A new equation of state of salt-free flexible-chain polyelectrolyte solution: phase equilibria and osmotic pressure

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We develop a first-principle equation of state of salt-free polyelectrolyte solution in the limit of infinitely long flexible polymer chains in the framework of a field-theoretical formalism beyond the linear Debye-Hueckel theory and predict a liquid-liquid phase separation induced by strong correlation attraction. As a reference system we choose a set of two independent ideal subsystems – charged macromolecules immersed in a structureless oppositely charged background created by counterions (polymer one component plasma) and counterions immersed in oppositely charged background created by polymer chains (hard-core one component plasma). We calculate the excess free energy of polymer one component plasma in the framework of Modified Random Phase Approximation, whereas a contribution of charge densities fluctuations of neutralizing backgrounds we evaluate at the level of Gaussian approximation. We show that our theory is in a very good agreement with the results of Monte-Carlo and MD simulations for critical parameters of liquid-liquid phase separation and osmotic pressure in a wide range of monomer concentration above the critical point, respectively.

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I. INTRODUCTION

It is well known that thermodynamic and structural properties of polyelectrolyte solutions in homogeneous state mainly determined by the correlation attraction of like-charged particles which is related to long-range Coulomb interaction. Moreover, in polyelectrolyte solutions the collective effects relating to strong correlated monomer concentration fluctuations due to chain structure of macromolecules and excluded volume interactions between monomers in a regime of semi-dilute solution also play a crucial role. Thus, a combination of these effects complicates a theoretical description of thermodynamics of polyelectrolyte solution in wide ranges of monomer concentration and temperature.

At present, it is well known that in salt-free flexible chain polyelectrolyte solutions a liquid-liquid phase separation due to strong correlation attraction can take place. This is evidenced by multiple theoretical works and results of Monte-Carlo simulation. However, to best of our knowledge there are no theoretical models which would able to predict correct critical parameters of such pure electrostatic phase transition. The problem due to which the theoretical values of the critical parameters significantly deviate from results of Monte-Carlo simulation is three-fold. Firstly, in a series of studies the correlation attraction into the total Helmholtz free energy omitted or described at the level of Debye-Hückel approximation, although the critical point of the discussed electrostatic phase transition located far from the range of applicability of linear Debye-Hückel theory. In work the contribution of correlation attraction was described at the level of mean-spherical approximation (MSA) that allowed to obtain a good agreement with simulation results for critical temperature but underestimated critical monomer concentration. The second reason is related to the fact that most existing theoretical works do not take into account the effects of monomer concentration fluctuations in the regime of semi-dilute polymer solution, which as was already mentioned above should be important for polyelectrolyte solutions as well as for solutions of neutral polymers. In order to evaluate a contribution of non-electrostatic interactions into the total free energy of the solution usually authors use some variants of mean-field approximation, within which the fluctuation effects are fully ignored. Finally, all above mentioned theoretical models based on the implicit assumption that contributions of electrostatic and non-electrostatic interactions are independent each other. We would like to stress that methodology which
based on a procedure of "construction" of the total free energy by using the expressions obtained within different theoretical approaches strictly speaking cannot be justified from first principles of statistical thermodynamics.

In reference\textsuperscript{19} addressed an interesting observation that one can obtain reasonable values of the critical parameters if use the modified random phase approximation (MRPA) for calculation of the electrostatic contribution into the free energy of the solution. MRPA was developed in works\textsuperscript{20,21} and in contrast on standard random phase approximation (RPA) contains a concept of ultraviolet cut-off in procedure of integration over vectors of reciprocal space. The parameter of ultraviolet cut-off determined from the condition of equality between number of degrees of freedom of the system and number of collective variables which contribute into the total free energy numerated by elements of reciprocal space. Therefore, cut-off parameter within MRPA related to the number density of particles. It is surprising that MRPA allows to obtain very accurate interpolation formulas for excess free energy of one component plasma (OCP) and hard-core one component plasma (HCOCP) in wide ranges of temperature and number density – from regime of linear Debye-Hueckel theory to strong coupling regime\textsuperscript{20,21}.

In work\textsuperscript{30} in the framework of a field-theoretical approach interpolation formulas for excess free energy, correlation length, and effective Kuhn length of the segment of polymer chain for semi-dilute solution of neutral polymer chains were obtained. It should be emphasize, that obtained by authors interpolation formulas contain all limiting laws predicted in earlier works within the scaling approach\textsuperscript{8}. An availability of interpolation formula for excess free energy of semi-dilute polymer solution offers new opportunities for its application to theoretical description of more complicated polymer systems in the framework of thermodynamic perturbation theory (TPT), as well as the Carnahan-Starling interpolation formula for free energy of hard sphere system widely used for theoretical description of thermodynamics of different low-molecular weight fluids\textsuperscript{27}.

The presented in reference\textsuperscript{19} observation and results proposed in reference\textsuperscript{30} motivated us attempt to develop a statistical theory of salt-free polyelectrolyte solution which could take into account simultaneously the effect of correlation attraction of charged monomers and counterions beyond the linear Debye-Hueckel theory, collective effects relating to the fluctuations of monomer concentration in the regime of semi-dilute solution and mutual influence of these effects. We formulate the theoretical model basing on some variant of
TPT formalism, which was developed in works\textsuperscript{31,32}. As reference system we choose a set of two independent subsystems – charged polymer chains immersed in a structureless oppositely charged background created by counterions (polymer one component plasma) and counterions (which we model as charged hard spheres) immersed in oppositely charged background created by polymer chains (hard-core one component plasma). We calculate the excess free energy of polymer one component plasma in the framework of MRPA. We show that our theory is in a very good agreement with the results of Monte-Carlo and MD simulations for critical parameters of electrostatic phase transition and dependence of osmotic pressure on monomer concentration in a region that is above the critical point, respectively.

II. THEORY

In this section we present a theoretical model based on TPT formalism in order to describe the thermodynamics of salt-free flexible chain polyelectrolyte solution. We assume that charged polymer chains and counterions immersed in a good solvent which modelled as structureless dielectric medium with dielectric permittivity $\varepsilon$. Moreover, we take into account an excluded volume of monomers and counterions modeling their as hard spheres of diameter $d$. For simplicity we also assume that each monomer has a fixed charge $-e$, whereas counterions have opposite charge $+e$ (a case of monovalent counterions). Thus a free energy of the solution one can write within canonical ensemble in a following form

$$F = -k_B T \ln Z,$$

where a partition function $Z$ of the solution takes the form

$$Z = \frac{1}{N_p!N_c!} \int d\Gamma_p \int d\Gamma_c e^{-\beta H},$$

where

$$H = H^{(c)}_{e.v.} + H^{(p)}_{e.v.} + H^{(pc)}_{e.e.} + \frac{1}{2} (\hat{\rho}_p V_c \hat{\rho}_p) + \frac{1}{2} (\hat{\rho}_c V_c \hat{\rho}_c) + (\hat{\rho}_p V_c \hat{\rho}_c)$$

is a model Hamiltonian of the system, where the following short-hand notations have been introduced

$$(fV_c g) = \int dx \int dy f(x)V_c(x - y)g(y),$$

$$V_c(x - y) = \frac{1}{\varepsilon |x - y|}$$
is a Coulomb potential,

$$\hat{\rho}_p(x) = -e \sum_{i=1}^{N_p} \int_0^N ds \delta(x - R_i(s))$$  \hspace{1cm} (5)$$

is a microscopic charge density of monomers,

$$\hat{\rho}_c(x) = e \sum_{j=1}^{N_c} \delta(x - r^c_j)$$  \hspace{1cm} (6)$$

is a microscopic charge density of counterions,

$$H^{(p)}_{\text{e.v.}} = \frac{k_BT_w}{2} \sum_{i,j=1}^{N_p} \int_0^N ds_1 \int_0^N ds_2 \delta(R_i(s_1) - R_j(s_2))$$  \hspace{1cm} (7)$$

is Hamiltonian of excluded volume interaction monomer-monomer; $w = \frac{2\pi d^3}{3}$ is a second virial coefficient of excluded volume interaction of hard spheres of diameter $d$;

$$H^{(c)}_{\text{e.v.}} = \frac{1}{2} \sum_{i \neq j} V_{hc}(r^c_i - r^c_j)$$  \hspace{1cm} (8)$$

is Hamiltonian of excluded volume interaction of counterion-counterion;

$$V_{hc}(r) = \begin{cases} \infty, & |r| \leq d \\ 0, & |r| > d. \end{cases}$$  \hspace{1cm} (9)$$

is a hard-core potential,

$$H^{(pc)}_{\text{e.v.}} = \sum_{i,j=1}^{N} \int_0^N ds V_{hc}(r^c_i - R_j(s))$$  \hspace{1cm} (10)$$

is Hamiltonian of excluded volume interaction of counterion-monomer. Moreover, has been introduced the following notations:

$$\int d\Gamma_p(\ldots) = \int \mathcal{D}R_1 \ldots \int \mathcal{D}R_{N_p} e^{-\frac{b}{2\pi^2} \sum_{j=1}^{N_p} \int_0^N ds R_j^2(s)} (\ldots)$$  \hspace{1cm} (11)$$

is a measure of integration over the configurations of polymer chains, $b$ is a Kuhn length of the segment, $N_p$ is a number of polymer chains, $N$ is a degree of polymerization of polymer chains;

$$\int d\Gamma_c(\ldots) = \Lambda_c^{-3N_c} \int_{V} d\mathbf{r}_1^c \ldots \int_{V} d\mathbf{r}_{N_c}^c (\ldots)$$  \hspace{1cm} (12)$$

is a measure of integration over a phase space of counterions, $N_c$ is a total number of counterions, $V$ is a volume of the system. The symbol $\int \mathcal{D}R(\ldots)$ in (11) denotes a functional
integration over configurations of the polymer chain. Moreover, we determine a following normalization condition:

\[ \int \mathcal{D}R e^{-\frac{N}{2d^2} \int_0^{d_{R,0}} ds R^2(s)} = V. \] (13)

In order to take into account a monomer-counterion excluded volume interaction we use an assumption

\[ \int d\Gamma_c \int d\Gamma_p e^{-\beta H^{(pe)}_{c,v}(\cdot)} \to \int d\Gamma'_c \int d\Gamma'_p(\cdot), \] (14)

where

\[ \int d\Gamma'_c(\cdot) = \Lambda_c^{-3N_c} \int_{V-NN_pv_m} d\mathbf{r}_c \int_{V-NN_pv_{mc}} d\mathbf{r}_c(\cdot), \] (15)

\( v_{mc} = v_{cm} = v_c = v_m = \pi d^3/6 \). The approximation (14) is a simplest way to include into the theory depletion effect\footnote{26}. In the renormalized measure \( \int d\Gamma'_p(\cdot) \) we have the following normalization condition

\[ \int \mathcal{D}R e^{-\frac{3}{2d^2} \int_0^{d_{R,0}} ds R^2(s)} = V_f, \] (16)

where \( V_f = V - N_c v_{cm} \) is a free volume for monomers. The model Hamiltonian \footnote{3} one can rewrite by the following way

\[ H = H_{POCP} + H_{HCOCP} + H_{pert}, \] (17)

where

\[ H_{POCP} = H^{(p)}_{e,v} + \frac{1}{2} (\hat{\rho}_p V_c \hat{\rho}_p) + (\hat{\rho}_p V_c \rho_c) + \frac{1}{2} (\rho_c V_c \rho_c) \] (18)

is a Hamiltonian of polymer one component plasma (POCP),

\[ H_{HCOCP} = H^{(c)}_{e,v} + \frac{1}{2} (\hat{\rho}_c V_c \hat{\rho}_c) + (\hat{\rho}_c V_c \rho_p) + \frac{1}{2} (\rho_p V_c \rho_p) \] (19)

is a Hamiltonian of hard-core one component plasma (HCOCP);

\[ H_{pert} = (\delta \hat{\rho}_c V_c \delta \hat{\rho}_p) \] (20)

is a perturbation part of the total Hamiltonian; \( \rho_c = e N_c V_f \) is an average charge density of counterions, \( V_f = V - N_c v_{cm} \) is a free volume for counterions (monomers), \( \rho_p = -\rho_c \) is an average charge density of monomers, \( \delta \hat{\rho}_p(\mathbf{x}) = \hat{\rho}_p(\mathbf{x}) - \rho_p \) is a local fluctuation of charge density of monomers, \( \delta \hat{\rho}_c(\mathbf{x}) = \hat{\rho}_c(\mathbf{x}) - \rho_c \) is a local fluctuation of charge density of counterions. We would like to stress that a set of charged flexible polymer chains immersed in a structureless neutralizing background we shall call throughout the paper as polymer...
one component plasma (POCP). Using the formalism of TPT we shall use a set of two independent ideal subsystems as a reference system – POCP of charged macromolecules and HCOCP of counterions. Hence, we get

\[ Z = Z_R \langle e^{-\beta H_{\text{pert}}} \rangle_R, \]  

(21)

where symbol \( \langle (\cdot) \rangle_R \) denotes an averaging over microstates of the reference system.

\[ \langle (\cdot) \rangle_R = \frac{1}{Z_R} \int d\Gamma_R e^{-\beta H_R(\cdot)}, \]  

(22)

\[ Z_R = \exp \left[ -\beta F_{\text{POCP}} - \beta F_{\text{HCOCP}} \right] \]  

(23)

is a partition function of the reference system; \( H_R = H_{\text{HCOCP}} + H_{\text{POCP}} \) is a Hamiltonian of the reference system. Thus an expression for the total Helmholtz free energy \( F \) within the TPT approach has a following form

\[ \beta F = \beta F_{\text{POCP}} + \beta F_{\text{HCOCP}} - \ln \langle e^{-\beta (\delta \rho_c V_c \delta \rho_p)} \rangle_R. \]  

(24)

The expression for density of excess free energy of HCOCP has a following form

\[ \frac{\mathcal{F}_{\text{HCOCP,ex}}}{n_m k_B T} = \frac{4\eta - 3\eta^2}{(1-\eta)^2} + \frac{3}{4} \left[ \ln \left( \Theta + cZ_0 \Gamma_c \right) - c \Gamma_c \left( 3 - \frac{2Z_0}{\Theta} \right) \right] - \]  

\[- \frac{3}{2} \left( \frac{c \Gamma_c Z_0}{\Theta} \right)^{3/2} \arctan \left( \sqrt{\frac{\Theta}{c \Gamma_c Z_0}} \right), \]  

(25)

where \( \Gamma_c = l_B \left( \frac{4\pi n_m'}{3} \right)^{1/3} \) is a plasma parameter, \( \eta = \frac{\pi d n_m'}{6} \) is packing fraction of counterions, \( n_m' = n_m / \left( 1 - \frac{\pi d n_m}{6} \right) \) is a renormalized concentration of monomers (counterions), \( l_B = e^2/\varepsilon k_B T \) is a Bjerrum length, \( n_m = N_p N/V \) is concentration of monomers (counterions), and \( c = \frac{2}{3} \left( \frac{4}{\pi^2} \right)^{1/3} \) is a number constant. Moreover, the following notations have been introduced

\[ Z_0 = \frac{(1-\eta)^4}{1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4}, \]  

(26)

\[ \Theta = 1 + \frac{6 \lambda_B \eta^2 (1-\eta)^4 (16 - 11\eta + 4\eta^2)}{5d \left( 1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4 \right)^2}. \]  

(27)

The equation (25) very accurate describes the thermodynamic properties of HCOCP in wide ranges of number density and temperature – from range of applicability of Debye-Hueckel theory to strong coupling regime. Applying an analogous approach to calculation of free
energy of POCP as well as for HCOCP\cite{21}, we arrive at the following expression (see Appendix A):

\[ \mathcal{F}_{\text{POCP,ex}} = \mathcal{F}_{\text{POCP,e.v.}} + \mathcal{F}_{\text{POCP,cor}}, \quad (28) \]

where correlation contribution into the free energy of POCP can be determined by the expression

\[ \mathcal{F}_{\text{POCP,cor}} = -n_m k_B T g(\omega, \sigma), \quad (29) \]

where

\[ g(\omega, \sigma) = \frac{3}{4} \left( \omega - \ln \left( 1 + \omega + \frac{\omega}{\sigma^2} \right) \right) + \]

\[ + \frac{3\sqrt{2}}{4} \frac{\omega \left( \sqrt{\omega} - \sqrt{\omega^2 - 4} \right)}{\sigma^{3/2}} \arctan \frac{\sqrt{\omega^2 + \sqrt{\omega^2 (\omega^2 - 4)}}}{2\omega} + \]

\[ + \frac{3\sqrt{2}}{4} \frac{\omega \left( \sqrt{\omega} + \sqrt{\omega^2 - 4} \right)}{\sigma^{3/2}} \arctan \frac{\sqrt{\omega^2 - \sqrt{\omega^2 (\omega^2 - 4)}}}{2\omega}, \quad (30) \]

\[ \omega = c \Gamma_m, \quad \Gamma_m = \Gamma_c = l_B \left( \frac{4\pi n_m^3}{3} \right)^{1/3} \]

is a plasma parameter of monomers, \( \sigma = \left( 9\pi^2 n_m^3 \right)^{1/3} \sqrt{\frac{4\pi b^2 \alpha}{9}} \)

is a dimensionless parameter. The non-electrostatic part \( \mathcal{F}_{\text{POCP,e.v.}} \) of the excess free energy of POCP can be determined by the expression which obtained by Edwards and Muthukumar within a field-theoretical approach\cite{30}:

\[ \frac{\mathcal{F}_{\text{POCP,e.v.}}}{k_B T} = \frac{1}{24\pi \xi^3} - \frac{9wn_m'}{8\pi \alpha \xi b^2} + \frac{wn_m'^2}{4}, \quad (31) \]

where correlation length \( \xi \) takes the form

\[ \xi = \frac{1}{2} \left( \frac{9}{4\pi n_m' b^2 \alpha} + \sqrt{\left( \frac{9}{4\pi n_m' b^2 \alpha} \right)^2 + \frac{2\alpha b^2}{3wn_m'}} \right), \quad (32) \]

and expansion factor \( \alpha \) of neutral polymer chain satisfies the following equation

\[ \alpha^3 - \alpha^2 = \frac{48w\xi}{\pi b^4}. \quad (33) \]

The expressions (31), (32) and (33) determine the density of free energy of solution of flexible polymer chains with excluded volume and qualitatively describe thermodynamic properties of the solution in regime of good solvent from regime of semi-dilute polymer solution to concentrated regime\cite{20}. 

Further, let us calculate the fluctuation correction to free energy of the reference system at the level of Gaussian approximation. Using the standard Hubbard-Stratonovich transformation we rewrite the partition function of the solution in the following form

\[ Z = Z_R \int \frac{D\Psi}{C} e^{-\frac{1}{2\beta} \langle \Psi, \hat{V}^{-1} \Psi \rangle} \langle e^{i\delta \hat{\rho} \cdot \Psi} \rangle_R, \]  

where

\[ \hat{V}(x - y) = \begin{pmatrix} 0 & V_c(x - y) \\ V_c(x - y) & 0 \end{pmatrix}, \]  

\[ \Psi(x) = \begin{pmatrix} \Psi_p(x) \\ \Psi_c(x) \end{pmatrix}, \]  

is a vector of auxiliary fields,

\[ \delta \hat{\rho}(x) = \begin{pmatrix} \delta \hat{\rho}_p(x) \\ \delta \hat{\rho}_c(x) \end{pmatrix}, \]  

is a vector of fluctuations of local charge densities. Moreover, the additional notations have been introduced

\[ \langle \Psi, \hat{V}^{-1} \rangle = \int dx \int dy \sum_{\alpha, \delta} \Psi_\alpha(x) \left( \hat{V}^{-1} \right)_{\alpha\delta}(x - y) \Psi_\delta(x) \]  

and

\[ \langle \Psi, \delta \hat{\rho} \rangle = \int dx \sum_{\alpha} \Psi_\alpha(x) \delta \hat{\rho}_\alpha(x). \]  

An operator \( \hat{V}^{-1} \) can be determined by the following integral relation

\[ \int dz \sum_{\delta} \left( \hat{V}^{-1} \right)_{\alpha\delta}(x - z) \hat{V}_{\delta\gamma}(z - y) = \delta_{\alpha\gamma}(x - y). \]  

Performing some cumbersome calculations (see Appendix B) we arrive at the expression

\[ \beta \mathcal{F}_{ex} = \beta \mathcal{F}_{POCP_{ex}} + \beta \mathcal{F}_{HCOP_{ex}} + \beta \mathcal{F}_{pert}, \]  

where the density of the perturbation part of the total density of free energy of the solution at the level of Gaussian approximation takes the form

\[ \beta \mathcal{F}_{pert} = \frac{1}{2} \int \frac{dk}{(2\pi)^3} \ln \left( 1 - \langle \delta \hat{\rho}_p(k) \delta \hat{\rho}_p(-k) \rangle_{POCP} \langle \delta \hat{\rho}_c(k) \delta \hat{\rho}_c(-k) \rangle_{HCOP} \hat{V}_c^2(k) \right), \]  

where \( \hat{V}_c(k) = \frac{4\pi}{i k^2} \) is a Fourier image of Coulomb potential, \( \langle \delta \hat{\rho}_p(k) \delta \hat{\rho}_p(-k) \rangle_{POCP} \) is a Fourier image of correlation function of microscopic charge density fluctuations of POCP,
and \( \langle \delta \hat{\rho}_c(k) \delta \hat{\rho}_c(-k) \rangle_{\text{HCOCP}} \) is a Fourier image of correlation function of microscopic charge density fluctuations of HCOCP. The latter has been obtained within the Gaussian approximation in work\(^\text{31}\) and can be written in the following form

\[
\langle \delta \hat{\rho}_c(k) \delta \hat{\rho}_c(-k) \rangle_{\text{HCOCP}} = \frac{Z_0 e^2 n'_m k^2}{k^2 + 4\pi n'_m l_B Z_0}. \tag{43}
\]

The corresponding expression for POCP also obtained within Gaussian approximation (see Appendix A) has a following form

\[
\langle \delta \hat{\rho}_p(k) \delta \hat{\rho}_p(-k) \rangle_{\text{POCP}} = \frac{n'_m e^2 S(k) k^2}{k^2 + 4\pi n'_m l_B S(k)}, \tag{44}
\]

where \( S(k) = \frac{n'_m \xi^3}{1+k^2 \xi^2} \) is a well known expression for the structure factor of semi-dilute polymer solution\(^\text{3}\).

Substituting (43) and (44) into (42) and calculating integral we arrive at

\[
\beta F_{\text{pert}} = \frac{1}{12\pi \xi^3} (G(u, v) - G(u, 0)), \tag{45}
\]

where \( u = \sqrt{4\pi l_B n'_m ^2 \xi^5}, \ v = \sqrt{4\pi l_B n'_m ^2 Z_0 \xi^2}, \) and function \( G(u, v) \) has a form

\[
G(u, v) = 1 + v^3 + \frac{\sqrt{2} \left( 2u^2 + (v^2 + 1) \sqrt{(v^2 - 1)^2 - 4u^2 - v^4 - 1} \right) \sqrt{v^2 + 1 + \sqrt{(v^2 - 1)^2 - 4u^2}}}{4\sqrt{u^2 + v^2}} + \frac{\sqrt{2} \left( 2u^2 - (v^2 + 1) \sqrt{(v^2 - 1)^2 - 4u^2 - v^4 - 1} \right) \sqrt{v^2 + 1 - \sqrt{(v^2 - 1)^2 - 4u^2}}}{4\sqrt{u^2 + v^2}}. \tag{46}
\]

Thus, we obtain the analytical expression for excess free energy of salt-free polyelectrolyte solution which taking into account the correlation attraction of charged particles, monomer concentration fluctuations in the regime of semi-dilute solution and mutual influence of these effects. It should be noted that the contributions of electrostatic and non-electrostatic interactions are not independent.

### III. NUMERICAL RESULTS AND DISCUSSION

Turning to the numerical calculation we introduce the dimensionless monomer concentration \( \tilde{n}_m = n_m d^3 \), temperature \( \tilde{T} = k_B T \tilde{d}_c^4 \), and second virial coefficient \( \tilde{w} = w d^3 \). In addition we assume that \( b = d \). Moreover, we determine the dimensionless osmotic pressure \( \tilde{\Pi} = \frac{\Pi d^4}{\varepsilon d} \).
Figure 1. The osmotic pressure $\tilde{\Pi}$ as a function of the monomer concentration at different temperatures $\tilde{T}$. As seen at sufficiently low temperature there is a Van-der-Waals loop that indicates the liquid-liquid phase separation.

Fig.1 demonstrates dependencies of the osmotic pressure on monomer concentration at different temperature $\tilde{T}$. As seen from Fig.1 at sufficiently low temperature a Van-der-Waals loop arises, that is indicates a liquid-liquid phase separation in the solution. Using the standard conditions of equality between chemical potentials and osmotic pressures of coexisting phases we obtain a coexistence curve of the liquid-liquid phase separation with an upper critical point (see Fig.2). As seen from Fig.2 the obtained coexistence curve is highly asymmetric that is in agreement with the results of Monte-Carlo computer simulation\textsuperscript{18}. Fig.2 shows also a comparison of the critical points obtained within different theories (including present theory) and Monte-Carlo computer simulation. The values of the critical parameters which have been obtained by the extrapolation of simulation results for $N \to \infty$ in work\textsuperscript{18} are following: $\tilde{T}_c = 0.2$ and $\tilde{n}_{m,c} = 0.09$. The Muthukumar theory\textsuperscript{23} predicts highly underestimated both critical parameters: $\tilde{T}_c = \tilde{n}_{m,c} = 1/64\pi \approx 0.005$. The theory developed by Jiang and co-authors based on MSA as was already mentioned in the Introduction predicts a good value of critical temperature but underestimated critical monomer concentration, namely $\tilde{T}_c = 0.245$ and $\tilde{n}_{m,c} = 0.01$. Our theory yields the critical parameters $\tilde{T}_c = 0.2$ and $\tilde{n}_{m,c} = 0.12$ that are in very good agreement with the results of Monte-Carlo simulation.
Figure 2. The coexistence curve of salt-free polyelectrolyte solution obtained within present theory and comparison of critical points calculated within theory of Jiang et.al\textsuperscript{25}, present theory and Monte-Carlo simulations\textsuperscript{18}. As seen, the critical point that is calculated within our theory is in very good agreement with the results of Monte-Carlo simulations.

It is instructive to regard how our theory can describe the thermodynamic properties of polyelectrolyte solution in the region above the critical point. Fig. 3 shows the comparison between the dependencies of the osmotic pressure on monomer concentration calculated within present theory and within MD simulation at \( \tilde{T} = 1.2 \) in wide range of monomer concentration\textsuperscript{37}. As seen from Fig. 3, our theory gives very good agreement with the results of MD simulation. Also our results are in very good agreement with a numerical calculation within PRISM theory\textsuperscript{39}. It should be noted, that two qualitatively different regimes of the osmotic pressure behavior take place. At a region of the small monomer concentration where the entropy of the mobile counterions gives a basic contribution into the osmotic pressure there is a linear dependence on monomer concentration (\( \tilde{\Pi} \sim \tilde{n}_m \)), whereas in concentrated regime we observe an essentially nonlinear behavior (\( \tilde{\Pi} \sim \tilde{n}_m^{9/4} \)). The predicted scaling law has been also obtained within a Monte-Carlo simulation\textsuperscript{38} and numerical calculations based on PRISM theory\textsuperscript{39}. 
IV. SUMMARY

In this study we developed a first-principle statistical theory of salt-free flexible chain polyelectrolyte solution in the regime of good solvent which based on the thermodynamic perturbation theory formalism and predicted the liquid-liquid phase separation arising due to strong correlation attraction of charded particles. Taking into account the correlation attraction of charged particles beyond the linear Debye-Hueckel theory and strong correlated monomer concentration fluctuations in the regime of semi-dilute polymer solution we developed an equation of state for salt-free polyelectrolyte solution which able to predict an accurate values of the critical parameters of liquid-liquid phase separation and values of osmotic pressure in wide range of monomer concentration in the region above the critical point. We would like to stress that our theory allows to get accurate values of the critical parameters without concept of charge renormalization (counterion condensation). As well known, the counterion condensation is an essentially nonlinear effect\textsuperscript{34,35} and consequently cannot be described within linear Debye-Hueckel type theory. However, our theoretical model go beyond the simple linear theory, so that it should take into account implicitly the effect of charge renormalization.
The limitation of the present theoretical model is related to the fact that it can be applied only to polyelectrolyte solution of sufficiently long polymer chains (i.e., in a case $N \to \infty$). However, as was shown in theoretical works\cite{23,24} and confirmed by means of Monte-Carlo and MD simulations in references\cite{18,37} the degree of polymerization of the polyelectrolyte chains has only a weak effect on thermodynamic properties of salt-free solution. In other words, if the degree of polymerization more than $\sim 30$, then thermodynamic quantities of polyelectrolyte solution in the regime of semi-dilute solution already does not depend on length of polymer chains.

The developed in present study accurate equation of state can be applied to theoretical description of thermodynamic properties of polyelectrolyte solutions with a small adding of low-molecular weight salts within the thermodynamic perturbation theory using the ionic strength as a small parameter of perturbation. In addition, the obtained equation of state can be applied to theoretical description of ingomogeneous polyelectrolyte solution as a part of a functional of free energy within the classical density functional theory instead the equation of state of simple one-component plasma\cite{40} to take into account more accurately the contribution of correlation attraction.

In conclusion, we would like to speculate about the reasons why a set of two independent one-component plasmas can be used for theoretical description of thermodynamics of salt-free polyelectrolyte solution near the critical point. As was predicted in reference\cite{17} and confirmed by Monte-Carlo simulation in work\cite{18}, the charged macromolecules near the critical point form a network from polyelectrolyte aggregates due to the strong correlation attraction. Thus, in this case the charged network can be regarded as a weakly fluctuating background neutralizing the charge of counterions, whereas the mobile counterions immersed in the polymer network can be regarded as neutralizing background for charged macromolecules. Thus, in order to evaluate the contribution of remaining effects that are related to the fluctuations of charge densities of the neutralizing backgrounds which undergo only slight fluctuations one can use the Gaussian approximation.

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V. APPENDIX A: DERIVATION OF FORMULAS (29) AND (44)

In this Appendix we give the derivation of expressions for excess free energy (29) and correlation function of charge density fluctuations (44) of POCP.

Let us represent the partition function of POCP in the following form

\[
Z_{POCP} = e^{\beta E_{self}} \int d\Gamma_p e^{-\beta H_{POCP,e.v.} - \beta H_{POCP,el}},
\]

where \( H_{POCP,e.v.} = \frac{k_B T w}{2} \sum_{i,j=1}^{N_p} \int_0^N \int_0^N ds_1 ds_2 \delta (\mathbf{r}_i(s_1) - \mathbf{r}_j(s_2)) \)

is a contribution into Hamiltonian of excluded volume interaction monomer-monomer,

\[
\int d\Gamma_p (\cdot) = \int D\mathbf{R}_1.. \int D\mathbf{R}_{N_p} e^{-\frac{3}{2\sigma^2} \sum_{j=1}^{N_p} \int ds \mathbf{R}_j^2(s)} (\cdot)
\]

is a measure of integration over configurations of Gaussian polymer chains,

\[
H_{POCP,el} = \frac{1}{2} (\hat{\rho}_p V_c \hat{\rho}_p) + (\rho_b V_c \hat{\rho}_p) + \frac{1}{2} (\rho_b V_c \rho_b)
\]

is a contribution into Hamiltonian of electrostatic interactions monomer-monomer, monomer-background, and background-background, \( \rho_b = -\langle \hat{\rho}_p(x) \rangle_{n.ch.} \) is charge density of neutralizing background, \( \beta E_{self} = \frac{\beta N N_p e^2}{2 k_B T} V_c(0) \) is an electrostatic self-energy of monomers,

\[
V_c(x - y) = \frac{1}{\varepsilon |x - y|}
\]

is a Coulomb potential.

Now let us calculate the partition function (47) in the framework of TPT formalism which proposed in reference 29. As a reference system we choose a set of neutral polymer chains with excluded volume. As was already mentioned in the main text, for free energy of such system there is an interpolation formula which taking into account effect of strongly correlated monomer concentration fluctuations in regime of semi-dilute polymer solution 30. Hence, we get

\[
Z_{POCP} = Z_{n.ch.} e^{\beta E_{self}} \left< e^{-\frac{\beta}{2} \langle \delta \hat{\rho}_p V_c \delta \hat{\rho}_p \rangle} \right>_{n.ch.},
\]

where \( \delta \hat{\rho}_p(x) = \hat{\rho}_p(x) - \langle \hat{\rho}_p(x) \rangle_{n.ch.} \) is a local charge density fluctuation of monomers; \( Z_{n.ch.} \) is a partition function of solution of neutral polymer chains. The symbol \( \langle (\cdot) \rangle_{n.ch.} \) denotes an averaging over microstates of solution of neutral polymer chains.
Applying to (52) a standard Hubbard-Stratonovich transformation one can get

$$Z_{\text{POCP}} = Z_{\text{n.ch.}} e^{\beta E_{\text{self}}} \int \mathcal{D}\varphi \frac{1}{C} e^{-\frac{1}{2\beta} (\varphi V_c^{-1} \varphi) \langle e^{i(\delta\hat{\rho}_p\varphi)} \rangle_{\text{n.ch.}}},$$  \hspace{1cm} (53)

where

$$C = \int \mathcal{D}\varphi e^{-\frac{1}{2\beta} (\varphi V_c^{-1} \varphi)}$$  \hspace{1cm} (54)

is a normalization constant; moreover, for simplicity the following short-hand notations have been introduced

$$\langle \varphi V_c^{-1} \varphi \rangle = \int d\mathbf{x} \int d\mathbf{y} \varphi(\mathbf{x}) V_c^{-1}(\mathbf{x} - \mathbf{y}) \varphi(\mathbf{y})$$  \hspace{1cm} (55)

and

$$\langle \delta\hat{\rho}_p \varphi \rangle = \int d\mathbf{x} \delta\hat{\rho}_p(\mathbf{x}) \varphi(\mathbf{x}).$$  \hspace{1cm} (56)

The kernel of reciprocal operator $V_c^{-1}$ can be determined by the relation

$$\int d\mathbf{z} V_c(\mathbf{x} - \mathbf{z}) V_c^{-1}(\mathbf{z} - \mathbf{y}) = \delta(\mathbf{x} - \mathbf{y}).$$  \hspace{1cm} (57)

Truncating a cumulant expansion in (53) in second order

$$\langle e^{i(\delta\hat{\rho}_p\varphi)} \rangle_{\text{n.ch.}} = \exp \left[ i \left( \langle \delta\hat{\rho}_p \rangle \varphi \right) - \frac{1}{2} \left( \varphi \langle \delta\hat{\rho}_p \delta\hat{\rho}_p \rangle \varphi \right) - \ldots \right],$$  \hspace{1cm} (58)

we obtain

$$Z_{\text{POCP}} \approx Z_{\text{n.ch.}} e^{\beta E_{\text{self}}} \int \mathcal{D}\varphi \frac{1}{C} e^{-\frac{1}{2\beta} (\varphi V_c^{-1} \varphi) - \frac{1}{2} \left( \varphi \langle \delta\hat{\rho}_p \delta\hat{\rho}_p \rangle \varphi \right) - \ldots},$$  \hspace{1cm} (59)

where the symbol $\langle (\cdot) \rangle_{\text{c}}$ denotes the cumulant averaging \cite{33}. Performing the calculation of Gaussian integral (59), we arrive at

$$Z_{\text{POCP}} = Z_{\text{n.ch.}} e^{\beta E_{\text{self}}} \exp \left[ \frac{V}{2} \int \frac{dk}{(2\pi)^3} \left( \frac{\kappa_p^2}{k^2} - \ln \left( 1 + \frac{\kappa_p^2}{k^2} (1 + S(k)) \right) \right) \right],$$  \hspace{1cm} (60)

where $\kappa_p = \sqrt{4\pi l_B n_m}$. Following the idea which proposed in references \cite{20,21} we introduce the ultraviolet cut-off in the integration over wave vectors $k$ in (60). In order to obtain the cut-off parameter $\Lambda$, we assume that total number of collective variables $\delta\hat{\rho}_p(k)$ which contribute into the total free energy of POCP is equal to the total number of degrees of freedom of POCP, i.e. $3NN_p$. Therefore, we have the relation

$$2V \frac{4\pi}{(2\pi)^3} \int_0^\Lambda dk k^2 = 3NN_p,$$  \hspace{1cm} (61)

17
from which we obtain the expression for cut-off parameter

$$\Lambda = (9\pi^2 n_m)^{1/3}. \quad (62)$$

The prefactor 2 in the left-hand side of (62) means that during the summation (integration) we have to take into account both real and imaginary parts of collective variable $\delta \hat{\rho}_p(k)$. Thus, keeping in mind ultraviolet cut-off (62) and calculating integral in (60) we obtain

$$F_{POCP} = F_{POCP,e.v.} + F_{POCP,el}, \quad (63)$$

where

$$F_{POCP,el} = -n_m k_B T g(\omega, \sigma), \quad (64)$$

and

$$g(\omega, \sigma) = \frac{3}{4} \left( \omega - \ln \left( 1 + \frac{\omega}{\sigma^2} \right) \right) +$$

$$+ \frac{3\sqrt{2}}{4} \frac{\omega \left( \sqrt{\omega \sigma} - \sqrt{\omega \sigma^2 - 4} \right)}{\sigma^{3/2} \sqrt{\omega \sigma + \sqrt{\omega (\omega \sigma^2 - 4)}}} \arctan \sqrt{\frac{\omega \sigma^2 + \sqrt{\omega \sigma^2 (\omega \sigma^2 - 4)}}{2\omega}} +$$

$$+ \frac{3\sqrt{2}}{4} \frac{\omega \left( \sqrt{\omega \sigma} + \sqrt{\omega \sigma^2 - 4} \right)}{\sigma^{3/2} \sqrt{\omega \sigma - \sqrt{\omega (\omega \sigma^2 - 4)}}} \arctan \sqrt{\frac{\omega \sigma^2 - \sqrt{\omega \sigma^2 (\omega \sigma^2 - 4)}}{2\omega}} \quad (65)$$

is a dimensionless function. Moreover, the following notations have been introduced: $\omega = c \Gamma_m$, $\Gamma_m = l_B \left( \frac{4\pi n_m}{3} \right)^{1/3}$ is a plasma parameter of monomers, $c = \frac{2}{3} \left( \frac{4}{\pi^2} \right)^{1/3}$ is a number constant, $\sigma = (9\pi^2 n_m)^{1/3} \sqrt{\frac{4\pi \alpha b^2}{9}}$ is a dimensionless parameter.

Now let us present a calculation of correlation function (44) of the local charge density of POCP at the level of Gaussian approximation using a method of generating functional. The partition function of POCP immersed in imaginary auxiliary external field $i\psi(x)$ takes the form

$$Z[\psi] = Z_{n.ch} e^{\beta E_{self}} \left< e^{-\frac{1}{2}(\delta \hat{\rho}_p V_c \delta \hat{\rho}_p) + i(\psi \delta \hat{\rho}_p)} \right>_{n.ch.}. \quad (66)$$

Now, let us introduce the following generating functional

$$\mathcal{P}[\psi] = \frac{Z[\psi]}{Z[0]}, \quad (67)$$

where $Z[0] = Z_{POCP}$. Thus the correlation function of local charge density of POCP can be determined by the double functional derivation of the generating functional $\mathcal{P}[\psi]$, i.e.

$$\langle \delta \hat{\rho}_p(x) \delta \hat{\rho}_p(y) \rangle_{POCP} = -\frac{\delta^2 \mathcal{P}[\psi]}{\delta \psi(x) \delta \psi(y)} \bigg|_{\psi=0}, \quad (68)$$
Using the Hubbard-Stratonovich transformation for the partition function $Z[\psi]$ we obtain

$$Z[\psi] = Z_{n.ch.} \int \frac{\mathcal{D}\varphi}{C} e^{-\frac{1}{\beta} \int (\varphi V_c^{-1} \varphi) + \frac{i}{2} (\psi \delta \hat{\rho}_p + i(\psi \delta \hat{\rho}_p))} \langle e^{i(\varphi \delta \hat{\rho}_p)} \rangle_{n.ch.}. \tag{69}$$

Thus, we get a following functional representation for generating functional $\mathcal{P}[\psi]$

$$\mathcal{P}[\psi] = \frac{1}{Z_{pert}} \int \frac{\mathcal{D}\varphi}{C} e^{-\frac{1}{\beta} (\varphi V_c^{-1} \varphi) + \frac{i}{2} (\varphi V_c^{-1} \varphi) - \frac{1}{2\beta} (\varphi V_c^{-1} \varphi) - \frac{1}{2\beta} (\varphi V_c^{-1} \varphi)} \langle e^{i(\varphi \delta \hat{\rho}_p)} \rangle_{n.ch.}. \tag{70}$$

where

$$Z_{pert} = \int \frac{\mathcal{D}\varphi}{C} e^{-\frac{1}{\beta} (\varphi V_c^{-1} \varphi) + \frac{i}{2} (\varphi V_c^{-1} \varphi) - \frac{1}{2\beta} (\varphi V_c^{-1} \varphi) - \frac{1}{2\beta} (\varphi V_c^{-1} \varphi)} \langle e^{i(\varphi \delta \hat{\rho}_p)} \rangle_{n.ch.}. \tag{71}$$

is a perturbative part of the partition function. Performing a shift of integration variable $\varphi \to \varphi - \psi$ we obtain

$$\mathcal{P}[\psi] = \frac{1}{Z_{pert}} \int \frac{\mathcal{D}\varphi}{C} e^{-\frac{1}{\beta} (\varphi V_c^{-1} \varphi) + \frac{i}{2} (\varphi V_c^{-1} \varphi) - \frac{1}{2\beta} (\varphi V_c^{-1} \varphi) - \frac{1}{2\beta} (\varphi V_c^{-1} \varphi)} \langle e^{i(\varphi \delta \hat{\rho}_p)} \rangle_{n.ch.}. \tag{72}$$

Using the cumulant expansion in integrand

$$\langle e^{i(\varphi \delta \hat{\rho}_p)} \rangle_R = e^{i \int d\varphi(x)(\delta \hat{\rho}_p(x))_c - \frac{1}{2} \int d\varphi(x)(\delta \hat{\rho}_p(x))_c \varphi(x) \varphi(\psi) \ldots} \tag{73}$$

and truncating it in the second order one can get

$$\mathcal{P}[\psi] \simeq \frac{1}{Z_{pert}} \int \frac{\mathcal{D}\varphi}{C} e^{-\frac{1}{\beta} (\varphi V_c^{-1} \varphi) + \frac{i}{2} (\varphi V_c^{-1} \varphi) - \frac{1}{2\beta} (\varphi V_c^{-1} \varphi)} \langle e^{i(\varphi \delta \hat{\rho}_p)} \rangle_{n.ch.}. \tag{74}$$

Where the kernel of integral operator $D^{-1}$ can be determined by the following way

$$D^{-1}(\mathbf{x} - \mathbf{y}) = V_c^{-1}(\mathbf{x} - \mathbf{y}) + \beta \langle \delta \hat{\rho}_p(\mathbf{x}) \delta \hat{\rho}_p(\mathbf{y}) \rangle_c. \tag{75}$$

Analogously, truncating the cumulant expansion in second order in $Z_{pert}$ and calculating the Gaussian integral we obtain

$$\mathcal{P}[\psi] \simeq \exp \left[ -\frac{1}{2\beta} \left( \psi V_c^{-1} \psi \right) + \frac{1}{2\beta} \left( \psi V_c^{-1} D V_c^{-1} \psi \right) \right] = \exp \left[ -\frac{1}{2\beta} \left( \psi G \psi \right) \right], \tag{76}$$

where

$$G = V_c^{-1} - V_c^{-1} D V_c^{-1} = V_c^{-1} \left( I - D V_c^{-1} \right) = V_c^{-1} \left( I - (V_c^{-1} + A)^{-1} V_c^{-1} \right) =$$

$$= V_c^{-1} \left( I - (I + V_c A)^{-1} \right) = V_c^{-1} (I + V_c A)^{-1} (I + V_c A - I) =$$

$$= V_c^{-1} (I + V_c A)^{-1} V_c A = V_c^{-1} V_c A (I + V_c A)^{-1} = A (I + V_c A)^{-1}, \tag{77}$$
and $A$ is an integral operator which can be represented as

$$A(x - y) = \beta \langle \hat{\rho}_p(x)\hat{\rho}_p(y) \rangle_R = \beta e^{2n_m} S(x - y), \quad (78)$$

$I$ is an identity operator, $S(x - y)$ is a structure factor of neutral polymer chain in the good solvent. Using the relation (77) we obtain

$$\langle \hat{\rho}_p(x)\hat{\rho}_p(y) \rangle_{POCP} = \frac{1}{\beta} G(x - y) = \frac{1}{\beta} \int \frac{dk}{(2\pi)^3} \frac{\tilde{A}(k)}{1 + \tilde{A}(k)V_c(k)} e^{ik(x-y)}, \quad (79)$$

where

$$\tilde{A}(k) = \beta e^{2n_m} S(k). \quad (80)$$

Thus we arrive at the following expression for Fourier image of correlation function of charge density fluctuations of POCP

$$\langle \hat{\rho}_p(k)\hat{\rho}_p(-k) \rangle_{POCP} = \frac{e^{2n_m} S(k)}{1 + \beta e^{2n_m} V_c(k) S(k)}. \quad (81)$$

Substituting the expression for $\tilde{V}_c(k)$ into (81) we arrive at (44).

VI. APPENDIX B: DERIVATION OF FORMULA (42)

In this Appendix we present a derivation of formula (42) for perturbation part of the total free energy. The partition function of solution within TPT has a form

$$Z = Z_R \int \frac{D\Psi}{C} e^{-\frac{1}{2}(\Psi,\hat{V}^{-1}\Psi)} \langle e^{i(\hat{\rho}_p)R} \rangle_R, \quad (82)$$

Further we can introduce a following definition for perturbative part of the partition function

$$Q_{pert} = \frac{Z}{Z_R} = \int \frac{D\Psi}{C} e^{-\frac{1}{2n}(\Psi,\hat{V}^{-1}\Psi)} e^{i(\hat{\rho}_p)R} - \frac{1}{2}(\Psi,\hat{\rho}_p)R \Psi =$$

$$= \int \frac{D\Psi}{C} e^{-\frac{1}{2}(\Psi,\hat{W}^{-1}\Psi)}, \quad (83)$$

where identity $\langle \hat{\rho}(x) \rangle_R = 0$, and definition for the inverse operator $\hat{W}^{-1}$

$$\hat{W}^{-1}(\vec{x} - \vec{y}) = \hat{V}^{-1}(\vec{x} - \vec{y}) + \beta \langle \hat{\rho}(\vec{x})\hat{\rho}(\vec{y}) \rangle_R \quad (84)$$

have been taken into account. Further, calculating a Gaussian integral (83) we obtain

$$Q_{pert} = \exp \left[ \frac{V}{2} \int \frac{dk}{(2\pi)^3} \ln \frac{\det (\hat{V}^{-1}(k))}{\det (\hat{W}^{-1}(k))} \right], \quad (85)$$

(20)
where matrices $\hat{W}^{-1}(k)$ и $\hat{V}^{-1}(k)$ can be determined as

$$
\hat{W}^{-1}(k) = \begin{pmatrix}
\beta \langle \delta \hat{\rho}_p(k) \delta \hat{\rho}_p(-k) \rangle_{POCP} & -\frac{1}{V_c(k)} \\
-\frac{1}{V_c(k)} & \beta \langle \delta \hat{\rho}_c(k) \delta \hat{\rho}_c(-k) \rangle_{HCOCP}
\end{pmatrix},
$$

(86)

$$
\hat{V}^{-1}(k) = \begin{pmatrix}
0 & -\frac{1}{V_c(k)} \\
-\frac{1}{V_c(k)} & 0
\end{pmatrix}.
$$

(87)

Further, calculating the determinants of matrices (86) and (87), substituting results into (85), and keeping in mind that $\beta F_{pert} = -\frac{1}{V} \ln Q_{pert}$, we obtain the formula (42).

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