Counterion adsorption theory of dilute polyelectrolyte solutions: Apparent molecular weight, second virial coefficient, and intermolecular structure factor

M. Muthukumar^{a)}

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA

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Polyelectrolyte chains are well known to be strongly correlated even in extremely dilute solutions in the absence of additional strong electrolytes. Such correlations result in severe difficulties in interpreting light scattering measurements in the determination of the molecular weight, radius of gyration, and the second virial coefficient of charged macromolecules at lower ionic strengths from added strong electrolytes. By accounting for charge-regularization of the polyelectrolyte by the counterions, we present a theory of the apparent molecular weight, second virial coefficient, and the intermolecular structure factor in dilute polyelectrolyte solutions in terms of concentrations of the polymer and the added strong electrolyte. The counterion adsorption of the polyelectrolyte chains to differing levels at different concentrations of the strong electrolyte can lead to even an order of magnitude discrepancy in the molecular weight inferred from light scattering measurements. Based on counterion-mediated charge regularization, the second virial coefficient of the polyelectrolyte and the interchain structure factor are derived self-consistently. The effect of the interchain correlations, dominating at lower salt concentrations, on the inference of the radius of gyration and on molecular weight is derived. Conditions for the onset of nonmonotonic scattering wave vector dependence of scattered intensity upon lowering the electrolyte concentration and interpretation of the apparent radius of gyration are derived in terms of the counterion adsorption mechanism. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4736545>]

I. INTRODUCTION

Polyelectrolyte chains dispersed in polar solvents are correlated by electrostatic forces over distances very much larger than their individual sizes in infinitely dilute solutions. Such strong correlations present numerous difficulties in experimentally characterizing isolated polyelectrolyte molecules in terms of their sizes and shapes.^{1–15} Depending on the polarizability of the solution and chemical details of the ionizable groups of the polyelectrolyte chains, a certain number of counterions dissociate from the chains. The extent of counterion release, which in turn depends on the polymer concentration and polymer conformations, and the amount of any added strong electrolyte, dictates the electrostatic correlation length for intra- and interchain interactions and the colligative properties of the solution. In this paper, by accounting for the charge-regularization of the polyelectrolyte by counterion adsorption at varying experimental conditions, we derive expressions for the molecular weight, radius of gyration, second virial coefficient, and intermolecular structure factor to be used in interpreting light scattering experiments on dilute polyelectrolyte solutions. This theory is complementary to the previous theoretical works^{16–28} where the degree of ionization of the polyelectrolyte has been fixed.

Light scattering is one of the most commonly used methods in the determination of the molecular weight, radius of

gyration, and the second virial coefficient of macromolecules in dilute solutions. As embodied in the Zimm plot,^{29–31} the inverse scattering intensity $I^{-1}(q)$, as a function of the scattering wave vector q , of a dilute solution containing macromolecules of uniform molecular weight M in a solvent is given by

$$\frac{1}{I(q)} \sim \frac{Kc_p}{R_\theta} = \begin{cases} \frac{1}{M} \left(1 + \frac{q^2 R_g^2}{3} + \dots \right), & qR_g \ll 1, c_p \rightarrow 0 \\ \frac{1}{M} + B_2 c_p + \dots, & q \rightarrow 0 \end{cases}, \quad (1)$$

where R_g and B_2 are the radius of gyration and the second virial coefficient, respectively, of the polymer and c_p is the monomer concentration. R_θ is the Rayleigh ratio proportional to the scattered intensity and K (defined below) is a factor depending on the c_p -dependence of the refractive index of the solution. Experimentally measured Kc_p/R_θ at small values of q and c_p provide an accurate determination of M , R_g , and B_2 for uncharged macromolecules. Implementation of the above formula for salt-free polyelectrolyte solutions fails terribly. The molecular weight inferred from the Zimm plot can be an order of magnitude smaller than the true value and furthermore it depends on whether the form factor or the osmotic compressibility is used in the extrapolation. The value of R_g^2 as inferred from Eq. (1) can be nonmonotonic as the salt concentration is decreased, first increasing and then decreasing. It can even be negative at low salt concentrations. Under these conditions, a plot of Kc_p/R_θ versus q^2 is nonmonotonic at small values of q . As $q \rightarrow 0$, there is an up-turn in the inverse

^{a)}E-mail: muthu@polysci.umass.edu.

scattered intensity resulting in challenges to interpret the light scattering data.

Some of the difficulties in characterizing polyelectrolyte molecules using light scattering can be traced to wrong usage of theory in recent publications, in contrast with the classic literature six decades ago.^{21,22} Equation (1), derived for a two-component uncharged solution, is not applicable for solutions of polyelectrolytes which are multi-component. A salt-free polyelectrolyte solution must be treated as a three-component system consisting of the charged polymer, counterion, and the solvent even if the scattering contrast of the counterions is negligible, as already recognized by Mysels²¹ and Prins and Hermans²² some time ago. Considering a solution of volume V and refractive index $\tilde{n}$ made of $(r + 1)$ components, each with n_i molecules, Brinkman and Hermans,³² Kirkwood and Goldberg³³ and Stockmayer³⁴ derived the Rayleigh ratio as

$$R_\theta = \frac{2\pi^2 \tilde{n}^2 V k_B T}{\lambda^4} \sum_{i=0}^r \sum_{j=0}^r \left(\frac{\partial \tilde{n}}{\partial n_i} \right)_V \left(\frac{\partial \tilde{n}}{\partial n_j} \right)_V \frac{A^{ij}}{|A|}, \quad (2)$$

where λ is the wavelength of the incident plane-polarized monochromatic light and $i = 0, 1, 2, \dots, r$ denote the solvent, solute number 1, solute number 2, etc. $|A|$ is the determinant of the matrix A whose elements are

$$A_{ij} = \left(\frac{\partial \mu_i}{\partial n_j} \right)_{V, T, n_{k \neq j}}, \quad (3)$$

where μ_i is the chemical potential of the i th component. $k_B T$ is the Boltzmann constant times the absolute temperature. A^{ij} is the cofactor of the matrix A . For a two-component system, Eq. (2) does indeed reduce to Eq. (1),

$$\frac{K c_p}{R_\theta} = \frac{1}{M}, \quad (4)$$

in the limit of $c_p \rightarrow 0$, where K is

$$K = \frac{2\pi^2 \tilde{n}^2}{\lambda^4} \left(\frac{\partial \tilde{n}}{\partial c_p} \right)^2. \quad (5)$$

On the other hand, when a solution consists of n macroions, each with αN ionized groups, $\alpha n N$ counterions and n_+ cations and n_- anions from a strong electrolyte, Prins and Hermans²² showed that Eq. (2) leads to

$$\frac{K c_p}{R_\theta} = \frac{1}{M} \left[1 + \frac{\alpha N}{\left(1 + \frac{2M}{\alpha N} \frac{c_s}{c_p} \right)} \right], \quad (6)$$

where $c_p = nM/V$ and $c_s = n_+/V = n_-/V$. This formula gives the crossover behavior of the apparent molecular weight M_{app} between the salt-free and salty limits,

$$\frac{K c_p}{R_\theta} \equiv \frac{1}{M_{app}} = \begin{cases} \frac{1}{M} (1 + \alpha N), & c_s = 0 \\ \frac{1}{M}, & c_s \gg c_p \end{cases} \quad (7)$$

in contrast to the difficulty associated with the use of Eq. (1). Extensions of the above formula, originally derived for colloidal particles and macroions without considerations of internal conformations, to flexible polyelectrolytes and other structural characteristics such as R_g and the structure factor are yet to be developed.

Although the correct limits of the apparent molecular weight is captured by the above formula, it is based on the assumption that the degree of ionization is fixed at a constant value for all values of c_s . There is a growing body of experimental work,^{35–40} simulations^{41–47} and theory^{48–60} which shows that the degree of ionization of a chain changes as the experimental conditions change. For the present situation, as c_s is increased, the chemical potential of the electrolyte ions that are oppositely charged to the polymer increases resulting in an enhanced adsorption of the counterions on the polymer. As a consequence, the effective degree of ionization of the polymer must be a decreasing function of c_s . In this paper, we extend our previous work⁵⁶ on the charge-regularization of the polymer as c_s is varied by combining polymer conformations and counterion adsorption. Based on the concentrations of the various species in the charge-regulated equilibrium, we implement the Kirkwood-Goldberg-Stockmayer formula (Eq. (2)) and derive expressions for the apparent molecular weight. Using the derived effective degree of ionization, we derive the pair potential between two chains and discuss the effect of intermolecular structure factor in interpreting light scattering data. The nonmonotonicity of $I^{-1}(q)$ with q^2 arising from the intermolecular correlations is addressed within the framework of counterion adsorption. Quantitative results are presented for a few representative examples pertinent to experimental conditions.

The rest of the paper is organized as follows. After defining the model in Sec. II, the theory is presented in Sec. III. Calculated results on the apparent molecular weight, radius of gyration, and second virial coefficient are given in Sec. IV, followed by a concluding section.

II. MODEL

Let a dilute solution of volume V contain n_0 solvent molecules and n polyelectrolyte chains. Each of the polyelectrolyte chains is assumed to have N repeat units, each of monomer length ℓ_0 . In order to consider situations where the polymer chain is synthesized as a random copolymer of ionizable and unionizable repeat units, we define the fraction of ionizable repeat units per chain as q_0 . This is the maximum allowed charge fraction per chain. Even if the polymer chain is a homopolymer made of identical ionizable groups as repeat units, only a fraction of these units are ionized on average. Let m and $(q_0 N - m)$ be the number of unionized and ionized repeat units among a total of $q_0 N$ ionizable groups. The average degree of ionization α is $1 - m/(q_0 N)$. We assume that the total charge from the charged units ($\alpha q_0 N$) is smeared uniformly throughout the chain backbone so that each repeat unit has the charge $\alpha q_0 N e$, where e is the value of the electronic charge. There are $n_c = \alpha q_0 n N$ monovalent counterions in the solution arising from the dissociation of the ionizable groups of the polymer chains. In addition, there are n_+ cations and n_- anions with valencies z_+ and z_- , respectively.

The partition sum Z of the system is written as the product of three factors,

$$Z = Z_1 Z_2 Z_3, \quad (8)$$

where Z_1 is the combinatorial factor arising from the indistinguishability of the molecules or ions belonging to each of the species in the system,

$$Z_1 = \frac{1}{n!n_0!n_c!n_+!n_-!} = \frac{1}{n!n_0! \prod_{\beta=c,+, -} n_\beta!}. \quad (9)$$

The combinatorial factor associated with randomly choosing m repeat units out of q_0N units for adsorbing counterions is

$$Z_2 = \left[\frac{(Nq_0)!}{m!(Nq_0 - m)!} \right]^n. \quad (10)$$

In reality, the process of adsorption of counterions on the polymer is cooperative and not random. However, in the present model, the cooperativity of counterion adsorption is not included.

The third factor Z_3 is due to all other contributions arising from chain conformations and distributions of all species subject to the various potential interactions in the system. The chain connectivity is written in the Edwards path integral representation, where the contour length of a chain is $L = N_k \ell$, where N_k and ℓ are, respectively, the Kuhn number of segments per chain and the Kuhn length. Since each Kuhn segment can be made of several repeat units, we assign z_p as the number of ionizable repeat units per Kuhn segment. Z_3 is modeled as

$$Z_3 = \int \prod_{\beta=1}^n \delta \mathbf{R}_\beta(s_\beta) \times \prod_{\beta'=s, c, +, -} \int \prod_{j=1}^{n'_\beta} d\mathbf{r}_j e^{-\frac{3}{2} \sum_\beta \int_0^L ds_\beta \left(\frac{\partial \mathbf{R}_\beta(s_\beta)}{\partial s_\beta} \right)^2 - U}, \quad (11)$$

where $\int \delta \mathbf{R}_\beta(s_\beta)$ denotes the path integral over the chain conformations with $\mathbf{R}_\beta(s_\beta)$ representing the position vector of s_β th arc length variable along the chain contour. The potential energy U is made of many contributions,

$$U = U_{pp} + U_{ps} + U_{ss} + U_{p,ions} + U_{ions,ions} + U_{ad}. \quad (12)$$

The potential interaction between the polymer segments is taken as

$$U_{pp} = \frac{1}{2} \sum_{\beta=1}^n \sum_{\beta'=1}^n \int_0^L \frac{ds_\beta}{\ell} \int_0^L \frac{ds_{\beta'}}{\ell} \{ w_{pp} \delta[\mathbf{R}_\beta(s_\beta) - \mathbf{R}_{\beta'}(s_{\beta'})] + \frac{\alpha^2 z_p^2 q_0^2 \ell_B}{|\mathbf{R}_\beta(s_\beta) - \mathbf{R}_{\beta'}(s_{\beta'})|} \}. \quad (13)$$

The first term on the right hand side parametrizes the short-range pairwise interaction as a pseudopotential of strength w_{pp} . The second term is the Coulomb interaction where ℓ_B is the Bjerrum length

$$\ell_B = \frac{e^2}{4\pi\epsilon_0\epsilon k_B T}, \quad (14)$$

with ϵ_0 and ϵ being the permittivity of vacuum and the temperature dependent uniform dielectric constant of the solution. The short-ranged interaction between polymer segments and solvent and between solvent molecules are parametrized

with w_{ps} and w_{ss} , respectively as

$$U_{ps} = \sum_{\beta=1}^n \int_0^L \frac{ds_\beta}{\ell} \sum_{j=1}^{n_0} w_{ps} \delta(\mathbf{R}_\beta(s_\beta) - \mathbf{r}_j), \quad (15)$$

and

$$U_{ss} = \frac{1}{2} \sum_{j=1}^{n_0} \sum_{j'=1}^{n_0} w_{ss} \delta(\mathbf{r}_j - \mathbf{r}_{j'}). \quad (16)$$

Similarly the Coulomb interactions between the polymer and ions and between the dissociated ions are taken as

$$U_{p,ions} = \sum_{\beta=1}^n \int_0^L \frac{ds_\beta}{\ell} \sum_{\beta'=c,+, -} \sum_{j_{\beta'}=1}^{n_{\beta'}} \frac{\alpha z_p q_0 z_{\beta'} \ell_B}{|\mathbf{R}_\beta - \mathbf{r}_{j_{\beta'}}|}, \quad (17)$$

and

$$U_{ions,ions} = \frac{1}{2} \sum_{\beta=c,+, -} \sum_{\beta'=c,+, -} \sum_{j_\beta=1}^{n_\beta} \sum_{j_{\beta'}=1}^{n_{\beta'}} \frac{z_\beta z_{\beta'} \ell_B}{|\mathbf{r}_{j_\beta} - \mathbf{r}_{j_{\beta'}}|}. \quad (18)$$

The last term U_{ad} of Eq. (12) represents the adsorption energy of all $(1 - \alpha)q_0nN$ counterions adsorbing to the polymer chains. Each of the ionizable monomers of the polyelectrolyte chains in isolation has an intrinsic ionization equilibrium depending on the specific chemical details of the monomer and the polarizability of the solvent in its immediate vicinity. We treat the ionization equilibrium of an isolated monomer (when it is not a part of the chain) with an intrinsic ionization constant K_i which is taken as a parameter. Since this equilibrium constant is the exponential of the free energy change accompanying the ionization process and the structure of pairwise electrostatic energy is proportional to the Bjerrum length, we write K_i as⁵⁶

$$K_i \equiv e^{-\delta \tilde{\ell}_B}, \quad (19)$$

where the Bjerrum length is made dimensionless with the Kuhn length,

$$\tilde{\ell}_B \equiv \frac{\ell_B}{\ell}. \quad (20)$$

The parameter δ is an equivalent representation of the intrinsic ionization constant K_i ,

$$\delta \tilde{\ell}_B \equiv -2.303 \log K_i \equiv 2.303 p K_i. \quad (21)$$

Using this parameter δ or equivalently the intrinsic pK_i of the ionizable repeat unit, the total adsorption energy due to adsorption of $(1 - \alpha)q_0nN$ counterions is given as⁵⁶

$$U_{ad} = -nNq_0(1 - \alpha)\delta \tilde{\ell}_B. \quad (22)$$

By combining all of the above equations, the Helmholtz free energy F as given by

$$F = -k_B T \ln Z \quad (23)$$

is derived in Sec. III by integrating the various degrees of freedom and making suitable assumptions to allow analytical calculations. It is convenient to define the monomer concentration of the polymer $c = nN/V$ and the concentration of the added monovalent salt $c_s = n_+/V = n_-/V$ in the respective

dimensionless units,

$$\tilde{c} \equiv c\ell_0^3 = \frac{nN\ell_0^3}{V}, \quad \tilde{c}_s \equiv c_s\ell_0^3 = \frac{n_+\ell_0^3}{V} = \frac{n_-\ell_0^3}{V}, \quad (24)$$

where ℓ_0^3 is assumed as the monomer volume.

III. THEORY

Based on the above model, we derive expressions for the Helmholtz free energy, the second virial coefficient of the polyelectrolyte chain, and the interchain structure factor.

A. Helmholtz free energy

Substitution of Eqs. (9)–(12) into Eq. (8) yields

$$Z = \frac{1}{n!n_0!} \left[\frac{(Nq_0)!}{m!(Nq_0 - m)!} \right]^n \int \prod_{\beta=1}^n \delta \mathbf{R}_{\beta}(s_{\beta}) \times \int \prod_i^{n_0} d\mathbf{r}_i e^{-\frac{3}{2} \sum_{\beta=1}^n \int_0^L ds_{\beta} (\frac{\partial \mathbf{R}_{\beta}(s_{\beta})}{\partial s_{\beta}})^2 - U_{pp} - U_{ps} - U_{ss} - U_{ad}} Z_{b,ion}, \quad (25)$$

where $Z_{b,ion}$ is the partial partition sum defined as integrating out all degrees of freedom of all dissociated counterions and electrolyte ions,

$$Z_{b,ion} = \frac{1}{\prod_{\beta=c,+,-} n_{\beta}!} \int \prod_i^{n_c + \sum_{\gamma} n_{\gamma}} d\mathbf{r}_i e^{-U_{p,ions} - U_{ions,ions}}. \quad (26)$$

The index γ represents the cations and anions of the electrolyte. In order to perform the above integral, it is convenient to introduce the collective coordinate for the dissociated ions,⁵²

$$\rho(\mathbf{r}) = \sum_{i=1}^{n_c + \sum_{\gamma} n_{\gamma}} z_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (27)$$

and its Fourier transform

$$\hat{\rho}(\mathbf{k}) = \frac{1}{V} \sum_{i=1}^{n_c + \sum_{\gamma} n_{\gamma}} z_i e^{-i\mathbf{k} \cdot \mathbf{r}}. \quad (28)$$

Assuming that the probability distribution function of $\hat{\rho}(\mathbf{k})$ is Gaussian, obeying the central limit theorem, $Z_{b,ion}$ becomes (see Ref. 52 for details)

$$Z_{b,ion} = \frac{V^{n_c + \sum_{\gamma} n_{\gamma}} e^{\frac{V\kappa^3}{12\pi}}}{n_c! \prod_{\gamma} n_{\gamma}!} \times e^{\frac{a^2 z_p^2 q_0^2}{2} \sum_{\beta=1}^n \int \frac{ds_{\beta}}{\ell} \sum_{\beta'=1}^n \int \frac{ds_{\beta'}}{\ell} \int \frac{d^3 k}{(2\pi)^3} \frac{U_{k,0}^2}{(U_{k,0} + 1/\rho_0)} e^{i\mathbf{k} \cdot [\mathbf{R}_{\beta}(s_{\beta}) - \mathbf{R}_{\beta'}(s_{\beta'})]}}, \quad (29)$$

where

$$U_{k,0} = \frac{4\pi \ell_B}{k^2}, \quad (30)$$

$$\rho_0 = \frac{z_c^2 n_c + \sum_{\gamma} z_{\gamma}^2 n_{\gamma}}{V}, \quad (31)$$

and

$$\kappa^2 = \frac{4\pi \ell_B}{V} \left(z_c^2 n_c + \sum_{\gamma} z_{\gamma}^2 n_{\gamma} \right), \quad (32)$$

with κ^{-1} being the Debye length arising from all dissociated ions.

The familiar Debye-Hückel contribution³¹ of $-V\kappa^3/12\pi$ to the free energy arising from the mean field correlation of all dissociated ions, although not neutral, is apparent in Eq. (29). It is also evident from Eq. (29) that the integration over the degrees of freedom of all dissociated ions results in an attractive component to the inter-segment electrostatic potential energy. This attractive component, in combination with the repulsive inter-segment Coulomb interaction, results in an effective screened Coulomb interaction between the segments. This is seen by substituting Eq. (29) into Eq. (25) with the result⁵²

$$Z = \frac{V^{n_c + \sum_{\gamma} n_{\gamma}} e^{\frac{V\kappa^3}{12\pi}}}{n!n_0!n_c! \prod_{\gamma} n_{\gamma}!} \left[\frac{(Nq_0)!}{m!(Nq_0 - m)!} \right]^n \int \prod_{\beta=1}^n \delta \mathbf{R}_{\beta}(s_{\beta}) \int \prod_{i=1}^{n_0} d\mathbf{r}_i e^{-U_{ps} - U_{ss} - U_{ad}} \times e^{-\frac{3}{2} \sum_{\beta=1}^n \int_0^L ds_{\beta} (\frac{\partial \mathbf{R}_{\beta}(s_{\beta})}{\partial s_{\beta}})^2 - \frac{1}{2} \sum_{\beta=1}^n \int \frac{ds_{\beta}}{\ell} \sum_{\beta'=1}^n \int \frac{ds_{\beta'}}{\ell} \int \frac{d^3 k}{(2\pi)^3} \tilde{U}_k e^{i\mathbf{k} \cdot [\mathbf{R}_{\beta}(s_{\beta}) - \mathbf{R}_{\beta'}(s_{\beta'})]}}, \quad (33)$$

with

$$\tilde{U}_k = w_{pp} + \frac{4\pi \alpha^2 z_p^2 q_0^2 \ell_B}{(k^2 + \kappa^2)}. \quad (34)$$

The two terms on the right hand side are the Fourier transforms of the short-ranged excluded volume interaction and

the screened Coulomb interaction between segments, respectively. The averaging over the dissociated ions generates the net effect of modifying the Coulomb interaction into the screened Coulomb interaction. It must be noted that the averaging of the subunit ionization (Eq. (10)) is different from the averaging of the dissociated ions and is performed at fixed κ .

By writing U_{ps} and U_{ss} in terms of the average concentrations of the polymer and solvent,

$$\int \prod_{i=1}^{n_0} d\mathbf{r}_i e^{-U_{ps}-U_{ss}} \simeq V^{n_0} e^{-V w_{ps} c c_0 - V w_{ss} c_0^2/2} \quad (35)$$

with $c = nN/V$ and $c_0 = n_0/V$. Instead of this crude mean-field approximation for the uncharged part, it is possible to perform better approximations as in our previous work.^{49,52} Since the main focus of the present paper is in the electrostatic aspects, Eq. (35) is sufficient.

Combining Eqs. (23), (33), and (35), we get

$$F = F_s + F_{h0} + F_{sa} + F_{ad} + F_{fl,i} + F_p, \quad (36)$$

where the various contributions to the free energy are defined as follows. The contribution F_s from the translational entropy of solvent, counterions and salt ions is

$$\frac{F_s}{k_B T} = n_0 \ln \tilde{c}_0 + n_c \ln \tilde{n}_c + \sum_{\gamma} n_{\gamma} \ln \tilde{n}_{\gamma} - n_0 - n_c - \sum_{\gamma} n_{\gamma}. \quad (37)$$

Here, the concentrations in the argument of the logarithm are made dimensionless with ℓ_0^3 as in Eq. (24),

$$\tilde{c}_0 = \frac{c_0 \ell_0^3}{V}, \tilde{n}_c = \frac{n_c \ell_0^3}{V}, \tilde{n}_{\gamma} = \frac{n_{\gamma} \ell_0^3}{V}. \quad (38)$$

The enthalpic contribution of polymer-solvent interactions F_{h0} is

$$\frac{F_{h0}}{k_B T} = V w_{ps} c c_0 + \frac{1}{2} V w_{ss} c_0^2. \quad (39)$$

The entropic contribution from the adsorbed counterions F_{sa} is

$$\frac{F_{sa}}{k_B T} = n q_0 N [\alpha \ln \alpha + (1 - \alpha) \ln(1 - \alpha)]. \quad (40)$$

The free energy of adsorption of counterions to the polymer chains F_{ad} is

$$\frac{F_{ad}}{k_B T} = -n q_0 N (1 - \alpha) \delta \tilde{\ell}_B. \quad (41)$$

The free energy contribution from the fluctuations in the distribution of dissociated ions $F_{fl,i}$ is given by the Debye-Hückel term³¹

$$\frac{F_{fl,i}}{k_B T} = -\frac{V \kappa^3}{12\pi}. \quad (42)$$

The free energy F_p of all polymer chains with short-ranged excluded volume interaction and the screened electrostatic interaction between segments is given by

$$e^{-\frac{F_p}{k_B T}} = \frac{1}{n!} \int \prod_{\beta=1}^n \delta \mathbf{R}_{\beta}(s_{\beta}) \exp \left[-\frac{3}{2} \sum_{\beta=1}^n \int_0^L ds_{\beta} \left(\frac{\partial \mathbf{R}_{\beta}(s_{\beta})}{\partial s_{\beta}} \right)^2 \right] \\ \times \exp \left[-\frac{1}{2} \sum_{\beta=1}^n \sum_{\beta'=1}^n \left\{ w_{pp} \delta(\mathbf{R}_{\beta}(s_{\beta}) - \mathbf{R}_{\beta'}(s_{\beta'})) \right. \right. \\ \left. \left. + \alpha^2 q_0^2 z_p^2 \ell_B \frac{e^{-\kappa |\mathbf{R}_{\beta}(s_{\beta}) - \mathbf{R}_{\beta'}(s_{\beta'})|}}{|\mathbf{R}_{\beta}(s_{\beta}) - \mathbf{R}_{\beta'}(s_{\beta'})|} \right\} \right]. \quad (43)$$

If adsorption on the polymer is from counterion of the polymer and another specific counterion from the strong electrolyte, it is in principle necessary to introduce two different values of the parameter δ as the pK_i values for these ions can be different. If we assume that these two kinds of counterions are chemically identical, then F_s of Eq. (37) needs to be replaced by

$$\frac{F_s}{k_B T} = n_0 \ln \tilde{c}_0 + (n_c + n_+) \ln(\tilde{n}_c + \tilde{c}_s) \\ + n_- \ln \tilde{c}_s - (n_c + n_+) - n_-, \quad (44)$$

where we have assumed that the polymer is a polyanion and the counterions are positively charged. Furthermore, if the finite size of the dissociated ions needs to be taken into account, the extended Debye-Hückel form for the electrostatic correlation energy of ions may be used for $F_{fl,i}$,

$$\frac{F_{fl,i}}{k_B T} = -\frac{V}{4\pi a^3} \left[\ln(1 + \kappa a) - \kappa a + \frac{1}{2} \kappa^2 a^2 \right], \quad (45)$$

where a is the diameter of all dissociated ions, taken to be the same. This result is valid even for the non-neutral background of unadsorbed counterions and salt ions.⁵⁵ In the limit of $\kappa a \rightarrow 0$, the above equation reduces to Eq. (35).

Combining Eqs. (36)–(44), the free energy F is a function of the degree of ionization α . Performing the minimization of F with respect to α gives the equilibrium value of α as a function of c and c_s for different values of ℓ_B , q_0 , and N . The resultant F with this value of α is then used to calculate the chemical potentials of the various components from which the theoretical value of the scattered intensity and apparent molar mass follow. Some typical results on these quantities and the radius of gyration are given in Sec. IV.

B. Second virial coefficient

Using the grand canonical ensemble and Mayer's cluster theory of multi-component solutions, the osmotic pressure Π of a dilute salt-free polyelectrolyte solution specified above is given by³¹

$$\frac{\Pi}{k_B T} = c_c + c + S - c_c \frac{\partial S}{\partial c_c} - c \frac{\partial S}{\partial c}, \quad (46)$$

where c_c is the counterion concentration and

$$S = -B_2 c^2 + \frac{\kappa^3}{12\pi} + O(c^{5/2}). \quad (47)$$

The second virial coefficient B_2 appearing in the above equation is

$$B_2 = \frac{1}{2} \int_0^{\infty} [1 - e^{-\frac{U(R)}{k_B T}}] 4\pi R^2 dR, \quad (48)$$

where $U(R)$ is the interchain interaction energy as a function of the separation distance R between the centers of mass of any two chains. With the inter-segment potential given by Eq. (43), $U(R)$ is written as

$$U(R) = U_{exc}(R) + U_{el}(R), \quad (49)$$

with

$$\frac{U_{exc}(R)}{k_B T} = \int_0^L ds_\alpha \int_0^L ds_\beta w_{pp} \delta[\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\beta(s_\beta)] \quad (50)$$

and

$$\frac{U_{el}(R)}{k_B T} = \int_0^L ds_\alpha \int_0^L ds_\beta \alpha^2 q_0^2 z_p^2 \ell_B \frac{e^{-\kappa |\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\beta(s_\beta)|}}{|\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\beta(s_\beta)|}. \quad (51)$$

Here the positions of the monomers s_α and s_β belonging to the α th and β th chains are $\mathbf{R}_\alpha(s_\alpha)$ and $\mathbf{R}_\beta(s_\beta)$ with respect to the centers of mass of the chains. Choosing the origin of the coordinate system as the center of mass of the α th chain, the positions of s_α and s_β are $\mathbf{R}_\alpha(s_\alpha)$ and $\mathbf{R}_\beta(s_\beta) - \mathbf{R}$.

The pair potential U_{exc} between two chains with solely short-range excluded volume interaction was originally calculated by Flory and Krigbaum.^{29,61} Defining the segmental density profile $\rho_p(\mathbf{r})$ of a chain as

$$\rho_p(\mathbf{r}) = \int_0^L ds_\alpha \delta(\mathbf{R}_\alpha(s_\alpha) - \mathbf{r}), \quad (52)$$

U_{exc} follows from Eq. (50) as

$$\frac{U_{exc}(R)}{k_B T} = w_{pp} \int d\mathbf{r} \rho_p^2(\mathbf{r}). \quad (53)$$

Assuming that $\rho_p(\mathbf{r})$ can be approximated by the Gaussian distribution,

$$\rho_p(\mathbf{r}) = N_k \left(\frac{3}{2\pi R_g^2} \right)^{3/2} e^{-\frac{3r^2}{2R_g^2}}, \quad (54)$$

the Flory-Krigbaum potential becomes

$$\frac{U_{exc}(R)}{k_B T} = w_{pp} N_k^2 \left(\frac{3}{4\pi R_g^2} \right)^{3/2} e^{-\frac{3R^2}{4R_g^2}}. \quad (55)$$

We now obtain an expression for $U_{el}(R)$ by invoking the same assumption of Flory and Krigbaum for the segmental density profile, except that R_g appropriately accounts for the intrachain excluded volume and electrostatic interactions as derived in Ref. 56. Using the Fourier transform $\hat{\rho}_p(\mathbf{k})$ of Eq. (52), we get

$$\frac{U_{el}(R)}{k_B T} = \int \frac{d^3k}{(2\pi)^3} \frac{4\pi\alpha^2 q_0^2 z_p^2 \ell_B}{(k^2 + \kappa^2)} e^{-i\mathbf{k}\cdot\mathbf{R}} \hat{\rho}_p(\mathbf{k}) \hat{\rho}_p(-\mathbf{k}). \quad (56)$$

With the assumed Gaussian distribution for $\rho_p(\mathbf{r})$ in Eq. (54),

$$\hat{\rho}_p(\mathbf{k}) = N_k e^{-k^2 R_g^2/6}, \quad (57)$$

the angular integration in Eq. (56) gives

$$\frac{U_{el}(R)}{k_B T} = \frac{2}{\pi} \frac{N^2 \alpha^2 q_0^2 \ell_B}{R} \int_0^\infty dk \frac{k}{(k^2 + \kappa^2)^2} \sin(kR) e^{-k^2 R_g^2/3}, \quad (58)$$

where $N_k z_p$ is taken as N . Performing the integration yields

$$\frac{U_{el}(R)}{k_B T} = \frac{N^2 \alpha^2 q_0^2 \ell_B}{2R} e^{\kappa^2 R_g^2/3} \left\{ e^{-\kappa R} \operatorname{erfc}\left(\frac{\kappa R_g}{\sqrt{3}} - \frac{\sqrt{3}R}{2R_g}\right) - e^{\kappa R} \operatorname{erfc}\left(\frac{\kappa R_g}{\sqrt{3}} + \frac{\sqrt{3}R}{2R_g}\right) \right\}, \quad (59)$$

where erfc is the complementary error function. In the limits of $\kappa = 0$ and $\kappa \rightarrow \infty$, U_{el} becomes

$$\frac{U_{el}(R)}{k_B T} = \begin{cases} \frac{N^2 \alpha^2 q_0^2 \ell_B}{R} \operatorname{erf}\left(\frac{\sqrt{3}R}{2R_g}\right), & \kappa = 0 \\ \frac{4\pi N^2 \alpha^2 q_0^2 \ell_B}{\kappa^2} \left(\frac{3}{4\pi R_g^2}\right)^{3/2} e^{-\frac{3R^2}{4R_g^2}}, & \kappa \rightarrow \infty \end{cases}. \quad (60)$$

As the screened electrostatic interaction becomes short-ranged at higher salt concentrations, $U_{el}(R)$ is the same as the Flory-Krigbaum potential of Eq. (55) with w_{pp} replaced by $4\pi\alpha^2 q_0^2 z_p^2 \ell_B / \kappa^2$. In the $\kappa = 0$ limit, $U_{el}(R)$ essentially decays as $1/R$. For convenience, we define the dimensionless quantities

$$\frac{R}{R_g} \equiv t, \kappa R_g \equiv \kappa^*, \frac{\ell_B}{R_g} \equiv \ell_B^*. \quad (61)$$

In terms of these, $U_{el}(R)$ follows from Eq. (59) as

$$\frac{U_{el}(R)}{k_B T} \equiv \frac{U_{el}^*(t)}{k_B T} \equiv N^2 \alpha^2 q_0^2 \ell_B^* g(t, \kappa^*), \quad (62)$$

where

$$g(t, \kappa^*) = \frac{1}{2t} e^{(\kappa^*)^2/3} \left\{ e^{-\kappa^* t} \operatorname{erfc}\left(\frac{\kappa^*}{\sqrt{3}} - \frac{\sqrt{3}t}{2}\right) - e^{\kappa^* t} \operatorname{erfc}\left(\frac{\kappa^*}{\sqrt{3}} + \frac{\sqrt{3}t}{2}\right) \right\}. \quad (63)$$

Substitution of the above equations in Eq. (48) gives the electrostatic part of the second virial coefficient $B_{2,el}$ as

$$B_{2,el} = \left(\frac{4}{3} \pi R_g^3 \right) \beta (N^2 \alpha^2 q_0^2 \ell_B^*, \kappa^*), \quad (64)$$

where

$$\beta (N^2 \alpha^2 q_0^2 \ell_B^*, \kappa^*) \equiv \frac{3}{2} \int_0^\infty dt t^2 [1 - e^{-\frac{U_{el}^*(t)}{k_B T}}], \quad (65)$$

with $U_{el}^*(t)/k_B T$ given by Eq. (62). The crossover behaviors of $U_{el}(R)$ and salt concentration dependence of $B_{2,el}$ are discussed in Sec. IV.

C. Interchain structure factor

Although the solution considered here is dilute, the chains can be significantly correlated by the electrostatic interaction at lower salt concentrations. Therefore, the interchain structure factor must be accounted for in interpreting light scattering data especially in salt-free solutions. According to the theory of light scattering, the structure factor $S(q)$ is given as²⁹⁻³¹

$$S(\mathbf{q}) = P(\mathbf{q}) \left[1 - \frac{c}{N} v(\mathbf{q}) \right], \quad (66)$$

where $\mathbf{q}$ is the scattering wave vector and the form factor $P(\mathbf{q})$ of a chain is

$$P(\mathbf{q}) = \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N \langle e^{-i\mathbf{q} \cdot \mathbf{R}_{ij}} \rangle, \quad (67)$$

with $\mathbf{R}_{ij}$ being the distance vector between the i th and j th monomers of the chain. In the $\mathbf{q} \rightarrow 0$ limit,

$$P(\mathbf{q}) = 1 - \frac{q^2 R_g^2}{3} + \dots, \quad q R_g \ll 1. \quad (68)$$

Allowing completely random orientations of chains, $v(\mathbf{q})$ of Eq. (66) is given by

$$v(\mathbf{q}) = \int_0^\infty [1 - e^{-U(R)/k_B T}] \frac{\sin(qR)}{qR} 4\pi R^2 dR, \quad (69)$$

with $U(R)$ being the interchain potential.

In the present paper, we are interested in small q limit. Therefore, by expanding $\sin(qR)$, we have

$$v(\mathbf{q}) = v_0 - v_2 q^2 + \dots, \quad (70)$$

where

$$v_0 = 2B_2, \quad (71)$$

in view of Eq. (48), and

$$v_2 = \frac{1}{6} \int_0^\infty [1 - e^{-U(R)/k_B T}] 4\pi R^4 dR. \quad (72)$$

Using the dimensionless variables t , κ^* , and ℓ_B^* , the electrostatic part $v_{2,el}$ of this is written as

$$v_{2,el} = \left(\frac{4}{3} \pi R_g^3 \right) R_g^2 \beta_2 (N^2 \alpha^2 q_0^2 \ell_B^*, \kappa^*), \quad (73)$$

with

$$\beta_2 (N^2 \alpha^2 q_0^2 \ell_B^*, \kappa^*) = \frac{1}{2} \int_0^\infty dt t^4 [1 - e^{-U_{el}^*(t)/k_B T}]. \quad (74)$$

The dependence of $v_{2,el}$ on the salt concentration c_s will be discussed in Sec. IV. Substitution of the above expressions for $P(\mathbf{q})$ and $v(\mathbf{q})$ in Eq. (66) gives

$$S(q) = \left(1 - \frac{c}{N} v_0\right) - q^2 \left[\frac{R_g^2}{3} \left(1 - \frac{c}{N} v_0\right) - \frac{c}{N} v_2 \right] + O(q^4). \quad (75)$$

Use of this result for the structure factor in the expression for the scattered intensity gives

$$\frac{Kc}{R_\theta} = \frac{1}{N_{app}(1 - \frac{c}{N} v_0)} \left\{ 1 + q^2 \left[\frac{R_g^2}{3} - \frac{cv_2}{N(1 - \frac{c}{N} v_0)} \right] + O(q^4) \right\}. \quad (76)$$

The common practice in light scattering experiments is to use the Zimm plot of Kc/R_θ versus q^2 , and obtain the molecular weight and the radius of gyration from the intercept and slope, respectively. When interchain correlations are taken into account, as seen in Eq. (76), there is an additional contribution to the apparent molar mass. In addition, the initial

slope can be negative if

$$\frac{cv_2}{N(1 - \frac{c}{N} v_0)} > \frac{R_g^2}{3}. \quad (77)$$

Under these circumstances, the radius of gyration inferred from the Zimm plot at very small scattering wave vectors would be aberrant from the true radius of gyration. This is due to the contribution of the second term inside the square brackets of Eq. (76). In the limit of large q ($qR_g \gg 1$), $S(q)$ is proportional to $q^{-1/\nu}$, where ν is the size exponent defined through $R_g \sim N^\nu$. Therefore,

$$\frac{Kc}{R_\theta} \sim q^{1/\nu}. \quad q R_g \gg 1. \quad (78)$$

As a result, when Eq. (77) is satisfied, the Zimm plot of Kc/R_θ versus q^2 is nonmonotonic with an initial negative slope at small q , reaching a minimum, and then increasing at large q values. An illustration of this feature will be presented in Sec. IV.

IV. RESULTS AND DISCUSSION

A. Apparent molar mass

Consider a solution consisting of n_0 solvent molecules, n polyelectrolyte chains (each of N monomers and maximum fraction of charged monomers q_0), n_1 monovalent co-ions from the dissociated salt, n_1 monovalent counterions from the dissociated salt, and $\alpha q_0 n N$ counterions from the polyelectrolyte chains. In the notation of Sec. II, each segment now is a monomer and $z_p = 1$. When the counterions from the polymer and the salt are chemically identical, the Helmholtz free energy of Eq. (36) is rewritten as

$$\begin{aligned} \frac{F}{k_B T} = & \sum_{i=0,1} n_i \left[\ln \left(\frac{n_i \ell_0^3}{V} \right) - 1 \right] + n \left[\ln \left(\frac{n \ell_0^3}{V} \right) - 1 \right] \\ & + (n_1 + \alpha q_0 n N) \left[\ln \left(\frac{(n_1 + \alpha q_0 n N) \ell_0^3}{V} \right) - 1 \right] \\ & + q_0 n N [\alpha \ln \alpha + (1 - \alpha) \ln(1 - \alpha)] - q_0 n N (1 - \alpha) \delta \tilde{\ell}_B \\ & + \frac{F_{el}}{k_B T} + \frac{1}{2} w_{ss} \frac{n_0^2}{V} + w_{ps} \frac{N n n_0}{V}, \end{aligned} \quad (79)$$

where $\tilde{\ell}_B \equiv \ell_B / \ell$, and ℓ_0^3 is the monomer volume. $F_{el}/k_B T$ includes the electrostatic excluded volume interactions between the polymer segments, the interchain correlations, and the Debye-Hückel correlations among dissociated ions,

$$\frac{F_{el}}{k_B T} \equiv \frac{F_p}{k_B T} - \frac{V \kappa^3}{12\pi}, \quad (80)$$

with F_p given by Eq. (43) and the inverse Debye length κ given by Eq. (32).

The minimization of the free energy with respect to α gives the optimum value of α at different values of the parameters of the theoretical model. Writing the free energy in terms of the equilibrium value of α thus obtained, the chemical potentials of the polymer component (μ_2) and the salt component (μ_1) are calculated. Taking the derivatives of μ_1 and μ_2 with respect to n_1 and n , we calculate the required factors in obtaining the Rayleigh ratio. The apparent molecular weight from the calculated Rayleigh ratio is then expressed in terms of the concentrations of the polyelectrolyte and salt and the various parameters.

1. Degree of ionization

In the infinitely dilute solutions, where we consider isolated chains, the optimum value of the degree of ionization is obtained by minimizing F with respect to α yielding

$$\ln\left(\frac{\alpha}{1-\alpha}\right) + \ln\left[\frac{(n_1 + \alpha q_0 N n) \ell_0^3}{V}\right] + \delta \tilde{\ell}_B = 0. \quad (81)$$

In obtaining this, we have assumed that $\partial(F_{el}/k_B T)/\partial\alpha$ is negligible in comparison with the other terms in the above equation. Inclusion of $\partial(F_{el}/k_B T)/\partial\alpha$ requires numerical work and our previous numerical work⁵⁶ has shown that this term can be safely ignored as long as the chain is not near any drastic conformational change such as the coil-globule transition. In terms of the dimensionless polymer concentration $\tilde{c} \equiv N n \ell_0^3 / V = c \ell_0^3$ and the salt concentration $\tilde{c}_s \equiv n_1 \ell_0^3 / V = c_s \ell_0^3$, the above equation leads to

$$\frac{\alpha(\tilde{c}_s + \alpha q_0 \tilde{c})}{(1-\alpha)} = K_i, \quad (82)$$

where K_i is defined in Eq. (19). The physically allowed value of α follows from the above quadratic equation as

$$\alpha = \frac{(\tilde{c}_s + K_i)}{2q_0\tilde{c}} \left(-1 + \sqrt{1 + \frac{4q_0\tilde{c}K_i}{(\tilde{c}_s + K_i)^2}} \right). \quad (83)$$

In the limit of $\tilde{c} \rightarrow 0$,

$$\alpha = \frac{K_i}{(\tilde{c}_s + K_i)} \left[1 - \frac{q_0\tilde{c}K_i}{(\tilde{c}_s + K_i)^2} + \dots \right], \quad (84)$$

and additionally for $\tilde{c}_s \rightarrow 0$,

$$\alpha = 1 - \frac{q_0\tilde{c}}{K_i} + \dots, \quad \tilde{c} \rightarrow 0, \tilde{c}_s/K_i \rightarrow 0. \quad (85)$$

In the limit of $\tilde{c}_s \rightarrow \infty$, Eq. (84) gives

$$\alpha = \frac{K_i}{\tilde{c}_s} + \dots, \quad \tilde{c} \rightarrow 0, K_i/\tilde{c}_s \rightarrow 0. \quad (86)$$

Therefore, the degree of ionization changes from unity at salt-free conditions to a small value at higher salt concentrations varying inversely with $\tilde{c}_s$. This behavior is illustrated in Fig. 1(a), where α is plotted against $\tilde{c}_s$ for $K_i = e^{-10}$, $q_0 = 0.2$, and $\tilde{c} = 10^{-7}$. The choice of the parameters corresponds to the Coulomb strength parameter $\tilde{\ell}_B = 3$ (corresponding roughly to the case of flexible polyelectrolytes such as sodium(polystyrene sulfonate) in aqueous solutions at room temperature) and the dielectric mismatch parameter

FIG. 1. (a) Plot of α versus $\tilde{c}_s$ for $q_0 = 0.2$, $K_i = e^{-10}$, and $\tilde{c} = 10^{-7}$. (b) Plot of α versus $\tilde{c}$ for $q_0 = 0.2$, $K_i = e^{-10}$, and $\tilde{c}_s = 10^{-7}$.

$\delta = 3.33$. This implies that the value of the intrinsic pK_i parameter is 4.343. The value of q_0 may be identified with the degree of quaternization of poly(vinyl pyridinium)-like polyelectrolytes. It is seen from Fig. 1(a) that the effective degree of ionization decreases as the salt concentration is increased. At higher salt concentrations in the solution, the chemical potential of the adsorbing ions is higher and as a result the adsorbed number of counterions is higher. Therefore the degree of ionization is lower at higher salt concentrations. The extent of this decrease in α as a function of c_s depends additionally on K_i , $\tilde{\ell}_B$, and c , as discussed in Ref. 56. While the dependence on the salt concentration is significant, the dependence on the polymer concentration is weak. A typical result is shown in Fig. 1(b) for $\tilde{c}_s = 10^{-7}$, $K_i = e^{-10}$, and $q_0 = 0.2$. It is clear that α changes only weakly with an increase in polymer concentration in contrast to the dependence on salt concentration. Figs. 1(a) and 1(b) give the typical crossover behaviors for the dependence of the degree of ionization between the limits of Eqs. (85) and (86). For the values of the variables considered here the results of α calculated approximately, but analytically, match well with the full numerical results of Ref. 56.

2. Apparent degree of polymerization

For the present situation, the Rayleigh ratio given by Eq. (2) becomes

$$R_\theta = \frac{2\pi^2 \tilde{n}^2 V}{\lambda^4} \left(\frac{\partial \tilde{n}}{\partial n} \right)_V \times \frac{\left(\frac{\partial \mu_1 / k_B T}{\partial n_1} \right)}{\left[\left(\frac{\partial \mu_1 / k_B T}{\partial n_1} \right) \left(\frac{\partial \mu_2 / k_B T}{\partial n} \right) - \left(\frac{\partial \mu_1 / k_B T}{\partial n} \right) \left(\frac{\partial \mu_2 / k_B T}{\partial n_1} \right) \right]}, \quad (87)$$

where μ_1 and μ_2 follow from Eq. (79) as

$$\frac{\mu_1}{k_B T} = \ln \tilde{c}_s + \ln(\tilde{c}_s + \alpha q_0 \tilde{c}), \quad (88)$$

and

$$\frac{\mu_2}{k_B T} = \ln \left(\frac{\tilde{c}}{N} \right) + \alpha q_0 N \ln(\tilde{c}_s + \alpha q_0 \tilde{c}) + q_0 N [\alpha \ln \alpha + (1 - \alpha) \ln(1 - \alpha) - (1 - \alpha) \delta \tilde{\ell}_B]. \quad (89)$$

Combining Eqs. (87)–(89), along with some tedious algebra (due to the dependence of α on $\tilde{c}$ and $\tilde{c}_s$ through Eq. (83)), we get the Rayleigh ratio R_θ . Further defining Kc/R_θ (with K defined by Eq. (5)) as the reciprocal of the apparent degree of polymerization N_{app} (proportional to the apparent molecular weight), we get N_{app} as

$$\frac{Kc}{R_\theta} \equiv \frac{1}{N_{app}} = \frac{1}{N} \left\{ 1 + \frac{x q_0 \alpha N}{\left[1 + \frac{(1+x) \tilde{c}_s}{q_0 \alpha \tilde{c}} \right]} \right\}, \quad (90)$$

where

$$\alpha = \frac{(\tilde{c}_s + K_i)}{2q_0 \tilde{c}} (-1 + s), \quad (91)$$

$$x = 1 + q_0 \tilde{c} \left[\frac{(-1 + s)}{2q_0 \tilde{c}} - \frac{2K_i}{s(\tilde{c}_s + K_i)^2} \right] \quad (92)$$

with

$$s \equiv \sqrt{1 + \frac{4q_0 \tilde{c} K_i}{(\tilde{c}_s + K_i)^2}}. \quad (93)$$

Before presenting the crossover behavior of N_{app} in terms of c and c_s , we look at the limits of salt-free and salty conditions. In the salt-free case, Eqs. (90)–(93) give

$$\frac{1}{N_{app}} = \frac{1}{N} + \frac{q_0}{\sqrt{1 + \frac{4q_0 \tilde{c}}{K_i}}}, \quad \tilde{c}_s = 0. \quad (94)$$

In the limit of $\tilde{c} \rightarrow 0$, this reduces to

$$\frac{1}{N_{app}} = \frac{1}{N} [(1 + q_0 N) + O(c)], \quad \tilde{c}_s = 0, c \rightarrow 0. \quad (95)$$

Thus the inverse of the apparent degree of polymerization is the maximum fraction of charge per chain in the salt-free limit for long enough chains,

$$\frac{1}{N_{app}} \rightarrow q_0, \quad c_s = 0, c \rightarrow 0, q_0 N \gg 1. \quad (96)$$

Thus, N_{app} can be significantly smaller than N in salt-free conditions. On the other hand, for large salt concentrations,

the second term of Eq. (90), by decreasing as $1/\sqrt{c_s}$, becomes negligible in comparison with unity so that the apparent degree of polymerization approaches the true degree of polymerization,

$$\frac{1}{N_{app}} = \frac{1}{N} + O(c), \quad \frac{\tilde{c}}{\tilde{c}_s} \rightarrow 0. \quad (97)$$

Thus the true molecular weight is recovered in the high-salt regime. The crossover behavior of N_{app} between the limits given by the above two equations follows from Eq. (90) as

$$\left(\frac{1}{N_{app}} - \frac{1}{N} \right) = \frac{x q_0 \alpha}{\left[1 + \frac{(1+x) \tilde{c}_s}{q_0 \alpha \tilde{c}} \right]}. \quad (98)$$

The deviation in the inverse of the molecular weight $\Delta(1/N)$ as defined by the left hand side of the above equation is plotted against the salt concentration in Fig. 2. As discussed above, the deviation vanishes at high salt concentrations and is the maximum in the zero salt limit. It must be noted that the crossover behavior given by Eq. (90) based on the counterion adsorption model of self-regulating polymer charge is qualitatively similar to that given by Eq. (6) based on fixed degree of ionization at all salt concentrations. However, there are significant differences in the quantitative nature of the crossover. While the result from Eq. (6) is independent of q_0 at zero salt, this asymptotic value is determined by q_0 in our present theory, as given by Eq. (94). In Fig. 2, this effect is illustrated for different values of q_0 , by fixing the ionization equilibrium constant K_i to be e^{-9} . Here the monomer concentration is kept at $c = 10^{-5}$ M. The salt concentration is expressed in molarity. The curves from the top to bottom correspond to $q_0 = 1.0, 0.5$, and 0.2 . At $c_s = 0$, $\Delta(1/N)$ approaches the asymptotic value given by Eq. (94). Basically, $1/N_{app}$ approaches $1/N + q_0$. As the salt concentration increases, the deviation is reduced in a cooperative manner due to the charge-regularization of the polymer, to eventually become negligible. Lower levels of salt concentration are needed to get rid off the deviation in $1/N$ for lower values of the maximum charge fraction q_0 .

The q_0 -dependence of $\Delta(1/N)$ for $c_s = 0$ can be absorbed by normalizing the deviation in $1/N$ in accordance with

FIG. 2. Plot of $\left(\frac{1}{N_{app}} - \frac{1}{N} \right)$ versus c_s (in molarity) for $c = 10^{-5}$ M and $K_i = e^{-9}$. The values of maximum charge fraction q_0 are 1.0, 0.5, and 0.2, respectively, from top curve to the bottom curve.

FIG. 3. Plot of $(\frac{1}{N_{app}} - \frac{1}{N})\sqrt{1+4q_0\tilde{c}/K_i}/q_0$ versus $t \equiv \tilde{c}_s/\tilde{c}$. (a) $q_0 = 1.0, 0.5, 0.2$, and 0.05 , respectively, from the top curve to the bottom curve for $k \equiv K_i/\tilde{c} = 10^3$. (b) $q_0 = 1.0$ and $k \equiv K_i/\tilde{c} = 10^3$ (top curve) and 1 (bottom curve).

Eq. (94). Defining ϕ as

$$\phi = \left(\frac{1}{N_{app}} - \frac{1}{N} \right) \frac{\sqrt{1+4q_0\tilde{c}/K_i}}{q_0}, \quad (99)$$

the deviation is plotted in Fig. 3(a) against $\tilde{c}_s/\tilde{c}$ for different values of q_0 . Here, $K_i/\tilde{c}$ is taken as 10^3 , which is a reasonable value corresponding to $\tilde{c} \sim 10^{-7}$ and $K_i \sim 10^{-4}$. As seen from Fig. 3(a), the recovery of the correct molecular weight can be achieved at lower salt concentrations for lower maximum charge fraction of the polyelectrolyte. The effect of pK_i on the deviation in $1/N$ is illustrated in Fig. 3(b) for $q_0 = 1.0$. The top and bottom curves correspond to $K_i/\tilde{c} = 10^3$ and 1 , respectively. By shifting down the pK_i by two units, the deviation becomes substantially smaller for moderate salt concentrations, as seen in Fig. 3(b).

B. Radius of gyration

The effect of counterion adsorption on the dependence of the radius of gyration on the salt concentration has already been addressed in Ref. 56. Here, we briefly note the key result. The expansion factor for the mean square end-to-end distance

$\tilde{\ell}_1$ is given by

$$\tilde{\ell}_1^{5/2} - \tilde{\ell}_1^{3/2} = \frac{4}{3} \left(\frac{3}{2\pi} \right)^{3/2} w_p p \sqrt{N} + \frac{4}{3} \sqrt{\frac{6}{\pi}} \alpha^2 \tilde{\ell}_B \tilde{\ell}_1 N^{3/2} \Theta(a), \quad (100)$$

where $\Theta(a)$ is

$$\Theta(a) = \frac{\sqrt{\pi}}{2a^{5/2}} \left[(a^2 - 4a + 6)e^a \operatorname{erfc}(\sqrt{a}) - 6 - 2a + 12\sqrt{\frac{a}{\pi}} \right], \quad (101)$$

with

$$a = \frac{\tilde{\kappa}^2 \tilde{\ell}_1 N}{6}, \quad (102)$$

and

$$\tilde{\kappa}^2 = 4\pi \tilde{\ell}_B (\alpha \tilde{c} + 2\tilde{c}_s). \quad (103)$$

Here, we have taken $z_p = 1$, $q_0 = 1$, and $N_k = N$ for simplicity. Within the approximation of uniform swelling of the polyelectrolyte chain, the average radius of gyration is given by

$$\frac{R_g}{\ell} \equiv \tilde{R}_g = \sqrt{\frac{N \tilde{\ell}_1}{6}}. \quad (104)$$

By substituting α from Eq. (83) into the above equations, $\tilde{\ell}_1$ and $\tilde{R}_g$ are calculated as functions of K_i , $\tilde{\ell}_B$, w , c , and c_s . Although we have used an analytically tractable approximation for α in the above equations, the present scheme gives results in excellent agreement with the numerical results of Ref. 56 by reproducing Figs. 4(a) and 4(b) of Ref. 56. As typical examples, for $N = 1000$, $\tilde{\ell}_B = 3$, $\delta = 3.5$, $w = 0$, $\tilde{c} = 0.0005$, the values of $\tilde{R}_g$ are 60.18, 17.9, and 13.08, respectively, at $\tilde{c}_s = 10^{-5}$, 10^{-3} , and 0.005 . These values are higher than the Gaussian chain value of $\tilde{R}_{g\theta} = 12.91$.

C. Interchain pair potential

The interchain pair potential is calculated from Eqs. (59) and (62). For $N = 1000$, $\tilde{\ell}_B = 3$, $\delta = 3.5$, $w = 0$, $\tilde{c} = 0.0005$, the function $g(t, \kappa^*)$ is plotted in Fig. 4 against

FIG. 4. Interchain distance dependence of the reduced pair potential for different values of κR_g for $N = 1000$, $\tilde{\ell}_B = 3$, $\delta = 3.5$, $w = 0$, and $\tilde{c} = 0.0005$.

FIG. 5. Dependence of the pair potential on the interchain distance for $N = 1000$, $\ell_B = 3$, $\delta = 3.5$, $w = 0$, and $\tilde{c} = 0.0005$. (a) $\tilde{c}_s = 10^{-5}$ and (b) $\tilde{c}_s = 0.005$.

$t = R/R_g$ for different values of κ^* . It is a decreasing function of the distance R between the centers of mass of the two chains extending up to $R \sim 3R_g$. As the salt concentration increases, the function g decreases as expected due to enhanced electrostatic screening between the chains. However, care must be exercised in interpreting the curves for the three different values of κ^* . For a given polymer concentration, salt concentration, and choices of the parameters K_i , ℓ_B , N , and q_0 , α is first calculated. This is then used in the calculations of κ and R_g . Thus for a given set of parameters, there is a unique combination of α , κ , and R_g . For example, $\kappa^* = 4.0501$, 4.9225 , and 8.0311 (the curves in Fig. 4) correspond to $\tilde{c}_s = 10^{-5}$, 10^{-3} , and 0.005 , respectively, with the corresponding values of $\tilde{R}_g$ being 60.18 , 17.9 , and 13.08 . Therefore, for each curve in Fig. 4, there is one unique value of R_g . The explicit result of the pair potential is given directly by Eq. (59). Representative results are given in Figs. 5(a) and 5(b), for $\tilde{c}_s = 10^{-5}$ and 0.005 (for the same values of the other parameters mentioned above for constructing Fig. 4). In the low salt concentration limit, the pair potential drops from about $140k_B T$ to zero at about the interchain distance comparable to three times the radius of gyration. In the case of higher salt concentration $\tilde{c}_s = 0.005$, $U(R)$ is only a fraction of $k_B T$ when the chains are too close and then it falls off to zero at about three times the radius of gyration.

FIG. 6. Dependence of β and β_2 on salt concentration for $N = 1000$, $\ell_B = 3$, $\delta = 3.5$, $w = 0$, and $\tilde{c} = 0.0005$.

D. Second virial coefficient and structure factor

The ratio of the second virial coefficient B_2 to the volume of the chain $4\pi R_g^3/3$ is β given by Eq. (65). Similarly, the coefficient of the quadratic term v_2 involved in the interchain structure factor is written as a product of $4\pi R_g^5/3$ and β_2 (Eq. (74)). The coefficients β and β_2 are evaluated by the above described procedure. For each set of parameters (N , ℓ_B , K_i , q_0 , w , c , and c_s), there is a unique set of values for α , κ , R_g , B_2 , and v_2 . As an example, for $N = 1000$, $\ell_B = 3$, $\delta = 3.5$, $w = 0$, and $\tilde{c} = 0.0005$, the calculated values of β and β_2 are presented in Fig. 6 as functions of the salt concentration $\tilde{c}_s$. By factoring out the chain volume (which in turn depends on the salt concentration) in the second virial coefficient, the coefficient β does not diverge at low salt concentrations. Specifically, for the above chosen values of the parameters, values of β are 13.40 , 10.51 , 3.65 , and 0.02 at $\tilde{c}_s = 10^{-5}$, 10^{-4} , 10^{-3} , and 10^{-2} , respectively. The corresponding values of β_2 are 26.00 , 17.58 , 3.74 , and 0.01 . It is to be noted that β_2 is larger than β at lower salt concentrations below $\tilde{c}_s \sim 0.001$ and this trend is reversed at higher salt concentrations. This behavior contributes to the nonmonotonic behavior of the scattered intensity with q^2 , as discussed below. It is to be noted that the above results pertain only to the electrostatic part of the second virial coefficient (since we have taken $w_{pp} = 0$). The contribution from the short-range excluded volume effect can be easily calculated by repeating the above steps. Also, the second virial coefficient terms involving small ions are assumed to be negligible in comparison with that for the polyelectrolyte chain.

E. Apparent radius of gyration

The radius of gyration of the macromolecule is obtained from the initial slope in the plots of Kc/R_θ versus q^2 . Due to contributions from the interchain correlations, the experimentally extracted radius of gyration from such plots can be quite different from the true radius of gyration. Defining the coefficient of the q^2 term inside the braces of Eq. (76) as $R_{g,app}^2/3$,

FIG. 7. Discrepancy between the true radius of gyration and the apparent radius of gyration as measured from the initial slopes of Kc/R_θ vs. q^2 plots. At very low salt concentrations, the initial slopes can be negative ($N = 1000$, $\bar{\ell}_B = 3$, $\delta = 3.5$, $w = 0$, and $\tilde{c} = 0.0005$).

we have

$$R_{g,app}^2 = R_g^2 - \frac{3cv_2}{N(1 - \frac{cv_0}{N})}. \quad (105)$$

Substitution of Eq. (73) in the above equation gives the deviation between the apparent radius of gyration and the true radius of gyration to the leading order in polymer concentration as

$$R_{g,app}^2 = R_g^2 \left[1 - \frac{4\pi\tilde{c}}{N} \beta_2 R_g^3 + \dots \right]. \quad (106)$$

Since R_g increases as the salt concentration is lowered, the contribution from the interchain correlations becomes substantial. This contribution reduces the value of the apparent radius of gyration in comparison with the true radius of gyration. It is to be noted that the correction term is proportional to the ratio of c to the polymer overlap concentration, although the coefficient β_2 is dependent on the ionization equilibrium. A comparison of true R_g^2 and the apparent $R_{g,app}^2$ is given in Fig. 7 as a function of the salt concentration for $N = 1000$, $\bar{\ell}_B = 3$, $\delta = 3.5$, $w = 0$, and $\tilde{c} = 0.0005$. The deviation becomes quite severe at lower salt concentrations, leading to the nonmonotonic variation of $R_{g,app}^2$ as the salt concentration is reduced. In fact, $R_{g,app}^2$ can become negative for $\tilde{c}_s$ below 5×10^{-4} (for the present set of parameter values), corresponding to the onset of negative slope at small q^2 in the plots of Kc/R_θ versus q^2 . This is a general phenomenon as long as the condition of Eq. (77) is satisfied.

V. CONCLUSIONS

A theory for analyzing light scattering data in dilute polyelectrolyte solutions is presented based on the varying extent of counterion adsorption on the polyelectrolyte chains as the experimental conditions are changed. For a given system of solvent, temperature, polymer concentration, polymer length, and monovalent salt concentration, the theory is derived with the supposition of one nonuniversal parameter, namely the intrinsic ionization constant K_i for the isolated ion-pair of the

ionizing monomeric group in the particular solvent. By accounting for the ionization equilibrium between the ionizing monomeric group and its counterion, we have derived the average degree of ionization for the chain, Debye length, radius of gyration, second virial coefficient, interchain structure factor, and the initial slope of plots of inverse scattering intensity versus square of the scattering wave vector. As the degree of ionization is allowed to self-regulate, the derived quantities form a unique set of inter-dependent properties in terms of the parameter K_i . This theory is different from the other approaches in the literature for interpreting light scattering data, all based on the assumption that the degree of ionization is fixed at all experimental conditions.

The main results of the theoretical predictions are as follows. By combining the present counterion adsorption theory with the theory of light scattering from multi-component solutions by Kirkwood-Goldberg-Stockmayer, we have derived expressions for the inverse scattering intensity at zero scattering angles. The apparent molecular weight extrapolated from the experimental data in this limit is asymptotically the reciprocal of the maximum charge fraction of the polymer chain in salt-free conditions and it approaches the true molecular weight as the salt concentration is increased. The degree of ionization decreases with an increase in salt concentration, and as a result the radius of gyration decreases monotonically with salt concentration. The decrease of radius of gyration with an increase in salt concentration and the recovery of true molecular weight only at high salt concentrations are in agreement with light scattering data.^{1,2,4} However, quantitative details of deviations of the extrapolated molecular weight from the true molecular weight at lower salt concentrations are yet to be established to enable comparison with the present theoretical predictions.

We have derived an approximate analytical formula for the interchain pair potential in terms of the self-regulating degree of ionization and radius of gyration, as a function of the distance between the centers of mass of the chains. The potential becomes insignificant at distances of about three times the radius of gyration. The potential at shorter interchain distances is higher at lower salt concentrations. The second virial coefficient of the chain, calculated from the derived interchain pair potential, is proportional to the chain volume, with the coefficient increasing only modestly with lowering of the salt concentration. The avoidance of divergence of the second virial coefficient at low salt concentrations is due to the finite amount of counterions and dissociated ions in the system.

We have addressed the role of interchain structure factor in dilute solutions in interpreting the light scattering data. The coefficient of q^2 in the interchain structure factor affects the apparent value of the radius of gyration extracted from the plots of Kc/R_θ versus q^2 . In the limit of very low polymer concentrations, we have provided an expression for the apparent radius of gyration. As the salt concentration is reduced, the apparent radius of gyration $R_{g,app}$ deviates significantly from its true value. $R_{g,app}^2$ exhibits a nonmonotonic feature, first increasing and then decreasing, as the salt concentration is continuously decreased. On the other hand, the true R_g increases continuously. In addition, $R_{g,app}^2$ can become even negative at lower salt concentrations corresponding to

a negative initial slope in the plots of Kc/R_θ versus q^2 . The condition for the onset of this negative slope is derived. Under these circumstances, the scattered intensity exhibits a peak at an intermediate scattering wave vector. In the present theory, the onset of such scattering peak is not due to the average distance between chains in dilute solutions, but due to the self-regulating degree of ionization and interchain interactions. The occurrence of the peak in the scattered intensity at intermediate scattering wave vectors is a well established experimental feature of polyelectrolyte solutions at low salt concentrations. However, simultaneous analysis of the radius of gyration, apparent molecular weight, second virial coefficient, and the scattering peak position is not yet carried out in experiments. It is hoped that the present theory would facilitate such an analysis by comparing the predictions with experimental data.

Another important complication in the light scattering measurements from dilute solutions of similarly charged polyelectrolyte chains is the common appearance of the slow mode representing the presence of large yet unknown structures. This issue is not addressed in the present work.

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