Complexation of oppositely charged polyelectrolytes: Effect of discrete charge distribution along the chain

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Similar to the Debye-Hückel plasma, charged groups of oppositely charged polyelectrolytes attract each other. We find exact expression for the correlation free energy of electrostatic attraction in polyelectrolytes within the random phase approximation. The obtained expression is shown to be valid in dilute, semidilute, concentrated solutions, and melts. In this theory we explicitly take into account positions of charged groups on the chains and examine both charge and polymer concentrations fluctuations. The existence of the critical point in θ solvent is demonstrated. The theory reproduces scaling results and describes the system beyond the scaling approximation.

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I. INTRODUCTION

Complexation of oppositely charged polyelectrolytes plays crucial role in living nature [1,2] and numerous industrial applications [3–6]. That is why understanding of peculiarities of electrostatic interactions in such systems is a topical problem in modern polymer science. Polyelectrolytes are macromolecules containing some fraction of charged groups and similar to the Debye-Hückel plasma, attractive electrostatic forces act between the charged groups in solutions of oppositely charged macromolecules. However, in contrast to the ideal gas of the ions, small thermodynamic fluctuations of charges on polymer chains are able to induce complexation or precipitation of the chains because polymers are known to be "poor" in entropy.

Theoretical description of the fluctuations induced electrostatic attraction in oppositely charged polyelectrolytes has a history of two decades. A pioneer theory by Borue and Erukhimovich was based on the random phase approximation (RPA) [7,8]. Using the gradient term for the entropy of a polymer chain, the authors could get analytical expression for the free energy [7,8]. Further theoretical approaches improved "polymeric ingredients" of the model considering the Debye function as a density-density correlation function and taking into account finite size of the charged groups [9,10]. Theories beyond the RPA were developed in Refs. [11,12].

All theories mentioned above are common in a sense that they examine charges on the chains which are homogeneously "smeared" along the chains even in the case if their fraction f is small enough. In other words, the charge concentration fluctuations $\xi^\pm(\mathbf{r})$ are assumed to be proportional to the polymer concentration fluctuations $\psi^\pm(\mathbf{r})$, $\xi^\pm(\mathbf{r}) = f\psi^\pm(\mathbf{r})$, at any length scales. That is why the electrostatic self-energy of polyanions and polycations has a finite value in such models. The approaches with smeared charges are adequate in a certain (intermediate) range of values of polymer concentration and fraction of charged groups, and they break down otherwise. For example, fluctuations induced

electrostatic interactions in dense, segregated multilayers of polycations and polyanions are vanishing within such models because polymer concentration fluctuations are suppressed in melts. On the other hand, charge fluctuations exist even in melts and they induce electrostatic attraction that cannot be described within continuous models.

In this paper, we propose a theory that explicitly takes into account concentration fluctuations of *charged groups* which (according to the definition) have discrete distribution along the chain. This theory allows to describe fluctuations induced electrostatic interactions in solutions of oppositely charged polyelectrolytes for any polymer concentrations including dilute, semidilute, and concentrated regimes. Furthermore, this theory is applicable for spatially homogeneous and nanosegregated melts of oppositely charged polyelectrolytes. We find exact expression for the correlation free energy and some of its asymptotic forms within the RPA. Phase behavior of counterions-free solution in θ solvent is analyzed. Our approach reveals existence of the critical point and can describe dense systems beyond the scaling approximation.

II. MODEL

Let us consider counterions-free solution of oppositely charged linear chains in a volume *V*. For the sake of simplicity we assume that polycations and polyanions have identical primary structures. The chain consists of *N* segments, each of the size *a*, and charged groups are regularly distributed along the chain: each $i\sigma$th, $i=1,2,\ldots,z$, segment carries an elementary charge *e* (+*e* for polycations and −*e* for polyanions), so that the fraction of the charged groups and their total number per chain ("valency" of the chain) are $f=1/\sigma$ and $z=N/\sigma$, respectively. The nonelectrostatic interactions of monomer units with the solvent are θ like, i.e., correspond to three-body repulsion.

To interrelate density fluctuations of various structural units of the chains, let us derive the free energy functional which depends on charge concentration fluctuations

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$$\xi^{\pm}(\mathbf{r}) = \sum_{i=1}^{\Pi/2} \sum_{j=1}^{z} \delta(\mathbf{r} - \mathbf{r}_{j\sigma}^{i}) - \frac{f\rho}{2},$$

and on polycation (polyanion) concentration fluctuations

$$\psi^{\pm}(\mathbf{r}) = \sum_{i=1}^{\Pi/2} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_{j}^{i}) - \frac{\rho}{2}.$$

Here Π is the number of polymer chains in the solution and $\rho = \Pi N / V$ is the average polymer concentration. The entropic contributions of polycations and polyanions to the functional are statistically independent and can be calculated separately

$$\delta F^{\pm}(\xi^{\pm}, \psi^{\pm}) = F^{\pm}(\xi^{\pm}, \psi^{\pm}) - F^{\pm}(0,0),$$

$$\frac{F^{\pm}(\xi^{\pm}, \psi^{\pm})}{k_B T} = -\ln \left\langle \delta \left(\xi^{\pm}(\mathbf{r}) - \sum_{i=1}^{\Pi/2} \sum_{j=1}^{z} \delta(\mathbf{r} - \mathbf{r}_{j\sigma}^{i}) + \frac{f\rho}{2} \right) \right.$$
$$\left. \times \delta \left(\psi^{\pm}(\mathbf{r}) - \sum_{i=1}^{\Pi/2} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_{j}^{i}) + \frac{\rho}{2} \right) \right\rangle, \quad (1)$$

where angle brackets denote thermodynamic average (integration over microscopic coordinates) with the statistical weight of the Gaussian chain, $w_{jj'}^{i} = \text{const} \times \exp[-3(\mathbf{r}_{j}^{i} - \mathbf{r}_{j'}^{i})^2 / (2a^2 |j - j'|)]$, whereas different chains are assumed to be uncorrelated. Calculation of Gaussian integrals in Eq. (1) can be done in a standard way [13] introducing Fourier transforms

$$\delta \left(\xi^{\pm}(\mathbf{r}) - \sum_{i=1}^{\Pi/2} \sum_{j=1}^{z} \delta(\mathbf{r} - \mathbf{r}_{j\sigma}^{i}) + f\rho/2 \right)$$
$$= \int D\varphi^{\pm}(\mathbf{r}) \exp \left\{ i \int d\mathbf{r} \varphi^{\pm}(\mathbf{r}) \xi^{\pm}(\mathbf{r}) - i \sum_{i=1}^{\Pi/2} \sum_{j=1}^{z} \varphi^{\pm}(\mathbf{r}_{j\sigma}^{i}) \right.$$
$$\left. + i \int d\mathbf{r} \varphi^{\pm}(\mathbf{r}) f\rho/2 \right\},$$

$$\delta \left(\psi^{\pm}(\mathbf{r}) - \sum_{i=1}^{\Pi/2} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_{j}^{i}) + \rho/2 \right)$$
$$= \int Dv^{\pm}(\mathbf{r}) \exp \left\{ i \int d\mathbf{r} v^{\pm}(\mathbf{r}) \psi^{\pm}(\mathbf{r}) - i \sum_{i=1}^{\Pi/2} \sum_{j=1}^{N} v^{\pm}(\mathbf{r}_{j}^{i}) \right.$$
$$\left. + i \int d\mathbf{r} v^{\pm}(\mathbf{r}) \rho/2 \right\}, \quad (2)$$

and expanding the exponents into the series in powers of small concentration fluctuations (the second and third terms in the exponents) up to the square [with respect to $\varphi^{\pm}(\mathbf{r})$ and $v^{\pm}(\mathbf{r})$] terms. Further integrations over $\varphi^{\pm}(\mathbf{r})$ and $v^{\pm}(\mathbf{r})$ result in the following free energy functional

$$\frac{\delta F^{\pm}(\xi^{\pm}, \psi^{\pm})}{k_B T} = \frac{N}{\rho} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{\Delta_q} (A_q \xi_{\mathbf{q}}^{\pm} \xi_{-\mathbf{q}}^{\pm} + B_q \psi_{\mathbf{q}}^{\pm} \psi_{-\mathbf{q}}^{\pm}$$
$$- 2C_q \xi_{\mathbf{q}}^{\pm} \psi_{-\mathbf{q}}^{\pm}), \quad (3)$$

where $\psi_{\mathbf{q}}^{\pm}$ and $\xi_{\mathbf{q}}^{\pm}$ are Fourier transforms of the polymer

and charge concentration fluctuations, $\mathbf{q}$ is the wave vector, $\Delta_q = A_q B_q - C_q^2$, $A_q = \Sigma_{i=1}^{N} \Sigma_{j=1}^{N} \exp\{-\alpha|i-j|\}$, $B_q = \Sigma_{i=1}^{z} \Sigma_{j=1}^{z} \exp\{-\alpha\sigma|i-j|\}$, and $C_q = \Sigma_{i=1}^{z} \Sigma_{j=1}^{N} \exp\{-\alpha|i\sigma-j|\}$, $\alpha = a^2 q^2 / 6$. The excluded volume interactions of monomer units of polycations and polyanions can be examined within the Flory-Huggins theory, $F_{vol} = k_B T / a^3 \int d\mathbf{r} \{[1 - \phi(\mathbf{r})] \ln[1 - \phi(\mathbf{r})] + \chi\phi(\mathbf{r})[1 - \phi(\mathbf{r})]\}$, where polymer (polycations + polyanions) volume fraction $\phi(\mathbf{r})$ is weakly fluctuating, $\phi(\mathbf{r}) = \rho a^3 + \psi^+(\mathbf{r})a^3 + \psi^-(\mathbf{r})a^3$, and θ condition means that the parameter $\chi = 1/2$. Expanding F_{vol} into the series in powers of $\psi^{\pm}(\mathbf{r})$, one gets $F_{vol} = F_{vol}(\phi) + \delta F_{vol}$,

$$\frac{\delta F_{vol}}{k_B T} = \frac{a^3 \phi}{2(1-\phi)} \int d\mathbf{r} [\psi^+(\mathbf{r}) + \psi^-(\mathbf{r})]^2 + \cdots$$
$$= \frac{a^3 \phi}{2(1-\phi)} \int \frac{d\mathbf{q}}{(2\pi)^3} (\psi_{\mathbf{q}}^+ + \psi_{\mathbf{q}}^-)(\psi_{-\mathbf{q}}^+ + \psi_{-\mathbf{q}}^-) + \cdots, \quad (4)$$

where $\phi = \rho a^3$. Finally, electrostatic interactions between charged segments contribute [14]

$$\frac{\delta F_{Coul}}{k_B T} = \frac{l}{2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{(\xi_{\mathbf{q}}^+ - \xi_{\mathbf{q}}^-)(\xi_{-\mathbf{q}}^+ - \xi_{-\mathbf{q}}^-)}{q^2}, \quad (5)$$

where l is proportional to the Bjerrum length $l_B = e^2 / (\epsilon k_B T)$, $l = 4\pi l_B$, and ϵ is the dielectric constant of the solvent. The total free energy functional takes the form: $\delta F_{tot} = \delta F^+ + \delta F^- + \delta F_{vol} + \delta F_{Coul}$. If we "fix" some profile of polymer density fluctuations ($\psi^{\pm}$) and want to calculate the equilibrium charge concentration fluctuations corresponding to these fixed ψ^+ and ψ^-, we have to minimize δF_{tot} over $\xi^{\pm}$:

$$\xi_{\mathbf{q}}^{\pm} = \frac{\dfrac{2NC_q}{\rho\Delta_q}\psi_{\mathbf{q}}^{\pm} + \dfrac{lC_q}{q^2 A_q}(\psi_{\mathbf{q}}^+ + \psi_{\mathbf{q}}^-)}{\dfrac{2NA_q}{\rho\Delta_q} + \dfrac{2l}{q^2}}. \quad (6)$$

Thus, the relation of $\xi^{\pm}$ and $\psi^{\pm}$ is more complicated ($q-$ or scale dependent) than in the models with smeared charges, $\xi^{\pm} = f\psi^{\pm}$. Equation (6) reproduces continuous model only in limit $q \to 0$, $\xi^+ = \xi^- = f(\psi^+ + \psi^-)/2$.

The contribution of the charge and monomer concentrations fluctuations to the electrostatic free energy of spatially homogeneous state of the solution is calculated in a standard way [15,16]

$$\frac{F_{corr}}{k_B T} = -\ln \int D\xi^+ D\xi^- D\psi^+ D\psi^- \exp \left\{ -\frac{\delta F_{tot}}{k_B T} \right\}$$
$$+ \ln \int D\xi^+ D\xi^- D\psi^+ D\psi^- \exp \left\{ -\frac{\delta F_{tot}}{k_B T} \bigg|_{l=0} \right\} - F_{self}, \quad (7)$$

where integration over $\psi^{\pm}$ means minimization over these functions because δF_{Coul} does not depend on $\psi^{\pm}$. Integration over $\xi^{\pm}$ can be done in a similar way as that presented in Refs. [15,16]. F_{self} in Eq. (7) corresponds to the self-energy of the pointlike charges [14] on the chains which has to be subtracted from the correlation free energy to provide convergency. The result takes the form

$$\frac{F_{corr}}{k_B T} = \frac{V}{2} \int \frac{d\mathbf{q}}{(2\pi)^3} \left[\ln\left(1 + \frac{l\rho B_q}{Nq^2}\right) - \frac{l\rho}{\sigma q^2} \right],$$

$$B_q = \sum_{i=1}^{z} \sum_{j=1}^{z} \exp\{-\alpha\sigma|i-j|\} = z \coth(\alpha\sigma/2) - \frac{1 - \exp(-\alpha N)}{2 \sinh^2(\alpha\sigma/2)},$$

$$\alpha = \frac{a^2 q^2}{6}. \tag{8}$$

III. DISCUSSION

The fact that F_{corr} contains only function B_q means that the excluded volume interactions in θ solvent do not contribute to the correlation free energy. This effect is quite predictable and related to independence of the Gaussian statistics of a chain in the θ solvent on triple repulsion of monomer units. On the contrary, even weak selectivity of the solvent to polycations and polyanions, which can be described by conventional Flory-Huggins expression with different polycation solvent (χ_+), polyanion solvent (χ_-), and polycation-polyanion ($\chi_\pm$) interactions parameters

$$F_{vol} = \frac{k_B T}{a^3} \int d\mathbf{r} \{\phi_s(\mathbf{r})\ln \phi_s(\mathbf{r}) + \chi_+ \phi_+(\mathbf{r})\phi_s(\mathbf{r})$$

$$+ \chi_- \phi_-(\mathbf{r})\phi_s(\mathbf{r}) + \chi_\pm \phi_+(\mathbf{r})\phi_-(\mathbf{r})\},$$

$$\phi_\pm(\mathbf{r}) = \phi/2 + \psi^\pm(\mathbf{r})a^3,$$

$$\phi_s(\mathbf{r}) = 1 - \phi_+(\mathbf{r}) - \phi_-(\mathbf{r}), \tag{9}$$

provides dependence of the correlation free energy on all structural functions (A_q, B_q, and C_q) and interactions parameters. This more complicated regime will be analyzed in forthcoming publication.

In the case of homogeneous melt of polycations and polyanions, the excluded volume interactions are screened, $\delta F_{vol} = 0$, and incompressibility of the melt means that $\psi_{\mathbf{q}}^- = -\psi_{\mathbf{q}}^+$. Minimizing Eq. (3) over $\psi_{\mathbf{q}}^+$, one gets $\delta F^+ + \delta F^-$ as a functional of $\xi^\pm$. Taking $\delta F_{tot} = \delta F^+ + \delta F^- + \delta F_{Coul}$ and using Eq. (7) with integration over $\xi^\pm$ only, we obtain exactly the same expression as done by Eq. (8), where the polymer volume fraction has to be set equal to unity, $\rho a^3 = 1$.

Therefore, Eq. (8) is valid for solutions and melts and has clear physical meaning both at small and high values of the polymer concentration. Below the overlap polymer volume fraction of the Gaussian chains $\phi^* \sim N^{-1/2}$, $\phi \ll \phi^*$, polyions are not aggregated and adopt Gaussian conformation if intrachain electrostatic repulsion is weaker than the energy of thermal motion, $z^2 l/(aN^{1/2}) \ll 1$. In the limit $l\phi z^2/a \ll 1$, $z \gg 1$, Eq. (8) takes the form

$$\mathcal{F}_{corr} = \frac{F_{corr}}{k_B T V} = \frac{\sqrt{6}}{3\pi^{3/2}} \frac{\rho}{N} \frac{lz^2}{a\sqrt{N}} - \frac{1}{12\pi}\left(\frac{l\rho z^2}{N}\right)^{3/2} + \cdots \tag{10}$$

Here the first term is the self-energy of the chains (the interaction energy of charges within the chains). The energy of

each individual chain corresponds to the energy of homogeneously charged sphere, $\sim Q^2/R$, of the charge $Q = ez$ and the radius $R \sim aN^{1/2}$. The second term is the correlation free energy of the Debye-Hückel plasma of z-valent ions having concentration ρ/N [17]. Indeed, interactions between the chains in very dilute solution can be treated as interactions between pointlike z-valent ions. The first term in Eq. (10) is obtained by approximation $\ln[1 + l\rho B_q/(Nq^2)] \approx l\rho B_q/(Nq^2)$ and by expansion of B_q into the series in powers of $\alpha\sigma$. The main contribution to the second term comes from small values of q at which $B_q \approx z^2$.

In the opposite limit of relatively high polymer concentrations, $l\phi z^2/a \gg 1$, $l\phi/a \ll 1$, $z \gg 1$, the correlation free energy takes the form

$$\mathcal{F}_{corr} = \frac{f^{3/2}}{3\pi a^3}\left[\left(\frac{3l\phi}{a}\right)^{3/4} - \frac{1}{10}\left(\frac{3l\phi}{a}\right)^{5/4} + \cdots\right]. \tag{11}$$

One of the ways to get this expression is calculation of the chemical potential with Eq. (8), $\mu_{corr} = \partial \mathcal{F}_{corr}/\partial\rho$. In μ_{corr}, B_q is approximated as $B_q \approx 2z/\alpha\sigma$ at $\alpha\sigma \ll 1$, $\alpha N \gg 1$. The first leading term of the expansion (11) is exactly equal to that of the model with smeared charges [8,11]. Despite a positive value this term is responsible for attraction because its contribution to the osmotic pressure, $\pi_{corr} = \rho\partial \mathcal{F}_{corr}/\partial\rho - \mathcal{F}_{corr}$, is negative. Finally, in the limit of high concentrations (concentrated solution or melt), $l\phi z^2/a \gg 1$, $l\phi/a \gg 1$, $z \gg 1$, $\mathcal{F}_{corr}$ takes the form

$$\mathcal{F}_{corr} = -\frac{(l\rho f)^{3/2}}{12\pi}, \tag{12}$$

if we approximate $B_q \approx z$ at $\alpha\sigma \gg 1$. This expression coincides with the correlation free energy of the ideal plasma of monovalent ions. Indeed, if subchains connecting two neighboring charges in the chain overlap, the charged units cannot be treated as smeared along the chain. The higher the concentration, the better applicability of the expression for the ideal gas. Equation (12) is obtained in the limit $l\phi/a \gg 1$. However, it has to be noticed that if the Bjerrum length is much larger than the size of the segment $[l_B/a = l/(4\pi a) > 10]$ [18], the charged groups strongly associate and assumption of weak charge fluctuations (RPA) breaks down. Therefore, an accuracy of Eq. (12) is not so high for solutions but quite reasonable for the melt. Equation (12) is negative what means that $\mathcal{F}_{corr}$ is nonmonotonous function of ϕ: first it grows with ϕ, Eqs. (10) and (11), and then becomes negative. Numerically integrated $\mathcal{F}_{corr}$, Eq. (8), and the corresponding osmotic pressure are compared with those of the model with homogeneous charge distribution in Fig. 1. Considerable disagreement of these two models is detectable at high concentrations. $\mathcal{F}_{corr}$ in the discrete model reveals completely different behavior, Fig. 1(a), and π_{corr} in this model demonstrates stronger attraction between charged units, Fig. 1(b). The stronger interactions in the discrete model can be clarified by the following evident example. If we smear equal positive and negative charges throughout some volume homogeneously, one gets zero electrostatic energy. On the other hand, if we fill in this volume by discrete charges, the energy of electrostatic interactions will be nonzero. In other
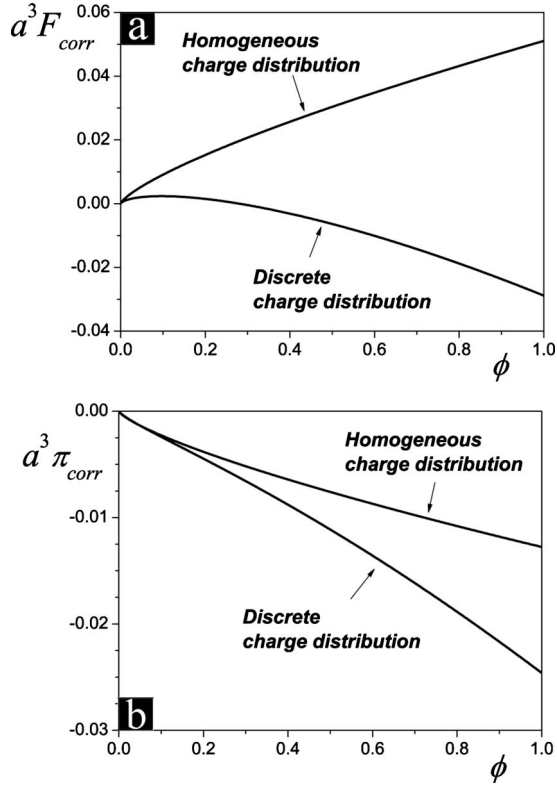
FIG. 1. The correlation free energies (a) and the correlation osmotic pressures (b) as functions of the polymer volume fraction ϕ. $N=10^3$, $l/a=4\pi$, and $f=0.1$.

words, following terminology of inhomogeneous polymer networks [13] one can say that discreteness of charges can be treated as extra quenched fluctuations which together with annealed (thermal) ones enhance total charge fluctuations and, therefore, electrostatic interactions.

Phase behavior of the counterions-free solution of oppositely charged polyelectrolytes in θ solvent can be described with the free-energy $\mathcal{F}$ including correlation free energy, Eq. (8), the free energy of translational motion of the chains, $\mathcal{F}_{tr}=(\phi/N)\ln\phi$, and the energy of the excluded volume interactions, $\mathcal{F}_{vol}=(1-\phi)\ln(1-\phi)+\phi(1-\phi)/2$. In contrast to the model with smeared charges where $\mathcal{F}_{corr}$ has a form of the first term in Eq. (11), our model reveals existence of the critical point defined as $\partial^2\mathcal{F}/\partial\phi^2=0$, $\partial^3\mathcal{F}/\partial\phi^3=0$. Analysis of these two equations allows us to conclude that the critical value of the polymer volume fraction corresponds to the overlap concentration, $\phi_c\sim N^{-1/2}$, and the critical value of the fraction of the charged units is determined from the condition $l\phi_c z^2/a\sim1$, i.e., $f_c\sim N^{-3/4}(a/l)^{1/2}$. The latter result coincides with a condition of coil-globule crossover in the case of single molecule of charge-symmetric diblock polyampholyte obtained within the scaling approximation [18,19]. The spinodals obtained for different lengths of the molecules via numerical solution of equation $\partial^2\mathcal{F}/\partial\phi^2=0$ are presented in Fig. 2 in variables $\phi-f$ ($\log_{10}-\log_{10}$ plot). Spatially homogeneous state of the solution is stable in regions below each of the curves. The longer the molecules, the smaller fraction of charged groups on the chains initiates phase separation. The slope of the dashed straight line corresponds to
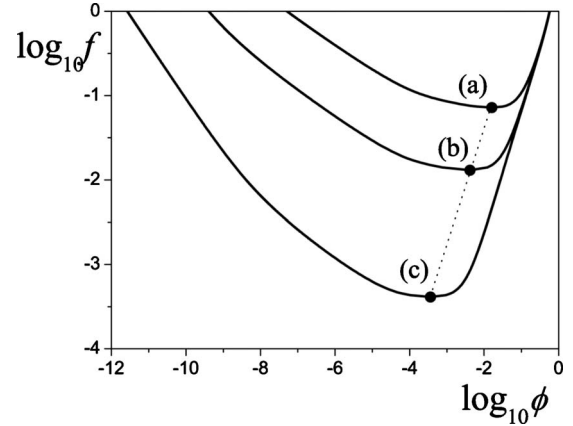

FIG. 2. $\log_{10}\phi-\log_{10}f$ spinodals of macrophase separation of oppositely charged polyelectrolytes in θ-solvent at different values of the number of segments in the chain: $N=10^2$ (a), 10^3 (b), and 10^5 (c). Spatially homogeneous state of the solution is stable below each of the curves. Collinear black circles correspond to the critical points. $l/a=4\pi$.

$3/2$ ($f_c\sim\phi_c^{3/2}(a/l)^{1/2}$). Above the critical point, the polymer volume fraction in diluted phase drops with f considerably and becomes vanishing far from the critical point. Here, the equilibrium concentration of the dense phase can be calculated by equating the osmotic pressure of the solution to zero, $\pi=\phi\partial\mathcal{F}/\partial\phi-\mathcal{F}=0$, Fig. 3. In this figure, we compare results of the discrete and continuous models. In agreement with our aforementioned arguments, the polymer volume fraction of the dense phase is higher for the discrete model.

Within the model with continuous charge distribution or in the regime of intermediate values of polymer concentration, Eq. (11), $\mathcal{F}_{corr}\sim f^{3/2}(l\phi/a)^{3/4}$, the polymer volume fraction of the dense phase can be calculated analytically in the limit of small fraction of the charged groups, $f\ll1$, if we expand $\mathcal{F}_{vol}$ into the series in powers of ϕ and neglect $\mathcal{F}_{tr}$, $\phi\sim f^{2/3}(l/a)^{1/3}\ll1$. This result coincides with the scaling one which was obtained for diblock polyampholytes [18,19]. However, the scaling exponent $\nu=2/3$ is valid only in limited range of f values, when the number of charged units per
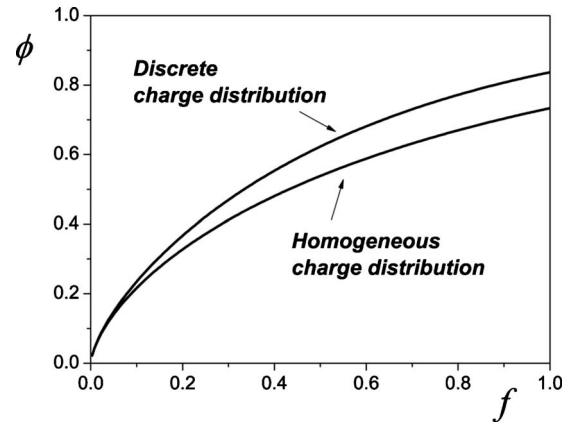

FIG. 3. The polymer volume fraction of the dense phase, ϕ, as a function of the fraction of charged groups, f. $N=10^5$ and $l/a=4\pi$.
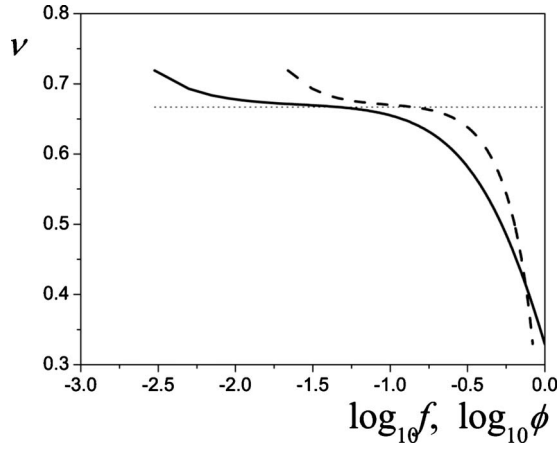
FIG. 4. $\log_{10} f - \nu$ (solid) and $\log_{10} \phi - \nu$ (dashed) curves, where ϕ is the equilibrium polymer volume fraction of the dense phase. In this curves, horizontal lines interrelate f and ϕ: intersections of any horizontal line with the curves determine equilibrium ϕ and value of f at which the volume fraction is calculated. The dotted line corresponds to the scaling exponent $\nu = 2/3$. $N = 10^5$, and $l/a = 4\pi$.

electrostatic blob [18,19] is large enough and continuous model is justified. If in the discrete model we approximate dependence of the polymer volume fraction in dense phase by a power function, $\phi = const \cdot f^\nu$, the exponent ν can exceed $2/3$ (small values of f and ϕ) or be smaller (high fraction of charged groups and polymer concentrations), Fig. 4. In Fig. 4, ν is defined as $\nu = \partial \log_{10} \phi / \partial \log_{10} f$, where ϕ is calculated from equality of the osmotic pressure of the solution to zero, $-\ln(1 - \phi) - \phi - \phi^2/2 + a^3 \pi_{corr} = 0$. Deviations of ν from $2/3$ can be explained by the decrease in the number of charged groups per blob (it can become less than one group per blob) in the case of small f and inapplicability of the electrostatic blobs concept at $\phi \sim 1$.

Applicability of RPA is justified if the electrostatic correlation length of a system is much larger than the characteristic distance between the charged groups. For example, in the Debye-Hückel plasma of monovalent ions of concentration c, the Debye screening (correlation) length $r_D = (lc)^{-1/2}$ must be much larger than the intercharge distance $r \sim c^{-1/3}$, $r_D \gg r$, i.e., $cl^3 \ll 1$. It also means that the thermal energy of the ions, $\sim c$, is much larger than the absolute value of the energy of electrostatic interactions between the ions, $\sim (lc)^{3/2}$, and aggregation of the ions (ion pair formation) cannot be described at the RPA level. In contrast to the ideal gas, complexation of oppositely charged polymers can be described within the RPA because polymers are known to be poor in entropy. At small enough values of polymer concentration, the continuous model is justified, Eq. (11), and the RPA coincides with the scaling treatment of the system [18,19]. In the scaling treatment, the correlation length is equal to the size of the electrostatic blob, $\xi_{el} \sim a(lf^2/a)^{-1/3}$, which is much larger than the intercharge distance, r
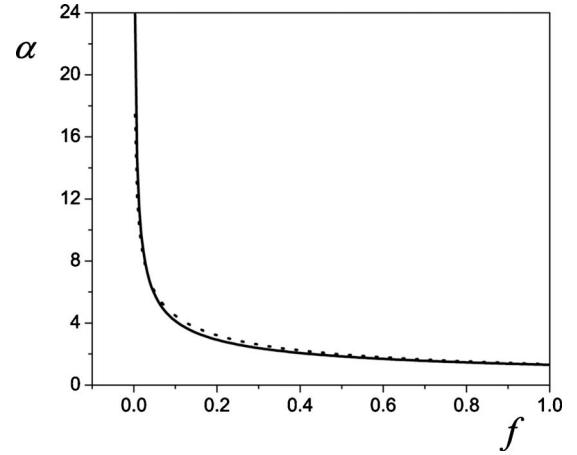

FIG. 5. Dimensionless correlation length $\alpha = (r_{corr}/r)^3$ as a function of the fraction of charged groups, f, for solution in θ-solvent (dotted) and melt (solid). $N = 10^5$ and $l/a = 4\pi$.

$\sim a(f\phi)^{-1/3} \sim a(f^5 l/a)^{-1/9}$, $\xi_{el} \gg r$ (each blob contains many charged groups), i.e., $f(l/a)^2 \ll 1$. Fulfillment of the latter inequality corresponds to applicability criterion for the continuous model, $\phi l/a \ll 1$ [see Eq. (11)], at $\phi \sim (f^2 l/a)^{1/3}$. Taking into account that $|\pi_{corr}| \sim r_{corr}^{-3}$, one can introduce applicability criterion for the discrete model as $\alpha \equiv (r_{corr}/r)^3 = \phi f/|\pi_{corr}| \gg 1$ in the whole range of ϕ and f values. $f - \alpha$ dependence is plotted in Fig. 5. The dotted line corresponds to the solution in θ-solvent far from the critical point. The polymer volume fraction ϕ of the dense phase (precipitant) is determined from the equality of the osmotic pressure to zero at each value of f. The correlation length of the melt ($\phi = 1$) is depicted by solid line in Fig. 5. It is seen that $\alpha > 1$ and RPA is applicable for both systems in the whole range of f values. However, better accuracy is achieved at smaller f values.

In conclusion, we developed a theory that correctly describes fluctuations induced attraction of charged units in solutions of oppositely charged polyelectrolytes for any values of polymer concentration and fraction of charged groups. This theory gives rise to stronger attraction between the charged groups due to analysis of their discrete distribution. We predict existence of the critical point and indicate a range of applicability of the scaling theory in counterions-free solution. Analytical expressions of the correlation free energy are obtained for various regimes.

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