Theory of competitive counterion adsorption on flexible polyelectrolytes: Divalent salts

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The 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 the Bjerrum length, salt concentration, and local dielectric heterogeneity as physical variables in the system. Self-consistent calculations of effective charge and size of the polymer show that divalent counterions replace condensed monovalent counterions in competitive adsorption. The theory further predicts that at modest physical conditions for a flexible polyelectrolytes such as sodium polystyrene sulfonate in aqueous solutions polymer charge is compensated and reversed with increasing divalent salt. Consequently, the polyelectrolyte shrinks and reswells. Lower temperatures and higher degrees of dielectric heterogeneity between chain backbone and solvent enhance condensation of all species of ions. Complete diagrams of states for the effective charge calculated as functions of the 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 (for low Coulomb strengths) or coion condensation (for high Coulomb strengths). Consideration of ion-bridging by divalent counterions leads to a first-order collapse of polyelectrolytes in modest presence of divalent salts and at higher Coulomb strengths. The authors' theoretical predictions are in agreement with the generic results from experiments and simulations. © 2008 American Institute of Physics. [DOI: [10.1063/1.2940199](https://doi.org/10.1063/1.2940199)]

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 ϵ , and is given by

$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon k_B T}, \quad (1.1)$$

where e is the electron charge, ϵ_0 is the vacuum permittivity, and k_B is the Boltzmann constant. The other one is the Debye screening length κ^{-1} , which sets the length scale for the screening of electrostatic interactions due to the dissociated ions, and is given by

$$\kappa^2 = 4\pi l_B \sum_i Z_i^2 c_i, \quad (1.2)$$

where the sum is over all species (i) of mobile ions of valency Z_i and number concentration c_i . In addition to the above two, a third length scale can be conceived¹ related to the dielectric heterogeneity, which accounts for the difference in the dielectric constant in the vicinity of the polymer 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 nonmonotonic dependence of the average conformation of flexible polyelectrolyte chains on temperature is now well-known from computer simulations and experiments. At very high temperatures, the chains in dilute salt-free solutions are in their athermal states with self-avoiding-walk 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 even beyond the excluded volume swelling due to intermonomer repulsion. At even lower temperatures, counterions condense on the chains sufficiently reducing the net polymer charge, and, consequently, the chains tend to contract. The presence of small-molecular monovalent salts has long been known to enhance this condensation effect, and the resulting contraction occurs at higher temperatures. Monovalent salts, however, gradually shrink flexible polyelectrolyte chains at temperatures that are still typically way below modest temperatures (e.g., room temperature for aqueous solutions). The 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 contract polyelectrolytes close to its Gaussian size at room temperatures. Further, the addition of a higher amount of divalent salt can even reverse the

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charge on the polymer (the phenomenon known as *overcharging*, *charge inversion*, or *charge reversal*) at certain physical conditions.

The condensation of counterions on flexible polyelectrolyte chains has traditionally been addressed in the Manning model² originally designed for infinitesimally thin and infinitely long rodlike molecules. However, Manning's argument has been found inadequate¹ for flexible polyelectrolytes. Flexibility allows significant bending of molecules due to charge compensation at lower temperatures, further 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 the precipitation of chains for high counterion valence, initial theories³ considered the translational free energy of the polyions and salt ions along with the screened Coulomb interaction between charges. With prefixed values of the excluded volume exponent ν (i.e., prefixed radius of gyration R_g), the free energy was minimized in terms of counterion species, and the correlated multivalent ions were shown⁴ to induce attraction between monomers (through “ion-bridging”) capable of collapsing a chain. The 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 addressed⁵ 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 similar to Manning's argument. A two-state (rodlike and collapsed) model for condensation predicted⁶ that the chain collapse occurs when the total charge of the 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^{6,7} treats the collapsed state 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^{8–13} and simulations¹⁴ have shown that added cations with higher valence are more effective in compacting 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 (Refs. 15–17) molecules. It was further noticed^{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 contracted with virtually negligible net charge on it, is predicted to be very small in recent simulations,²⁰ which otherwise observe definite overcharging. Although rapid shrinkage of chain dimensions due to charge neutralization at higher salt concentrations or lower temperatures is abundantly observed in experiments^{21–23} and in simulations,^{24–27} charge reversal by multivalent salt is not universally observed.²⁸ Very recent experiments, however, have lent support to both charge inversion^{29,30} and counterion mediated attraction³¹ in biological polyelectrolytes such as DNA.

An effective two-parameter theory³² considered the adsorption process of counterions and formation of mono- and dicomplexes between negatively charged monomers and positively charged divalent 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 conformations at various physical conditions. To address the chain entropy of flexible polyelectrolytes and its role in counterion distribution, Muthukumar developed¹ 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 conformational free energy of the polymer. The adsorption theory¹ considers continuous values for the size (R_g) of a single chain treated as a continuous curve, which provides an appropriate description of entropy of a flexible chain. The theory treats salt-free as well as salty conditions with monovalent counterions in dilute solutions of a flexible polyelectrolyte. 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 (below Gaussian dimensions) due to short-ranged dipole interactions at low temperatures.^{26,27} In addition to the length scales l_B (Bjerrum length) and κ^{-1} (Debye length) in the charged system, the adsorption theory uses the concept of a dielectric mismatch parameter δ , 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^{33–35} solvent. In generic polyelectrolyte solutions, δ is the ratio of the bulk to local dielectric constants, and the distance from the backbone in which ϵ assumes its bulk value sets a new length scale. This mismatch in ϵ , if substantial, creates 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 to contract a chain to its Gaussian conformation at modest temperatures [say, the room temperature at which $l_B \sim 7$ Å for sodium polystyrene sulfonate (NaPSS) in water] only at a large concentration of an added monovalent salt.

In this paper, we extend Muthukumar's adsorption theory¹ to include divalent counterions. The basic concept still relies on the competition between the electrostatics of the adsorbed ions and the entropy of the 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 the extent of the adsorbed ions as functions of temperature, the degree of dielectric mismatch, and the concentration of the divalent salt (BaCl_2). In addition to the adsorption of monovalent and divalent counterions (Na^+ and Ba^{++} , respectively), we also take into account the attachment of negative salt coions (Cl^-), as previous theories^{7,32} and simulations²⁸ indicate substantial presence of coions near the chain backbone. The conformational free energy of the system depends on the extent of adsorption of various ionic species on the chain backbone as well as on the size of the polymer, and all contributing factors remain nonlinearly 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 to the Gaussian conformation of the polyelectrolyte chain. With further increase of the divalent salt concentration, adsorbed divalent counterions overcharge, and, consequently, reexpand chains. This occurs for significantly large ranges of physical parameters δ and l_B . A substantial fraction of salt coions (Cl^-) also adsorbs on the monomer-divalent ion-pairs. The coion condensation reduces the degree of overcharging but does not eliminate it. However, for modest temperatures and in a generic solvent (water at room temperature), there is always a critical degree of dielectric heterogeneity below which neither chain shrinkage 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 the salt concentration, temperature, and the dielectric mismatch parameter are relatively robust functions of l_B , κ^{-1} , and δ , 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 adsorption of all types of counterions and coions resulting in the achievement of the isoelectric point at lower divalent salt concentrations. A typical state diagram for poly-

FIG. 1. (Color online) Sketch of the 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 the net effective charge (degree of ionization) of 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 the 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. The dashed part of the isoelectric line is beyond the validity of the Debye-Hückel theory employed here.

electrolyte charge is predicted (Fig. 1) in which below a critical Coulomb strength (proportional to $1/T$, $1/\epsilon$, or δ) there is no overcharging with increasing divalent salt. Above this critical strength, electrostatics is strong enough to adsorb sufficient number of counterions inducing overcharging. For higher salt concentrations, we expect recharging of the polyelectrolyte due to either screening of electrostatics³⁶ (for low Coulomb strengths) or coion (Cl^-) condensation (for high Coulomb strengths). The dashed line indicates that in this regime of the salt concentration the theory only predicts qualitative results. 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.

Another interesting phenomenon related to the collapse of polyelectrolytes is ion-bridging which is believed to be observed in many experiments.¹⁰⁻¹² Ion-bridging is an electrostatic interaction in which a single divalent cation adsorbs on two nonbonded negatively charge monomers. Therefore, the bridges effectively induce between monomers a long-ranged attractive interaction capable of collapsing the chain to conformations way below its Gaussian value. We address this ion-bridging interaction for certain physical conditions and present a simple theory that predicts a first-order chain collapse for moderate conditions. This phenomenon is analyzed in detail in Sec. III G.

The rest of the article is organized as follows: In Sec. II,

FIG. 2. (Color online) 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 ϵ . Possible charge complexes for each monomer: (a) Monomer (-1) , (b) monomer-monovalent $(-1, +1)$, (c) monomer-divalent $(-1, +2)$, (d) monomer-divalent-monocoion $(-1, +2, -1)$, and (e) a bridging configuration of monomer-divalent-monomer. The dielectric constant ϵ_i 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 adsorbed ions.

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

II. THEORY

Following Muthukumar's work with monovalent salt,¹ we consider a linear flexible polyelectrolyte chain of N monomers in a solution of volume Ω , 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, Na^+ from NaCl) is chemically identical to the counterion from the polymer (say, Na^+ from NaPSS). Similarly, the coions from both types of salts are of the same species (say, Cl^- from NaCl and BaCl_2). At any time, both monovalent and divalent counterions (say, Ba^{++} from BaCl_2 as divalent counterions) can adsorb on separate monomers. In addition, the Ba^{++} -monomer ion-pair is viewed as a positive monovalent ion, and the negative coions (Cl^-) will adsorb on some of these pairs as counterions (see Fig. 2). 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 Ba^{++} -monomer ion-pairs ($M_3 \leq M_2$), the effective (or average) degree of ionization of the entire chain will be $f = (N - M_1 - 2M_2 + M_3)/N$.

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 (Na^+), n_2 divalent counterions (Ba^{++}), and $n_1 + 2n_2$ coions (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 theory¹ 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 discussed below, the number of variational variables becomes five when the electrostatic bridging by divalent ions is considered.

As before,¹ the free energy F has six contributions of F_1 , F_2 , F_3 , F_4 , F_5 , and F_6 related, respectively, to (i) the entropy of the mobility of the adsorbed counterions and coions along the polymer backbone, (ii) translational entropy of the unadsorbed counterions and coions (including salt ions) which are mobile within the volume Ω , (iii) fluctuations in electrostatic interactions (Debye-Hückel) among all unadsorbed counterions and coions except the polymer, (iv) the unscreened electrostatic (Coulomb) energy of the monomer-counterion bound pairs (both monovalent and divalent counterions) and the 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 arising from the various distributions of the adsorbed counterions and coions, we note that there are N monomers, M_1 adsorbed monovalent counterions (Na^+), $M_2 - M_3$ adsorbed divalent counterions (Ba^{++}) with no coion (Cl^-) condensation, and M_3 ion-triplets (monomer- Ba^{++} - Cl^-) in the system. Therefore, $N - M_1 - M_2$ monomers remain bare charged with no ions adsorbed on them. Consequently, the partition function is

$$Z_1 = \frac{N!}{(N - M_1 - M_2)! M_1! (M_2 - M_3)! M_3!}. \quad (2.1)$$

We define

$$\alpha_1 = \frac{M_1}{N}, \quad \alpha_2 = \frac{M_2}{N}, \quad \alpha_3 = \frac{M_3}{N}. \quad (2.2)$$

Using $F_1 = -k_B T \ln Z_1$, we have

$$\begin{aligned} \frac{F_1}{Nk_B T} &= (1 - \alpha_1 - \alpha_2) \log(1 - \alpha_1 - \alpha_2) + \alpha_1 \log \alpha_1 \\ &\quad + (\alpha_2 - \alpha_3) \log(\alpha_2 - \alpha_3) + \alpha_3 \log \alpha_3. \end{aligned} \quad (2.3)$$

The above expression implies following two obvious constraints:

$$\alpha_1 + \alpha_2 \leq 1 \quad \text{and} \quad \alpha_3 \leq \alpha_2. \quad (2.4)$$

To determine the translational entropy of the unadsorbed ions which are distributed in the bulk volume Ω , 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 coions (Cl^-). Therefore, the partition function related to the translational entropy in volume Ω is

$$\begin{aligned} Z_2 &= \frac{\Omega^{N-M_1+n_{1+}+n_{2+}-M_2+n_{1+}+2n_{2+}-M_3}}{(N-M_1+n_{1+})!(n_{2+}-M_2)!(n_{1+}+2n_{2+}-M_3)!} \\ &= \frac{\Omega^{N-M_1-M_2-M_3+2n_{1+}+3n_{2+}}}{(N-M_1+n_{1+})!(n_{2+}-M_2)!(n_{1+}+2n_{2+}-M_3)!}. \end{aligned} \quad (2.5)$$

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

$$N = \rho\Omega, \quad n_{1+} = \frac{c_{s1}N}{\rho}, \quad n_{2+} = \frac{c_{s2}N}{\rho}. \quad (2.6)$$

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

$$\begin{aligned} \frac{F_2}{Nk_B T} &= \left(1 - \alpha_1 + \frac{c_{s1}}{\rho}\right) \log(\rho(1 - \alpha_1) + c_{s1}) \\ &\quad + \left(\frac{c_{s2}}{\rho} - \alpha_2\right) \log(c_{s2} - \rho\alpha_2) \\ &\quad + \left(\frac{c_{s1}}{\rho} + 2\frac{c_{s2}}{\rho} - \alpha_3\right) \log(c_{s1} + 2c_{s2} - \rho\alpha_3) \\ &\quad - \left\{ (1 - \alpha_1 - \alpha_2 - \alpha_3) + 2\frac{c_{s1}}{\rho} + 3\frac{c_{s2}}{\rho} \right\}, \end{aligned} \quad (2.7)$$

with the constraint

$$M_2 \leq n_{2+}. \quad (2.8)$$

The free energy contribution from the correlations of all dissociated ions is given by the Debye–Hückel electrostatic free energy

$$F_3 = -k_B T \frac{\Omega \kappa^3}{12\pi}, \quad (2.9)$$

where the inverse Debye length κ is given by

$$\kappa^2 = 4\pi l_B \sum_i Z_i^2 n_i / \Omega. \quad (2.10)$$

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. For our present case,

$$\begin{aligned} \kappa^2 &= 4\pi l_B \{N - M_1 + n_{1+} + 4(n_{2+} - M_2) + n_{1+} + 2n_{2+} - M_3\} / \Omega \\ &= 4\pi l_B (N - M_1 - 4M_2 - M_3 + 2n_{1+} + 6n_{2+}) / \Omega \\ &= 4\pi l_B \{\rho(1 - \alpha_1 - 4\alpha_2 - \alpha_3) + 2c_{s1} + 6c_{s2}\}. \end{aligned} \quad (2.11)$$

Using the definitions from Eq. (2.6) we reach

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

To determine the electrostatic energy gain due to the adsorption of all sorts of ions (Na^+ , Ba^{++} , and Cl^-), we recount different ion-pairs and triplets which form after adsorption. 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^{++} ion, and $\alpha_3 N$ triplets of monomer(-1), and Ba^{++} and Cl^- ions. In addition, $(1 - \alpha_1 - \alpha_2)N$ monomers(-1) bear the original charge. In Muthukumar's theory,¹ the dielectric mismatch parameter δ was conceived to address a local dielectric constant ϵ_l in the vicinity of the chain backbone. Experiments have shown³³ ϵ_l to be almost an order of magnitude less than its bulk value ϵ (around 78 in water) near polyelectrolyte or protein backbone. The dielectric constant increases exponentially^{34,35} from the low value (corresponding to the material made from the chain-backbone) to its full bulk value over a distance of 1–10 Å from the chain monomers. $\delta = (\epsilon_l / \epsilon_d)$ was introduced,¹ where d is the dipole length of the monomer-monovalent counterion ion-pair. The value of d is probably comparable to the Bjerrum length l_B . A glance at Fig. 2 reveals that δ in the above form only applies to the monomer-monovalent (Na^+) and monomer-divalent (Ba^{++}) ion-pairs but not to the divalent counterion-monovalent coion ($\text{Ba}^{++}-\text{Cl}^-$) 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^{++} -monomer, $\text{Ba}^{++}-\text{Cl}^-$, and Cl^- -monomer), and the interpretation of δ is not simple. We introduce a parameter δ_2 for the monomer- $\text{Ba}^{++}-\text{Cl}^-$ triplet. δ_2 is expected to be less than 4δ (the value it would have assumed if there were two point charges, $+2e$ and $-2e$, respectively), but the determination of its actual value would require a microscopic treatment. In principle, δ_2 would be a function of δ . For simplicity, we assume all ions and monomers to be of the same size, and estimate δ_2 as follows.

First of all, we write the electrostatic energy of adsorption in terms of δ and δ_2 ,

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

where $\tilde{l}_B = l_B / l$ and the terms containing δ are written following Ref. 1. Note that if one assumes that the local dielectric constant ϵ_l applies only to the Ba^{++} -monomer pair, but not to the $\text{Ba}^{++}-\text{Cl}^-$ pair ($\epsilon = \epsilon_{\text{water}}$ in that case), then δ_2 turns out to be

$$\delta_2 = \left(2 + \frac{2}{\delta}\right) \delta. \quad (2.14)$$

This should be the lowest value of δ_2 . On the other hand, if ϵ_l applies to both Ba^{++} -monomer and $\text{Ba}^{++}-\text{Cl}^-$ pairs, then

$$\delta_2 = 4\delta. \quad (2.15)$$

This should be the highest value of δ_2 . In practice, δ_2 is likely to be somewhere between these two limiting values.

We choose the dielectric constant to be ϵ_l (the local value pertaining to the chain backbone) for the Ba^{++} -monomer pair and $(\epsilon_l + \epsilon_{\text{bulk}})/2$ for the $\text{Ba}^{++}-\text{Cl}^-$ pair. Then, δ_2 turns out to be

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

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 δ_2 , we later show that the basic qualitative results do not change if δ_2 is assigned any value in the range mentioned above. Therefore, we 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^{1,37} in which one starts from the Edwards Hamiltonian,

$$\begin{aligned} H = & \frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathcal{R}(s)}{\partial s} \right)^2 + \frac{w}{2} \int_0^L ds \int_0^L ds' \delta(\mathcal{R}(s) \\ & - \mathcal{R}(s')) + \frac{l_B}{2} \int_0^L ds \int_0^L ds' \frac{1}{|\mathcal{R}(s) - \mathcal{R}(s')|} \exp \\ & - \kappa |\mathcal{R}(s) - \mathcal{R}(s')|, \end{aligned} \quad (2.17)$$

where $L=Nl$, $\mathcal{R}(s)$ 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:

$$\langle R^2 \rangle = Nll_1 \equiv Nl^2 \tilde{l}_1 = 6R_g^2, \quad (2.18)$$

where $\tilde{l}_1 \sim l_1/l$. 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

$$\begin{aligned} \frac{F_5}{Nk_B T} = & \frac{3}{2N} (\tilde{l}_1 - 1 - \log \tilde{l}_1) + \frac{4}{3} \left(\frac{3}{2\pi} \right)^{3/2} \frac{w}{\sqrt{N} \tilde{l}_1^{3/2}} \\ & + 2 \sqrt{\frac{6}{\pi}} f^2 \tilde{l}_B \frac{N^{1/2}}{\tilde{l}_1^{1/2}} \Theta_0(a), \end{aligned} \quad (2.19)$$

where

$$\begin{aligned} \Theta_0(a) = & \frac{\sqrt{\pi}}{2} \left(\frac{2}{a^{5/2}} - \frac{1}{a^{3/2}} \right) \exp(a) \text{erfc}(\sqrt{a}) + \frac{1}{3a} + \frac{2}{a^2} \\ & - \frac{\sqrt{\pi}}{a^{5/2}} - \frac{\sqrt{\pi}}{2a^{3/2}}, \end{aligned} \quad (2.20)$$

where

$$a \equiv \tilde{\kappa}^2 N \tilde{l}_1^2 / 6. \quad (2.21)$$

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

$$f = 1 - \alpha_1 - 2\alpha_2 + \alpha_3. \quad (2.22)$$

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).

Until now we have considered the electrostatic interaction only between monomers the effective charge of which, with or without condensed ions, is nonzero. 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- Na^+ pair and a monomer- $\text{Ba}^{++}-\text{Cl}^-$ triplet would be treated equally by F_5 , although they have different electrostatic effects. Similarly, a monomer- Ba^{++} pair would be simply treated as a $+1$ charge, although the pair has 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 below its Gaussian size in the presence of monovalent counterions at very low temperatures (i.e., when the degree of ionization is negligible). In the previous paper,¹ these correlations among neutral ion-pairs and between neutral ion-pairs and charged monomers were addressed by short-ranged δ -function potentials which led to a free energy contribution of the following form:

$$\frac{F_6}{Nk_B T} \sim \frac{4}{3} \left(\frac{3}{2\pi} \right)^{3/2} w_i \delta^2 \tilde{l}_B^2 \frac{1}{\sqrt{N} \tilde{l}_1^{3/2}}, \quad (2.23)$$

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 attraction 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 attraction⁴² may induce. We leave out the short-ranged correlation effects between the dipoles near the isoelectric point in our present analysis. In Sec. III G, we present an ion-bridging theory based on our model predicting the global instability of a polyelectrolyte chain. The point worthy of note here is that the bridging interaction reduces²⁸ 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, we assume w to

FIG. 3. (Color online) Competitive displacement of monovalent counterions by divalent counterions: Fractions of adsorbed ions ($\alpha_1, \alpha_2, \alpha_3$), the 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 δ values plotted against the divalent salt concentration. For a Gaussian chain, $\tilde{l}_1 = 1$. Other parameters are $N = 1000$, $\tilde{\rho} = 0.0005$, $\tilde{l}_B = 3.0$, $w = 0$, and $\tilde{c}_{s1} = 0$. Note, for lower δ , there is no overcharging. For higher δ , almost all divalent counterions adsorb on the chain replacing the monovalent ones. The number of adsorbed coions (α_3) closely follow α_2 for this particular value of δ . 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 $\tilde{c}_{s2}$ is further increased.

be high enough to render the bridging effect negligible. Although we assume w to be zero except in Sec. III G, choosing nonzero positive values of w only brings minor quantitative changes to our results (and that even only near the isoelectric point) in the “no-bridging” scenario. When bridging is included (Sec. III G), however, w is a very important parameter affecting the salt concentration or the Coulomb strength required for the first-order transition to the collapsed state.

III. RESULTS AND DISCUSSION

The total free energy $F = F_1 + F_2 + F_3 + F_4 + F_5$ is given in terms of the fraction of adsorbed counterions and coions (α 's), the size of the polymer (l_1), temperature and the bulk dielectric constant (l_B), the degree of polymerization (N), the monomer density (ρ), monovalent and divalent salt concentrations (c_s 's), and local dielectric mismatch parameters (δ and δ_2). The goal is to self-consistently determine the fractions of the adsorbed ions (α_1 , α_2 , and α_3) and the size ($R_g = \sqrt{Nl_1/6}$) 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. These are the Bjerrum length (l_B) related to the Coulomb interaction and the Debye length (κ^{-1}). In addition, this formalism invokes a third length scale due to the dielectric mismatch parameter δ . Therefore, the important parameters on which we base our analysis are l_B , the salt concentrations (c_{s1} and c_{s2}), and δ .

A. Competitive adsorption

We start with an isolated polyelectrolyte chain 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 $\delta = 2.5$ and 1.5 , respectively, to illustrate the role of the parameter δ . Generally at higher values of δ , fractions of adsorbed ion species are expected to increase. We notice that (Fig. 3) both divalent counterions and negative monovalent coions (α_2 and α_3 , respectively) adsorb progressively in higher numbers with increasing divalent salt concentration. The number of monovalent counterions (α_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 parameter (as shown below in the diagrams of charged states). The variables chosen in this specific calculation are the degree of polymerization $N = 1000$ and the 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 sulfonate (NaPSS) in water at room temperature]. δ_2 is given by Eq. (2.16) throughout the paper, unless noted otherwise. For $\delta = 1.5$, only 5% of the monomers are neutralized by monovalent counterions for the salt-free 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 δ value, almost all available divalent counterions adsorb displacing the monovalent

lent counterions with increasing c_{s2} . Negative monovalent coions (Cl^-) also adsorb on the monomer-divalent ion-pair substantially. f decreases monotonically and *reverses sign* when c_{s2} is still well below the monomer concentration ρ . At $c_{s2} \sim 80\%$ of ρ , α_1 drops below 5% and α_2 is about 80% implying that almost all available divalent counterions have adsorbed. 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. The number of condensed monovalent ions, however, decreases to zero monotonically.

For the lower value of δ , 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. Chain contraction

In Fig. 3(b), we have noticed that the polyelectrolyte net charge due to the adsorption of divalent counterions becomes negligible as soon as the salt concentration reaches half the polymer concentration ($c_{s2} \sim \rho/2$). Consequently, the chain shrinks 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 the degree of ionization f of the polyelectrolyte decreases moderately and monotonically, and never changes sign. Consequently, the size ($\tilde{l}_1$ 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 shrinks to Gaussian statistics near this isoelectric point.

This continuous shrinkage of a generic polyelectrolyte (NaPSS) chain in water occurs for modest values of δ , at a modest presence of the divalent salt, and at room temperature. This phenomenon has been noticed theoretically,⁶ in experiments,^{10,29,30,43} and simulations.^{20,28}

C. 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 δ in our theory plays an important role in the charge reversal induced by counterion adsorption. Temperature is also an important factor regulating the relative weight of the electrostatic energy gain of ion adsorption. To show these effects, we plot the degree of ionization f and the expansion factor $\tilde{l}_1$

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

of the chain as functions of Bjerrum length l_B (inverse temperature and bulk dielectric constant) for various δ values in Fig. 5. The other parameters are $N=1000$, $\tilde{\rho}=0.0005$, $\tilde{c}_{s1}=0$, and $\tilde{c}_{s2}=0.0005=\tilde{\rho}$. The concentrations of the divalent salt and the polymer are chosen to be equal to ensure the availability of enough divalent ions to adsorb on every monomer if physical conditions permit. In Fig. 5(a), we notice that there is negligible adsorption for $\delta=1$ (which is the comparable value of δ in simulations^{20,28}). Similar to the monovalent case [Figs. 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 two-fold for divalent ions). At no temperature there is overcharging for $\delta=1$. For $\delta=1.5$, we start to see nominal overcharging which only manifests through a little reswelling of the chain. The absolute value of overcharging is less than 1% at these δ values and we can extend our prediction of the lower threshold value of the dielectric heterogeneity to be 1.5 for the whole range of temperature (threshold $\delta \approx 1.7$ for $\tilde{l}_B=3.0$). There is, however, a drastic qualitative change in the

FIG. 5. (Color online) Dependency of overcharging on $\tilde{l}_B$: The degree of ionization (f) in (a) and the size expansion factor ($\tilde{l}_1$) in (b) of the polyelectrolyte plotted against $\tilde{l}_B$ for different values of δ . Parameters are $N=1000$, $\bar{\rho}=0.0005$, $\tilde{c}_{s1}=0$, and $\tilde{c}_{s2}=0.0005$. Collapse and subsequent overcharging occur for higher values of δ . The isoelectric point is reached at lower values of $\tilde{l}_B$ for higher values of δ . The absolute value of overcharging for $\delta=1.5$ – 1.7 is less than 2%. This overcharging behavior contrasts with s. 2(a) and 3 in Ref. 1 for monovalent salts.

dependencies of f and R_g on $\tilde{l}_B$ for δ 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 δ as expected (T^{-1} and δ , both favor higher degree of adsorption). The absolute value of the maximum overcharge and the reswelled size increase with δ 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 δ value is high enough (as we increase $\tilde{l}_B$) to have repulsion between monomers stronger than that at the point of maximal *swelling*. Another point of note is that for higher temperatures, just as for monovalent counterions, only a fraction of available divalent ions adsorb. The optimal temperature at which the chain reexpansion is maximum shifts to a higher value with higher values of δ . For very low temperatures, sufficient number of negative coions (Cl^-) adsorb to gradually reneutralize the chain for all δ values.

To further explore the issue of overcharging, we plot f

FIG. 6. (Color online) Dependency of overcharging on δ : Fractions of adsorbed ions ($\alpha_1, \alpha_2, \alpha_3$), the degree of ionization (f) in (a), and the expansion factor ($\tilde{l}_1$) in (b), plotted against the δ -parameter for $\tilde{l}_B=3.0$. Other parameters are the same as in Fig. 5. Charge neutralization occurs for $\delta \sim 1.7$; overcharging is possible at this $\tilde{l}_B$ value only if $\delta > 1.7$. Cl^- adsorption (α_3) is higher for higher values of δ , and that reduces overcharging.

and $\tilde{l}_1$ against δ for $\tilde{l}_B=3$ in Fig. 6. The other parameters are the same as in Fig. 5. At room temperature in aqueous solutions, there can be no overcharging unless δ is higher than a threshold value which is around 1.7 for NaPSS. Only for δ as high as 1.7, the dielectric heterogeneity would be strong enough to electrostatically guide enough divalent cations to be adsorbed and, consequently, reverse the charge of the chain. The strong sensitivity of the total charge and conformation of the polymer to δ is manifested 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 δ changing only from 1 to 1.7. For very high values of δ , Cl^- ions condense progressively at higher numbers to reduce overcharging.

D. Condensation of coions

In a monomer $\text{Ba}^{++}-\text{Cl}^-$ 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 δ or the range of the local dielectric constant ϵ_l . We assume that all triplets in the system have this specific colinear arrangement in which the line joining

FIG. 7. (Color online) Effect of dielectric mismatch for the coion: The fraction of adsorbed Cl^- ions (α_3), the degree of ionization f in (a) and (b) for $\delta=2.5$ and 1.5 , respectively, and the expansion factor ($\tilde{l}_1$) in (c) and (d) for the same δ values plotted against δ_2 for its whole physical range possible for the respective value of δ . Other parameter values are the same as in Fig. 6. For the higher $\delta=2.5$, progressively higher values of δ_2 reduce and finally eliminate overcharging (and, consequently, the reexpansion of the chain) by increasing α_3 . For $\delta=1.5$ (no overcharging at any temperature), fractions of both adsorbed divalent counterions and monovalent coions, α_2 and α_3 , respectively, increase to leave f (and R_g) approximately unchanged.

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 the lowest values permitted by physical conditions of the strength parameter δ_2 related to the formation of the triplet have been determined in terms of δ through Eqs. (2.14) and (2.15). Although suggested by a few authors,³⁵ 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 Eq. (2.16) is different from ϵ . 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., δ) exclusively determines the value of δ_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 size l of the monomer. To illustrate that these approximations do not compromise the generality of the conclusions, 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 δ_2 . We vary δ_2 from its lowest [Eq. (2.14)] to its highest value [Eq. (2.15)] for a specific value of δ . In Fig. 7(a), we choose $\delta=2.5$, for which overcharging is evident for $\tilde{l}_B=3.0$. Other parameters are: $N=1000$, $\tilde{\rho}=0.0005=\tilde{c}_{s2}$, and $\tilde{c}_{s1}=0$. We notice that with increasing δ_2 a progressively larger number of Cl^- ions condense on the chain. This reduces overcharging and close to the highest value of δ_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 δ_2 values) reduce the de-

gree 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 δ_2 has negligible effect on both f and R_g in this case. However, fractions of both condensed divalent counterions and monovalent coions (α_2 and α_3 , respectively) increase with δ_2 , keeping the overall degree of ionization (f) approximately unaltered.

E. 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-F_5) as functions of the critical parameters. The major conclusion of the theory¹ has been that the equilibrium distribution of the adsorbed counterions and the size of the polyelectrolyte are determined essentially by a competition between the translational entropy of dissociated ions and the Coulomb energy gain of adsorbed 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 ($\tilde{c}_{s2}=0.0005$, 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 adsorption energy F_4 [Eq. (2.13)]. For higher temperatures (lower $\tilde{l}_B$'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 gain in F_4 . The

FIG. 8. (Color online) Contributions to free energy: Separate parts of the free energy for a fixed divalent salt concentration ($\tilde{c}_{s2}=0.0005$) as functions of (a) the Bjerrum length $\tilde{l}_B$ and (b) the dielectric mismatch strength (δ). (a) $\delta=2.5$ and (b) $\tilde{l}_B=3.0$. Parameters are $N=1000$, $\tilde{\rho}=0.0005$, and $\tilde{c}_{s1}=0$. 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 adsorbed ions, and F_{tot} (solid)=total free energy. For a fixed salt concentration, the major competition is between the translational entropy (increases with temperature) and the Coulomb attraction (increases with both $\tilde{l}_B$ and δ). The similarity in the roles of $\tilde{l}_B$ and δ is evident.

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 δ 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 $\tilde{l}_B$ and δ . According to this adsorption theory, reduction of any of temperature, the bulk dielectric constant ϵ , or the local dielectric constant ϵ_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 $\tilde{l}_B$ and δ .

F. Diagrams of charged states

We have proposed earlier a tentative state diagram (Fig. 1) of the total charge f (or the degree of ionization

FIG. 9. (Color online) (a) The state diagram of the effective charge of the polymer (f) for $\tilde{l}_B=3.0$ as functions of the dielectric mismatch δ and the divalent salt concentration $\tilde{c}_{s2}$. Parameters are $N=1000$, $\tilde{\rho}=0.0005$, and $\tilde{c}_{s1}=0$. Charged states are A, D with negative and B, C with 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 $\tilde{c}_{s2}$. Other parameters, states, and lines are the same as in (a).

$=1-\alpha_1-2\alpha_2+\alpha_3$) 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 ($\tilde{l}_B$), the divalent salt concentration ($\tilde{c}_{s2}$), and the dielectric mismatch parameter (δ). 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. Figures 9 and 10 describe the complete limiting charged states, parts of which have already been discussed in detail in the 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 $\tilde{c}_{s2}$ and the dielectric mismatch parameter δ . The state diagram is qualitatively similar to the proposed one (Fig. 1), with the strength of the Coulomb interaction being represented by δ [Eq. (2.13)], $\tilde{l}_B$ being fixed. To explain the diagram, we first choose a specific value of $\delta=2.5$ [see Figs. 3(b) and 4 also]

FIG. 10. (Color online) The state diagram of the total charge density on the polymer (f) at a fixed divalent salt concentration ($\tilde{c}_{s2}=0.0005$) as functions of the dielectric mismatch strength δ and the Bjerrum length $\tilde{l}_B$. Other parameters are the same as in Fig. 9. Charged states are A with negative, B, C with positive, and C1 with zero. Lines are isoelectric (solid), maximum overcharging (dot), and zero charge (dash and dot-dash).

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 coions (Cl^-) are available in the solution and some of them adsorb 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 δ , because a higher fraction of divalent counterions would remain dissociated in the solution due to a lower Coulomb energy gain. For values of δ higher than ≈ 3 , a substantial fraction of monovalent counterions of the polymer (Na^+) too, remain adsorbed on the chain and the chain charge is neutralized with fewer divalent counterions. If δ is less than ≈ 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 adsorption. The line of minimum charge (for δ less than ≈ 1.7) expectedly continues to be the line of maximum charge reversal (for δ greater than ≈ 1.7). For very high salt concentrations, the Coulomb interaction is progressively screened and all adsorbed ions begin to rejoin the solution (not included in the state diagram). We must, however, be cautioned that the DH approximation [and, consequently, F_3 in Eq. (2.12)] is not 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)]

$$c_{s2-\text{max}} \approx (24\pi l_B^3)^{-1}. \quad (3.1)$$

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 redissolution of condensed ions at least an order of magnitude higher in 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 slopes of the isoelectric lines (branch one in Figs. 9(a) and 9(b)) are opposite at high Coulomb strengths because in the latter case a higher degree of Cl^- adsorption at high l_B requires more divalent salt to neutralize the chain.

The state diagram as a function of $\tilde{l}_B$ and δ for a fixed salt concentration $\tilde{c}_{s2}=0.0005$ (equal to the monomer concentration) is presented in Fig. 10. One essential characteristic is that the degree of ionization remains steadily 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-dashed line) generally decreases with higher values of δ (higher electrostatic energy gain). The magnitude of the degree of ionization as a function of $\tilde{l}_B$ for fixed values of δ can be obtained in Fig. 5, and as a function of δ for a fixed value of $\tilde{l}_B$ in Fig. 6. Both figures can be analyzed in conjunction with this state diagram. Point worthy of note is that there will be no overcharging regardless of how high l_B is if δ is less than a critical value ~ 1.50 (see Fig. 5). We previously had established the critical δ to be around 1.7 for $\tilde{l}_B=3.0$. It is to be noted that although we see overcharging for δ between 1.5 and 1.7 for $\tilde{l}_B > 3.0$ the actual absolute value of excess charge is negligible (less than 2%) in this range.

G. Effect of bridging

We now consider the bridging configuration of non-bonded monovalent monomers mediated by divalent counterions. Let us assume that some of the adsorbed divalent ions participate in bridging. When bridging is included, the minimization of the free energy needs to be performed with respect to five variables. In our theory, we will address the bridging interaction as an effective two-body interaction between monomers with uncompensated charge. The pronounced shrinking of individual polyelectrolyte coils (such as polyacrylate chains¹⁰) in the presence of divalent ions has

long been observed in light-scattering experiments and viscosity measurements. The shrinkage has been interpreted as intramolecular coil collapse^{10-12,44,45} induced by ion-bridging that has further been addressed^{11,46} as a hydrophobic intramolecular interaction. In response to an increasing salt to polymer ratio, a gradual shrinking of the polymer chains was observed¹² to be followed by a sharp collapse to a compact spherical shape (R_g/R_h going down from 1.5 to 0.8). To theoretically formulate this phenomenon, we note that a bridge formed by a divalent counterion is tantamount to a cross-link junction of functionality four,^{28,47} that, in turn, can be treated as an attractive two-body interaction of local nature (such as two-body excluded volume interaction). Therefore, in the presence of the bridging effects induced by divalent counterions, w in Eq. (2.19) is replaced by

$$w' = w + \frac{E_{\text{br}}}{k_B T} \alpha_{2b}, \quad (3.2)$$

where α_{2b} is the ratio of the number of divalent ions that participate in bridging (M_{2b}) to the number of monomers (i.e., $\alpha_{2b} = M_{2b}/N$). 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 (ϵ_l) since the divalent cation in the monomer-cation-monomer charge complex sits between and in the vicinity of both monomers (Fig. 2). With the definition¹ $\delta = \epsilon_l / \epsilon_d$, we have

$$E_{\text{br}} = -\frac{4e^2}{4\pi\epsilon_l d} + \frac{e^2}{4\pi\epsilon_d 2d} = -\frac{7}{2} \tilde{l}_B \delta k_B T. \quad (3.3)$$

We must add the third virial term in the chain free energy [F_5 , Eq. (2.19)] to maintain stability in the system in the case

of a negative w' . Combining Eqs. (3.2) and (3.3), therefore, the chain free energy takes the following form:

$$\begin{aligned} \frac{F_5}{Nk_B T} = & \frac{3}{2N} (\tilde{l}_1 - 1 - \log \tilde{l}_1) \\ & + \frac{4}{3} \left(\frac{3}{2\pi} \right)^{3/2} \left(w - \frac{7}{2} \tilde{l}_B \delta \alpha_{2b} \right) \frac{1}{\sqrt{N}} \frac{1}{\tilde{l}_1^{3/2}} \\ & + \frac{1}{N} \frac{w_3}{\tilde{l}_1^3} + 2 \sqrt{\frac{6}{\pi}} \tilde{l}_B \frac{N^{1/2}}{\tilde{l}_1^{1/2}} \Theta_0(a), \end{aligned} \quad (3.4)$$

where w_3 is the third-virial coefficient which is necessarily positive. Further, we note that if a fraction α_{2b} of the condensed divalent counterions participates 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 , Eq. (2.13)] is modified after the inclusion of the bridging interaction as

$$\frac{F_4}{Nk_B T} = -\alpha_1 \delta \tilde{l}_B - 2(\alpha_{2a} - \alpha_3) \delta \tilde{l}_B - \alpha_3 \delta_2 \tilde{l}_B, \quad (3.5)$$

where $\alpha_3 \leq \alpha_{2a}$. In addition, the entropic contribution to the free energy coming from the number of ways the adsorbed ions can be distributed [F_1 , Eq. (2.1)] will also be modified. Following the same arguments as in Sec. II A, we calculate the number of ways to distribute M_1 monovalent counterions (Na^+), $M_{2a} - M_3$ divalent counterions (Ba^{++}) (with no coion (Cl^-) adsorption), M_3 ion-triplets (monomer- Ba^{++} - Cl^-), and M_{2b} pairs of ion-bridges among N monomers (ignoring the permutations among the ion-bridges but taking into account of the double counting of them) to be

$$Z_1 = \frac{N!}{(N - M_1 - M_{2a} - 2M_{2b})! M_1! (M_{2a} - M_3)! M_3! (M_{2b})^2 2^{M_{2b}}}, \quad (3.6)$$

where $\alpha_{2a} \equiv M_{2a}/N$ and $\alpha_{2b} \equiv M_{2b}/N$. Therefore,

$$\begin{aligned} \frac{F_1}{Nk_B T} = & \alpha_{2b} \log 2 + (1 - \alpha_1 - \alpha_{2a} - 2\alpha_{2b}) \log(1 - \alpha_1 \\ & - \alpha_{2a} - 2\alpha_{2b}) + 2\alpha_{2b} \log \alpha_{2b} + \alpha_1 \log \alpha_1 + (\alpha_{2a} \\ & - \alpha_3) \log(\alpha_{2a} - \alpha_3) + \alpha_3 \log \alpha_3. \end{aligned} \quad (3.7)$$

The other parts of the free energy depend only on the numbers and valencies of different species of free ions, and therefore remain unaltered. They are given as 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 $F = \sum_i F_i$ is minimized now for a new set of five variational variables α_1 , α_{2a} , α_{2b} , α_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 $N=100$, $\tilde{\rho} = 0.0008$, $\tilde{l}_B = 3.0$, $\delta = 1.9$, $\tilde{c}_{s1} = 0$, $w = 2.0$, and $w_3 = 0.25$. For

very low divalent salt concentrations, the conformations are very similar to the case in which bridging is absent. At modest temperatures ($\tilde{l}_B = 3.0$ in water for NaPSS) and for low salt ($\tilde{c}_{s2} < 0.00027$), almost all added divalent counterions adsorb on the chain backbone, but they form 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 the electrostatic bridging free energy [Fig. 11(c)]. The Cl^- ions adsorb on the monomer-divalent ion-pair, as they do in the 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

FIG. 11. (Color online) Effect of bridging: The degree of ionization (f), fractions of adsorbed ions (α 's) (a), the size expansion factor ($\tilde{l}_1$) (b), and separate parts of the free energy (F 's) (c) as functions of the divalent salt concentration (c_{s2}) when monomer-bridging by divalent cations is taken into account. Parameters are $N=100$, $\tilde{\rho}=0.0008$, $\tilde{l}_B=3.0$, $\delta=1.9$, $\tilde{c}_{s1}=0$, $w=2.0$, and $w_3=0.25$. Bridging induces a first-order collapse transition with a sudden gain in the electrostatic ion-bridging energy. At the transition salt concentration, all monomer-divalent cation ion-pairs ("monocomplexes") give way to monomer-cation-monomer ion bridges ("dicomplexes").

higher Coulomb strength or divalent salt concentration to effect the bridging collapse. Before the collapse, the distribution of the adsorbed counterions and the polymer conformations are quite similar to those 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 quantitative changes to our results.

The sharp collapse of polyelectrolyte chains in solutions from a coil to a compact spherical globule with increasing number of divalent cations is strongly supported by experiments.⁴⁴ Regardless of the nature of the intermediate phases (for example, the pearl-necklace phase which is beyond the scope of our theory limited to uniform spherical expansion), the compact globular phase is found to be a certainty^{44,45} before the system reaches the precipitation phase boundary at which the cation-polyelectrolyte salt is formed. The value of the expansion factor we get ($\tilde{l}_1 \sim 0.08$) does agree quite well to the experimental values of neutral polymers in the globule phase. We notice that, in the collapsed state, the monovalent counterions adsorb on almost all of the remaining monomers [Fig. 11(a)] (also noticed in recent experiments⁴⁵) and the effective charge almost vanishes. This indicates that the polyelectrolyte in the collapsed state virtually behaves as a neutral polymer in poor solvent. In this case, the sign inversion of the excluded volume parameter (w) is effected by the attractive bridging interaction [Eq. (3.2)].

We further notice that the salt concentration $\tilde{c}_{s2}^*$, at which the polymer collapses, decreases with increasing Coulomb strength [Figs. 12(a) and 12(b)] further confirming that the first order collapse induced by the ion-bridging by divalent (or multivalent) cations is an electrostatic phenomenon. In addition, Fig. 12(c) shows that $\tilde{c}_{s2}^*$ varies approximately inversely with both forms of the Coulomb strength $\tilde{l}_B$ and δ . We find $\tilde{l}_B \tilde{c}_{s2}^* \approx 0.0006$ (for $\delta=2.5$) and $\delta \tilde{c}_{s2}^* \approx 0.0005$ (for $\tilde{l}_B=3.0$).

In conclusion, our model predicts a coil-globule transition, mediated by bridging due to divalent ions, which depends sensitively on temperature and the dielectric heterogeneity, as well as on the availability of divalent counterions.

IV. CONCLUSIONS

We have extended Muthukumar's theory¹ for the adsorption of monovalent counterions on a flexible polyelectrolyte by including divalent counterions. The divalent counterions replace the monovalent ones in the competitive adsorption process. For moderate values of the dielectric mismatch parameter (δ), temperature, and bulk dielectric constant ($\tilde{l}_B$), numbers of both the adsorbed divalent cations (Ba^{++}) and monovalent anions (Cl^-) increase and the number of the adsorbed monovalent cations (Na^+) decrease monotonically with an increasing concentration of the added divalent salt (BaCl_2). As observed in the 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 monomer concentration implying that almost all divalent cations added to the solution adsorb at those modest parameter values. With a further increase of the divalent salt concentration, the adsorbed divalent counterions overcharge the chain resulting in a reswelling of

FIG. 12. (Color online) 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 δ (b). In (a), $\tilde{l}_B=3.0$. In (b), $\delta=2.5$. All other parameters are the same as in Fig. 11. Lowering of $\tilde{c}_{s2}^*$ with the Coulomb strength indicates that the collapse is due to electrostatic interactions. $\tilde{l}_B$ and δ play similar roles, as expected. In (c) $\tilde{l}_B \tilde{c}_{s2}^* \approx 0.0006$ (for $\delta=2.5$) and $\delta \tilde{c}_{s2}^* \approx 0.0005$ (for $\tilde{l}_B=3.0$).

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 threshold value. The minimum degree of heterogeneity (δ) required to condense all available divalent cations marginally decreases with $\tilde{l}_B$. At room temperature in aqueous solutions ($\tilde{l}_B \sim 7 \text{ \AA}$), the adsorption theory predicts that δ must be at

least 1.7 to overcharge the polyelectrolyte. For higher values of $\tilde{l}_B$, the threshold value of δ decreases only up to 1.5.

We have developed the diagrams of charged states of the polymer in terms of three variables: $\tilde{l}_B$, κ , and δ . Both higher δ (lower ratio of local to bulk ϵ) and $\tilde{l}_B$ (lower temperature or bulk ϵ) facilitate ion adsorption of all types. Consequently, the isoelectric point (charge neutralization) and subsequent charge inversion are achieved at lower temperatures for higher δ and vice versa. The absolute value of the maximum charge reversal and simultaneous maximal reswelling increase with δ . 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 δ (≥ 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 ($\tilde{l}_B$ increased), progressively higher fractions of monovalent coions (Cl^-) adsorb 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 Ba^{++} and 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- Ba^{++} - Cl^- triplets as functions of the basic dielectric mismatch strength δ . It has been shown that the qualitative picture of the total effective charge and conformation of the polyelectrolyte remains unaltered although the distribution of counterions and coions around it may vary for a change in the triplet strength parameter (δ_2) within these limits. For an unrealistic value of the parameter closer to its higher limit, increased 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 adsorbed ions in shaping the counterion distribution around the polyelectrolyte chain. The electrostatic bridging of nonbonded monomers by divalent counterions leads to a first-order coil-globule transition at modest physical conditions. The salt concentration required for the transition to occur varies approximately inversely with the Coulomb strength. 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 the charge reversal and the coil-globule transition in the presence of divalent salts in dilute solutions of flexible polyelectrolytes.

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- ¹M. Muthukumar, *J. Chem. Phys.* **120**, 9343 (2004).
- ²G. S. Manning, *J. Chem. Phys.* **51**, 924 (1969).
- ³P. Gonzalez-Mozuelos and M. Olvera de la Cruz, *J. Chem. Phys.* **103**, 3145 (1995).
- ⁴M. Olvera de la Cruz, L. Belloni, M. Delsanti, J. P. Dalbiez, O. Spalla, and M. Drifford, *J. Chem. Phys.* **103**, 5781 (1995).
- ⁵P. S. Kuhn, Y. Levin, and M. C. Barbosa, *Macromolecules* **31**, 8347 (1998).
- ⁶F. J. Solis and M. Olvera de la Cruz, *J. Chem. Phys.* **112**, 2030 (2000).
- ⁷F. J. Solis, *J. Chem. Phys.* **117**, 9009 (2002).
- ⁸C. C. Conwell and N. V. Hud, *J. Cluster Sci.* **14**, 115 (2003).
- ⁹C. C. Conwell, I. D. Vilfan, and N. V. Hud, *Proc. Natl. Acad. Sci. U.S.A.* **100**, 9296 (2003).
- ¹⁰K. Huber, *J. Phys. Chem.* **97**, 9825 (1993).
- ¹¹Y. Ikeda, M. Beer, M. Schmidt, and K. Huber, *Macromolecules* **31**, 728 (1998).
- ¹²R. Schweins and K. Huber, *Eur. Phys. J. E* **5**, 117 (2001).
- ¹³M. Delsanti, J. P. Dalbiez, O. Spalla, L. Belloni, and M. Drifford, *ACS Symp. Ser.* **548**, 381 (1994).
- ¹⁴R. Chang and A. Yethiraj, *J. Chem. Phys.* **118**, 11315 (2003).
- ¹⁵T. T. Nguyen, I. Rouzina, and B. I. Shklovskii, *J. Chem. Phys.* **112**, 2562 (2000).
- ¹⁶T. T. Nguyen, A. Y. Grosberg, and B. I. Shklovskii, *J. Chem. Phys.* **113**, 1110 (2000).
- ¹⁷T. T. Nguyen, A. Y. Grosberg, and B. I. Shklovskii, *Phys. Rev. Lett.* **85**, 1568 (2000).
- ¹⁸Also see, H. Schiessel and P. Pincus, *Macromolecules* **31**, 7953 (1998).
- ¹⁹H. Schiessel, *Macromolecules* **32**, 5673 (1999).
- ²⁰P.-Y. Hsiao and E. Luijten, *Phys. Rev. Lett.* **97**, 148301 (2006).
- ²¹M. Beer, M. Schmidt, and M. Muthukumar, *Macromolecules* **30**, 8375 (1997).
- ²²V. M. Prabhu, M. Muthukumar, G. D. Wignall, and Y. B. Melnichenko, *Polymer* **42**, 8935 (2001).
- ²³For a nice review, see V. M. Prabhu, *Curr. Opin. Colloid Interface Sci.* **10**, 2 (2005).
- ²⁴M. J. Stevens and K. Kremer, *J. Chem. Phys.* **103**, 1669 (1995).
- ²⁵M. J. Stevens and K. Kremer, *Phys. Rev. Lett.* **71**, 2228 (1993).
- ²⁶S. Liu and M. Muthukumar, *J. Chem. Phys.* **116**, 9975 (2002).
- ²⁷R. G. Winkler, M. Gold, and P. Reineker, *Phys. Rev. Lett.* **80**, 3731 (1998).
- ²⁸S. Liu, K. Ghosh, and M. Muthukumar, *J. Chem. Phys.* **119**, 1813 (2003).
- ²⁹Y. Murayama, Y. Sakamaki, and M. Sano, *Phys. Rev. Lett.* **90**, 018102 (2003).
- ³⁰K. Besteman, K. Van Eijk, and S. G. Lemay, *Nat. Phys.* **3**, 641 (2007).
- ³¹X. Qiu, K. Andresen, L. W. Kwok, J. S. Lamb, H. Y. Park, and L. Pollack, *Phys. Rev. Lett.* **99**, 038104 (2007).
- ³²J. Wittmer, A. Johner, and J. F. Joanny, *J. Phys. II* **5**, 635 (1995).
- ³³E. L. Mehler and G. Eichele, *Biochemistry* **23**, 3887 (1984).
- ³⁴G. Lamm and G. R. Pack, *J. Phys. Chem. B* **101**, 959 (1997).
- ³⁵I. Rouzina and V. A. Bloomfield, *Biophys. J.* **74**, 3152 (1998).
- ³⁶V. M. Prabhu, E. J. Amis, D. P. Bossev, and N. Rosov, *J. Chem. Phys.* **115**, 4367 (2004).
- ³⁷M. Muthukumar, *J. Chem. Phys.* **86**, 7230 (1987).
- ³⁸I. Rouzina and V. A. Bloomfield, *J. Phys. Chem.* **100**, 9977 (1996).
- ³⁹B.-Y. Ha and A. J. Liu, *Phys. Rev. Lett.* **79**, 1289 (1997).
- ⁴⁰R. Golestanian, M. Kardar, and T. Liverpool, *Phys. Rev. Lett.* **82**, 4456 (1999).
- ⁴¹A. Yu. Grosberg, T. T. Nguyen, and B. I. Shklovskii, *Rev. Mod. Phys.* **74**, 329 (2002).
- ⁴²N. Gronbech-Jensen, R. J. Mashl, R. F. Bruinsma, and W. M. Gelbart, *Phys. Rev. Lett.* **78**, 2477 (1997).
- ⁴³Y. Zhang, J. F. Douglas, B. D. Ermi, and E. J. Amis, *J. Chem. Phys.* **115**, 4367 (2001).
- ⁴⁴G. Goerigk, R. Schweins, K. Huber, and M. Ballauff, *Europhys. Lett.* **66**, 331 (2004).
- ⁴⁵R. Schweins, G. Goerigk, and K. Huber, *Eur. Phys. J. E* **21**, 99 (2006).
- ⁴⁶K. A. Narh and A. Keller, *J. Polym. Sci., Part B: Polym. Phys.* **31**, 231 (1993).
- ⁴⁷M. Muthukumar, in *Molecular Basis of Polymer Networks*, Springer Proceedings in Physics, Vol. 42, edited by A. Baumgärtner and C. E. Picot (Springer, New York, 1989), p. 28.