Chain Collapse and Counterion Condensation in Dilute Polyelectrolyte Solutions

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A quantitative theory for polyelectrolytes in salt-free dilute solutions is developed. Depending on the electrostatic interaction strength, polyelectrolytes in solutions can undergo strong stretching (with polyelectrolyte dimension $R_g \sim l_B^{1/3} N$, where l_B is the Bjerrum length and N is the number of the chain segments) or strong compression (with $R_g \sim l_B^{-1/2} N^{1/3}$). A strong polymer collapse occurs as a first-order phase transition due to accompanying counterion condensation. [S0031-9007(98)06754-4]

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Many important synthetic and biological macromolecules are polyelectrolytes, and their properties differ significantly from that of the neutral polymers [1]. Importance of the former stimulates a variety of their analytical [2] and numerical [3] studies. However, even for a simple system of a salt-free solution of linear flexible polyelectrolytes (an electroneutral system of charged chains and counterions), many fundamental properties are still unclear.

The neutral chains undergo a collapse transition as the solvent quality decreases [1,4], but collapse and stretching of polyelectrolytes follow quite different laws. This happens due to a particular role of the counterions in these processes, which cannot be reduced only to a simple electrostatic screening and to an increase of the persistence length [5]. Under conditions of extreme dilution, for weakly charged polyelectrolytes, the counterions occupy the whole volume almost uniformly, with a very low concentration, owing to the entropy "forces." Under these conditions, polyelectrolytes tend to strong stretching caused by the strong (weakly screened) intersegment repulsions; the end-to-end distance of the chain in this case is proportional to the number of charged segments. Under a strong polyelectrolyte charge, when the electrostatic energy of polymer-counterion attraction is larger than the corresponding loss of entropy due to the counterion localization, an essential part of the counterions localizes in the close vicinity of the polyelectrolytes. This effect, called counterion condensation (e.g., [6]), leads to an effective polymer charge screening and can cause a decrease of the polymer size. This chain collapse can be even stronger than for the neutral chains.

In this Letter we present a new quantitative theory of polyelectrolytes in salt-free dilute solutions. We describe the polyelectrolyte dimension for a wide range of parameters, covering the area of the counterion condensation, and analyze the nature of the condensation.

Consider a dilute solution (electroneutral as a whole) of charged chains, each composed of $N \gg 1$ segments (monomers) with the bond length a. Let each monomer have a unit charge e (say, positive) so that N counterions of the opposite charge (say, negative) are present. Let $V = (4\pi/3)R_0^3$ be the volume per chain. We assume that the solution is very dilute, so that the condition $R_g \ll R_0$ always holds (R_g is the gyration radius of the chain) and we can concentrate on the one-chain problem. We write for the Bjerrum length $l_B = \beta e^2/\varepsilon$ (ε is the dielectric permittivity of the solvent, $\beta^{-1} \equiv k_B T$) and adopt the point-counterion approximation.

We write the Hamiltonian for the one-chain problem:

$$H = H_{\mathrm{n.ch}} + H_{\mathrm{el.ch}} + H_{\mathrm{c}} + H_{\mathrm{c-ch}}\,. \tag{1}$$

Here $H_{\mathrm{n.ch}}$ is the Hamiltonian of the neutral chain, which accounts for all non-Coulombic interactions between the monomers of the chain, $H_{\mathrm{el.ch}}$ accounts for the Coulombic interactions between the monomers of the chain, and H_{c} contains the ideal counterion part and the Coulombic part of the counterion-counterion interactions; finally, $H_{\mathrm{c-ch}}$ accounts for the Coulombic interactions between the counterions and the chain. It is convenient to write the Coulombic interactions in terms of the microscopic densities of counterions, $\hat{\rho}_c(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$, and of monomers, $\hat{\rho}_m(\mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{R}_j)$, where $\{\mathbf{r}_i\}$ and $\{\mathbf{R}_j\}$ are coordinates of the counterions and of the monomers, respectively. $H_{\mathrm{el.ch}}$ and $H_{\mathrm{c-ch}}$ read in this notation [7]

$$\beta H_{\mathrm{el.ch}} = \frac{l_B}{2} \int d\mathbf{r}\, d\mathbf{r}'\, \varphi(\mathbf{r} - \mathbf{r}')\hat{\rho}_m(\mathbf{r})\hat{\rho}_m(\mathbf{r}')\,, \tag{2}$$

$$\beta H_{\mathrm{c-ch}} = -l_B \int d\mathbf{r}\, d\mathbf{r}'\, \varphi(\mathbf{r} - \mathbf{r}')\hat{\rho}_m(\mathbf{r})\hat{\rho}_c(\mathbf{r}')\,, \tag{3}$$

where $(e^2/\varepsilon)\varphi(r) = (e^2/\varepsilon r)$ is the Coulomb potential. For the subsequent analysis it is worthwhile to map the counterion part, H_c, onto the Hamiltonian of the one-component plasma (OCP) [8]. The OCP model is formulated as follows: the point charges are immersed into the structureless compensating background of the opposite charge. The background charge density is $e\rho(\mathbf{r})$, and the average local density of the point charges (i.e., counterions) is equal to $\rho(\mathbf{r})$ [8]. The OCP Hamiltonian reads

$$H_{\mathrm{OCP}}[\rho(\mathbf{r})] = H_{\mathrm{c}} + H_{\mathrm{bb}}[\rho(\mathbf{r})] + H_{\mathrm{bc}}[\rho(\mathbf{r})], \qquad (4)$$

where $\beta H_{\mathrm{bb}} = (l_B/2)\int d\mathbf{r}\,d\mathbf{r}'\,\varphi(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r})\rho(\mathbf{r}')$ describes the background self-interaction, while $\beta H_{\mathrm{bc}} = -l_B\int d\mathbf{r}\,d\mathbf{r}'\,\varphi(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r})\hat{\rho}_c(\mathbf{r}')$ gives the energy of the background-counterion interaction. From Eq. (4) it follows that $H_{\mathrm{c}} = H_{\mathrm{OCP}} - H_{\mathrm{bc}} - H_{\mathrm{bb}}$.

To address the problem of the gyration radius of the chain, we consider the *conditional* free energy of the system, $F(R_{\mathrm{g}})$, as a function of the gyration radius R_{g}. We define an effective Hamiltonian of the neutral chain, $\overline{H}_{\mathrm{n.ch}}$, as $\exp(-\beta\overline{H}_{\mathrm{n.ch}}) \equiv D(R_{\mathrm{g}})\exp(-\beta H_{\mathrm{n.ch}})$, where the conditional function $D(R_{\mathrm{g}})$ is equal to unity if the coordinates of the monomers are consistent with the condition for the gyration radius to be R_{g}, otherwise it equals zero. Since for the systems with Hamiltonians $\overline{H}_{\mathrm{n.ch}}$ and H_{OCP} reliable estimates for the free energy are known, it is reasonable to write the total Hamiltonian as a sum of two parts: the reference part,

$$H_0 = \overline{H}_{\mathrm{n.ch}}(R_{\mathrm{g}}) + H_{\mathrm{OCP}}[\rho(\mathbf{r})], \qquad (5)$$

and the perturbation part,

$$\beta H' = \frac{l_B}{2}\int d\mathbf{r}\,d\mathbf{r}'\,\varphi(\mathbf{r}-\mathbf{r}')[\hat{\rho}_m(\mathbf{r})\hat{\rho}_m(\mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}')] - l_B\int d\mathbf{r}\,d\mathbf{r}'\,\varphi(\mathbf{r}-\mathbf{r}')[\hat{\rho}_m(\mathbf{r}) - \rho(\mathbf{r})]\hat{\rho}_c(\mathbf{r}'), \qquad (6)$$

and to use then the Gibbs-Bogoljubov inequality:

$$F(R_{\mathrm{g}}) \le F_{\mathrm{n.ch}}(R_{\mathrm{g}}) + F_{\mathrm{OCP}}[\rho(\mathbf{r})] + \langle H'\rangle_{H_0}. \qquad (7)$$

Here $F_{\mathrm{n.ch}}(R_{\mathrm{g}})$ is the free energy of the neutral chain with the gyration radius R_{g}. $F_{\mathrm{OCP}}[\rho(\mathbf{r})]$ is the free energy of the inhomogeneous OCP with the background charge density $\rho(\mathbf{r})$. Finally, $\langle H'\rangle_{H_0}$ is obtained by averaging the perturbation part, H', given by Eq. (6), over the reference Hamiltonian, H_0, given by Eq. (5). Minimizing the right-hand side of Eq. (7) with respect to the average density of the counterions $\rho(\mathbf{r})$, one obtains an estimate of the conditional free energy $F(R_{\mathrm{g}})$. Minimizing then $F(R_{\mathrm{g}})$ with respect to R_{g}, one finds the gyration radius.

The free energy of the neutral polymer is a sum of the elastic part, written in the Flory-type approximation [1] as $k_BT\gamma(\alpha^2 + \alpha^{-2})$ and the interaction part, written on the level of the second virial approximation [1] as $k_BTBN^2/(4\pi R_{\mathrm{g}}^3/3)$. Here α is the chain expansion factor, $\alpha^2 \equiv R_{\mathrm{g}}^2/R_{\mathrm{g.id}}^2$, with $R_{\mathrm{g.id}}$ being the mean-square gyration radius of the ideal chain, $R_{\mathrm{g.id}}^2 = Na^2/6$, $\gamma \simeq 9/4$ for Gaussian polymers [4], and B is the second virial coefficient. Here we consider the case of a good solvent, $B > 0$. With the reduced coefficient $B^* \equiv 6^{3/2}B/(3\pi a^3)$, we write for $F_{\mathrm{n.ch}}(R_{\mathrm{g}})$

$$\beta F_{\mathrm{n.ch}}(R_{\mathrm{g}}) \simeq \frac{9}{4}(\alpha^2 + \alpha^{-2} + B^*N^{1/2}\alpha^{-3}). \qquad (8)$$

The OCP part of the free energy in the local density approximation [8,9] reads

$$\beta F_{\mathrm{OCP}} = \int d\mathbf{r}\,\rho(\mathbf{r})\{\Psi_{\mathrm{OCP}}^{\mathrm{id}}[\rho(\mathbf{r})] + \Psi_{\mathrm{OCP}}^{\mathrm{cor}}[\rho(\mathbf{r})]\}, \qquad (9)$$

where $\Psi_{\mathrm{OCP}}^{\mathrm{id}}[\rho(\mathbf{r})] \equiv \ln[\Lambda_c^3\rho(\mathbf{r})] - 1$ refers to the ideal part of the OCP-free energy per ion (Λ_c is the thermal wavelength of the counterions), while $\Psi_{\mathrm{OCP}}^{\mathrm{cor}}[\rho(\mathbf{r})]$ refers to the excess or "correlation" part of the free energy [8]. This may be expressed in terms of the (local) "plasma" parameter $\Gamma = l_B/a_c$, where $a_c = \{3/[4\pi\rho(\mathbf{r})]\}^{1/3}$ is the (local) ion-sphere radius of the counterion. For $\Psi_{\mathrm{OCP}}^{\mathrm{cor}}$ a few accurate Padé fits exist (e.g., [10,11] and references therein). These, however, are rather cumbersome and contain many (e.g., six in [10]) empirical parameters. Here we use a simple and accurate first-principle expression for $\Psi_{\mathrm{OCP}}^{\mathrm{cor}}$ which has been obtained recently [11]:

$$\Psi_{\mathrm{OCP}}^{\mathrm{cor}}(\Gamma) = \frac{3}{4}[\ln(1 + c\Gamma) - c\Gamma] - \frac{3}{2}(c\Gamma)^{3/2}\arctan\frac{1}{\sqrt{c\Gamma}}, \qquad (10)$$

with $c \equiv (2/3)(2/\pi^2)^{1/3}$. This agrees within 1% to 2.5% with the Monte Carlo data for most of the range of Γ, and has a maximal deviation of $\approx$8% for $0.1 < \Gamma < 0.5$ [11].

Taking into account that $\langle\hat{\rho}_c(\mathbf{r})\rangle_{H_0} = \rho(\mathbf{r})$, we finally write the following for the perturbation part:

$$\beta\langle H'\rangle_{H_0} = \frac{l_B}{2}\int d\mathbf{r}\,d\mathbf{r}'[\varphi(\mathbf{r}-\mathbf{r}')g_2(\mathbf{r},\mathbf{r}') - 2\varphi(\mathbf{r}-\mathbf{r}')g_1(\mathbf{r})\rho(\mathbf{r}') + \varphi(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r})\rho(\mathbf{r}')], \qquad (11)$$

where $g_2(\mathbf{r},\mathbf{r}') = \langle\hat{\rho}_m(\mathbf{r})\hat{\rho}_m(\mathbf{r}')\rangle_{H_0}$ is the monomer pair correlation function and $g_1(\mathbf{r}) = \langle\hat{\rho}_m(\mathbf{r})\rangle_{H_0}$ is the monomer average density inside the macroion's core, i.e., in the volume confined by the gyration radius.

Now we note that the part of the free energy which depends on $\rho(\mathbf{r})$ may be written as follows (see, e.g., [9]):

$$\int d\mathbf{r}\,\rho(\mathbf{r})\Big[-e\phi_{\mathrm{ext}}(\mathbf{r}) + \frac{e}{2}\phi_{\mathrm{int}}(\mathbf{r}) + \Psi_{\mathrm{OCP}}^{\mathrm{cor}} + \Psi_{\mathrm{OCP}}^{\mathrm{id}}\Big], \qquad (12)$$

where $\varepsilon\phi_{\mathrm{ext}}(\mathbf{r}) = e\int d\mathbf{r}'\,\varphi(\mathbf{r}'-\mathbf{r})g_1(\mathbf{r}')$ is the "external" field provided by the charged chain and $\varepsilon\phi_{\mathrm{int}}(\mathbf{r}) = -e\int d\mathbf{r}'\,\varphi(\mathbf{r}'-\mathbf{r})\rho(\mathbf{r}')$ is the "internal" field which describes on the mean-field level interactions between counterions [9]. Discarding the correlation term $\Psi_{\mathrm{OCP}}^{\mathrm{cor}}$ in (12) one obtains the Poisson-Boltzmann (PB), i.e., the *mean-field* description of the system.

For the counterion density distribution we adopt here a simplified model. We introduce two characteristic densities: ρ_{in}, the average counterion density inside the macroion's core, and ρ_{out}, that for the outer region. This approximation implies that the size of the transient region where the density of the counterions changes from its in-core value to the bulk one is small compared to the gyration radius. From the normalization condition, $(4\pi/3)(R_0^3 - R_{\mathrm{g}}^3)\rho_{\mathrm{out}} + (4\pi/3)R_{\mathrm{g}}^3\rho_{\mathrm{in}} = N$, ρ_{out} is determined by ρ_{in}. It is convenient to use a dimensionless density, $\rho \equiv \rho_{\mathrm{in}}/n$, where $n = N/V_{\mathrm{g}}$ is the average in-core monomer density and $V_{\mathrm{g}} = (4\pi/3)R_{\mathrm{g}}^3$ is the gyration volume. The monomer correlation functions are approximated as $g_1 \approx n$, and $g_2 \approx n \times n = n^2$. Using these approximations one can find all contributions to the free energy (7); in particular,

$$\frac{\beta\langle H'\rangle_{H_0}}{N} = \frac{3}{5}\left(\frac{l_B}{R_{\mathrm{g}}}\right)(1-\rho)^2\left(1-\frac{2R_{\mathrm{g}}}{3R_0}\right)N\,, \tag{13}$$

where the terms $\mathcal{O}(R_{\mathrm{g}}^3/R_0^3)$ are omitted. The OCP part is also easily computed; it is somewhat cumbersome to be written explicitly for the general case. We analyze the behavior of the system in the limit $R_0 \gg R_{\mathrm{g}}$ and $N \gg 1$. Keeping for the free energy only leading terms with respect to vanishing R_{g}/R_0 and $1/N$, analyzing the relative contribution of different addendums, and omitting less significant ones, we finally arrive at the following result for the total (conditional) free energy:

$$\begin{aligned}\frac{\beta F(\alpha,\rho)}{N} \simeq{}& \frac{9}{4N}\left\{\alpha^2 + \frac{1}{\alpha^2} + \frac{B^* N^{1/2}}{\alpha^3}\right\} \\ &- 3(1-\rho)\ln R_0^* - \frac{3}{2}\left(\frac{2}{\pi^2}\right)^{1/3}\frac{l_B^*\rho^{4/3}}{N^{1/6}\alpha} \\ &+ \frac{3}{5}\,\frac{l_B^* N^{1/2}}{\alpha}(1-\rho)^2,\end{aligned} \tag{14}$$

with dimensionless $l_B^* \equiv l_B 6^{1/2}/a$ and $R_0^* \equiv R_0/a$. In the PB approximation the third term in (14) is omitted.

The equilibrium state of the system is determined by the free energy minimum with respect to both variables α and ρ. Equation (14) clearly demonstrates a competition for the equilibrium "in-core" counterion density ρ between the two largest (at $\rho < 1$) terms, which are the second and fourth on the right-hand side of Eq. (14). The second, negative term, large for $R_0^* \gg 1$, accounts for the counterion entropy. It tends to minimize the free energy by minimizing ρ; i.e., it drives the counterions away from the polyelectrolyte in order to fill uniformly the space of the one-chain cell. The positive fourth term (also large at $N \gg 1$) accounts for the free energy of screened Coulombic interaction between monomers. It is minimal if all of the counterions are condensed on the polymer, i.e., when $\rho = 1$. Thus mainly this two-term competition determines the equilibrium counterion density. The third term on the right-hand side of Eq. (14), which accounts for the counterion correlations, becomes important only if $\rho \to 1$. The following asymptotic cases give explicit solutions.

(i) If $l_B^* N^{1/2} \ll \alpha \ln R_0^*$, the second (negative) entropic term is the most important in Eq. (14) and $\rho \to 0$ as $\sim(R_{\mathrm{g}}/R_0)^3$. This case corresponds to the unscreened Coulombic interactions between the chain segments, so that the polyelectrolyte tends to expand, and $\alpha \gg 1$. We can write the leading terms as

$$\left.\frac{\beta F}{N}\right|_{\rho\to 0} \simeq \frac{9\alpha^2}{4N} + \frac{3}{5}\,\frac{l_B^* N^{1/2}}{\alpha} + \text{const.} \tag{15}$$

Thus the equilibrium α and R_{g} are, respectively,

$$\alpha \simeq \left(\frac{2}{15}\right)^{1/3} l_B^{*\,1/3} N^{1/2} \quad \text{or} \quad \frac{R_{\mathrm{g}}}{a} \sim l_B^{*\,1/3} N\,. \tag{16}$$

This is a regime of strong stretching of the polyelectrolyte.

(ii) If $l_B^* N^{1/2} \gg \alpha \ln R_0^*$, the fourth positive, inter-segment screened-Coulombic interaction term in Eq. (14) is essentially larger than the counterion entropic term, $\rho \simeq 1$ and $\alpha \ll 1$. Thus, in this case,

$$\left.\frac{\beta F}{N}\right|_{\rho\to 1} \simeq \frac{9B^*}{4N^{1/2}\alpha^3} - \frac{3}{2}\left(\frac{2}{\pi^2}\right)^{1/3}\frac{l_B^*}{N^{1/6}\alpha} \tag{17}$$

so that the equilibriums α and R_{g} read

$$\alpha \simeq 3\left(\frac{\pi}{4}\right)^{1/3}\frac{B^{*\,1/2}}{l_B^{*\,1/2}N^{1/6}} \quad \text{or} \quad \frac{R_{\mathrm{g}}}{a} \sim \frac{B^{*\,1/2}N^{1/3}}{l_B^{*\,1/2}}\,. \tag{18}$$

This is a regime of strong collapse of the polyelectrolyte. Note that the second (negative) term in (17) accounts for the counterion correlations; without this term (in the PB approximation) no chain collapse would be observed.

For the general case we solved the minimization problem numerically (again for the conditions $R_0 \gg R_{\mathrm{g}}$ and $N \gg 1$). We analyzed the dependences of R_{g} on l_B at fixed B^*, R_0^*, and N. The $R_{\mathrm{g}}(l_B^*)$ dependence for some particular B^*, R_0^*, and N is shown in Fig. 1. For small and large values of the reduced Bjerrum length, l_B^*, the radius R_{g} changes in accordance with the asymptotic Eqs. (16) and (18). Our findings are in qualitative agreement with the results of the numerical studies [3], where the same two different regimes in the $R_{\mathrm{g}}(l_B^*)$ dependence were observed. For intermediate l_B^* we find a sharp bend in the dependence of the equilibrium free energy on l_B^* and a discontinuity of its first-order derivatives.

We interpret this as a first-order phase transition from the strong stretching regime, with $\alpha \gg 1$, to the strong collapse regime, with $\alpha \ll 1$. This phase transition is accompanied (or driven) by the process of counterion condensation, when the counterion density changes from $\rho \ll 1$ (counterions are uniformly spread over the bulk) to $\rho \simeq 1$ (practically all counterions are confined inside the polyelectrolyte globule). After the counterion condensation the polyelectrolyte dimensions become significantly smaller than they would be for a neutral chain with the

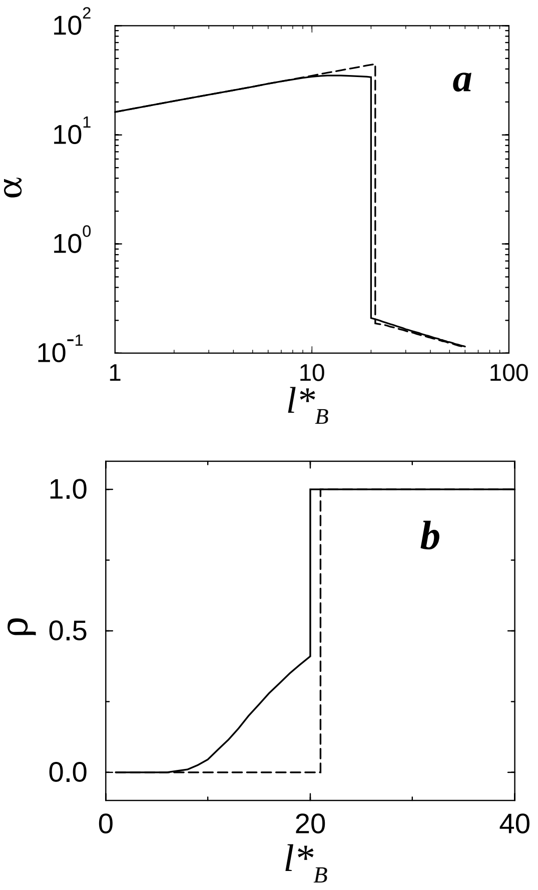

FIG. 1. (a) Dependences of the polyelectrolyte expansion factor α versus the reduced Bjerrum length, $l_B^* \equiv l_B\sqrt{6}/a$, calculated for $N = 10^3$, $R_0^* = 10^5$ with $B^* = 1$. A dramatic jumplike decrease of the polyelectrolyte size occurs along with the first-order phase transition due to the counterion condensation. (b) Dependences of the near-polyelectrolyte counterion density. Dotted curves refer to the numerical analysis of the simplified Eq. (14). Solid curves account for the next-order corrections with respect to R_g/R_0 and $1/N$.

same volume interactions (i.e., with the same virial coefficients [4]). One can explain this effect as follows: The correlation part of the OCP-free energy (ignored in the PB approximation) gives rise to a negative pressure which at $l_B^* \gg 1$ overcompensates the ideal chain and counterions entropic pressure. It may be balanced by the intersegment non-Coulombic repulsion but only at some degree of compression. Clearly, the PB approximation misses this phenomenon, i.e., it qualitatively fails for $l_B^* \gg 1$.

As it is seen from Fig. 1, for $R_0^* = 10^5$ and $N = 10^3$, the phase transition occurs at $l_B^* \simeq 20$. We found that with decreasing R_0^* and N the transition shifts to smaller l_B^* and becomes less pronounced. These values of l_B^* seem to be accessible for real polyelectrolyte solutions, and one can expect that the transition may be observed experimentally (we are not, however, aware of such observations). The change of the regime in the $R_g(l_B)$ dependence did not occur as a phase transition in [3], where simulations were performed for chains of 32 and 64 monomers. Since the present theory applies to the limit $N \gg 1$, we cannot conclude whether the transition (which becomes less sharp with decreasing N) disappears at some critical N larger than that used in [3]. We also believe that the phase transition found within the simple two-level model for the counterion density will persist for more realistic density distribution (at least for $N \gg 1$) [12].

In conclusion, we developed a simple theory of dilute salt-free linear polyelectrolyte solutions. We analyzed the dependence of the gyration radius of the chain on the Bjerrum length, l_B, which characterizes the strength of the Coulombic interactions in the system, and found two different regimes in this dependence, the same as were observed in numerical studies. Additionally, we detected a first-order phase transition from chain stretching to strong collapse, which is accompanied by the counterion condensation on the polyelectrolyte.

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