

## Invariance of density correlations with charge density in polyelectrolyte solutions

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We present a theory for the equilibrium structure of polyelectrolyte solutions. A simple and general optimization method is introduced that enables theories such as the random phase approximation to handle the strong repulsive forces present in such systems. Quantitative comparison is made with data from recent neutron-scattering experiments of randomly charged, hydrophilic polymers in salt-free, semidilute solution at various charge densities. We show that the invariance observed at high charge fraction may be the result of polymer-polymer correlations, rather than the conventional explanations involving counterion condensation.

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Polyelectrolytes are polymers with ionizable groups that dissociate in polar solvent leaving ions bound to the chain and counterions free in solution [1]. The study of polyelectrolytes has traditionally been driven by their omnipresence in living things [2], but there has been rapidly growing use of and interest in synthetic ones for technological applications [3].

In this article we focus on the general properties of polyelectrolytes and consider some recent intriguing experiments of Nishida, Kaji, and Kanaya (NKK) [4], and Essafi, Lafuma, and Williams (ELW) [5]. Counterion condensation [6] is commonly invoked as the cause of the invariance at high charge density observed in these experiments. While there is some ambiguity in the literature about what precisely is counterion condensation, it is generally regarded that the mechanism is not captured in any theory in which ion-counterion correlations are included only at the level of Debye-Hückel theory [6,7]. However, we show here that Debye-Hückel modeling of ion-counterion correlations, when accompanied by adequate treatment of polymer-polymer correlations, is sufficient to produce an invariance at high charge density.

There are few theories that can handle the strong repulsions and attractions present in polyelectrolyte solutions [8]. Further, there is currently no theory that provides reliable predictions for liquid structure in the semidilute regime—which is the region of greatest experimental interest. The theory of Laria, Wu, and Chandler [9] has been applied to examine density correlations there as a function of number density [10], but performs poorly at large, experimentally relevant, interaction energies and charge densities [11]. The theory of Donley, Rajasekaran, and Liu (DRL) seems to perform properly at large interaction energies and charge densities, but presently only for purely repulsive systems [12]. Despite its simple form, the random phase approximation

(RPA) can give reasonable predictions for the free energy of polyelectrolyte solutions [13]. Here, we propose that theories such as the RPA can be rendered adequate for density correlations given a suitable reinterpretation of the interaction potential [14]. Let

$$S_{MkM'k'}(r) = \langle [\hat{\rho}_{Mk}(\mathbf{r}) - \rho_{Mk}] [\hat{\rho}_{M'k'}(\mathbf{0}) - \rho_{M'k'}] \rangle \quad (1)$$

denote the density-density correlation function between a  $k$ -type monomer (or site) on a molecule of type  $M$  and a  $k'$ -type monomer on a molecule of type  $M'$  a distance  $r = |\mathbf{r}|$  apart. Here,  $\hat{\rho}_{Mk}(\mathbf{r})$  is the microscopic density of  $k$ -type monomers on molecules of type  $M$  at position  $\mathbf{r}$  with average value  $\rho_{Mk}$ . The brackets denote a thermodynamic average. The Fourier transform of  $S_{MkM'k'}(r)$  is the partial structure factor and links the theory to scattering experiments. The correlation function can be separated into *intra*- and *intermolecular* contributions,  $\Omega_{Mkk'}(r)$  and  $H_{MkM'k'}(r)$ , respectively,

$$S_{MkM'k'}(r) = \Omega_{Mkk'}(r) \delta_{MM'} + H_{MkM'k'}(r), \quad (2)$$

where  $\delta_{MM'}$  is the Kronecker delta. In this work, the molecular structure function  $\Omega_{Mkk'}(r)$  is assumed to be known. The intermolecular correlation function is  $H_{MkM'k'}(r) = \rho_{Mk} \rho_{M'k'} [g_{MkM'k'}(r) - 1]$ , where  $g_{MkM'k'}(r)$  is the radial distribution function. Thus, to compare with experiment we need a form for this function in terms of the potentials and molecular structures. Consider for simplicity a system where all the interactions can be decomposed as pair potentials  $u_{MkM'k'}(r)$  between sites. Here, we take these potentials to be hard core for distances  $r$  less than some range  $\sigma_{MkM'k'}$ , and Coulombic outside. Consider also a class of theories for which  $g_{MkM'k'}(r)$  is a function only of the interactions  $\{u\}$  and the total molecular structure functions  $\{\Omega\}$ . Theories in this class include the RPA and possible higher loop improvements, and the polymer version [15] of the theory of Chandler, Silbey, and Ladanyi [16]. One significant failure of theories such as the RPA is that they predict a negative  $g_{MkM'k'}(r)$  for short distances if the interaction  $u_{MkM'k'}(r)$  is strongly repulsive, even though the radial distribution function is intrinsically non-negative. This shortcoming is thought to be one reason that RPA underestimates the

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strength of the dependence of the structure factor peak position  $q_{\max}$  with polymer monomer number density  $\rho_m$  in the semidilute regime.

For short-range repulsive, e.g., hard-core, potentials one remedy to this deficiency was proposed by Andersen and Chandler (AC) [14]. Their idea was to replace the true potential  $u$  by an effective “optimized” one,  $\tilde{u}_{MkM'k'}(r)$ . For distances  $r < \sigma_{MkM'k'}$ ,  $\tilde{u}_{MkM'k'}(r)$  is selected so that the hard-core condition is satisfied, i.e.,  $g_{MkM'k'}(r) = 0$ . Outside the core,  $\tilde{u}_{MkM'k'}(r)$  can be set equal to the original potential  $u$  which is long ranged and presumably weak. In this way, higher-order diagrams neglected in the theory are summed in an approximate manner to enforce the core condition. When applied to the RPA, this optimization scheme is a generalization of the Mean Spherical Approximation (MSA) closure of the Ornstein-Zernike equation [17] and a closely related scheme has been shown to be diagrammatically proper for Chandler-Silbey-Ladanyi (CSL) theory [15]. This optimized RPA (ORPA), usually with long-range potentials absent, is more popularly known as Reference Interaction Site Model (RISM) for small molecules [18] and Polymer RISM (PRISM) for polymers [19].

Unfortunately this AC optimization is not very useful for polyelectrolytes. One reason is that the contact energy between ion and counterion seems to be less important than the interaction energy of the counterion with the whole chain. Hence, enforcing the hard-core behavior between opposite charges matters less than modeling correctly the chain structure, e.g., determining the bond length,  $b$ . A more important reason is that the repulsion between like-charged polymers is usually very large. This causes the radial distribution function to be effectively zero out to a distance that scales with the Debye-Hückel screening length with density in the semidilute regime, which is usually much larger than the hard-core distance [10,12,20]. Hence, enforcing the core condition produces little improvement in the theory for long polyelectrolytes.

The alternative scheme we propose here is to optimize the range of the pseudo-hard-core portion of  $\tilde{u}$ , and not just its amplitude. By this we mean that if  $g(r)$  is nearly zero out to some distance, then it makes little difference whether this exclusion zone is caused by a hard-core potential or a Coulombic one. This effective hard-core diameter  $\sigma_{MkM'k'}^{eff}$  is determined by requiring that  $g_{MkM'k'}(r)$  be non-negative everywhere (not just zero inside the core). The closure to the theory then is

$$g_{MkM'k'}(r) = 0, \quad r < \sigma_{MkM'k'}^{eff},$$

$$\tilde{u}_{MkM'k'}(r) = u_{MkM'k'}(r), \quad r > \sigma_{MkM'k'}^{eff}, \quad (3)$$

and the range  $\sigma_{MkM'k'}^{eff}$  of the effective hard-core interaction is chosen to have the smallest value such that  $g_{MkM'k'}(r) > 0$  for  $r > \sigma_{MkM'k'}^{eff}$  subject to the constraint that  $\sigma_{MkM'k'}^{eff} \geq \sigma_{MkM'k'}$ . With guesses for the  $\sigma_{MkM'k'}^{eff}$ 's, one can solve the RPA (or a similar theory) numerically in a manner very similar to what is done in PRISM. One then adjusts the  $\sigma_{MkM'k'}^{eff}$  by iteration. Equation (3), which we call “range optimiza-

tion,” is the primary theoretical result of this paper.

To compare with the scattering data of NKK and ELW, we show results for the range optimized version of RPA, denoted as RO-RPA. In the NKK and ELW experiments, the molecules were hydrophilic, sulfonated vinyl polymers that were linear and randomly charged, with monovalent ions and counterions. Small angle x-ray (SAXS) and neutron-(SANS) scattering methods were used to examine the equilibrium structure of polyelectrolytes and counterions in their salt-free solution, water. Previous experiments on polyelectrolytes have examined how density correlations in the liquid change with  $\rho_m$ . Here, though,  $\rho_m$  was held constant at a semidilute or near semidilute density and the per chain average fraction of charged monomers  $f$  was varied. Batches of polymers with different values of  $f$  were created and the scattered intensity  $I(q)$  as a function of wave-vector  $q$  was measured for each. NKK found that at small  $f$ , the peak position of  $I(q)$ ,  $q_{\max}$ , obeyed a power law, but at larger  $f \sim 0.4$  appeared to reach an asymptote. ELW extended these measurements to higher  $f$  and found that  $q_{\max}$  was effectively constant for  $f > 0.4$ . SANS measurements also allowed them to extract the polymer monomer-monomer structure factor  $\hat{S}_{mm}(q)$ . They found that at least for the range  $0.55 < f < 0.81$ ,  $\hat{S}_{mm}(q)$  was invariant for the wave vectors measured. A picture that ELW offer is that as one increases  $f$  above 0.4, the system acts as if the charges on the chain are renormalized such that the effective  $f$  is constant. Counterion condensation is usually given as the explanation.

The neutron-scattering data of ELW on poly(acrylamide-co-sodium-2-acrylamido-2-methylpropane sulfonate), or poly-AMAMPS, is sufficiently well characterized to allow quantitative comparison via  $\hat{S}_{mm}(q)$  [5]. We show results for  $\hat{S}_{mm}(q)$  for three models: the “minimal,” “primitive,” and “two state.” In all models the polymer chains are linear and rodlike. The chains are uniformly charged and all monomers are identical and have the same monomer valency,  $Z_m = f$ , which can be varied continuously from 0 to 1. The strength of the system interactions is characterized partly by the ratio of the Bjerrum length  $l_B = e^2 / (\epsilon k_B T)$  to the bond length  $b$ . Here,  $e$ ,  $\epsilon$ , and  $k_B T$  are the electron charge, solvent (water) dielectric constant, and thermal energy, respectively. In the models here, the effect of the salt-free solvent enters only through  $\epsilon$ . Both monomer and counterion are spherical and we set their diameters,  $\sigma$ , equal to each other and also equal to the bond length  $b$ . For ELW,  $l_B \approx 7.1 \text{ \AA}$ ,  $b \approx 2.5 \text{ \AA}$ , and  $\rho_m \sigma^3 \approx 3 \times 10^{-3}$ . The counterion density  $\rho_c$  was determined by charge neutrality,  $Z_m \rho_m + Z_c \rho_c = 0$  and counterion valency  $Z_c = -1$ . The chain length  $N$  was set to 400 so that the above density was well inside the semidilute regime and thus consistent with ELW. In the minimal model the system consists only of linear polymers, with the effect of counterions incorporated in a modified effective interaction between the polymers. Specifically, monomers on the same or different chains interact with a potential that is hard core for  $r < \sigma$ . Outside the core the potential has a screened, Debye-Hückel form:  $u_{mm}(r) = (Z_m^2 l_B / r) e^{-\kappa r}$ , where the inverse screening length  $\kappa = \sqrt{4\pi Z_c^2 l_B \rho_c}$ . In the primitive model, the system consists of linear polymers and counterions. Polymer monomers and

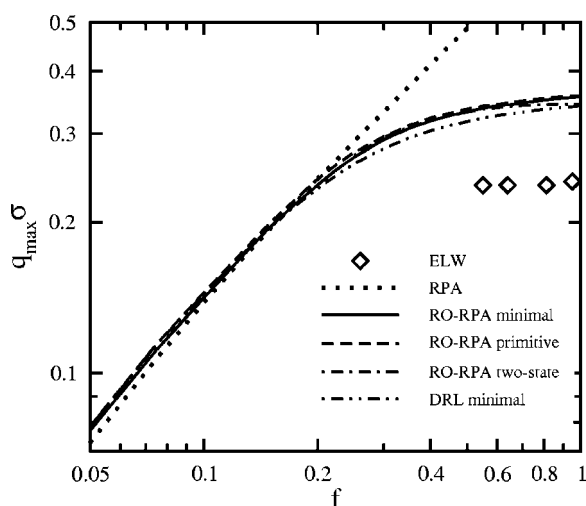


FIG. 1. Scaled peak wave vector  $q_{max}\sigma$  of the monomer-monomer partial structure factor  $\hat{S}_{mm}(q)$  as a function of the average fraction of charged monomers per chain  $f$  for  $l_B/b=2.85$  and  $\rho_m\sigma^3=3\times 10^{-3}$ . The meaning of the curves and symbols is shown within the figure.

counterions interact with a potential that is also hard core for  $r < \sigma$ . Outside the core the potential has a bare Coulomb form:  $u_{ij}(r) = Z_i Z_j l_B / r$ , where  $i$  or  $j$  denote monomers or counterions.

As we will see, comparison of the predictions of RO-RPA in the primitive model with simulation data [21] shows that RO-RPA tends to underestimate the strength of polymer-counterion correlations [11]. The two-state model is a common way to improve these correlations [6,13]. In this model counterions are divided into two species, free and condensed. In one version of the model, free ions are counterions as in the primitive model; the condensed ones are bound to the surface of the chain, but able to translate along its length. Each chain has the same number of condensed counterions,  $N_c$ . An average  $N_c$  is determined by constructing a free energy for the system and then minimizing it with respect to  $N_c$ . For a given  $N_c$  we computed the intramolecular structure functions  $\Omega_{Mkk'}(r)$  for the polymer-condensed counterion “molecule” by a single chain Monte Carlo simulation. Here, the intramolecular effective interaction between chain monomers and condensed counterions was taken to have a screened Debye-Hückel form similar to above, but the inverse screening length  $\kappa = \sqrt{4\pi l_B(Z_m^2 \rho_m + Z_c^2 \rho_c)}$  was due to both ions and counterions. We calculated the free energy using the “charging” formula [18], assuming that the molecular structure was constant during the charging. This constancy is not correct obviously; however, the goal here is not a value for the free energy, but the position of its minimum with respect to  $N_c$ . We expect for the minimum that this approximation is a reasonable one.

Figures 1 and 2 show results for the peak position  $q_{max}$  and peak height  $\hat{S}_{mm}(q_{max})$  of the monomer-monomer partial structure factor. The solid, dashed, and dashed-dotted lines correspond to results of RO-RPA using the minimal, primitive, and two-state models, respectively. Results from the RPA are also shown as dotted lines. Diamonds are data of

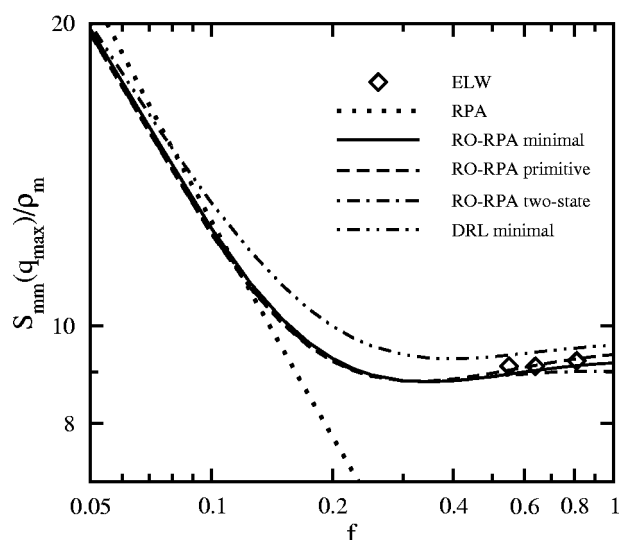


FIG. 2. Scaled peak height of the monomer-monomer partial structure factor  $\hat{S}_{mm}(q_{max})/\rho_m$  as a function of the average fraction of charged monomers per chain  $f$ . The conditions are the same as in Fig. 1. The meaning of the curves and symbols is shown within the figure.

ELW. At small  $f$ ,  $q_{max}$  increases and  $\hat{S}_{mm}(q_{max})$  decreases with increasing  $f$  for both RPA and RO-RPA, with the theories in approximate quantitative agreement. On the other hand, at large  $f \geq 0.4$ , it is clear that range optimization completely changes the character of the RPA theory. In contrast to the RPA, RO-RPA in the minimal model predicts that both quantities become pretty much constant, in agreement with NKK [4] and ELW [5]. Note that adding explicit counterions and condensed counterions produces only moderate improvement in the theoretical trends [22]. To provide additional evidence of the validity of the RO-RPA theory in the minimal model, we also show results (dot-dot-dashed lines) of the DRL theory [12] in the minimal model. DRL is an approximation to the “two-chain” equation for  $g(r)$  [9,23]. As can be seen, this theory also produces an invariance at large  $f$  and agrees almost quantitatively with RO-RPA at all values of  $f$ . Agreement between RO-RPA and experiment for  $\hat{S}_{mm}(q_{max})$  is very good with the former predicting values less than 5% lower than the latter. Agreement for  $q_{max}$  is less satisfactory with RO-RPA predicting values about 35% higher than experiment. The most probable cause of this discrepancy is our neglect of chain flexibility since the Debye-Hückel screening length  $\xi$  is about  $5\sigma$  at large  $f$ , implying a flexible chain on scales larger than that. If the chains were partially collapsed, then the repulsion and average distance between monomers on different chains would be larger. Thus  $q_{max}$  would decrease and  $\hat{S}_{mm}(q_{max})$  would increase. On the other hand, if the solvent—which is “good” for poly-AMAMPS—were included explicitly, then  $\hat{S}_{mm}(q_{max})$  would decrease. An explanation for the invariance with  $f$  seen by the theory is due to screening: as  $f$  increases, the repulsion between polymer chains increases; on the other hand, charge neutrality forces more and more counterions into the solution which increases the screening between polymers. At small  $f$ ,

polymer and counterion correlations are weak, but at large  $f$  they increase such that one reaches a balance between polymer-polymer repulsion and counterion screening.

In conclusion, we have presented an optimization scheme that improves substantially the predictive power of the RPA theory for the structure of polyelectrolyte solutions. We showed that this range-optimized RPA, applied to polyelectrolytes models of varying detail, yields all trends exhibited in the experimental data of ELW at large monomer charge,  $f$ , and is in moderate agreement with their data for the peak position and height. Notably, the invariance at large  $f$  is predicted even in the minimal model, where the effect of counterions is treated strictly at only the Debye-Hückel level, and without invoking more complex mechanisms such as those

commonly involving counterion condensation. This behavior resulted from the proper treatment of polymer-polymer correlations allowed by the range-optimization procedure. Consequently, further improvements of our chain model, namely to include flexibility, may be necessary to draw detailed conclusions about the origins of the effects seen in ELW. The range optimization procedure, as applied to the RPA, may be adequate, but is general enough to be employed in other theories if necessary.

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