LETTER TO THE EDITOR

Counterion correlations and attractions in dense polyelectrolyte solutions

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Abstract
We study concentrated solutions of highly charged polyelectrolyte solutions beyond the mean-field approximation by explicitly taking into account the effects of both counterion and polymer chain fluctuations. One part of the fluctuating counterion densities moves freely throughout the bulk. The second counterion density component consists of a fraction of counterions fluctuating along the length of the chains. The degree of condensation and the effective intra-chain potential are determined self-consistently. We observe the effects of this interaction which is attractive over short distances and can lead to a collapse as a sufficiently high level of counterion condensation is achieved.

Mean-field theory has been very useful in determining some of the properties of polyelectrolyte solutions. However, it has also been known for many years that by itself the theory does not explain many of the observed behaviours of such systems. While mean-field (Poisson–Boltzmann) theory was successfully used to explain charge renormalization in polyelectrolytes as introduced by Oosawa/Manning for rod-like molecules [1] additional considerations are needed to address, for example, the ubiquitous attractive interaction between macroions of like charge. This has been observed in numerous experimental studies [2–4] and has also been the subject of a number of simulation studies [5, 6].

There is a general consensus that the origin of like-charge attraction is due to charge correlations. Several theoretical studies have looked at the effects of charge correlations on the properties of charged macromolecules [7–9] and surfaces [10]. Most of these studies, however, have tended to focus on charge correlations on single macromolecules [11] or with molecules with simple geometry, such as rods or spherical colloidal particles. The source of the attractive interactions in macromolecules can be due to (1) a Wigner crystal of counterions on the polyion [12], (2) specific binding of counterions to the polyion [13], or (3) thermal fluctuations [7] depending on the temperature and the bare charge density of the polyion. However, recent simulations [6] seem to indicate only a short-range correlated counterion cloud for finite diameter rods. It is found experimentally that the condensation of counterions of increasing valence leads to stronger attractive interactions and a subsequent collapse of the chain.

The study of homogeneously charged polyelectrolyte solutions *without charge correlations* has a long history [14–19]. Polyelectrolyte solutions at finite monomer concentrations are of particular interest since they are most relevant to experiment. In addition, recent careful scattering experiments have also probed attractive interaction and the polyelectrolyte peak height at higher chain concentration and varying valences. Nishida *et al* [20] have investigated the phase diagram of salt-free polyelectrolytes, while Zhang *et al* [21] and Dubois and Boué [22] looked at the effects of counterion valences. Simulations have also addressed multivalence (see for example the recent work by Chang and Yethiraj [23]).

Counterion correlations in polyelectrolyte solutions have attracted much attention in the recent literature [24–26]. However, a self-consistent description of the effect of *fluctuations* on the degree of counterion condensation and vice versa is still lacking. Furthermore, recent experimental studies [27] have highlighted the need for phase diagrams which can relate the properties of the polyelectrolytes and counterions to phase boundaries between condensed (collapsed) and uncondensed states. We attempt to address this by performing a systematic expansion in the density fluctuations of *all* the degrees of freedom. Our results are thus most accurate for concentrated solutions but should give valuable insights to the semi-dilute regime. We will not make direct comparisons with experiments here but rather set up a formalism which can be used to study a variety of polyelectrolyte systems at non-zero concentrations.

In this letter we investigate the statistical mechanics of a system of counterions and flexible polyelectrolyte chains beyond the mean-field (Poisson–Boltzmann) approximation. We evaluate self-consistently the saddle point (giving the mean-field equations) and go *beyond* the mean field by calculating the quadratic fluctuations about it. In evaluating the partition function, we perform the following calculational trick which allows us to obtain the correct saddle-point equations. The counterions are split into two (arbitrary) groups with one group of counterions moving in the close proximity of the chains, while the other 'free' counterions move throughout the remaining volume of the system. We shall call the counterions in proximity to the chain 'condensed' for want of a better term. We calculate the free energy of the system allowing the exchange of counterions between the two groups. In other words, we calculate a partition sum over all counterion configurations by summing over *all possible* fractions of condensed ions, enabling us to calculate the most likely (optimum) fraction of condensed ions as a function of all system parameters. We keep track of all the Coulomb interactions between 'condensed' counterions (moving along the chain contours), free counterions (moving in the bulk), and the polyelectrolyte. A systematic expansion in the density fluctuations of chains and of both free and condensed counterions is performed. Our main approximation is that the bulk densities are almost homogeneous, enabling truncation of the fluctuations at quadratic order. The free energy is minimized with respect to the fraction of 'condensed' ions. A nontrivial coupling of counterion degrees of freedom to the chain degrees of freedom produces new physics and *changes* the value of the condensed fraction. We investigate the dependence of the fraction of condensed ions on system parameters, and calculate the chain structure factor expected from scattering experiments.

We treat the condensed counterions in a similar way to Lau *et al*'s analysis of counterion condensation near a charged plate [10]. The polymer chain degrees of freedom will be expressed in terms of quadratic density fluctuations, following closely the description of polyelectrolyte melts given by Borsali and Vilgis [15]. Our treatment of *free* counterions resembles that of Olvera de la Cruz *et al* [28] but we do not fix the condensed fraction but rather calculate it self-consistently taking account of the entropy and Coulomb energy of both free and condensed ions. Recently a model of free and condensed *monovalent* counterions has been developed by Muthukumar [29] in which the actions between condensed ions are

approximated by dipoles. We keep the full Coulomb interaction, allowing us to address high valence counterion systems.

We consider $\mathcal{N}$ flexible polyelectrolyte chains of equal lengths L with linear charge density $-\lambda e$ which is neutralized by N counterions of charge ze moving in the volume V. Additional salt provides $2M$ ions of charges $\pm ze$ to the counterions. A fraction f of the number of counterions N is presumed to be condensed on the chain. Since, in principle, salt ions can also condense, $0 \leqslant f \leqslant (1 + M/N)$.

Calculation of the free energy entails integration over the polymer, counterion and salt ion degrees of freedom. The polymer chain conformations are given by $r_i(s)$, where s is the arc length. Condensed counterions are located at positions $\{s_j\}$ along the polymer contour which have spatial coordinates coupled to the polymer $\{r(s_j)\}$. The positions of the free uncondensed counterions are denoted by z_i whereas the salt ions with the same sign of charge as the polyelectrolyte are located at positions z_i'.

For flexible (Gaussian) chains the (functional) integral over each polymer conformation $[\mathrm{d}r_i(s)]$ is accompanied by the Wiener measure, $\exp[-3/2\ell^2 \int_0^L \mathrm{d}s(\partial r_i/\partial s)^2]$. Here ℓ is the Kuhn length. The Coulomb energy due to the interactions between *all* the different charged components determines the Boltzmann weight.

We choose to express all lengths in terms of the Kuhn length ℓ (dimensionless quantities are identified by ˜). The volume fraction of polyelectrolyte chain segments is given by $\Phi_0 = \mathcal{N}L\ell^2/V \equiv \mathcal{N}L/(\ell\tilde{V})$. Dimensionless average condensed, bulk positive and bulk negative counterion densities, defined by $\Phi_0\tilde{c}_0 = fN/\tilde{V}$, $\tilde{n}_0^+ = ((1-f)N + M)/\tilde{V}$, and $\tilde{n}_0 = M/\tilde{V}$, respectively, must sum with the total chain charges for electrical neutrality: $(\tilde{\lambda}/z - \tilde{c}_0)\Phi_0 + \tilde{n}_0^+ - \tilde{n}_0 = 0$.

We define the densities of the charged species (polyions, counterions, positive and negative salt ions respectively),

$$\varrho(r) + \Phi_0 = \sum_i^{\mathcal{N}} \int_0^{L/\ell} \mathrm{d}s\, \delta\left(\tilde{r}_i(s) - \tilde{r}\right), \qquad c(s) + \tilde{c}_0 = \sum_{j=1}^{fN} \delta\left(s - s_j\right)$$

$$n^+(r) + \tilde{n}_0^+ = \sum_{i=1}^{(1-f)N+M} \delta\left(z_i - r\right), \qquad n^-(r) + \tilde{n}_0^- = \sum_{i=1}^{M} \delta\left(z_i' - r\right)$$

where the spatial density fluctuation has been split from the homogeneous background densities. Adding them together defines the total charge density $\rho(x) = (-\tilde{\lambda} + z\tilde{c}_0)\varrho(x) + zn^+(x) + zn^-(x) + \sum_{i=1}^{\mathcal{N}}\int \mathrm{d}s\, zc(s)\delta(r_i(s) - x)$. The Coulomb energy is therefore given by $\tilde{\ell}_\mathrm{B} k_B T/2 \int \mathrm{d}^3x\, \mathrm{d}^3x'\, \rho(x)\rho(x')/|x - x'|$ where we have defined the dimensionless *Bjerrum length* as $\tilde{\ell}_\mathrm{B} = e^2/(4\pi\epsilon_0 k_\mathrm{B}T\ell)$. We note the conversion of the linear density of the condensed counterions $c(s) + \tilde{c}_0$ into a volume density by multiplication by $\delta(r(s) - x)$.

We introduce another functional integral $[\mathrm{d}\phi]$ over a field ϕ conjugate to the total charge density, via a Hubbard–Stratonovich transformation and by making use of $-\nabla^2|x - x'|^{-1} = 4\pi\delta(x - x')$. The *complete* classical partition function for the flexible polyions, counterions and co-ions interacting electrostatically is therefore

$$Z(f) = \mathrm{Tr}\, e^{-\beta\mathcal{H}} = C(N, M, f)J_\phi \int [\mathrm{d}\tilde{r}(s)][\mathrm{d}\tilde{\phi}(x)] \prod_{i=1}^{(1-f)N+M} \mathrm{d}^3z_i \prod_{k=1}^{M} \mathrm{d}^3z'_k \prod_{j=1}^{fN} \mathrm{d}s_j$$

$$\times \exp\left\{-\frac{3}{2}\sum_{i=1}^{\mathcal{N}}\int_0^{L/\ell} \mathrm{d}s\left(\frac{\partial r_i}{\partial s}\right)^2 - \frac{1}{8\pi z^2\tilde{\ell}_\mathrm{B}}\int_{\tilde{V}} \mathrm{d}^3x\left(\nabla\tilde{\phi}(x)\right)^2\right.$$

$$\left. + \frac{\mathrm{i}}{z}\int_{\tilde{V}} \mathrm{d}^3x\, \rho(x)\tilde{\phi}(x)\right\}. \tag{1}$$

where $C(N, M, f) = \frac{1}{M!} \frac{1}{[(1-f)N+M]!} \frac{1}{(fN)!}$ is a combinatorial factor and J_ϕ is a normalizing Jacobian.

The partition function is evaluated as follows [30]. In a first step the integrals over the positions of the point-like ions z_i, z_i' and s_j are performed transforming into the collective degrees of freedom c, n^+, n^-. Then (functional) integrations over the densities c, n^+, n^- are evaluated approximately using the steepest descent method which entails finding the saddle point (giving the mean-field equations) and the quadratic fluctuations about it [31].

The second step involves transforming from polymer conformation $r(s)$ to collective polymer segment density $\varrho(x)$. For dense polymer systems this is achieved by the well-known random phase approximation (RPA) which gives a Gaussian distribution for ϱ [32],

$$Z_q(f) = \frac{1}{(fN)!} \frac{1}{[(1-f)N+M]!} J_\phi J_\varrho e^{[(1-f)N+M]\ln \tilde{V} + fN \ln(L/\ell)}$$

$$\times \int [d\varrho] [d\phi] \exp\left\{ -\frac{1}{2} \int_x \int_{x'} \varrho G_0^{-1} \varrho + i \int_x \phi \left(-\frac{\tilde{\lambda}}{z} + \tilde{c}_0 \right) \varrho \right\}$$

$$\times \exp\left\{ -\frac{1}{2z^2\tilde{\ell}_B} \int_x \left[\frac{(\nabla\phi)^2}{4\pi} + z^2\tilde{\ell}_B \left(\frac{\tilde{\lambda}}{z}\Phi_0 + 2\tilde{n}_0^- \right) \phi^2 \right] - \frac{1}{2}\tilde{c}_0 \int_x \phi^2 \varrho \right\} \quad (2)$$

where $(\int_x \equiv \int_{\tilde{V}} d^3x)$ and $G_0^{-1}(x)$ is the inverse flexible chain structure factor, well approximated in Fourier space [32] by

$$G_0(k) = 6\tilde{R}_g^2 \Phi_0/(1 + k^2 R_g^2/2)$$

where $\tilde{R}_g^2 = L/(6\ell)$ is the (non-interacting chain) radius of gyration.

Most terms in equation (2) are familiar. We identify the Debye–Hückel (DH) inverse operator $\hat{V}_{DH}^{-1} \equiv \frac{1}{4\pi z^2\tilde{\ell}_B}(-\nabla^2 + \tilde{\kappa}^2)$ and its equivalent real-space potential $V_{DH}(r) = z^2\tilde{\ell}_B e^{-\tilde{\kappa}|\tilde{r}|}/|\tilde{r}|$, with dimensionless DH screening length $1/\tilde{\kappa}$, where $\tilde{\kappa}^2 = 4\pi z^2\tilde{\ell}_B[2\tilde{n}_0^- + \frac{\tilde{\lambda}}{z}\Phi_0]$.

The term in $\phi^2 \varrho$ in the exponential in the integrand in equation (2) is new and central to our results. It arises from the coupling of the condensed counterion density along the chain contour to the electric potential ϕ via the polymer fluctuation. Its origin is the integration over condensed counterion arc-length locations $\int(\prod_j ds_j) \exp(i \int d^3x \phi(x)\delta(x - r(s_j)))$.

We integrate *exactly* over the Coulomb field ϕ and then keep all polymer density fluctuations in the resulting expression to quadratic order. The term linear in the density vanishes due to charge neutrality and we obtain an effective interaction term between *chain segments* $V_{eff} \equiv (\frac{\tilde{\lambda}}{z})^2[(1-f)^2 V_{DH} - \frac{f^2}{2} V_{DH}^2]$. This contains contributions (a) from the renormalized polymer backbone charge $(1-f)\tilde{\lambda}$ repelling with a Debye–Hückel potential, and (b) the condensed counterion fraction $f\tilde{\lambda}$ causing attraction screened at half the DH length. It is important to note that the latter part has a *different* Bjerrum length dependence in the prefactor, i.e. $\tilde{\ell}_B^2$, than for the DH part. We note that the screening is due to the *all of the* counterions (even those not in the bulk). As the degree of condensation f increases, the attractive part to the effective interaction becomes stronger.

The remaining, quadratically truncated polymer density fluctuation functional integral is $\int[d\varrho] \exp[1/2 \int \varrho S^{-1} \varrho] = \int[d\varrho] \exp[1/2 \int \varrho(G_0^{-1} + \tilde{\lambda}^2 V_{eff})\varrho]$ and it can be used to read off the polymer chain structure factor in terms of the dimensionless momentum transfer vector q:

$$S_f(q) = \left[\left(\frac{1 + q^2\tilde{R}_g^2/2}{6\tilde{R}_g^2\Phi_0} \right) + \frac{4\pi(1-f)^2\tilde{\lambda}^2\tilde{\ell}_B}{q^2 + \tilde{\kappa}^2} - 2\pi f^2 z^2 \tilde{\lambda}^2 \tilde{\ell}_B^2 \frac{1}{q} \arctan\left(\frac{q}{2\tilde{\kappa}} \right) \right]^{-1}. \quad (3)$$

The fraction of condensed counterion $f^\star$ is determined by minimizing the free energy $-\beta F_q(f) = \ln Z_q(f)$ with respect to f.
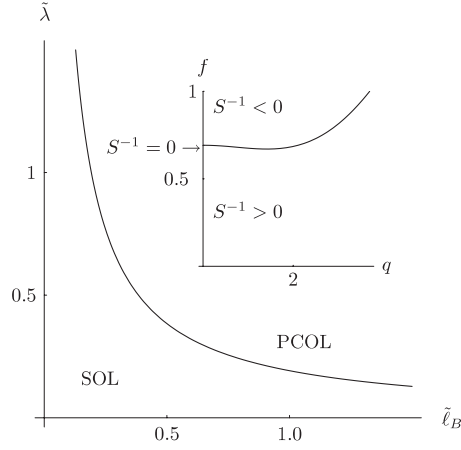
Figure 1. The phase diagram shows the region in $\tilde{\ell}_B$ and $\tilde{\lambda}$ in which the chains are always in solution (SOL). Outside this region we find possible chain collapse (PCOL). In the PCOL domain a situation such as in the inset occurs, which shows a typical line at which $S_f^{-1}(q)$ becomes zero-valued and then negative (where the theory breaks down) for some values of q for available values of the condensed fraction f. The SOL region excludes any such cases from occurring for $0 \leqslant f \leqslant 1 + z\tilde{n}_0/\tilde{\lambda}\Phi_0$. (Parameter values used: $\tilde{R}_g^2 = 10.0$, $\Phi_0 = 0.05$. Main graph: $n_0 = 0.0$; inset: $\tilde{\lambda} = 8.0$, $\tilde{\ell}_B = 0.5$, and $n_0 = 0.01$).

$$0 = \left. \frac{\mathrm{d}\frac{z\beta F_q(f)}{\tilde{\lambda}\Phi_0 V}}{\mathrm{d}f} \right|_{f^\star} = \psi_0(f^\star N + 1) - \psi_0\left((1 - f^\star)N + M + 1\right)$$

$$- \ln\frac{\Phi_0}{1 - \Phi_0} + \frac{z}{4\pi^3\tilde{\lambda}\Phi_0}\int' \mathrm{d}^3k \left[\frac{\mathrm{d}S^{-1}}{\mathrm{d}f}\right]_{f^\star} S_{f^\star} \tag{4}$$

Here $\psi_0(x)$ is the digamma function resulting from derivatives of $\ln\Gamma(fN+1)$. A small length cutoff q_c models the hard-core repulsion chains eventually must experience at short distances and is indicated by a prime on the integral sign. For numerical work we chose $q_c = 10$ throughout, corresponding to a hard-core length-scale of 0.1ℓ. For the data presented by us here $\tilde{\kappa} < 0.6$ (or a Debye length greater than 1.66ℓ), and as long as $q_c \gg \tilde{\kappa}$, we find that the values of $f^\star$ do not depend strongly on the value of q_c. $1/q_c$ is also much smaller than the values of radius of gyration used in plots $\sqrt{10} \simeq 3.2$.

Values of $f^\star$ are obtained from equation (4) by numerically performing the integration and solution. (Numerically, we approximate the combination of digammas above well using $\ln[f/(1 - f + z\tilde{n}_0/\tilde{\lambda}\Phi_0)]$.) The $S_f(q)$ of equation (3) can become singular for sufficiently large values of $f \in [0, 1 + z\tilde{n}_0/\tilde{\lambda}\Phi_0]$, depending on the remaining system parameters. This indicates failure of our homogeneity assumptions and a possible collapse of the polymers due to effective attraction. We call this region 'PCOL' in figure 1. We note that if the condition $1/(6\tilde{R}_g^2\Phi_0) > \pi z^2\tilde{\lambda}^2\tilde{\ell}_B^2(1 + z\tilde{n}_0/\tilde{\lambda}\Phi_0)^2/\tilde{\kappa}$ is fulfilled, the system is always within the 'SOL'-region. This is seen by observing that $S_f^{-1}(q) \geqslant 1/(6\tilde{R}_g^2\Phi_0) - \pi z^2\tilde{\lambda}^2\tilde{\ell}_B^2(1 + z\tilde{n}_0/\tilde{\lambda}\Phi_0)^2/\tilde{\kappa}$. Consequently, decreases in radius of gyration, backbone charge density, valence or Bjerrum length and salt concentration move the system into the 'SOL'-region.

Figure 2(a) displays the trend of increasing condensation as the temperature is lowered. Condensation weakens as the backbone charge density decreases (figure 2(b)). We note that
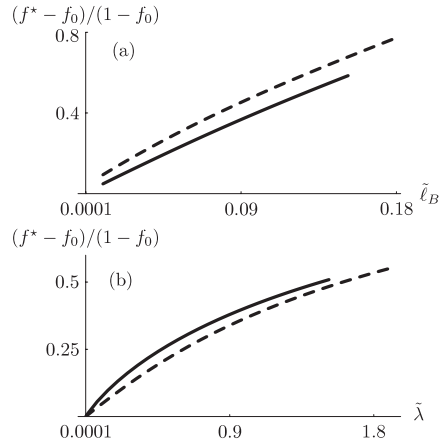
Figure 2. We plot numerical solutions of $f^\star$, in (a) as a function of $\tilde{\ell}_B$ for $\tilde{n}_0 = 0.0$ (solid) and $\tilde{n}_0 = 0.03$ (dashed), with $\Phi_0 = 0.1$, $\tilde{\lambda} = 1.0$, and $\tilde{R}_g^2 = 10.0$. In (b) the dependence of $f^\star$ on the bare backbone charge density $\tilde{\lambda}$ is shown for $\Phi_0 = 0.1$ (solid) and $\Phi_0 = 0.05$ (dashed) where $\tilde{\ell}_B = 0.1$, $\tilde{n}_0 = 0.0$, and $\tilde{R}_g^2 = 10.0$. The lines terminate when values outside the guaranteed chain solution regime are reached (cf figure 1).
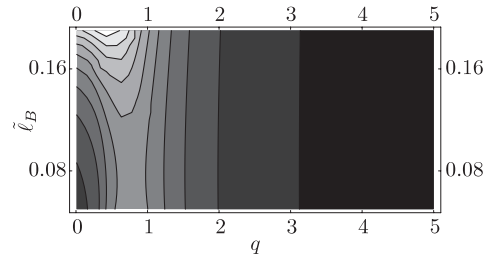

Figure 3. A contour plot of the structure factor as $\tilde{\ell}_B \propto 1/T$ varies is depicted. The plot clearly shows the polyelectrolyte peak (lighter areas represent greater scattering intensity). Appropriate values of $f^\star$ were computed numerically. Otherwise the parameter values are $\tilde{\lambda} = 1.0$, $\Phi_0 = 0.1$, $\tilde{n}_0^+ = 0.0$, and $\tilde{R}_g^2 = 10.0$.

counterion condensation is the result of a competition between counterion entropy and the electrostatic interaction with the macroion. If entropy wins, there will be a uniform density of ions in the solution; if the electrostatic interaction wins, the counterions are condensed in the vicinity of the macroion. For non-zero volume fraction of polyelectrolyte it is clear that a fraction $f_0 = \Phi_0$ of the counterions must be close to the chains even when there is no electrostatic interaction between the counterions and the chains. Therefore a clearer indication of this entropy–energy competition is the renormalized condensed fraction $\frac{f^\star - f_0}{1 - f_0}$, which is plotted in figure 2.

As is typical of polyelectrolyte solutions [21, 22, 20], the structure factor $S_{f^\star}(q)$ (figure 3) features the emergence of the polyelectrolyte peak at finite q and sufficiently small Bjerrum length. For $f = 0$ the results of Vilgis and Borsali [15] are recovered, in which the peak position scales as $q_{max} \propto \Phi_0^{1/4}$.

A pertinent experimental example which has been thoroughly studied is λ-phage DNA (48502 bp, $R_g \sim 10\,000$ Å), for which we can define the parameters $\ell \simeq 500$ Å and $\lambda^{-1} = 1.7$ Å, for which $\tilde{\lambda} = 294$, and using the Bjerrum length in water, 7 Å, we have

Table 1. We list values of $f^\star$ for increasing valences in systems where $\tilde{\ell}_B = 0.05$, $\tilde{\lambda} = 1.0$, $\tilde{R}_g^2 = 10$, $\Phi_0 = 0.1$, and $\tilde{n}_0 = 0.0$. As expected, the results indicate that increasing valence causes stronger condensation (and by implication, in our model, a significant increase in the attraction of the effective chain–chain interaction).

z	1	2	3
$f^\star$	0.292	0.556	0.884
q_{peak}	0.743	0.507	0.0

$\tilde{\ell}_B = 0.014$, which at $\Phi_0 \sim 0.02$ mg ml^{-1}, valence $z = 3$ (spermidine) and $n_0 = 5$ mM [27] lies in the PCOL region of the phase diagram (see figure 1).

Experiments indicate that counterion valence strongly affects the attraction and condensation, these effects becoming increasingly dominant as counterions are changed from monovalent, to divalent, to trivalent. This is in agreement with our results where the valence, backbone charge density, and the Bjerrum length always occur in the combinations $\tilde{\lambda}/z$ and $z^2 \tilde{\ell}_B$, defining equivalent temperatures and charge densities for different valences. Table 1 lists the valence dependence of $f^\star$ for equivalent temperatures and backbone charge densities. The measurements of Zhang *et al* [21] of a polyelectrolyte peak at smaller q_{peak} for higher valences are supported by our model.

Summarizing, we have shown that combined condensed and bulk counterion fluctuations, treated to quadratic order, produce a charge renormalization of the chain backbone with a rich dependence on monomer concentration, counterion density and degree of ionization. The fluctuations also cause an effective, short-range intra-chain attraction, which decreases with increasing temperature. Eventually, increasing condensation leads to a possible collapse of the polymer chains. This collapse is promoted by increasing the radius of gyration, backbone charge density, counterion valence and salt concentration. The criterion for this is expressed through $S_f^{-1}(q) = 0$ for any values of $0 \leqslant f \leqslant 1 + z\tilde{n}_0/\tilde{\lambda}\Phi_0$. In contrast to isolated rods [1], we find no discernible sharp condensation transition for counterions on flexible, dense homogeneous chains. We have found that increasing the Bjerrum length or charge density along the chain increases the degree of condensation $f^\star$. Furthermore, numerical investigations suggest the trends that $f^\star$ increases weakly with increases of the radius of gyration or of counterion or monomer concentrations (at least when these concentrations are low). We intend to extend this work to calculate the scattering from labelled condensed counterions [33] and to predict effective interaction parameters between different species of polyelectrolyte [27].

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