \approx 0.12,$$

$$\Delta\mu_{dis} \approx -\frac{l\tau^2}{12\pi a}[\ln(\rho l a^2\tau^2 m^3) - C_1 + 1] - \frac{(l\tau)^{3/2}\rho^{1/2}}{8\pi}. \tag{B10}$$

The first term in $\mathcal{F}_{dis}$ can be derived from Eq. (16) in the limit $m\tau \gg 1$, if we set $t_y \approx \pi/y$ in the logarithmic term.

APPENDIX C: COMPLETELY ORDERED STATE

Integration of Eq. (16) with the structural function of the completely ordered state, Eq. (20), over the angle between vectors $\hat{\mathbf{u}}$ and $\mathbf{q}$ results in

$$\mathcal{F}_{ord} = \frac{4}{(2\pi)^2 L^3}\int_0^\infty dy\,y^2\left[\omega\frac{1+m\tau t_y}{y^2} - \left(1+\omega\frac{1+m\tau t_y}{y^2}\right)\ln\left(1+\omega\frac{1+m\tau t_y}{y^2}\right)\right],$$

$$t_y = \frac{\sin^2(y)}{y^2}, \qquad \omega = l\tau\rho L^2/4. \tag{C1}$$

It is worthwhile first to calculate the derivative of $\mathcal{F}_{ord}$ with respect to the parameter ω,

$$\frac{\partial\mathcal{F}_{ord}}{\partial\omega} = -\frac{4}{(2\pi)^2 L^3}\int_0^\infty dy(1+m\tau t_y)\ln\left(1+\omega\frac{1+m\tau t_y}{y^2}\right). \tag{C2}$$

1. Large number of charged units per chain, $m\tau \gg 1$

It is clear that the completely ordered state of the solution cannot be attained at very low polymer concentrations. Therefore, we confine ourselves to consideration of the case $\omega m\tau \gg 1$. It means that for the polyelectrolyte regime, $l \sim a$, the polymer volume fraction $\phi \sim \rho a^3$ should be larger than $1/(m^3\tau^2)$, $\phi \gg 1/(m^3\tau^2)$. In the limit of the large number of charged units per chain, $m\tau \gg 1$, such an assumption does not reduce the generality of our approach and covers a very wide concentration range including even the dilute regime, $1/(m^3\tau^2) \ll \phi < \phi^* \sim 1/m^2$. The derivative in Eq. (C2) can be written as

$$\frac{\partial\mathcal{F}_{ord}}{\partial\omega} \approx -\frac{1}{\pi^2 L^3}\left[m\tau\int_0^\xi dy\,t_y\ln\left(1+\omega m\tau\frac{t_y}{y^2}\right) + \int_\xi^\infty dy\,\ln\left(1+\frac{\omega}{y^2}\right)\right], \tag{C3}$$

where $\xi \sim \sqrt{m\tau} \gg 1$. Depending on ω one can distinguish two regimes. At $\omega < \xi^2$ the first integral in the square brackets of Eq. (C3) can be written as the sum of two terms,

$$\begin{aligned}\int_0^\xi dy\,t_y\ln\left(1+\omega m\tau\frac{t_y}{y^2}\right) &\approx \int_0^{\omega^{1/4}\xi^{1/2}} dy\,t_y\ln\left(\frac{\omega m\tau t_y}{y^2}\right) + \omega m\tau\int_{\omega^{1/4}\xi^{1/2}}^{\xi} dy\,\frac{t_y^2}{y^2}\\ &\approx \frac{\pi}{2}\ln(\omega m\tau) + \int_0^\infty dy\,t_y\ln\left(\frac{t_y}{y^2}\right) + O\left(\frac{1}{\omega^{1/4}\xi^{1/2}}\right)\end{aligned} \tag{C4}$$

and the second integral takes the form

$$\begin{aligned}\int_\xi^\infty dy\,\ln\left(1+\frac{\omega}{y^2}\right) &= \sqrt{\omega}\left(\pi - 2\arctan\frac{\xi}{\sqrt{\omega}}\right) - \xi\ln\left(1+\frac{\omega}{\xi^2}\right)\\ &= O\left(\frac{\omega}{\xi}\right) \quad \text{at} \quad \omega < \xi^2.\end{aligned} \tag{C5}$$

The other regime, $\omega > \xi^2$, is analyzed in a similar manner. The result in the main order of magnitude can be presented as

$$\frac{\partial\mathcal{F}_{ord}}{\partial\omega} \approx -\frac{1}{2\pi L^3} \times \begin{cases} m\tau[\ln(4\omega m\tau) + C_2] + \cdots & \text{at} \quad \omega < \xi^2\\ m\tau[\ln(4\omega m\tau) + C_2] + 2\sqrt{\omega} + \cdots & \text{at} \quad \omega > \xi^2,\end{cases} \tag{C6}$$

$$C_2 = \frac{2}{\pi}\int_0^\infty dy\,t_y\ln\left(\frac{t_y}{4y^2}\right) \approx -1.69.$$

2. Small number of charged units per chain, $m\tau \ll 1$

In this case Eq. (C2) takes the form

$$\frac{\partial\mathcal{F}_{ord}}{\partial\omega} \approx -\frac{1}{\pi^2 L^3}\int_0^\infty dy\,\ln\left(1+\frac{\omega}{y^2}\right) = -\frac{\sqrt{\omega}}{\pi L^3}. \tag{C7}$$

Comparing Eqs. (C6) and (C7) one can choose the value of $\partial\mathcal{F}_{ord}/\partial\omega$ at $\omega > \xi^2$ as the interpolation form covering all the considered limits. In this approximation the contribution of Coulomb interactions to the free energy, chemical potential and osmotic pressure of the completely ordered state of the solution have the form

$$\mathcal{F}_{ord} \approx -\frac{l\tau^2\rho}{8\pi a}[\ln(\rho l a^2\tau^2 m^3) + C_2 - 1] - \frac{(l\rho\tau)^{3/2}}{12\pi},$$

$$\Delta\mu_{ord} \approx -\frac{l\tau^2}{8\pi a}[\ln(\rho l a^2\tau^2 m^3) + C_2] - \frac{(l\tau)^{3/2}\rho^{1/2}}{8\pi},$$

$$\Delta p_{ord} \approx -\frac{l\tau^2\rho}{8\pi a} - \frac{(l\rho\tau)^{3/2}}{24\pi}. \tag{C8}$$

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