Invariance of density correlations with charge density in polyelectrolyte solutions

James P. Donley,1 David R. Heine,2 and David T. Wu2

1The Boeing Company, Huntington Beach, CA 92647
2Departments of Chemistry and Chemical Engineering, Colorado School of Mines, Golden, CO 80401
(Dated: March 22, 2022)

We present a theory for the equilibrium structure of polyelectrolyte solutions. The main element is a simple, new optimization scheme that allows theories such as the random phase approximation (RPA) to handle the harsh repulsive forces present in such systems. Comparison is made with data from recent neutron scattering experiments of randomly charged, hydrophilic polymers in salt-free, semi-dilute solution at various charge densities. Models with varying degrees of realism are examined. The usual explanation of the invariance observed at high charge density has been counterion condensation. However, when polymer-polymer correlations are treated properly, we find that modeling polymer-counterion correlations at the level of Debye-Hückel theory is sufficient.

PACS numbers: 61.20.Gy,61.25.Hq,82.35.Rs,87.15.-v

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

Theoretical study of them is one of the most challenging in the field of complex fluids, however, because of the strong repulsions and attractions present in such systems [3].

In this Letter, we present a scheme that allows a potentially large class of theories to deal properly with these strong long-range interactions. We demonstrate the utility of this approach by comparing with some recent intriguing experiments of Nishida, Kaji and Kanaya (NKK) [4], and Essafi, Lafuma and Williams (ELW) [5]. Counterion condensation [6] commonly is 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 at the level of Debye-Hückel theory [3,6]. However, we show in the theory described below that Debye-Hückel modeling of ion-counterion correlations can itself produce an invariance at high charge density.

There are few theories that can handle the harsh repulsions and attractions in polyelectrolyte solutions [8]. Further, there is currently no theory that provides reliable predictions for liquid structure in the semi-dilute regime—which is the region of most experimental interest. The theory of Laria, Wu and Chandler [9] has been applied successfully 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 in some instances give reasonable predictions for the free energy of polyelectrolyte solutions [13]. Here, we assume that theories such as the RPA are also adequate for density correlations given a suitable reinterpretation of the interaction potential that appears in them [14]. Let

\[ S_{MM'}(r) = (\hat{\rho}_{MM'}(r) - \rho_{MM'}) \]  

be 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 = |r| apart. Here, \( \hat{\rho}_{MM'}(r) \) is the microscopic density of k-type monomers on molecules of type M at position r with average value \( \rho_{MM'} \). The brackets denote a thermodynamic average. The Fourier transform of \( S_{MM'}(r) \) is the partial structure factor and links the theory to scattering experiments. The correlation function can be separated into intra- and inter-molecular pieces, \( \Omega_{MM'}(r) \) and \( H_{MM'}(r) \):

\[ S_{MM'}(r) = \Omega_{MM'}(r)\delta_{MM'} + H_{MM'}(r), \]

where \( \delta_{MM'} \) is the Kronecker delta. In this work, the molecular structure function \( \Omega_{MM'}(r) \) is assumed known. The intermolecular correlation function \( H_{MM'}(r) = \rho_{MM'}\rho_{M'M'} \) 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 a simple system where all the interactions can be decomposed as pair potentials \( u_{MM'}(r) \) between sites. Here, we take these potentials to be hard-core for distances r less than some range \( \sigma_{MM'} \), and Coulombic outside. Consider also a class of theories for which \( g_{MM'}(r) \) 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 failure of theories such as the RPA is that they predict a negative $g_{MM'K'}(r)$ for short distances if the interaction $u_{MM'K'}(r)$ 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 strength of the dependence of $g_{MM'}$ with $\rho_m$ in the semi-dilute 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 a pseudo or optimized one, $\hat{u}_{MM'K'}(r)$. For distances $r < \sigma_{MM'K'}$, $\hat{u}_{MM'K'}(r)$ takes a value such that the hard-core condition is satisfied, i.e., $g_{MM'K'}(r) = 0$. Outside the core, $\hat{u}_{MM'K'}(r)$ 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 MSA closure of the Ornstein-Zernike equation [17] and a closely related scheme has been shown to be diagrammatically proper for CSL theory [15]. This optimized RPA or ORPA, usually with long-range potentials absent, is more popularly known as RISM for small molecules [13] and PRISM for polymers [16].

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 for semi-dilute densities which is usually much larger than the hard-core distance [11,12,20]. Hence, enforcing the core condition produces little improvement in the theory for long polyelectrolytes.

An alternative scheme is to optimize the range of the pseudo-hard-core portion of $\hat{u}$, and not just its amplitude. By this we mean that if $g(r)$ is nearly zero out to some distance, then it makes no difference whether this exclusion zone is caused by a hard-core potential or a Coulombic one. This effective hard-core diameter $\sigma_{MM'K'}^{\text{eff}}$ is determined by requiring that $g_{MM'K'}(r)$ be non-negative everywhere (not just zero inside the core). The closure to the theory then is:

$$
\begin{align*}
g_{MM'K'}(r) &= 0, & r < \sigma_{MM'K'}^{\text{eff}}, \\
\hat{u}_{MM'K'}(r) &= u_{MM'K'}(r), & r > \sigma_{MM'K'}^{\text{eff}},
\end{align*}
$$

The range $\sigma_{MM'K'}^{\text{eff}}$ of the hard-core interaction is chosen to have the smallest value such that $g_{MM'K'}(r) > 0$ for $r > \sigma_{MM'K'}^{\text{eff}}$ subject to the constraint that $\sigma_{MM'K'}^{\text{eff}} \geq \sigma_{MKM'}$. With guesses for the $\sigma_{MKM'}$s, one can solve the RPA (or similar theory) numerically in a manner very similar to what is done in PRISM. One then adjusts the $\sigma_{MKM'}^{\text{eff}}$ by iteration. Eq. (3) is the primary result of this paper.

For simplicity, we show results for the range optimized version of RPA, denoted as RO-RPA. We compare with scattering data of NKK and ELW. In these 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. Previous experiments on polyelectrolytes have examined how density correlations in the liquid change with polymer monomer number density $\rho_m$. Here, though, $\rho_m$ was held constant at a semi-dilute or near semi-dilute 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 wavevector $q$ was measured for each. NKK found that at small $f$, the peak position of $I(q)$, $q_{\text{max}}$, 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 $q_{\text{max}}$ was effectively constant for $f > 0.4$. SANS measurements also allowed them to extract the polymer monomer-monomer structure factor $S_{mm}(q)$. They found that at least for the range $0.55 < f < 0.81$, $S_{mm}(q)$ was invariant for the wavevectors 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 polyAMAPS is sufficiently well characterized to allow quantitative comparison via $S_{mm}(q)$ [5]. We show results for $S_{mm}(q)$ for three models, the “minimal”, “primitive” and “two-state”. In all models the polymer chains are linear and rod-like. The chains are uniformly charged and all monomers are identical so that the 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 $l_B = e^2/(kT)$ to the polymer bond length $b$. Here, $e$, $\epsilon$ and $kT$ 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 equal to the bond length $b$. For ELW, $l_B \approx 7.1A$, $b \approx 2.5A$ 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 500. In the minimal model the system consists only of linear polymers. Monomers on the same chain or different chains interact with a potential which is hard-core for $r < \sigma$. Outside the core the potential has a screened Debye-Hückel form: $u_{ij}(r) = \frac{Z^2_{i} Z^2_{j}}{\kappa r} \rho_{c}$, where the inverse screening length $\kappa = \sqrt{4 \pi Z^2_{i} Z^2_{j}}$. In the primitive model, the system consists of linear polymers and counterions. Polymer monomers and counterions interact with a potential which is also hard-core for $r < \sigma$. Outside the core the potential has a bare Coulomb form: $v_{ij}(r) = \frac{Z^2_{i} Z^2_{j}}{r}$, where $i$ or $j$ denote monomers or counterions.

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 ones are counterions as in the primitive model, and 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 $\Omega_{ijkl}(r)$ 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 $\kappa = \sqrt{4 \pi l_B (Z^2_{m} \rho_{m} + Z^2_{c} \rho_{c})}$ 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 $q_{\text{max}}$ and peak height $S_{\text{mm}}(q_{\text{max}})$ 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 ELW. At small $f$, both quantities seem to obey power laws: $q_{\text{max}} \sim f^{\alpha}$ and $S_{\text{mm}}(q_{\text{max}}) \sim f^{-\eta}$. All RO-RPA models predict $\alpha \approx 2/3$ and $\eta \approx 0.9$. For flexible hydrophilic polyelectrolytes $\alpha$ is expected to be 1/3 [4, 22]. The difference is due probably to our modeling the chains as rods while they are predicted to be rod-like only for a restricted range of lengthscales [22]. We know of no data for $\eta$ for polyelectrolytes. 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 [3]. Note that adding explicit counterions and condensed counterions produces only moderate improvement in the theoretical trends [22]. As a check on the validity of the RO-RPA theory, we
also show results (dot-dot-dashed lines) of the DRL theory in the minimal model. DRL is an approximation to the “two-chain” equation for $g(r)$. 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 $S_{mm}(q_{\text{max}})$ is very good with the former predicting values less than 5% lower than the latter. Agreement for $q_{\text{max}}$ 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 $\xi \sim 5\sigma$ 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 $q_{\text{max}}$ would decrease and $S_{mm}(q_{\text{max}})$ would increase. On the other hand, if the solvent—which is “good” for poly-AMAMPS—were included explicitly then $S_{mm}(q_{\text{max}})$ would decrease. An explanation for this 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 a new optimization scheme that appears to improve substantially the predictive power of the RPA theory for the structure of polyelectrolyte solutions. We showed that this range-optimized RPA in the minimal model yields all trends exhibited in the experimental data of ELW at large $f$ and is in moderate agreement with that data for the peak position and height. The crudeness of our chain model, however, precludes us from drawing any firm conclusions about the origins of the effects seen in ELW. On the other hand, since the minimal model does predict an invariance and the comparison is reasonable enough, it is apparent that a number of questions need to be answered before the cause(s) of this phenomenon is determined. But it is interesting that a model of screened Coulomb chains can produce effects that would normally be associated with more complex mechanisms such as counterion condensation.

We thank John G. Curro, Andrea J. Liu, John D. McCoy, Monica Olvera de la Cruz and Craig E. Pryor for helpful conversations and correspondence.

---
* Electronic address: james.p.donley@boeing.com
† Present Address: Sandia National Laboratories, Albuquerque, NM 87185