

Communication: Counter-ion solvation and anomalous low-angle scattering in salt-free polyelectrolyte solutions

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We investigate the influence of counter-ion solvation on the homogeneity of salt-free polyelectrolyte solutions based on a coarse-grained model that includes an explicit solvent. We show that the solvation of the counter-ions can cause a transformation between a nearly homogeneous to a non-uniform polymer solution, in which there is both a chain clustering and the formation of large charge-free domains, i.e., “voids.” The emergence of these heterogeneous structures induced by counter-ion solvation is accompanied by the localization and formation of counter-ion rich domains that are symptomatic of emergent effective long-range attractive interchain interactions.

The clustering of charged particles having the same sign is a ubiquitous, but poorly understood phenomenon that is observed from atomic scales up to the largest observable structures of the universe.^{1,2} In particular, the clustering of charged particles has been reported in polyelectrolyte solutions,^{3–8} dusty plasmas,^{9–11} charged colloidal dispersions,^{12–16} and in superconductors.¹⁷ Langmuir¹⁸ rationalized the clustering of charged molecules in solution as being due to an effective long-range attractive interaction mediated by the counter-ions lying between like-charged particles, an idea also suggested by Feynman.¹⁹ In contrast to the direct observation of clustering of colloidal particles in many direct real space measurements,^{12–15} the mean field model of Derjaguin-Landau-Verwey-Overbeek (DLVO)^{20,21} of charged particle suspensions at equilibrium predicts that only purely repulsive electrostatic forces should exist between particles having a common charge. Sogami and Ise,^{22–24} as well as others,^{25,26} have clarified that the DLVO theory is only applicable to *weakly charged* particles and that particle clustering emerges experimentally when the charge density is sufficiently large to localize a significant number of counter-ions near the interface of the particles. Although there have been efforts to overcome the deficiencies of DLVO theory,²⁷ there is still no generally accepted theory of the structure and thermodynamics of highly charged particle suspensions that includes the effects of solvation.

In the present work, we are concerned with flexible polyelectrolyte solutions, which are even less well understood theoretically than highly charged colloidal suspensions. As with charged particle suspensions, there have been numerous scattering studies^{3,5–7} indicating a tendency of these solutions to be heterogeneous and there have been many models proposed to rationalize the origin of the attractive interaction responsible for the presumed large scale chain clustering.^{22,28–34}

Theoretical models introduced to rationalize this phenomenon have emphasized the importance of multivalent counter-ions, dipole-dipole and quadrupole interactions complexes with polymers,^{7,34,35} hydrogen bonding, and cation- π interactions.³⁶ Ray and Manning^{37,38} have emphasized that this clustering phenomenon is even more prevalent in experimental studies of polyelectrolyte solutions with *monovalent* counter-ions and this observation raises questions for understanding the nature of polyelectrolyte solutions from a theoretical standpoint. Attractive interactions, mediated through ion solvation, between monovalent ions having the same sign have been observed in molecular dynamics simulations by Zangi,³⁹ implying that the clustering of ions of the same sign can also arise in simple salt solutions.

The ubiquitous nature of this clustering phenomenon motivates us for the search of a more generic physical explanation. Our modeling is based on a previously introduced solvent polyelectrolyte model^{40–42} that includes both an explicit solvent and counter-ions, along with energetic parameters that govern the relative affinity of the solvent for the counter-ions. This model accounts for the short-ranged interactions of the solvent needed to address counter-ion and polymer solvation, while at the same time it enables long time and relatively large scales simulations that are required to study the associative behavior of polyelectrolyte solutions. We find that the competitive associative interactions of the counter-ions between polymer backbone and the solvent molecules lead to the formation of large scale polyelectrolyte clusters and void formation, i.e., regions depleted of both polymers and counter-ions, but rich in solvent.

We employ a bead-spring model of Lennard-Jones (LJ) segments bound by stiff harmonic bonds suspended in explicit LJ solvent particles, some of which are charged to represent counter-ions. All macro-ion segments, dissolved ions, and solvent particles are assigned the same mass m , size σ , strength of interaction ε , and all dissolved ions are monovalent. We set ε and σ as the units of energy and length; the cutoff distance for LJ interaction potential is $r_c = 2.5\sigma$. The parameters between different particle types are set equal to unity, except for the en-

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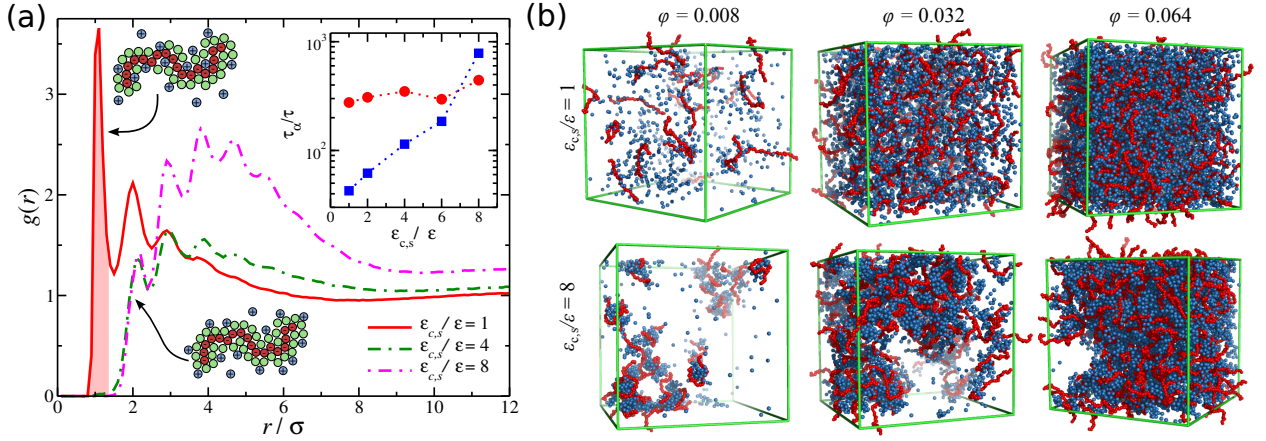


FIG. 1. (a) Pair correlation function, $g(r)$, between the polyelectrolyte segments and the counter-ions for different dispersion energies between the counter-ions and the solvent, $\epsilon_{c,s}/\epsilon$, at charge fraction $\phi = 0.032$. The highlighted area corresponds to interfacial counter-ions. Inset shows the structural relaxation time τ_α , obtained from the intermediate scattering function for the polymer segments (circles) and counter-ions (squares) as function of $\epsilon_{c,s}$ and normalized by the reduced unit of time, τ . (b) Screenshots of the polyelectrolyte solutions at different concentrations and dispersion energies between the solvent and counter-ions. The solvent (neutral) particles are rendered invisible for clarity.

ergy interaction parameter between the solvent particles and the counter-ions $\epsilon_{c,s}$, which reflects the solvent affinity for the counter-ions, in a separate paper, we consider the experimental estimate of $\epsilon_{c,s}$.⁴³ All polyelectrolyte chains have $M_w = 41$ segments carrying a $-e$ charge per segment, where e is the elementary charge and the total polyelectrolyte charge is $Z_p = -M_w e$. The bonds between polymer segments are connected via a stiff harmonic spring, $V_H(r) = k(r - l_0)^2$, where $l_0 = \sigma$ is the equilibrium length of the spring, and $k = 1000 \epsilon/\sigma^2$ is the spring constant.

The system is composed of a total of $N = 256\,000$ particles in a periodic cube of side L and volume V . The system includes N_p polyelectrolyte chains and $N_+ = N_p |Z_p|/e$ counter-ions; the number of neutral particles is $N_0 = N - N_+ - N_p M_w$ and we define the charge fraction as $\phi = (N_+ + N_p |Z_p|/e)/N$. Each system has an overall neutral total charge. All charged particles interact via the Coulomb potential with a cutoff distance $r_{c,c} = 10 \sigma$, and the particle-particle particle-mesh method is used for distances $r > r_{c,c}$.⁴⁴ The Bjerrum length was set equal to $l_B = e^2/(\epsilon_s k_B T) = 2.4 \sigma$, where T is the temperature, k_B is Boltzmann's constant, and ϵ_s is the dielectric constant of the medium. Our simulations were equilibrated at constant pressure and constant temperature conditions, i.e., reduced temperature $k_B T/\epsilon = 0.75$ and reduced pressure $\langle P \rangle \approx 0.02$, and production runs were performed at constant temperature and constant volume, maintained at equilibrium by a Nosé-Hoover thermostat. Typical simulations equilibrate for 4000τ and data is accumulated over a $10\,000 \tau$ interval, where $\tau = \sigma(m/\epsilon)^{1/2}$ is the time unit; the time step used was $\Delta t/\tau = 0.005$. For comparison, we also consider an implicit solvent model at the same volume and temperature as our explicit solvent model, except that there is no solvent and all LJ

interactions are described by Weeks-Chandler-Andersen potential.

Polyelectrolytes have a fraction of their counter-ions dissolved into the solvent, and it is expected that the variation of $\epsilon_{c,s}$ to influence the competitive binding between the counter-ions and the solvent particles along the polyelectrolyte backbone. For weak dispersion interactions, $\epsilon_{c,s}/\epsilon = 1$, some counter-ions have the tendency to “condense” along the polyelectrolyte backbone (see Fig. 1a); counter-ions that are located at distances $r < 1.1 \sigma$ from any polyelectrolyte segment are labeled as interfacial counter-ions.^{42,45} A fraction of counter-ions, however, are located at longer distances, but remain associated with the polyelectrolyte chain in the form of an ionic cloud surrounding the chains. These two counter-ions states are transient with a constant dynamic exchange of counter-ions between them.^{41,42,46} When the dispersion energies start to become stronger $\epsilon_{c,s}/\epsilon > 2$, more interfacial counter-ions become dissolved in the solvent and for $\epsilon_{c,s}/\epsilon > 4$ the average number of interfacial counter-ions is approximately zero. The solvated counter-ions remain loosely associated with the polyelectrolyte chains via the long-range Coulomb interactions, resulting in the enrichment of the diffuse counter-ion cloud around the polyelectrolyte chains at $r/\sigma \approx 2$ to 6 ; see Fig. 1a. Another consequence of the high solvent affinity for the counter-ions is that the counter-ion mobility is significantly reduced, due to the sluggish dynamics of the solvation layer around the counter-ions; see the inset of Fig. 1a. In other words, the affinity of the solvent for the counter-ions greatly influences the spatial-temporal distribution of counter-ions without greatly altering the electrostatic character of the solution.

The spatial reorganization of the counter-ions associated with their solvation has a profound influence on

the structure of the polyelectrolyte chains in the solution. This is apparent in the screenshots presented in Fig. 1b. For low polyelectrolyte concentrations and $\varepsilon_{c,s}/\varepsilon = 8$, we observe the formation of solvent domains rich in counter-ions and the polyelectrolyte chains wrapping around them. The counter-ion rich domains may form aggregates, bringing the polyelectrolyte chains in close proximity. For higher concentrations, the chain clustering leads to the formation of even larger clusters that eventually start to percolate across the simulation cell. Beyond this point, we observe the formation of voids, see Fig. 1b. These voids are charge-free bounded space regions, but they are occupied by neutral solvent particles. The voids, observed before in suspension of highly charged colloids,^{12–16} remain stable over long time periods at equilibrium conditions. Computation of structural correlations (such as radial distribution function and static structure factor) of these solution indicate no detectable evolution in time or sensitivity to simulation box size, suggesting that this heterogeneity corresponds to some type of supramolecular assembly.

To probe the structural nature of polyelectrolyte solutions at larger length scales, we use the static structure factor, $S(q)$, which describes the mean correlations in the positions of particles and q is the wave number. Uncharged polymer chains in solution exhibit a monotonic decrease in $S(q)$; see Fig. 2. For salt-free polyelectrolytes, $S(q)$ exhibits a primary peak located on a scale intermediate on the order of the polymer size and its location is influenced by the polymer concentration,^{47,48} molecular architecture,⁴⁹ and charge valence.⁷ Another characteristic feature of these complex liquids is the sharp upturn of the intensity of $S(q)$ at the low q -region, which is variable with the particular system and this scattering feature is often attributed to the chain clustering,^{3,5,7} as observed in highly charged colloidal systems.^{12–16} Representative $S(q)$ data for monovalent salts of highly charged polystyrene sulfonate in water⁷ are presented in inset of Fig. 2, and qualitatively similar data is found for DNA, dendrimers, proteins, and other biological and synthetic polyelectrolytes.⁵⁰ However, we are not aware of any theoretical model of polyelectrolyte solutions that reproduces these structural features.

In our polyelectrolyte model, we find that increasing $\varepsilon_{c,s}$ results in the primary peak shifting to larger q -values (Fig. 2), meaning that the average distance between the polyelectrolyte chains is reduced. This effect is coupled to a sharp rise in $S(q)$ at the low q -region, which is indicative of the emergence of a long-ranged attractive interactions between the polyelectrolyte chains and the formation of large heterogeneous structures. If we treat the solvent as a continuum fluid in our polyelectrolyte model as implicit solvent, as in the “standard restricted primitive model”, then we find no low-angle enhancement of scattering intensity; see Fig. 2. Counter-ion solvation clearly leads to *qualitative* changes in the scattering intensity of polyelectrolyte solutions. Moreover, the low angle scattering properties of polyelectrolyte so-

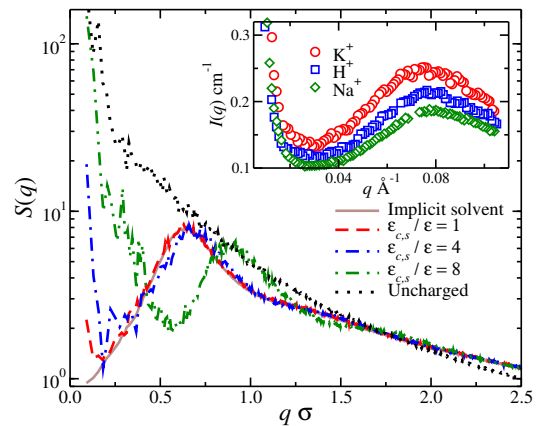


FIG. 2. Static structure factor at different dispersion energies between the solvent and counter-ions $\varepsilon_{c,s}$, for polyelectrolyte solutions with charge fraction of $\varphi = 0.032$. Results for uncharged polymers at the same polymer concentration are also presented. Inset: Small angle scattering intensity results of salt-free polystyrene sulfonate solutions having a (0.2 mol/L) polymer concentration with several monovalent counter-ions, based on data acquired in the measurements of Ref. 7.

lutions are strongly correlated with changes in the solution viscosity and the slow mode relaxation time from dynamic scattering measurements⁷ so that the dynamic clustering of these solutions is clearly implicated in the properties on polyelectrolyte solutions. The clustering of the polyelectrolytes appears to take the form of poly-disperse branched clusters of polymer chains so that no well-defined peak in $S(q)$ serves to define their average size. A quantification of this dynamic chain clustering will require the simulation of larger systems.

Additionally, we find that the solvent affinity for the counter-ions influences the height of the primary peak and the scaling of the location of the primary peak (q_{peak}) with polyelectrolyte concentration ($\rho_p = N_p/V$), see Supplementary Information (SI). Previously, the scale $q_{\text{peak}} \sim \rho_p^\mu$ was observed with our model,⁴⁹ where μ is near $1/2$ for $\varepsilon_{c,s}/\varepsilon = 1$ consistent with experimental observations.⁴⁷ Here, we find that the magnitude of this exponent becomes smaller with increasing $\varepsilon_{c,s}$, e.g., $\mu \approx 0.36$ for $\varepsilon_{c,s}/\varepsilon = 4$. A deviation from $\mu = 1/2$ can be expected since de Gennes’ prediction of $1/2$ exponent assumes that the polyelectrolyte solutions are homogeneous.⁵¹ While many studies reported exponent values close to de Gennes’ prediction, there are several experimental studies^{7,52–55} indicating exponent values in the range of 0.25 to 0.5. Our findings suggest that this variability in this exponent value reflects the degree of heterogeneity in polyelectrolyte solution arising from counter-ion and polymer solvation.

To understand the emergence of structural heterogeneity in polyelectrolyte solutions, and to quantify the effective interactions between polyelectrolyte chains, we cal-

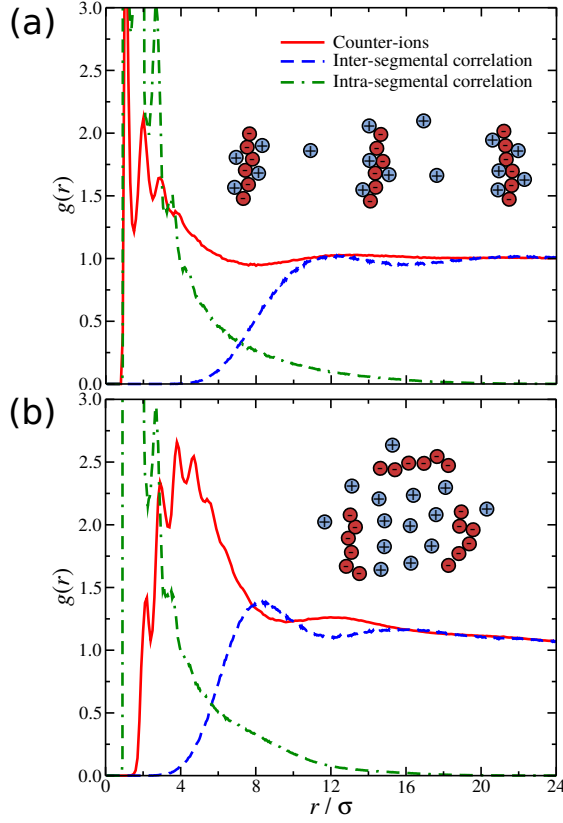


FIG. 3. The intra- and inter-correlation function for the polyelectrolyte segments, as well as, the correlation function between the polyelectrolyte segments and the counter-ions at different polyelectrolyte solutions with charge fraction $\varphi = 0.032$ and (a) $\varepsilon_{c,s}/\varepsilon = 1$; (b) $\varepsilon_{c,s}/\varepsilon = 8$.

culate the pair correlations between of counter-ion with respect to polyelectrolyte segments, the inter- and intra-segmental correlations, see Fig. 3. For low values of $\varepsilon_{c,s}$, the counter-ions localize along the polyelectrolyte backbone, reducing the effective charge of the polyelectrolyte backbone. This “screening” effect of the polyelectrolyte chains leads to the formation of a homogeneous polyelectrolyte solution (Fig. 1b), because their effective inter-chain interaction is predominately repulsive. For higher values of $\varepsilon_{c,s}/\varepsilon > 2$, more interfacial counter-ions dissolve into the solvent, further enriching the counter-ion cloud described above. These counter-ions clouds are domains rich in positive charge that attract other neighboring negatively charged polyelectrolyte chains, thus bringing them closer together, Fig. 3b. This segregation in the spatial distributions of the charges is qualitatively consistent with ideas of Langmuir, Ise, and Feynman,^{18,19,24} and previous direct experimental observations of charge density waves in model polyelectrolyte materials.⁵⁶ Our findings suggest that the solvation of counter-ions is essential for $S(q)$ upturn in the low q -region, explaining the absence of this scattering feature in ionomer-type sys-

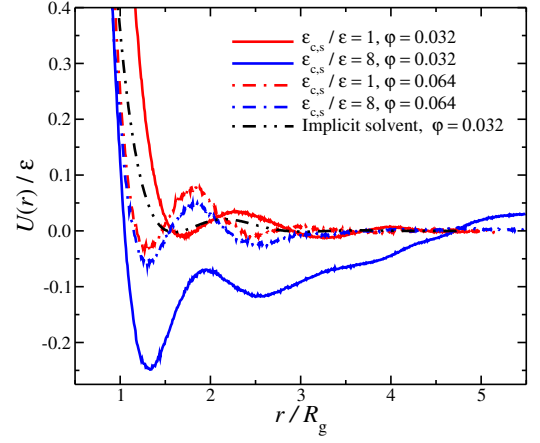


FIG. 4. Potential of mean force, $U(r)$, based on the inter-segmental pair correlations, as function of the distance normalized by average radius of gyration R_g .

tems, where the counter-ion solvation is limited.^{57,58}

The nature of the intersegmental interaction can be quantified by calculating the effective potential of mean force, $U(r) = -k_B T \ln[g(r)]$. For low polyelectrolyte concentration and $\varepsilon_{c,s}/\varepsilon = 8$, $U(r)$ exhibits an attractive well located at approximately $r \approx 1.3 R_g$, beyond which $U(r)$ decays slowly with distance, as seen in Fig. 4. The fact that the interchain interactions are characterized by a scale on the order of the overall polymer size (R_g), rather than the segmental size (σ), indicates that these interactions have a long-range nature, as found before in highly charged colloidal suspensions,^{12–16} further information about R_g is found in the supplementary information. Increasing the polymer concentration leads to a decrease in the strength of interchain attractions for $\varepsilon_{c,s}/\varepsilon = 8$, which reduces the chain clustering and correspondingly the voids become smaller in size, another simulation observation consistent with prior experimental observations on highly charged colloidal suspensions.⁵⁹ Reducing the affinity of the solvent for the counter-ions significantly reduces the depth of potential well, resulting in a relative homogeneous polyelectrolyte solution. We also observed that the depth of the attractive potential is diminished with divalent counter-ions, in agreement with observations discussed by Ray and Manning,^{37,38} and we plan to study polyelectrolyte solutions with higher valent ions in a separate paper.

Our study demonstrates that the counter-ion solvation is responsible for the emergence of long-range attractive inter-chains interactions associated with polymer clustering and void formation in salt-free like-charged polyelectrolyte solutions. In particular, we find that an increase in the counter-ion solvation results in the ionization of the polyelectrolyte backbone, the suppression of the counter-ion mobility, and the enrichment of the counter-ion cloud surrounding the polymers. The combination of these effects results in the formation of domains rich in solvated

counter-ions that give rise to long-range attractive interactions between the polyelectrolyte chains. Our results confirm the basic idea of like-attraction mediated via the intermediate “unlikes” species by the Langmuir-Ise-Feynman mechanism, basically “my enemy’s friend is my friend”. We note that void formation has been directly observed in “coacervates” polymers³⁶ and in DNA thin films.⁸ The control of chain clustering and void formation has great potential in applications ranging from drug delivery, the encapsulation of particles, and nanoparticle synthesis in dusty plasmas.

SUPPLEMENTARY MATERIAL

See supplementary material for information on polyelectrolyte peak in $S(q)$ and the radius of gyration results.

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Supplementary Information: Counter-ion solvation and anomalous low-angle scattering in salt-free polyelectrolyte solutions

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POLYELECTROLYTE PEAK

The polyelectrolyte peak in the static structure factor, $S(q)$, is one of key structural features of the polyelectrolyte solutions. In Fig. 1 we present the variation of the polyelectrolyte peak for different polyelectrolyte solutions, having different dispersion energies between the solvent and counter-ions $\varepsilon_{c,s}$.

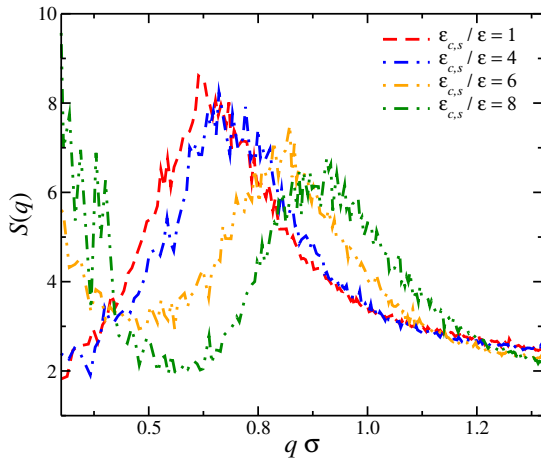


FIG. 1: Static structure factor $S(q)$ at different dispersion energies between the solvent and counter-ions $\varepsilon_{c,s}$, for polyelectrolyte solutions with charge fraction of $\varphi = 0.032$.

RADIUS OF GYRATION

The size of the polyelectrolyte chains can be described by the radius of gyration, R_g . We find a modest decrease of R_g with increasing the dispersion interaction between the solvent and the counter-ions, $\varepsilon_{c,s}$, see Fig. 2. Overall, the polyelectrolyte chains maintain worm-like configura-

tions. In previous work [1], we varied the molecular mass under fixed solvation conditions, $\varepsilon_{c,s}/\varepsilon = 1$, and arrived at the same general conclusion. The polymer chains have worm-like rather rod-like in our polyelectrolyte solution model. Contrast matching neutron scattering measurements of polyelectrolyte solutions allow for the estimation of individual chains and such measurements also indicate that the chains are worm-like [2].

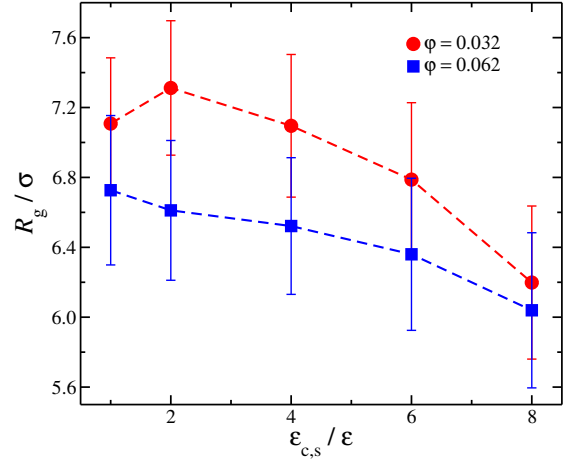


FIG. 2: Average radius of gyration, R_g , as function of the solvent affinity for the counter-ions, $\varepsilon_{c,s}$. The error-bars correspond to one standard deviation.

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