Theory of competitive counterion adsorption on flexible polyelectrolytes: Divalent salts

Arindam Kundagrami and M. Muthukumar

Department of Polymer Science and Engineering
University of Massachusetts at Amherst, Amherst, MA 01003

Counterion distribution around an isolated flexible polyelectrolyte in the presence of a divalent salt is evaluated using the adsorption model [M. Muthukumar, J. Chem. Phys. 120, 9343 (2004)] that considers Bjerrum length, salt concentration, and local dielectric heterogeneity as physical variables in the system. Self consistent calculations of effective charge and size of polymer show that divalent counterions replace condensed monovalent counterions in competitive adsorption. The theory further predicts that at modest physical conditions, polymer charge is compensated and reversed with increasing divalent salt. Consequently, the polyelectrolyte collapses and reswells, respectively. Lower temperatures and higher degrees of dielectric heterogeneity enhance condensation of all species of ions. Complete diagram of states for the effective charge calculated as functions of Coulomb strength and salt concentration suggest that (a) overcharging requires a minimum Coulomb strength, and (b) progressively higher presence of salt recharges the polymer due to either electrostatic screening (low Coulomb strength) or negative coion condensation (high Coulomb strength). A simple theory of ion-bridging is also presented which predicts a first-order collapse of polyelectrolytes. The theoretical predictions are in agreement with generic results from experiments and simulations.

I. INTRODUCTION

Understanding charged polymers has again become a major focus of the polymer community in the last few years. With respect to uncharged systems, there are two additional
length scales traditionally considered in theoretical treatments of salty polyelectrolyte solutions. One is the Bjerrum length \( l_B \), which sets the length scale for the strength of the Coulomb interaction at a particular temperature \( T \) in a specific solvent of dielectric constant \( \epsilon \), given by

\[
l_B = \frac{e^2}{4\pi\varepsilon_0\kappa_B T},
\]

where \( e \) is the electron charge, \( \varepsilon_0 \) is the vacuum dielectric constant, and \( \kappa_B \) is the Boltzmann constant. The other one is the Debye screening length \( \kappa^{-1} \), which sets the length scale for screening due to dissociated ions, given by

\[
\kappa^{-2} = 4\pi l_B \sum_i Z_i^2 c_i,
\]

where the sum is over all species (\( i \)) of mobile ions of valency \( Z_i \) and concentration \( c_i \). In addition to the above two, a third length scale can be conceived relating to the dielectric heterogeneity, which accounts for the difference in the dielectric constant in the vicinity of the chains and in the bulk solvent. In this paper, we consider these three length scales to theoretically determine the effective charge and conformation of a single isolated polyelectrolyte chain in the presence of divalent salts.

The typical non-monotonic dependence of the average conformation of flexible polyelectrolyte chains on temperature is now well-known. At very high temperatures, the chains in dilute salt-free solutions are in their athermal states with self-avoiding-walk (SAW) statistics. Although the chains are fully charged at these conditions, the electrostatic repulsion among monomers remains negligible compared to thermal fluctuations. As the temperature decreases, electrostatics becomes progressively important and the chains expand due to inter-monomer repulsion even beyond the excluded-volume swelling. At even lower temperatures, counterions condense on the chains sufficiently reducing the net polymer charge, and consequently the chains contract again. The presence of small-molecular monovalent salts has long been known to enhance this condensation effect, and the resulting collapse occurs at higher temperatures. Monovalent salts, however, collapse polyelectrolytes at temperatures that are still typically way below modest temperatures (e. g., room temperature for aqueous solutions). Presence of divalent (or multivalent) salts, however, induces a drastic qualitative change in polyelectrolyte behaviors. A modest number of divalent counterions in water can effectively neutralize and collapse polyelectrolytes at room temperatures. Further, addition of a higher amount of divalent salt can even reverse the charge on the polymer
(the phenomenon known as overcharging or charge inversion or charge reversal) at certain physical conditions.

The condensation of counterions on flexible polyelectrolyte chains has traditionally been covered in the Manning model originally designed for infinitesimally thin and infinitely long rod-like molecules. However, Manning’s argument has been found inadequate for flexible polyelectrolytes, particularly for complex systems with multivalent ions. Flexibility allows significant bending of molecules due to charge compensation at lower temperatures, allowing substantial changes in the conformational entropy of the polymer. Manning’s assumption that the discrete nature of the charged groups has a secondary effect becomes entirely invalid for multivalent ions. It is precisely this discreteness that is found responsible for complete charge compensation (and resulting contraction of polyelectrolytes) and subsequent overcharging at modest temperatures by multivalent salt counterions. This overcharging behavior is unexplainable within the Poisson-Boltzmann formalism which considers a continuum description of the charge density. In order to address precipitation of chains for high counterion valence, initial theories considered translational free energy of polyions and salt ions along with screened Coulomb interaction between charges. With prefixed values of the excluded volume exponent \( \nu \) (i.e., prefixed radius of gyration, \( R_g \)), the free energy was minimized in terms of counterion species, and the correlated multivalent ions were shown to induce attraction between monomers (through ion-‘bridging’) capable of collapsing a chain. Redissolution of chains was also observed at higher (multivalent) salt concentrations, but it was explained by a reduced bridging force due to electrostatic screening (as opposed to overcharging). Later, unscreened Coulomb interaction within condensed ion-pairs was first addressed without considering the chain entropy, and the theory predicted dependencies of the degree of ionization, \( f \), (which is the total effective charge density of polyelectrolytes after accounting for the condensed ions) on temperature and salt concentrations to be similar to Manning’s argument. A two-state (rod-like and collapsed) model for condensation predicted that chain collapse occurs when the total charge of multivalent cations equals to that of the ionizable groups of the polymer, implying the condensation of almost all added multivalent ions at modest temperatures. The two-state theory of condensed charges at low temperatures as an amorphous ionic solid similar to simple electrolytes (say, NaCl), and, therefore, still ignores the chain entropy and bending-related reorganization of condensed charges at low temperatures.
Generic experiments\textsuperscript{8,9,10,11,12,13} and simulations\textsuperscript{14} have shown that added cations with higher valence are more effective in compactifying a long DNA molecule (or a polyanion in general), and that implies a dominant electrostatic mechanism for polyelectrolyte collapse. Within the purview of this concept, the issue of overcharging induced by the addition of multivalent salts was investigated theoretically for rodlike DNA\textsuperscript{15,16,17} molecules. It was further noticed\textsuperscript{18,19} that there is a typical range in salt concentration, in which the short-ranged attractions between monomers are effective due to the proximity of the isoelectric point (at which the average effective charge of the polymer is zero). The total effective DNA charge was found to reverse sign if the multivalent salt concentration was increased above this range. This concentration window, within which a flexible chain remains collapsed with virtually negligible net charge on it, is predicted to be very small in recent simulations\textsuperscript{20}, which otherwise observe definite overcharging. Although rapid collapse due to charge neutralization for higher salt concentrations or lower temperatures is abundantly observed in experiments\textsuperscript{21,22,23} and in simulations\textsuperscript{24,25,26,27}, charge reversal by multivalent salt is not universally observed\textsuperscript{28}. Very recent experiments, however, have lent support to both charge inversion\textsuperscript{29,30} and counterion mediated attraction\textsuperscript{31} in biological polyelectrolytes such as DNA.

An effective two-parameter theory\textsuperscript{32} considered the adsorption process of counterions and formation of mono and di-complexes between negatively charged monomers and divalent positively charged salt ions. The theory predicted charge neutralization and subsequent charge-reversal of the chain backbone at moderate concentrations of divalent salts. The predictions, however, are limited to weak polyelectrolytes without consideration to the chain energy and hence chain configurations at various physical conditions. To address the chain entropy of flexible polyelectrolytes and its role in counterion distribution, Muthukumar developed\textsuperscript{1} a continuum theory of counterion condensation as an adsorption process. Condensation in this argument is facilitated at lower temperatures but, unlike in previous theories, is coupled with the configurational free energy of the polymer. The adsorption theory\textsuperscript{1} considers continuous values for the size ($R_g$) of a single chain treated as a continuous curve, which provide an appropriate description of entropy of a flexible chain. The theory treats the salt-free and salty conditions with monovalent counterions in dilute solutions of flexible polyelectrolytes. The parametric analysis of the competition between the translational entropy of counterions and the electrostatic energy gain of condensed ions reproduces
all classical results including the chain-collapse due to short-ranged dipole interactions at low temperatures.\textsuperscript{26,27} In addition to the length scales $l_B$ (Bjerrum length) and $\kappa^{-1}$ (Debye length) in the charged system, the adsorption theory uses the concept of a dielectric mismatch parameter, $\delta$, which captures the fact that the dielectric constant has much lower values near the chain backbone of a polyelectrolyte or protein than in the bulk solvent.\textsuperscript{33,34,35} In generic polyelectrolyte solutions, $\delta$ is the ratio of the bulk to local dielectric constants, and the range in which $\epsilon$ assumes its bulk value sets a new length scale. This mismatch in $\epsilon$, if substantial, will create higher potential gradients that can electrostatically guide counterions toward oppositely charged monomers. The theory showed that this may significantly increase counterion condensation at modest temperatures leading to a lower effective charge and smaller size of the polyelectrolyte. Monovalent counterions, however, was shown not to be able to collapse a chain completely at modest temperatures (say, the room temperature at which $l_B \sim 7\,\text{Å}$ in water).

In this paper, we extend Muthukumar’s adsorption theory\textsuperscript{1} to include divalent counterions. The basic concept still relies on the competition between the electrostatics of condensed ions and the entropy of free ions. The present model is intended to analyze the competitive displacement of monovalent counterions by divalent counterions when a salt-free dilute solution of flexible polyelectrolytes is mixed with a salt solution of divalent ions. As a specific example of this situation, we consider a single isolated polyelectrolyte (NaPSS) in a dilute solution (water) with monovalent counterions of its own but with no additional monovalent salt (NaCl) in general. We monitor the chain conformation and arrangement of condensed ions as functions of temperature, degree of dielectric mismatch, and concentration of divalent salt (BaCl\textsubscript{2}). In addition to the condensation of monovalent and divalent counterions (Na\textsuperscript{+} and Ba\textsuperscript{2+}, respectively), we also take into account the attachment of negative salt coions (Cl\textsuperscript{-}), as previous theories\textsuperscript{7,32} and simulations\textsuperscript{28} indicate substantial presence of negative coions near the chain backbone. The configurational free energy of the system depends on the extent of adsorption of various species of ions on the chain backbone as well as on the size of the polymer, and all contributing factors remain non-trivially coupled. These factors are assessed self-consistently with the important assumption of the adsorption theory being that the chemical potentials in the adsorbed and free states of the ions are the same. A numerical minimization of the free energy with respect to the fraction of condensed ions and the chain size determines the equilibrium values of the respective quantities.
The key conclusions are the following. In a competitive adsorption process, divalent ions displace the condensed monovalent ions at modest temperatures and for reasonable values of the dielectric mismatch parameter. At similar physical conditions, increasing divalent salt concentration can induce complete neutralization and resulting contraction of the polyelectrolyte chain. With further increase of divalent salt in the solution, condensed divalent counterions overcharge and reexpand chains for significantly large ranges of physical parameters $\delta$ and $l_B$. A substantial fraction of negative salt coions ($\text{Cl}^-$) also condenses on the monomer-divalent ion-pair which reduces the degree of overcharging but does not eliminate it. However, for modest temperatures in a generic solvent (water at room temperature), there is always a critical degree of dielectric heterogeneity below which neither chain collapse nor charge reversal occurs irrespective of the amount of divalent salt in solution. Further, the dependencies of the regularization of charge and size of the polymer on salt concentration, temperature, and the dielectric mismatch parameter are relatively robust functions of $l_B$, $\kappa^{-1}$, and $\delta$, not depending sensitively on the microscopic details of the charge complexes. For a moderate presence of salt, both the degree of ionization and chain size are typically smaller for divalent salts than for monovalent salts. A higher dielectric mismatch and a lower temperature enhance condensation of all types of counterions and coions resulting in the achievement of isoelectric point at lower divalent salt concentrations. A typical state diagram for polyelectrolyte charge is predicted (Fig. 1) in which below a critical Coulomb strength (proportional to $1/T$, $1/\epsilon$ or $\delta$) there is no overcharging with increasing divalent salt. Above this critical strength, electrostatics is strong enough to condense sufficient number of counterions inducing overcharging. For higher salt concentrations, we expect recharging of the polyelectrolyte due to either screening of electrostatics (low Coulomb strength) or negative coion ($\text{Cl}^-$) condensation (high Coulomb strength). The dashed line indicates that in this regime of salt concentration the theory only predicts qualitative results. If ion-bridging is present, a simple theory based on this model predicts first order chain collapse. Our theory shows that overcharging is an outcome of both correlation-induced adsorption related to the discreteness of divalent cations and dielectric heterogeneity related to the local chemical structure of polyelectrolytes.

The rest of the article is organized as follows: in Sec.II, we develop the theory and in Sec.III, we present the results discussing competitive adsorption (III.A), chain collapse (III.B), overcharging (III.C), coion condensation (III.D), free energy (III.E), state diagrams
for various regimes of polymer charge (III.F), and the bridging scenario (III.G). Conclusions are summarized in Sec.IV.

II. THEORY

Following Muthukumar’s work with monovalent salt\textsuperscript{1}, we consider a linear flexible polyelectrolyte chain of $N$ monomers in a solution of volume $\Omega$, with the center of mass of the chain at the origin of the coordinate system. Each monomer is monovalently charged (negative) and of length $l$. There can be either or both monovalent and divalent salts in the solution (say, water), which being electroneutral at all times will have a maximum of $N$ monovalent counterions in addition to the salt ions. We assume that the counterion from the monovalent salt (say, $\text{Na}^+$ from NaCl) is chemically identical to the counterion from the polymer (say, $\text{Na}^+$ from NaPSS). Similarly, the coions from both types of salts are of the same species (say, $\text{Cl}^-$ from NaCl and BaCl$_2$). At any time, both monovalent and divalent counterions (say, $\text{Ba}^{++}$ from BaCl$_2$ as divalent counterions) can condense on separate monomers. In addition, the $\text{Ba}^{++}$-monomer ion pair is viewed as a positive monovalent ion, and the negative coions ($\text{Cl}^-$) will condense on some of these pairs as counterions. Therefore, if $M_1$ monovalent counterions and $M_2$ divalent counterions get adsorbed on the chain ($M_1 + M_2 \leq N$), and $M_3$ (negative) coions condense on $\text{Ba}^{++}$-monomer ion pairs ($M_3 \leq M_2$), the effective (or average) degree of ionization of the entire chain is $f = (1 - M_1 - 2M_2 + M_3)/N$. $R_g$ is the radius of gyration of the chain. $c_{s1}$ and $c_{s2}$ are, respectively, the number concentrations of the added monovalent and divalent salts. Both types of salts are fully dissociated into $n_1$ monovalent counterions ($\text{Na}^+$), $n_2$ divalent counterions ($\text{Ba}^{++}$) and $n_1 + 2n_2$ negative coions ($\text{Cl}^-$). Therefore, $c_{s1} = n_{1+}/\Omega$ and $c_{s2} = n_{2+}/\Omega$. The free energy of the system, consisting of the chain, condensed and mobile counterions, and the solution, would depend on four independent variables: $M_1, M_2, M_3,$ and $R_g$. The theory\textsuperscript{1} aims to evaluate $M_1, M_2, M_3,$ and $R_g$ self-consistently by calculating the free energy $F$ of the system as a function of all these variables and electrostatic parameters. The equilibrium values of the four major variables are obtained by minimizing $F$ simultaneously with respect to these variables. Therefore, this requires an extension of the previous theory of minimization with two variables to a theory with four variables.

As before\textsuperscript{1}, the free energy $F$ has six contributions $F_1, F_2, F_3, F_4, F_5,$ and $F_6$ related,
respectively, to (i) entropy of mobility of the condensed counterions and coions on the polymer backbone, (ii) translational entropy of uncondensed counterions and coions (including salt ions) which are mobile within the volume Ω, (iii) electrostatic fluctuation interaction (Debye-Hückel) among all unadsorbed counterions and coions except the polymer, (iv) the unscreened electrostatic (Coulomb) energy of monomer-counterion pairs (both monovalent and divalent counterions) and monomer-counterion-coion triplets, (v) free energy of the polyelectrolyte with an average degree of ionization \( f \), and (vi) electrostatic correlation involving the neutral ion-pairs or ion-triplets along the backbone of the polymer.

A. The free energy

To determine the entropic contribution from the condensed counterion and coions, we note that there are \( N \) monomers, \( M_1 \) condensed monovalent counterions (Na\(^+\)), \( M_2 - M_3 \) condensed divalent counterions (Ba\(^{++}\)) with no negative coion (Cl\(^-\)) condensation, and \( M_3 \) ion-triplets (‘monomer-Ba\(^{++}\)-Cl\(^-\)’). Therefore, \( N-M_1-M_2 \) monomers remain bare charged with no ions condensed on them. Consequently, the partition function is

\[
Z_1 = \frac{N!}{(N-M_1-M_2)!M_1!(M_2-M_3)!M_3!}. \tag{2.1}
\]

We define,

\[
\alpha_1 = \frac{M_1}{N}; \quad \alpha_2 = \frac{M_2}{N}; \quad \alpha_3 = \frac{M_3}{N} \tag{2.2}
\]

Using \( F_1 = -K_B T \ln Z_1 \), we have,

\[
\frac{F_1}{Nk_BT} = (1 - \alpha_1 - \alpha_2) \log(1 - \alpha_1 - \alpha_2) + \alpha_1 \log \alpha_1 \tag{2.3}
\]

\[
+ (\alpha_2 - \alpha_3) \log(\alpha_2 - \alpha_3) + \alpha_3 \log \alpha_3.
\]

The above expression implies two obvious constraints:

\[
\alpha_1 + \alpha_2 \leq 1 \quad \text{and} \quad \alpha_3 \leq \alpha_2. \tag{2.4}
\]

To determine the translational entropy of the uncondensed ions which are distributed in the bulk volume \( \Omega \), we count as mobile ions: \( N - M_1 + n_{1+} \) monovalent counterions (Na\(^+\)), \( n_{2+} - M_2 \) divalent counterions (Ba\(^{++}\)), and \( n_{1+} + 2n_{2+} - M_3 \) monovalent negative coions
(Cl\(^{-}\)). Therefore, the partition function related to the translational free energy in volume \(\Omega\) would be

\[
Z_2 = \frac{\Omega^{N-M_1+n_1+n_2+n_2}-M_2+n_1+2n_2-M_3}{(N-M_1+n_1+M_2)!((n_1+2n_2-M_3)!)}
\]

\[
= \frac{(N-M_1+n_1+M_2)!((n_1+2n_2-M_3)!)}{(N-M_1+n_1)!((n_1+2n_2-M_3)!)}.
\]

Relating numbers of ions and their concentrations is helpful. We note

\[
N = \rho\Omega; \quad n_{1+} = \frac{c_{s1}N}{\rho}; \quad n_{2+} = \frac{c_{s2}N}{\rho}.
\]

With use of \(F_2 = -k_B T \ln Z_2\) and after some calculations we arrive at

\[
\frac{F_2}{Nk_B T} = (1 - \alpha_1 + \frac{c_{s1}}{\rho}) \log(\rho(1 - \alpha_1) + c_{s1}) + \left(\frac{c_{s2}}{\rho} - \alpha_2\right) \log(c_{s2} - \rho\alpha_2)
\]

\[
+ \left(\frac{c_{s1}}{\rho} + 2\frac{c_{s2}}{\rho} - \alpha_3\right) \log(c_{s1} + 2c_{s2} - \rho\alpha_3)
\]

\[- \left\{ (1 - \alpha_1 - \alpha_2 - \alpha_3) + \frac{2c_{s1}}{\rho} + \frac{3c_{s2}}{\rho} \right\}.
\]

Here, the constraint would be

\[
M_2 \leq n_{2+}.
\]

The free energy contribution from the correlations of all dissociated ions can be calculated in the electrostatic free energy

\[
F_3 = -k_B T \frac{\Omega\kappa^3}{12\pi},
\]

where the inverse Debye length \(\kappa\) is given by

\[
\kappa^2 = 4\pi l_B \sum_i Z_i^2 n_i / \Omega.
\]

This result is obtained from the Debye-Hückel (DH) theory and caution must be exercised to identify regimes where the DH theory is at best a gross approximation. Here, \(Z_i\) is the valency of the dissociated ion of the \(i\)-th species. In this case [see the text before Eq. (2.5)],

\[
\kappa^2 = 4\pi l_B \left\{ N - M_1 + n_{1+} + 4(n_2+ - M_2) + n_{1+} + 2n_2+ - M_3 \right\} / \Omega
\]

\[
= 4\pi l_B (N - M_1 - 4M_2 - M_3 + 2n_{1+} + 6n_{2+}) / \Omega
\]

\[
= 4\pi l_B \{ \rho(1 - \alpha_1 - 4\alpha_2 - \alpha_3) + 2c_{s1} + 6c_{s2} \}.
\]
Using the definitions from Eq. (2.6) we reach

$$\frac{F_3}{Nk_B T} = -\frac{1}{3} \sqrt{4\pi l_B^{3/2} \rho} \left( \rho (1 - \alpha_1 - 4\alpha_2 - \alpha_3) + 2c_{s1} + 6c_{s2} \right)^{3/2}. \quad (2.12)$$

To determine the electrostatic energy gain due to condensation of all sorts of ions (Na\(^+\), Ba\(^{2+}\), and Cl\(^-\)), we recount different ion pairs and triplets which form after condensation. On the polymer chain, there are \(\alpha_1 N\) pairs of 'monomer(-1) and Na\(^+\) ion', \((\alpha_2 - \alpha_3) N\) pairs of 'monomer(-1) and Ba\(^{2+}\) ion', and \(\alpha_3 N\) triplets of 'monomer(-1), Ba\(^{2+}\) and Cl\(^-\) ions'. In addition, \((1 - \alpha_1 - \alpha_2) N\) monomers(-1) remain charge uncompensated. In Muthukumar’s theory\(^1\), the dielectric mismatch parameter \(\delta\) was conceived to address a local dielectric constant \(\epsilon_l\) in the vicinity of the chain backbone. Experiments have shown\(^33\) \(\epsilon_l\) to be almost an order of magnitude less than its bulk value \(\epsilon\) (around 78 in water) near polyelectrolyte or protein backbone. The dielectric constant increases exponentially\(^34,35\) from the fractional to its full bulk value over a distance of 1-10 Å from the chain monomers. \(\delta = (\epsilon l / \epsilon_l d)\) was introduced\(^1\), where \(d\) is the dipole length of the monomer-monovalent counterion ion-pair. A glance at Fig. 2 reveals that \(\delta\) in above form only applies to the monomer-monovalent (Na\(^+\)) and monomer-divalent (Ba\(^{2+}\)) ion pairs, but not to the divalent counterion-monovalent monovalent (Ba\(^{2+}\)-Cl\(^-\)) ion pair in the monomer-divalent counterion-monovalent coion triplet. In an ion pair, there are two ions involved with a fixed distance between them. For the triplet, however, there are three lengths involved (for example, Ba\(^{2+}\)-monomer, Ba\(^{2+}\)-Cl\(^-\) and Cl\(^-\)-monomer), and interpretation of \(\delta\) is a bit tricky. We introduce a parameter \(\delta_2\) for the 'monomer-Ba\(^{2+}\)-Cl\(^-\)' triplet. \(\delta_2\) is expected to be less than 4\(\delta\) (the value it would have assumed if there were two point charges, +2\(e\) and -2\(e\), respectively), but the determination of its actual value would probably require a microscopic treatment. In principle, \(\delta_2\) would be a function of \(\delta\). For simplicity, we assume all ions and monomers to be of the same size, and determine \(\delta_2\) in what follows.

First of all, we write the electrostatic energy of condensation in terms of \(\delta\) and \(\delta_2\):

$$\frac{F_4}{Nk_B T} = -\alpha_1 \delta l_B - 2(\alpha_2 - \alpha_3) \delta l_B - \alpha_3 \delta_2 \delta l_B, \quad (2.13)$$

where \(\delta l_B = l_B / l\) and the terms containing \(\delta\) are written following Ref. 1 (with \(l \sim d\)). Note that if one assumes that the local dielectric constant \(\epsilon_l\) applies only to the Ba\(^{2+}\)-monomer pair, but not to the Ba\(^{2+}\)-Cl\(^-\) pair (\(\epsilon = \epsilon_{water}\) in that case), then \(\delta_2\) turns out to be

$$\delta_2 = \left(2 + \frac{2}{\delta}\right) \delta. \quad (2.14)$$
Those should be the lowest values for $\delta_2$. On the other hand, if $\epsilon_l$ applies to both Ba$^{++}$-monomer and Ba$^{++}$-Cl$^-$ pairs, then

$$
\delta_2 = 4\delta. \tag{2.15}
$$

Those should be the highest values for $\delta_2$. In practice, $\delta_2$ would be somewhere between these two limiting sets of values. We choose the dielectric constant to be $\epsilon_l$ for the Ba$^{++}$-monomer pair and $(\epsilon_l + \epsilon_{bulk})/2$ for the Ba$^{++}$-Cl$^-$ pair. Then, $\delta_2$ turns out to be

$$
\delta_2 = \left(2 + \frac{4}{\delta + 1}\right)\delta. \tag{2.16}
$$

Point worthy of note is that the repulsion between the monomer and the Cl$^-$ ion has been ignored; it would bring a very small correction in all three cases above. Although the counterion distribution and chain conformations are sensitively dependent on $\delta_2$, we later show that the very basic qualitative results do not change if $\delta_2$ is assigned any value in the range mentioned above. Therefore, we would use Eq. (2.16) in all of our representative calculations, unless mentioned otherwise.

The free energy of the flexible polyelectrolyte chain is obtained by the variational method\cite{1,37} in which one starts from the Edwards Hamiltonian,

$$
H = \frac{3}{2l} \int_0^L ds \left( \frac{\partial R(s)}{\partial s} \right)^2 + \frac{w}{2} \int_0^L ds \int_0^L d s' \delta (R(s) - R(s')) \tag{2.17}
$$

$$
+ \frac{l_B}{2} \int_0^L ds \int_0^L d s' \frac{1}{|R(s) - R(s')|} \exp -\kappa|R(s) - R(s')|,
$$

where $L = Nl$, $R(s)$ is the position vector of the chain at arc length $s$, and $w$ is the strength parameter for all short-ranged hydrophobic or excluded volume effects. An effective expansion factor $l_1$ is defined as follows:

$$
\langle R^2 \rangle = Nl_1 \equiv Nl_1 \tilde{l}_1 = 6R_g^2. \tag{2.18}
$$

Here, $\langle R^2 \rangle$ is the mean square end-to-end distance, and $l_1$ effectively measures the swelling of the chain compared to a Gaussian chain. Assuming uniform, spherically symmetric expansion or contraction of the chain, and by extremizing the free energy we obtain

$$
\frac{F_5}{Nk_BT} = \frac{3}{2N} \left( \tilde{l}_1 - 1 - \log \tilde{l}_1 \right) + \frac{4}{3} \left( \frac{3}{2\pi} \right)^{3/2} \frac{w}{\sqrt{N} \tilde{l}_1^{3/2}} \tag{2.19}
$$

$$
+ 2\sqrt{\frac{6}{\pi}} l_B^2 \tilde{l}_1^{-1/2} N^{1/2} \Theta_0(a),
$$
where
\[
\Theta_0(a) = \frac{\sqrt{\pi}}{2} \left( \frac{2}{a^{5/2}} - \frac{1}{a^{3/2}} \right) \exp(a) \text{erfc}(\sqrt{a}) + \frac{1}{2a} + \frac{2}{a^2} - \frac{\sqrt{\pi}}{a^{5/2}} - \frac{\sqrt{\pi}}{2a^{3/2}},
\]
(2.20)
where
\[
a \equiv \tilde{\kappa}^2 N l_1^2 / 6.
\]
(2.21)
Here, \(\tilde{\kappa} = \kappa l\). We further define two more dimensionless variables, \(\tilde{\rho} = \rho l^3\) and \(\tilde{c}_{si} = c_{si} l^3\), where \(i\) stands for the ion species. The important factor \(f\) is our previously defined average degree of ionization and is given by
\[
f = 1 - \alpha_1 - 2\alpha_2 + \alpha_3.
\]
(2.22)
The justification of using the variational result as the polymer free energy has been discussed in the previous paper\(^1\). We assume that similar arguments are still valid for this work. Any other alternative function of average degree of ionization \((f)\) and radius of gyration \((R_g)\) for \(F_5\) may be used in place of Eq. \((2.19)\).

Till now we have considered the electrostatic interaction only between monomers the effective charge of which, with or without condensed ions, is non-zero. In other words, the third-term in the polymer free energy \(F_5\) [Eq. \((2.19)\)] addresses the electrostatic interaction (within Debye-Hückel approximation) between monomers with non-zero effective monopole charges. Further, \(F_5\) considers only the monopole contribution of each ion-pair or ion-triplet. For example, a monomer-\(\text{Na}^+\) pair and a monomer-\(\text{Ba}^{++}\)-\(\text{Cl}^-\) triplet would be treated equally by \(F_5\), although they have quite different electrostatic effects. Similarly, a monomer-\(\text{Ba}^{++}\) pair would be simply treated as a \(+1\) charge, although the pair will have additional dipole effects. These additional dipole or higher order multipole effects would be critical when the average charge of the chain is close to zero. It has been shown\(^1,26,27\) that these ion-pair effects play a key role to collapse a chain in presence of monovalent counterions at very low temperatures (i.e, when the degree of ionization is negligible). In the previous paper\(^1\), this correlation among neutral ion-pairs and between neutral ion-pairs and charged monomers were addressed by short-ranged \(\delta\)-function potentials which led to free energy contribution of the form
\[
\frac{F_6}{Nk_B T} \sim \frac{4}{3} \left( \frac{3}{2\pi} \right)^{3/2} w_1 \delta^2 l_B^2 \frac{1}{\sqrt{N}} l_1^{-3/2},
\]
(2.23)
where \( w_i \)’s \(< 0\) are temperature dependent parameters, and are different for dipole-dipole and dipole-monopole interactions. These contributions are attractive and would modify the excluded volume interaction [the second term in \( F_5 \), Eq. (2.19)]. They can significantly reduce the size of the chain only around the isoelectric point \( (f \sim 0) \), and the type of collapse is generally continuous or second order.

In addition to the short-ranged dipole correlations, there can be long-ranged attraction between monomers mediated by multivalent counterions\(^{38,39}\). This attractive correlation between counterions may compensate the residual Coulomb repulsion of the chain even at higher degrees of ionization\(^{40}\), and the extended conformation of the chain may become unstable. This can as well be treated with the concept of ion ‘bridging’\(^{28,41}\). It is still not conclusively known what kind of collapse this correlation-induced long-ranged attraction may induce. We leave out the short-ranged correlation effects near the isoelectric point in our present analysis. In Section III.G, we give preliminary results of an ion bridging theory leading to global instability of a polyelectrolyte chain based on our model. The point worthy of note here is that the bridging interaction reduces\(^{28}\) the effective value of the excluded volume parameter \( w \). Therefore, for higher values of \( w \), only very high Coulomb strength or divalent salt concentration will allow the bridging effect to take place. In most of our analysis (only except Section III.G), we assume \( w \) to be high enough to render the bridging effect to be negligible. Although we assume \( w \) to be zero except in Section III.G, that will imply the ‘no-bridging’ scenario in which choosing non-zero positive value of \( w \) only brings minor quantitative changes to our results. When bridging is included (Section III.G), however, \( w \) is a very important parameter affecting the transition salt concentration or Coulomb strength.

A more detailed analysis of the role of multivalent cations in collapsing a polyelectrolyte and the related order of the transition will be presented in a future publication.

III. RESULTS AND DISCUSSION

We can express the total free energy \( F = F_1 + F_2 + F_3 + F_4 + F_5 \) in terms of the fraction of condensed counterions and coions \((\alpha\)'s\), size of the polymer \((l_1)\), temperature and bulk dielectric constant \((l_B)\), degree of polymerization \((N)\), monomer density \((\rho)\), monovalent and divalent salt concentrations \((c_s \)'s\), and local dielectric mismatch parameters \((\delta \text{ and } \delta_2)\). The goal is to self-consistently determine the fractions of condensed ions \((\alpha_1, \alpha_2, \text{ and } \alpha_3)\) and the
size \( R_g = \sqrt{\langle Nll_1/6 \rangle} \) that minimize the free energy. It is a simultaneous minimization with respect to four variables \((\alpha_1, \alpha_2, \alpha_3, \tilde{l}_1)\) instead of two in the previous paper\(^1\), and it is best performed numerically. Compared to a neutral system, there are two additional length scales in a charged system. They are the Bjerrum length \((l_B)\) related to the Coulomb interaction and the Debye length \((\kappa^{-1})\) introduced by screening due to dissociated ions including salt ions. This formalism invokes a third length scale due to the dielectric mismatch parameter \(\delta\). Therefore, the important parameters on which we base our analysis are \(l_B\), the salt concentrations \((c_{s1} \text{ and } c_{s2})\), and \(\delta\).

**A. Competitive adsorption**

We start with an isolated polyelectrolyte at low concentrations and at modest temperatures. In the first observation, the concentration of the divalent salt \((c_{s2})\) is increased from while keeping the concentration of the monovalent salt at zero \((c_{s1} = 0)\). We have chosen a higher and a lower value of \(\delta = 2.5 \text{ and } 1.5\), respectively. Generally at higher values of \(\delta\), fractions of condensed ion species are expected to increase. We notice that [Fig. 3] both divalent counterions and negative monovalent coions condense progressively in higher numbers \((\alpha_2 \text{ and } \alpha_3, \text{ respectively})\) with increasing divalent salt concentration. The number of monovalent counterions \((\alpha_1)\), however, decreases with increasing \(c_{s2}\). This implies that in this competitive adsorption process, condensed monovalent counterions, when challenged by a divalent salt, are replaced by divalent counterions. This happens for the entire physical range of the dielectric mismatch paremeter (we will later show in the diagrams of charged states). The variable values chosen in this specific calculation are degree of polymerization \(N = 1000\) and monomer density \(\tilde{\rho} = \rho l^3 = 0.0005\) at \(\tilde{l}_B = 3.0\) (value related to flexible polymers of the type sodium polystyrene sulphonate (NAPSS) in water at room temperature). \(\delta_2\) is given by Eq. \((2.16)\) throughout the paper, unless noted otherwise. For \(\delta = 1.5\), only 5% of monomers are neutralized by monovalnt counterions at no salt situation \((c_{s1}, c_{s2} = 0)\) [Fig. 3(a)] whereas the number increases to 35% for \(\delta = 2.5\) [Fig. 3(b)]. At this higher \(\delta\) value, almost all available divalent counterions condense displacing the monovalent counterions with increasing \(c_{s2}\). Negative monovalent coions \((\text{Cl}^-)\) also condense on the monomer-divalent ion-pair substantially. \(f\) decreases monotonically and *reverses sign* when \(c_{s2}\) is still well below the monomer concentration \(\rho\). At \(c_{s2} \sim 80\% \text{ of } \rho, \alpha_1\) drops below 5% and \(\alpha_2\) is about
80% implying that almost all available divalent counterions have condensed. The size of the chain decreases steeply [Fig. 3(d)] due to rapid neutralization, but increases beyond the isoelectric point \( (f = 0) \) due to repulsion among divalent cations that overcharge the chain. The size is dictated by the third term in Eq. (2.19) at these salt concentrations. For higher values of \( c_{s2} \), more negative coions condense on the chain to reduce the (over)charge of the chain marginally. Number of condensed monovalent ions, however, decrease to zero monotonically.

For the lower value of \( \delta \), the original sign of the polyelectrolyte charge \( (f) \) is preserved even at higher divalent salts [Fig. 3(a)] with the minimum absolute degree of ionization being around 0.27. Consequently, the size of the chain [Fig. 3(c)] remains substantially bigger than the Gaussian value for the entire range of salt concentration.

**B. The chain collapse**

In Fig. 3(b), we have noticed that the polyelectrolyte net charge due to condensation of divalent counterions becomes negligible as soon as the salt concentration reaches half the polymer concentration \( (c_{s2} \sim \rho/2) \). Consequently, the chain collapses to its Gaussian size at around this isoelectric point. To compare with the case of monovalent counterions, we plot both the degree of ionization \( f \) and the expansion factor \( \tilde{l}_1 \) at \( \tilde{l}_B = 3.0 \) in Fig. 4. The other parameters are: \( N = 1000, \delta = 2.5, \) and \( \tilde{\rho} = 0.0005 \). We notice that for the monovalent salt, degree of ionization \( f \) of the polyelectrolyte decreases moderately and monotonically, and never changes sign. Consequently, the size \( (l_1 \) or \( R_g \)) also decreases monotonically with the Gaussian statistics being obtained only at very high salt concentrations (or at very low temperatures). For the divalent salt, however, the isoelectric point is achieved as soon as there are sufficient number of divalent counterions available to neutralize the chain. That happens at a very low \( c_{s2} \). As a result, the polyelectrolyte collapses (Gaussian statistics) near this isoelectric point.

This collapse of a generic polyelectrolyte (NAPSS) in water occurs for modest values of \( \delta \), at a modest presence of the divalent salt, and at room temperature. This phenomenon has long been noticed theoretically, and very recently in experiments and simulations.
C. The issue of overcharging

Our theory predicts that charge neutralization and subsequent charge reversal would occur to an isolated flexible polyelectrolyte in aqueous solutions at room temperature and at a modest presence of a divalent salt. The parameter $\delta$ in our theory plays an important role in the charge reversal induced by counterion condensation. Temperature is also an important factor regulating the relative weight of electrostatic energy gain of ion condensation. To show these effects, we plot the degree of ionization $f$ and the expansion factor $\tilde{l}_1$ of the chain as functions of Bjerrum length $l_B$ (inverse temperature and bulk dielectric constant) for various $\delta$ values in Fig. 5. The other parameters are: $N = 1000$, $\tilde{\rho} = 0.0005$, $c_{s1} = 0$ and $c_{s2} = 0.0005 = \tilde{\rho}$. The concentrations of the divalent salt and the polymer is chosen to be equal to ensure the availability of enough divalent ions to condense over every monomer if physical conditions permit. In Fig. 5(a), we notice that there is negligible condensation for $\delta = 1$ (which is the comparable value of $\delta$ in simulations). Similar to the monovalent case [Fig. 2(a) and 3 in Ref. 1], the chain is neutralized only at very low temperatures (there is a factor of two in $l_B$ because the Coulomb energy gain for each ion-pair is twofold for divalent ions). At no temperature there is overcharging for $\delta = 1$. There is, however, a drastic qualitative change in the dependencies of $f$ and $R_g$ on $l_B$ for $\delta$ values 2 and above. At a particular temperature $T_0$, the chain is neutralized and if $T$ is further reduced, overcharging occurs (and the chain swells). $T_0$ is higher for higher values of $\delta$ as expected ($T^{-1}$ and $\delta$, both favor higher degree of condensation). The absolute value of maximum overcharge and re-swelled size increase with $\delta$ as well. In particular, the reswelled size is larger than the original swelling for $\delta = 4.0$. This is despite the absolute effective charge being lower at the maximal reswelling because, at this point, the Coulomb strength for this large $\delta$ value is high enough to have repulsion between monomers stronger than at point of maximal swelling as we increase $\tilde{l}_B$. Another point of note is that for higher temperatures, just as for monovalent counterions, only a fraction of available divalent ions condense. The optimal temperature at which the chain reexpansion is maximum shifts to a higher value with higher values of $\delta$. It might be instructive to note that we increase $c_{s2}$ in Fig. 3(b), by fixing the system at the abscissa value of 3 in Fig. 5 and staying on the $\delta = 2.5$ curve. For very low temperatures, sufficient number of negative coions (Cl$^-$) condense to gradually re-neutralize the chain for all $\delta$ values.
To further explore the issue of overcharging, we plot $f$ and $\tilde{l}_1$ against $\delta$ for $\tilde{l}_B = 3$ in Fig. 6. The other parameters are the same as in Fig. 6. At room temperature in aqueous solutions, there can be no overcharging unless $\delta > 1.7$. Only for $\delta$ as high as 1.7, the dielectric heterogeneity would be strong enough to electrostatically guide enough divalent ions that condense and reverse the charge of the chain. The strong sensitivity of the total charge and conformation of the polymer on $\delta$ is manifest in Fig. 6, in which $f$ decreases from about 93% to zero (and subsequently $\tilde{l}_1$ decreases from about 25 to 1 - the Gaussian value) for $\delta$ changing only from 1-1.7. For very high values of $\delta$, Cl$^-$ ions condense progressively at higher numbers to reduce overcharging.

**D. Condensation of Cl$^-$ ions**

In a monomer-Ba$^{++}$-Cl$^-$ ion-triplet, the colinear arrangement of the three charges, in the same order as written here, is electrostatically the most favorable one. This is true regardless of the strength of $\delta$ or the range of the local dielectric constant $\epsilon_l$. We assume that all triplets in the system have this specific colinear arrangement in which the line joining the charges is perpendicular to the chain backbone [see Fig. 2]. We have discussed before the ambiguity in determining the electrostatic energy gain per triplet formation. The highest and lowest values permitted by physical conditions of the strength parameter $\delta_2$ related to the formation of the triplet has been determined in terms of $\delta$ through Eqs. (2.14)-(2.15). Although suggested by a few authors, we did not consider a different local dielectric constant for isolated Ba$^{++}$ or Cl$^-$ ions. The dielectric constant relevant for the Coulomb interaction between the Ba$^{++}$ and Cl$^-$ ions in Eqn. (2.16) is different than $\epsilon$. This is because of the fact that these two ions are in the local environment of the chain backbone, and consequently, the local dielectric behavior of the polyelectrolyte (i.e., $\delta$) exclusively determines the value of $\delta_2$.

In this theory, to minimize the number of adjustable parameters, we assume that the sizes of the ions (Ba$^{++}$, Cl$^-$, and Na$^+$) are of the order of the size $l$ of the monomer. To illustrate that these approximations do not compromise the generality of the problem, we plot the fraction of condensed ions ($\alpha_1, \alpha_2, \alpha_3$), degree of ionization ($f$), and the size expansion factor ($\tilde{l}_1$) of the polymer as functions of $\delta_2$. We vary $\delta_2$ from its lowest [Eq. (2.14)] to its highest value [Eq. (2.15)] for a specific value of $\delta$. In Fig. 7(a), we choose $\delta = 2.5$, for which overcharging is evident for $\tilde{l}_B = 3.0$. Other parameters are: $N = 1000, \tilde{\rho} = 0.0005 = c_{52}$
and \( c_{s1} = 0 \). We notice that with increasing \( \delta_2 \), progressively larger number of \( \text{Cl}^- \) ions condense on the chain. This reduces overcharging and close to the highest value of \( \delta_2 \), overcharging would be marginally eliminated. This result has close resemblance to recent simulations\(^{20}\), where it is observed that smaller ion sizes (which leads to effectively higher \( \delta_2 \) values) reduce the degree of overcharging. In Fig. 7(b), we choose \( \delta = 1.5 \), for which there is no overcharging at \( \tilde{l}_B = 3.0 \). We notice that a change in \( \delta_2 \) has negligible effect on both \( f \) and \( R_g \) in this case. However, fractions of both condensed divalent counterions and monovalent coions (\( \alpha_2 \) and \( \alpha_3 \), respectively) increase with \( \delta_2 \), keeping the overall degree of ionization (\( f \)) approximately unaltered.

E. The free energy profile

One of the advantages of our equilibrium adsorption theory is that it is possible to compare the contributions of different factors in the total free energy (\( F_1 \) to \( F_5 \)) as functions of the critical parameters. The major conclusion of the theory\(^1\) has been that the equilibrium distribution of counterions and the size of the polyelectrolyte are determined essentially by the competition between the translational entropy of dissociated ions and the Coulomb energy gain of condensed ions. This is indeed borne out by our calculation in the presence of divalent salts too, as shown in Fig. 8. In Fig. 8(a), the separate parts of the free energy are plotted against the Bjerrum length \( \tilde{l}_B \) for a fixed divalent salt concentration (\( c_{s2} = 0.0005 \), equal to the monomer density) and for a specific strength of dielectric mismatch (\( \delta = 2.5 \)). The major contributions to the total free energy come from the translational entropy \( F_2 \) [Eq. (2.7)] and the Coulomb free energy \( F_4 \) [Eq. (2.13)]. For higher temperatures (lower \( l_B \)'s), the entropic term is favored as electrostatics remains negligible compared to thermal fluctuations. For lower temperatures, electrostatics becomes progressively relevant, and many ions condense reflecting substantial gains in \( F_4 \). The entropic contribution \( F_1 \) [Eq. (2.3)] related to the mobility of condensed ions along the backbone has negligible effect, and so does the Debye-Hückel contribution \( F_3 \) [Eq. (2.12)] at these salt concentrations.

In Fig. 8(b), similar free energy components are plotted against \( \delta \) at the same salt concentration and for \( \tilde{l}_B = 3.0 \). The curves in (a) and (b) are remarkably similar demonstrating the equivalence of the parameters \( l_B \) and \( \delta \). According to this adsorption theory, reduction of any of temperature, the bulk dielectric constant \( \epsilon \) or the local dielectric constant \( \epsilon_l \) (near
the hydrophobic regions of the chain backbone) by a similar factor would induce very similar effects to polyelectrolyte behaviors. This is especially valid for modest values of $l_B$ and $\delta$.

F. The diagrams of charged states

We have proposed earlier a tentative state diagram (Fig. 1) of the total charge $f$ (or the degree of ionization $=1-\alpha_1-2\alpha_2+\alpha_3$) of the polyelectrolyte. In this subsection, we present the actual state diagrams calculated from our theory, as functions of three major variables - the Bjerrum length ($l_B$), divalent salt concentration ($c_{s2}$) and the dielectric mismatch parameter ($\delta$). In what follows, one of these variables is fixed and the diagram of states (regions of negative and positive degree of ionization) is calculated numerically as functions of the other two. Figs. 9-10 describe the complete limiting charged states, parts of which have already been discussed in detail in preceding subsections.

In Fig. 9(a), the calculated state diagram at $\tilde{l}_B = 3.0$ is presented as a function of the divalent salt concentration $c_{s2}$ and the dielectric mismatch parameter $\delta$. The state diagram is qualitatively similar to the proposed one [Fig. 1], with the strength of the Coulomb interaction being represented by $\delta$ [Eq. (2.13)], and with $\tilde{l}_B$ being fixed. To explain the diagram, we first choose a specific value of $\delta = 2.5$ (see Figs. 3(b) and 4) and monitor the charged state with increasing divalent salt concentration. For low salt, there are not enough divalent counterions (Ba$^{++}$) to neutralize the chain and the polyelectrolyte preserves its sign of charge (state A) of salt-free conditions. At around $c_{s2} \sim \rho/2$, which is half the monomer concentration, the charge of the polymer becomes zero (on the locus of first isoelectric points - the solid line). If $c_{s2}$ is increased further, the polymer charge is reversed (state B), and at around $c_{s2} \sim \rho$, almost all monomers are neutralized by divalent counterions. The charge reversal is maximum at around this point (on the locus of maximum overcharging points - the dotted line). With $c_{s2}$ increasing even further, more negative coions (Cl$^-$) are available in the solution and some of them condense on the monomer-Ba$^{++}$ ion-pairs to reduce the degree of overcharging (state C). The first isoelectric points between states A and B are reached at a higher $c_{s2}$ for a lower $\delta$, because a higher fraction of divalent counterions would remain dissociated in the solution due to a lower Coulomb energy gain. For values of $\delta$ higher than $\simeq 3$, a substantial fraction of monovalent counterions of the polymer (Na$^+$) too remain condensed on the chain and the chain charge is neutralized with fewer divalent...
counterions. If $\delta$ is less than $\simeq 1.7$, the state of overcharging (state B) is never reached and with increasing salt concentration, the polymer charge goes through a minimum (on the locus of points of minimum charge - the dashed line) before increasing again due to Cl$^-$ ion condensation. The line of minimum charge (for $\delta$ less than $\simeq 1.7$) expectedly continues to be the line of maximum charge reversal (for $\delta$ greater than $\simeq 1.7$). For very high salt concentrations, the Coulomb interaction is progressively screened and all condensed ions begin to rejoin the solution (not included in the state diagram). We must, however, be cautioned that the Debye-Hückel (DH) approximation (and consequently $F_3$ in Eq. (2.12)) might not be valid at this high salt regime. A salt concentration for which the Debye length is equal to the Bjerrum length ($\kappa^{-1} \geq l_B$) can be tentatively set as the highest limit of validity of the DH theory. For divalent salts it turns out to be [see Eq. (2.11)]

$$c_{s2-max} \simeq \left(24\pi l_B^3\right)^{-1}.$$  \hfill (3.1)

The steepness of the state boundary (the locus of second isoelectric points - the dot-dashed line) implies that the polymer charge becomes zero again (only applicable for $\delta > 1.7$) due to re-dissolution of condensed ions at least an order higher salt concentrations.

The state diagram as a function of $l_B$ and $c_{s2}$ for a fixed value of $\delta = 2.5$ is presented in Fig. 9(b). The diagram is qualitatively similar to the previous one, although a much higher salt concentration (note the difference in the scale of the coordinate) is needed to reach the line of minimum charge (dashed) and the line of maximum overcharging (dotted) at low values of $\tilde{l}_B$ (higher temperatures). In this regime, electrostatics becomes progressively weaker with increasing temperature, and consequently lower fractions of available divalent ions condense. Regarding this diagram too, the degree of ionization and overcharging (absolute value of $f$) can be obtained for the particular value of $\tilde{l}_B = 3.0$ from Fig. 3(b).

The state diagram as a function of $l_B$ and $\delta$ for a fixed salt concentration $c_{s2} = 0.0005$ (equal to the monomer concentration) is presented in Fig. 10. One essential characteristic is that the degree of ionization remains steadily at zero (state C1) above a certain value of $\tilde{l}_B$ (i.e., below a certain temperature), because the Coulomb attraction is strong enough to make form the monomer-Ba$^{++}$-Cl$^-$ ion-triplet on every monomer location. This critical value of $\tilde{l}_B$ (on the lower boundary of the zero charge state - the dot-dot-dashed line) decreases with higher values of $\delta$ (higher electrostatic energy gain). The magnitude of the degree of ionization as a function of $\tilde{l}_B$ for fixed values of $\delta$ can be obtained in Fig. 5 and as a
function of \( \delta \) for a fixed value of \( l_B \) in Fig. 6. Both figures can be analyzed in conjunction with this state diagram. One small point worthy of note is that state D, although implying a non-zero degree of ionization of the same sign of the bare polymer charge, has virtually negligible charge in it that can be assumed to be zero.

**G. The bridging scenario: a simple theory**

In all previous discussion, we did not consider the bridging configuration of nonbonded monovalent monomers by divalent counterions. This ion-bridging phenomenon is electrostatic in nature and can significantly affect polyelectrolyte conformation if present. In this subsection we will give preliminary results of a simple theory based on our model. We assume that a fraction of condensed divalent ions participate in bridging. Therefore, when bridging is included the minimization of the free energy, as it will turn out, is with respect to five variables. Now, the bridge formed by divalent counterion tantamounts to a cross-link junction of functionality four$^{28}$, that in turn can be treated as an attractive two-body interaction of local nature (like two-body excluded volume interaction). Therefore, in the presence of bridging effects due to divalent counterions, \( w \) in Eq. (2.19) is replaced by,

\[
\begin{align*}
    w' &= w + \frac{E_{br}}{k_B T} \alpha_{2b},
\end{align*}
\]  

where \( \alpha_{2b} \) is the ratio of the number of divalent ions that participate in bridging to the number of monomers (i.e., \( \alpha_{2b} = M_{2b}/N \), where \( M_{2b} \) is the total number of divalent ions involved in bridging). \( E_{br} \) is the attractive energy associated with one bridge, and hence is negative. To calculate \( E_{br} \), the relevant dielectric constant should be the local one \( (\epsilon_l) \) since the divalent cation in the monomer-cation-monomer charge complex sits between and in the vicinity of both monomers. With the definition \( \delta = \epsilon l / \epsilon d \), where the distance between both ion pairs in the complex remains to be \( d = l \) (same as other condensed pairs), it turns out that

\[
\begin{align*}
    E_{br} &= - \frac{4e^2}{4\pi\epsilon_l d} + \frac{e^2}{4\pi\epsilon_l 2d} \\
    &= -\frac{7}{2} l_B \delta k_B T. 
\end{align*}
\]  

We must add the third virial term in the chain free energy \( (F_5, \text{ Eq. (2.19)}) \) to maintain stability in the system in case of a negative \( w' \). Combining Eqs. (3.2) and (3.3), therefore,
the chain free energy takes the form,

\[
\frac{F_5}{Nk_BT} = \frac{3}{2N} \left( \tilde{l}_1 - 1 - \log \tilde{l}_1 \right) + \frac{4}{3} \left( \frac{3}{2\pi} \right)^{3/2} \left( w - \frac{7}{2} \tilde{l}_B \delta \alpha_{2b} \right) \frac{1}{\sqrt{N}} \frac{1}{\tilde{l}_1^{3/2}} \tag{3.4}
\]

\[
+ \frac{1}{N} \frac{w_3}{\tilde{l}_1^3} + 2 \sqrt{\frac{6}{\pi}} f^2 \tilde{l}_B N^{1/2} \tilde{l}_1^{-1/2} \Theta_0(a),
\]

where \( w_3 \) is the third-virial coefficient which is necessarily positive. Further we note that if a fraction \( \alpha_{2b} \) of condensed divalent counterions participate in bridging, a fraction \( \alpha_{2a} = \alpha_2 - \alpha_{2b} \) does not. Therefore, the electrostatic energy related to the formation of monomer-cation monocomplexes \((F_4, \text{Eq. (2.13)})\) is modified after the inclusion of bridging interaction as,

\[
\frac{F_4}{Nk_BT} = - \alpha_1 \delta \tilde{l}_B - 2(\alpha_{2a} - \alpha_3) \delta \tilde{l}_B - \alpha_3 \delta_2 \tilde{l}_B, \tag{3.5}
\]

where \( \alpha_3 \leq \alpha_{2a} \). The other parts of the free energy remain unaltered and are given as: \( F_1 \) in Eq. (2.3), \( F_2 \) in Eq. (2.7), and \( F_3 \) in Eq. (2.12). In all these cases, \( \alpha_2 = \alpha_{2a} + \alpha_{2b} \).

The total free energy \( F = F_1 + \ldots + F_5 \) is minimized now for a new set of five variables, \( \alpha_1, \alpha_{2a}, \alpha_{2b}, \alpha_3 \) and \( \tilde{l}_1 \), and the polymer and counterions are free to explore every possible degree of freedom. The representative result is given in Fig. 11. The parameters chosen are: \( N = 100, \tilde{\rho} = 0.0008, \tilde{l}_B = 3.0, \delta = 1.9, \tilde{c}_{s1} = 0, w = 2.0, w_3 = 0.25 \). For very low divalent salt concentrations, the conformations are very similar to the case where bridging is absent. At modest temperatures \((\tilde{l}_B = 3.0 \text{ in water})\) and for low salt \((\tilde{c}_{s2} < 0.00027)\), almost all added divalent counterions condense, but they from monocomplexes (no bridging, Fig. 11(a)). At a particular \( \tilde{c}_{s2}^* \), which depends on the prevalent physical conditions, all divalent ions suddenly form dicomplexes (bridging) accompanied by a collapse of the chain [Fig. 11(b)], in which \( \tilde{l}_1 \ll 1 \) for \( \tilde{c}_{s2} > 0.00027 \) and a huge gain in electrostatic bridging free energy [Fig. 11(c)]. The Cl\(^-\) ions condense as they do for no-bridging scenario only if the divalent salt concentration is lower than the collapse concentration \( \tilde{c}_{s2}^* \). Above that, Cl\(^-\) ions become free as every condensed divalent cation is attached to two monomers. The effect of the excluded volume parameter \( w \) is evident in Eqs. (3.2) and (3.4) as they show that a higher \( w \) will require a higher Coulomb strength or divalent salt concentration to effect the bridging collapse. Until the collapse, the distribution of counterions and the polymer conformations are quite similar to that of the ‘no-bridging’ cases (see Fig. 3 for example). This explains our choice of \( w = 0 \) for the rest of the article (except for this subsection). In
the ‘no-bridging’ scenario, different positive values of \( w \) would only render minor qualitative changes to our results.

We further notice that the collapse concentration, \( c_{s2}^* \), decreases with increasing Coulomb strength [Fig. 12(a),(b)] confirming that the first order collapse induced due to ion-bridging by divalent (or multivalent) cations is an electrostatic phenomenon. In addition, Fig. 12(c) shows that \( c_{s2}^* \) roughly varies inversely with both forms of Coulomb strength, \( \tilde{l}_B \) and \( \delta \). This is a remarkable prediction for experimentalists and we find \( \tilde{l}_B c_{s2}^* \simeq 0.0006 \) (for \( \delta = 2.5 \)) and \( \delta c_{s2}^* \simeq 0.0005 \) (for \( \tilde{l}_B = 3.0 \)).

In conclusion, our model predicts a bridging transition, which we believe depends sensitively on temperature and dielectric heterogeneity, as well as on the availability of divalent counterions. At this point, we leave the rest of the bridging analysis for future publication.

IV. CONCLUSIONS

We have extended Muthukumar’s adsorption theory\(^1\) for condensation of monovalent counterions on a flexible polyelectrolyte by including divalent counterions. It is observed that the divalent counterions replace the monovalent ones in the competitive adsorption process. For moderate values of the dielectric mismatch parameter (\( \delta \)), temperature and bulk dielectric constant (\( \tilde{l}_B \)), numbers of both condensed divalent cations (\( \text{Ba}^{++} \)) and monovalent anions (\( \text{Cl}^{-} \)) increase and the number of condensed monovalent cations (\( \text{Na}^{+} \)) decrease monotonically with increasing concentration of added divalent salt (\( \text{BaCl}_2 \)). As observed in previous theories, experiments, and simulations, a moderate amount of divalent salt entirely compensates the polyelectrolyte (NaPSS) charge and consequently contracts the chain to its Gaussian size. The divalent salt concentration at which the charge neutralization takes place is roughly half the salt concentration implying that almost all divalent cations added to the solution condense at those modest parameter values. With further increase of divalent salt concentration, condensed divalent counterions overcharge the chain resulting in reswelling of the chain. This phenomenon is addressed for the first time theoretically for a flexible chain allowed to take all possible conformations. The charge reversal, however, is absent at modest temperatures regardless of the salt concentration if the dielectric heterogeneity is weaker than a critical value. The minimum degree of heterogeneity (\( \delta \)) required to condense all available divalent cations at a particular temperature and solution (\( \tilde{l}_B \)) increases with temperature.
At room temperature in aqueous solutions \((l_B \sim 7\text{Å})\), the adsorption theory predicts that the ratio of the bulk to local dielectric constant must be at least 1.7 to overcharge the polyelectrolyte.

It can be conceived that there are three length scales involved in the polyelectrolyte system analyzed by this adsorption theory. They are, the Bjerrum length \(l_B\) (representing the equilibrium temperature \(T\) of a solution with bulk dielectric constant \(\epsilon\)), the Debye length \(\kappa^{-1}\) (representing the salt concentration \(c_{si}\)), and the third one related to the strength of the dielectric heterogeneity in the vicinity of the polyelectrolyte backbone \((\delta)\). We have developed the diagrams of charged states of the polymer in terms of these three variables. Both higher \(\delta\) (lower ratio of local to bulk \(\epsilon\)) and \(l_B\) (lower temperature or bulk \(\epsilon\)) facilitate ion condensation of all types. Consequently, the isoelectric point (charge neutralization) and subsequent charge inversion are achieved at lower temperatures for higher \(\delta\) and vice versa. The absolute value of the maximum charge reversal and simultaneous maximal reswelling increase with \(\delta\). For a minimal dielectric mismatch \((\delta \sim 1)\), no overcharging is predicted for any temperature. This limit is the closest comparable to the simulations and it explains why in some simulations overcharging is never observed\(^{28}\).

For moderate values of \(\delta\) \((\geq 2)\), maximal overcharging and reswelling occurs at intermediate temperatures lower than that of the first isoelectric point (at which a moderate amount of divalent cations and a fraction of monovalent anions neutralize the chain). If temperature is further decreased \((l_B\) increased), progressively higher fraction of monovalent anions \((\text{Cl}^-)\) condense reducing the degree of overcharging. At low enough temperatures, regardless of the degree of dielectric heterogeneity, the second and trivial isoelectric point (at which all monomers are neutralized by the presence of both \(\text{Ba}^{++}\) and \(\text{Cl}^-\) ions) is achieved and the Gaussian statistics is reestablished.

We have determined the physical limits of the strength parameter for the formation of monomer-\(\text{Ba}^{++}\)-\(\text{Cl}^-\) triplets as functions of the basic dielectric mismatch strength \(\delta\). It has been shown that the qualitative picture of the total effective charge and conformation of the polyelectrolyte remain unaltered although the distribution of counterions and coions around it may vary for a change in the triplet strength parameter \((\delta_2)\) within these limits. For an unrealistic value of the parameter closer to its higher limit, increased \(\text{Cl}^-\) condensation may marginally eliminate overcharging at all physical conditions.

Analysis of the free energy highlights the competition between the entropic contribution
of dissociated ions and the electrostatic contribution of condensed ions in shaping the counterion distribution around the polyelectrolyte. The local dielectric constant and temperature have similar contribution to the electrostatics of the system (except at very high salt concentrations). If electrostatic bridging of non-bonded monomers by divalent counterions is effective due to a weak excluded volume effect, there is a first order collapse at modest conditions. The transition salt concentration varies approximately inversely with the Coulomb strength at modest conditions. In summary, our theory predicts that both electrostatics and the dielectric inhomogeneity near the backbone of the polymer (reflecting the nonuniversal chemical nature of the system) are responsible for charge reversal in polyelectrolyte systems.

V. ACKNOWLEDGEMENTS

Financial support for this work was provided by the NIH Grant No. 1R01HG002776-01, National Science Foundation (NSF) Grant No. 0605833, and MRSEC at the University of the Massachusetts, Amherst. Fruitful discussions with Zhaoyang Ou are gratefully acknowledged.

VI. REFERENCES

1. M. Muthukumar, J. Chem. Phys. 120, 9343 (2004).
2. G. S. Manning, J. Chem. Phys. 51, 924 (1969).
3. P. Gonzalez-Mozuelos and M. Olvera de la Cruz, J. Chem. Phys., 103 3145 (1995).
4. M. Olvera de la Cruz, L. Belloni, M. Delsanti, J. P. Dalbiez, O. Spalla, and M. Drifford, J. Chem. Phys., 103 5781 (1995).
5. P. S. Kuhn, Y. Levin, and M. C. Barbosa, Macromolecules, 31 8347 (1998).
6. F. J. Solis and M. Olvera de la Cruz, J. Chem. Phys., 112 2030 (2000).
7. F. J. Solis, J. Chem. Phys., 117 9009 (2002).
8. C. C. Conwell and N. V. Hud, J. Cluster Science, 14 115 (2003).
9. C. C. Conwell, I. D. Vilfan, and N. V. Hud, J. PNAS, 100 9296 (2003).
10. K. Huber, J. Phys. Chem., 97 9825 (1993).
11 Y. Ikeda, M. Beer, M. Schmidt, and K. Huber, Macromolecules, 31 728 (1998).
12 R. Schweins and K. Huber, Eur. Phys. J. E, 5 117 (2000).
13 M. Delsanti, J. P. Dalbiez, O. Spalla, L. Belloni, and M. Drifford, ACS Symp. Ser. 548, 381 (1994).
14 R. Chang and A. Yethiraj, J. Chem. Phys., 118 11315 (2003).
15 T. T. Nguyen, I. Rouzina, and B. I. Shklovskii, J. Chem. Phys., 112 2562 (2000).
16 T. T. Nguyen, A. Y. Grosberg, and B. I. Shklovskii, J. Chem. Phys., 113 1110 (2000).
17 T. T. Nguyen, A. Y. Grosberg, and B. I. Shklovskii, Phys. Rev. Lett., 85 1568 (2000).
18 Also see, H. Schiessel and P. Pincus, Macromolecules, 31 7953 (1998).
19 H. Schiessel, Macromolecules, 32 5673 (1999).
20 P-Y. Hsiao and E. Luijten, Phys. Rev. Lett., 97 148301 (2006).
21 M. Beer, M. Schmidt, and M. Muthukumar, Macromolecules, 30 8375 (1997).
22 V. M. Prabhu, M. Muthukumar, G. D. Wignall, and Y. B. Melnichenko, Polymer, 42 8935 (2001).
23 For a nice review, see V. M. Prabhu, Current Opinion in Colloid and Interface Science, 10 2 (2005).
24 M. J. Stevens and K. Kremer, J. Chem. Phys., 103 1669 (1995).
25 M. J. Stevens and K. Kremer, Phys. Rev. Lett., 71 2228 (1993).
26 S. Liu and M. Muthukumar, J. Chem. Phys. 116, 9975 (2002).
27 R. G. Winkler, M. Gold, and P. Reineker, Phys. Rev. Lett., 80 3731 (1998).
28 S. Liu, K. Ghosh and M. Muthukumar, J. Chem. Phys. 119, 1813 (2003).
29 Y. Murayama, Y. Sakamaki, and M. Sano, Phys. Rev. Lett., 90 018102 (2003).
30 K. Besteman, K. Van Eijk, and S. G. Lemay, Nature Physics, 3 641 (2007).
31 X. Qiu, K. Andresen, L. W. Kwok, J. S. Lamb, H. Y. Park, and L. Pollack, Phys. Rev. Lett., 99 038104 (2007).
32 J. Wittmer, A. Johner, and J. F. Joanny, J. Phys. II France 5, 635 (1995).
33 E. L. Mehler and G. Eichele, Biochemistry, 23 3887 (1984).
34 G. Lamm and G. R. Pack, J. Phys. Chem. B, 101 959 (1997).
35 I. Rouzina and V. A. Bloomfield, Biophys. J., 74 3152 (1998).
36 V. M. Prabhu, E. J. Amis, D. P. Bossev, and N. Rosov, J. Chem. Phys., 115 4367 (2004).
37 M. Muthukumar, J. Chem. Phys. 86, 7230 (1987).
FIGURE CAPTIONS

Fig. 1 Sketch of charged states for an isolated polyelectrolyte chain (of NaPSS type) in dilute solutions (water) in the presence of a divalent salt (of BaCl$_2$ type) as functions of the Coulomb strength ($l_B \sim (\epsilon T)^{-1}$) and the salt concentration. Points left to the isoelectric line (on which net effective charge (degree of ionization) on the polymer is zero) correspond to states in which the sign of polymer charge is unchanged (negative). However, there is a locus of points for intermediate values of salt concentration at which the net charge is a minimum. Right to the isoelectric line the effective polymer charge is reversed (positive). If the isoelectric point is crossed along the line of minimum charge from left to right, it becomes the line of maximum overcharging. Dashed part of the isoelectric line is beyond the Debye-Hückel limit.

Fig. 2 Schematic diagram of the system consisting of the isolated polymer chain, condensed counterions, dissociated mobile ions, and the solution as the background interacting only through the dielectric constant $\epsilon$. Possible charge complexes for each monomer: monomer (-1), monomer-monovalent (-1,+1), monomer-divalent (-1,+2), and monomer-divalent-monoion (-1,+2,-1). The dielectric constant $\epsilon_l$ in the vicinity of the chain is much lower than the bulk value. To reach equilibrium the major competition is between the translational entropy of the dissociated ions and the Coulomb energy gain of the condensed ions.

Fig. 3 Competitive displacement of monovalent counterions by divalent counterions: fraction of condensed ions ($\alpha_1, \alpha_2, \alpha_3$), degree of ionization ($f = 1 - \alpha_1 - 2\alpha_2 + \alpha_3$) in (a) and (b) for $\delta = 1.5$ and 2.5 respectively, and the expansion factor ($\tilde{l}_1 = $...
$6R_g^2/Nl^2$ in (c) and (d) for the same $\delta$ values plotted against the divalent salt concentration ($c_{s2} \sim 0.01c_s(M)$). For Gaussian chain, $\tilde{l}_1 = 1$. Other parameters are: $N = 1000, \tilde{\rho} = 0.0005, \tilde{l}_B = 3.0, w = 0$, and $c_{s1} = 0$. Note, for lower $\delta$, there is no overcharging. For higher $\delta$, almost all divalent counterions condense on the chain replacing the monovalent ones. The number of condensed negative coions ($\alpha_3$) closely follow $\alpha_2$ for this particular value of $\delta$. The sign of $f$ is reversed (overcharging) at some concentration of BaCl$_2$. Near the isoelectric point ($f \sim 0$), the chain is Gaussian due to minimal electrostatic repulsion. It swells due to overcharging if $c_{s2}$ is further increased.

**Fig. 4** Effect of valency of counterions: comparison of degree of ionization ($f$) in (a), and size expansion factor ($\tilde{l}_1$) in (b), of the polyelectrolyte in presence of either monovalent or divalent salt. $\delta = 2.5$ and other parameters are the same as in Fig. 3. $c_{s2} = 0$ is zero when $c_{s1}$ is added and vice versa. Divalent counterions can neutralize and consequently collapse the polymer at moderate conditions of $\tilde{l}_B = 3.0$. For monovalent counterions, collapse (to Gaussian chain) is only possible at very low temperatures. If $c_{s2}$ is increased beyond the isoelectric point, the chain expands due to overcharging.

**Fig. 5** Dependency of overcharging on $\tilde{l}_B$: degree of ionization ($f$) in (a), and size expansion factor ($\tilde{l}_1$) in (b), of the polyelectrolyte plotted against $\tilde{l}_B$ for different values of $\delta$. Parameters are: $N = 1000, \tilde{\rho} = 0.0005, c_{s1} = 0$, and $c_{s2} = 0.0005$. Collapse and subsequent overcharging occur for higher values of $\delta$. Isoelectric point is reached at lower $l_B$ for higher values of $\delta$. This overcharging behavior contrasts with Figs. 2(a) and 3 in Ref. 1 for monovalent salts.

**Fig. 6** Dependency of overcharging on $\delta$: fraction of condensed ions ($\alpha_1, \alpha_2, \alpha_3$), degree of ionization ($f$) in (a), and the expansion factor ($\tilde{l}_1$) in (b), plotted against the $\delta$-parameter for $\tilde{l}_B = 3.0$. Other parameters are the same as in Fig. 5. Charge neutralization occurs for $\delta$ about 1.7; overcharging is possible only if $\delta > 1.7$. Cl$^-$ condensation ($\alpha_3$) is higher for higher values of $\delta$, and that reduces overcharging.

**Fig. 7** Effect of dielectric mismatch for the coion: fraction of condensed Cl$^-$ ions ($\alpha_3$), degree of ionization $f$ in (a) and (b) for $\delta = 2.5$ and 1.5 respectively, and expansion factor ($\tilde{l}_1$) in (c) and (d) for the same $\delta$ values plotted against $\delta_2$ for its whole physical
range possible for the respective value of $\delta$. Other parameter values are the same as in Fig. 6. For higher $\delta = 2.5$, progressively higher values of $\delta_2$ reduce and finally eliminate overcharging (and consequently the reexpansion of the chain) by increasing $\alpha_3$. For $\delta = 1.5$ (no overcharging at any temperature), fraction of both condensed divalent counterions and monovalent coions, $\alpha_2$ and $\alpha_3$ respectively, increase to leave $f$ (and $R_g$) approximately unchanged.

**Fig. 8** Contributions to free energy: separate parts of the free energy for a fixed divalent salt concentration ($\tilde{c}_s^2 = 0.0005$) as functions of (a) Bjerrum length $\tilde{l}_B$ and (b) dielectric mismatch strength ($\delta$). For (a), $\delta = 2.5$ and (b), $\tilde{l}_B = 3.0$. Parameters are: $N = 1000, \tilde{\rho} = 0.0005, \tilde{c}_s^1 = 0$. Energies are: $F_1$ (dot) = entropy of mobility along the chain, $F_2$ (dash) = translational entropy of mobile ions, $F_3$ (dot-dash) = Debye-Hückel correlation between mobile ions, $F_4$ (dot-dash-dash) = Coulomb attraction between condensed ions and $F_{tot}$ (solid) = total free energy. For fixed salt concentration, the major competition is between the translational entropy (increase with temperature) and Coulomb attraction (increase with both $\tilde{l}_B$ and $\delta$). The similarity in the roles of $\tilde{l}_B$ and $\delta$ is evident.

**Fig. 9** (a) The state diagram of the total charge density of the polymer ($f$) for $\tilde{l}_B = 3.0$ as functions of the dielectric mismatch $\delta$ and the divalent salt concentration $\tilde{c}_s^2$. Parameters are: $N = 1000, \tilde{\rho} = 0.0005, \tilde{c}_s^1 = 0$. Charged states are: A,D - negative, B,C - positive (note: original polymer charge is negative). Lines are: isoelectric branch one (solid), maximum overcharging (dot), isoelectric branch two (dot-dash), and minimum charge (dash); (b) the state diagram of $f$ at a fixed dielectric mismatch strength ($\delta = 2.5$) as functions of the Bjerrum length $\tilde{l}_B$ and the divalent salt concentration $\tilde{c}_s^2$. Other parameters, states, and lines are the same as in (a).

**Fig. 10** The state diagram of the total charge density on the polymer ($f$) at a fixed divalent salt concentration ($\tilde{c}_s^2 = 0.0005$) as functions of the dielectric mismatch strength $\delta$ and the Bjerrum length $\tilde{l}_B$. Other parameters are the same as in Fig. 9. Charged states are: A,D - negative, B,C - positive, and C1 - zero. Lines are: isoelectric branch one (solid), maximum overcharging (dot), isoelectric branch two (dot-dash), minimum charge (dash), and zero charge (dash-dot-dot).
**Fig. 11** Effect of bridging: degree of ionization $(f)$, fractions of condensed ions $(\alpha$’s) (a), size expansion factor $(\tilde{l}_1)$ (b), and separate parts of the free energy $(F$’s) (c) as functions of divalent salt concentration $(c_{s2})$ when monomer-bridging by divalent cations is taken into account. Parameters are: $N = 100, \tilde{\rho} = 0.0008, \tilde{l}_B = 3.0, \delta = 1.9, c_{s1} = 0, w = 2.0, w_3 = 0.25$. Bridging induces a first-order collapse transition with a sudden gain in electrostatic ion-bridging energy. At the transition salt concentration, all monomer-divalent cation ion-pairs (’monocomplex’es) give way to monomer-cation-monomer ion bridges (’dicomplex’es).

**Fig. 12** Effect of Coulomb strength on collapse: the salt concentration $\tilde{c}_{s2}^*$, at which the first-order collapse occurs, as functions of $\tilde{l}_B$ (a), and $\delta$ (b). In (a), $\delta = 2.5$. In (b), $\tilde{l}_B = 3.0$. All other parameters are the same as in Fig. 11. Lowering of $\tilde{c}_{s2}^*$ with Coulomb strength indicates that the collapse is due to electrostatic interactions. $\tilde{l}_B$ and $\delta$ play similar roles, as expected. In (c): $\tilde{l}_B\tilde{c}_{s2}^* \simeq 0.0006$ (for $\delta = 2.5$) and $\delta\tilde{c}_{s2}^* \simeq 0.0005$ (for $\tilde{l}_B = 3.0$).
FIG. 1: Kundagrami et al., JCP
FIG. 2: Kundagrami et al., JCP
FIG. 3: Kundagrami et al., JCP
FIG. 4: Kundagrami et al., JCP
FIG. 5: Kundagrami et al., JCP
FIG. 6: Kundagrami et al., JCP
FIG. 7: Kundagrami et al., JCP
FIG. 8: Kundagrami et al., JCP
FIG. 9: Kundagrami et al., JCP
FIG. 10: Kundogrami et al., JCP
FIG. 11: Kundagrami et al., JCP
FIG. 12: Kundagrami et al., JCP