Structure of Polyelectrolyte Solutions

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We present a liquid-state theory for polyelectrolyte solutions. The theory predicts liquidlike structure on long length scales in dilute solution which disappears in semidilute solutions. The predictions of the theory for the static structure factor in tobacco mosaic virus solutions are in good agreement with light-scattering experiments in both dilute and semidilute solutions. Predictions for the scaling of the position of the maximum in the structure factor with concentration are consistent with experiments. [S0031-9007(96)01541-4]

Polyelectrolytes are charged macromolecules in solution. Their study is challenging from a theoretical standpoint because it involves the dual complexity arising from the polymeric nature of the molecules and the long-ranged nature of the Coulombic interactions. The many applications of these materials add to their importance, and consequently they have been studied extensively. Experiments on polyelectrolytes are notoriously difficult because of problems caused by trace impurities. Scattering experiments are particularly difficult because of the added problem of low excess scattering intensity in dilute solutions [1], and it is only recently that light [2,3], small angle x ray [4,5], and neutron scattering techniques [3] have been applied to study the structure of polyelectrolyte solutions.

In polyelectrolyte solutions, several interesting features are observed in the static structure factor $S(q)$ [2–5]. At low concentrations a primary and sometimes secondary peak is observed in the structure factor suggesting significant liquidlike layering on a length scale of the order of the size of the molecules. The primary peak in the structure factor broadens and moves to higher wave vectors as the concentration is increased suggesting that the liquidlike order *diminishes* as the concentration is *increased.* No interpretation of this behavior has been proposed [3,4]. Attention has also focused on the scaling of the position, q_{max}, of the peak in $S(q)$ with concentration. Most experiments show that $q_{max} \sim c^{\nu}$ where $\nu = \frac{1}{3}$ in dilute solutions and $\nu = \frac{1}{2}$ in semidilute solutions. These exponents are predicted by scaling theories. Other values of $\nu \approx 0.4$ are also observed [5], however, and remain unexplained.

In this work we present a simple theory for the structure of polyelectrolyte solutions that is consistent with all these experimental observations. We investigate the structure of rigid rodlike polyelectrolytes in salt-free solutions. This is a good model for tobacco mosaic virus (TMV) solutions for which extensive experiments are available [2,3]. Since the behavior of the static structure factor is very similar whether the molecules are rigid (TMV) or flexible (sodium polystyrene sulphonate) our analysis sheds light on the scattering from polyelectrolyte solutions in general. The theory provides an explanation for the experimental observations in terms of many-body packing effects which are important at low concentrations but become less important at high concentrations due to interpenetration of molecules.

The molecules are modeled as a collection of interaction sites arranged linearly in a rodlike configuration. Each particle consists of N charged hard spheres (or sites) with a spacing d between adjacent spheres. Each sphere has a diameter σ and carries a negative charge qe, where e is the charge on an electron. The total charge on each particle $Q = Nqe$. The effect of solvent and small ions is included into the potential of interaction between sites on the polyelectrolyte molecules. The resulting effective potential $\beta u(r)$ is approximated as the sum of a hard sphere and screened Coulomb interaction: $\beta u(r) = \infty$ for $r < \sigma$, and $\beta u(r) = \Gamma \exp(-\kappa r)/r$ for $r > \sigma$, where r is the distance between two sites. In the Debye-Hückel approximation, assuming spherical symmetry of the ionic atmosphere around each site, the coupling strength $\Gamma = q^2 l_B/(1 + \kappa\sigma)$, where $l_B \equiv \beta e^2/\epsilon$ is the Bjerrum length ($l_B \approx 7.14$ Å at room temperature), ϵ is the dielectric constant of the solvent, β^{-1} is Boltzmann's constant multiplied by the temperature, and κ is the inverse screening length. In salt-free solutions $\kappa = q\sqrt{4\pi l_B c_p}$, where c_p is the polyelectrolyte concentration defined by $c_p \equiv NN_M/V$, and N_M is the number of particles in a volume V.

We investigate the structure of solutions of these rods using the polymer reference interaction site model (PRISM) theory of Curro and Schweizer [6] which is based on the RISM theory of Chandler and Andersen [7]. The PRISM equation relates the intermolecular site-site total correlation function $h(r)$ [$\equiv g(r) - 1$, where $g(r)$ is the site-site pair correlation function] to the single chain structure factor and the direct correlation function $C(r)$ via a nonlinear integral equation given by (in Fourier space)

$$\hat{h}(q) = \hat{P}(q)\hat{C}(q)\hat{P}(q) + c_p\hat{P}(q)\hat{C}(q)\hat{h}(q), \quad (1)$$

where q is the Fourier transform variable, carets denote Fourier transforms, and $\hat{P}(q)$ is the single chain structure factor.

Given an expression for $\hat{P}(q)$ (which can be evaluated exactly for our model) and a closure relation between $h(r)$ and $C(r)$ we can solve for $g(r)$ and hence for the structure factor. We investigate several closure approximations and find that the only accurate one is the reference Laria-Wu-Chandler (R-LWC) closure suggested by Schweizer and Yethiraj [8] based on an approximation devised by Laria, Wu, and Chandler [9]. In this closure,

$$P * C * P(r) = P * C_0 * P(r) + P * (-\beta v) * P(r)$$
$$+ h(r) - h_0(r) - \ln \frac{g(r)}{g_0(r)}, \quad r > \sigma, \quad (2)$$

where the asterisks denote convolution integrals, and $v(r)$ is the tail potential: $v(r) = 0$ for $r < \sigma$ and $v(r) = u(r)$ otherwise. We use the exact core condition $g(r) = 0$ for $r < \sigma$. Functions with subscript "0" refer to correlation functions for a hard sphere rod fluid (with the charges turned off). These functions are obtained from the PRISM theory with the Percus-Yevick closure [6]. To be consistent with terminology in this field [1] we define a structure factor as $S(q) \equiv [\hat{P}(q) + c_p \hat{h}(q)]/\hat{P}(q)$ [this differs from the usual definition $S(q) = \hat{P}(q) + c_p \hat{h}(q)$].

We test this theory by comparing its predictions for $g(r)$ at infinite dilution to exact results from computer simulation. For $c_p = 0$,

$$g(r) = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i^1 - \mathbf{r}_j^2) e^{-\beta U(1,2)} \right\rangle_{\Omega_1 \Omega_2}, \quad (3)$$

where $\mathbf{r}_i^1$ and $\mathbf{r}_j^2$ are, respectively, the position of the ith bead on molecule 1 and the jth bead on molecule 2, $U(1, 2)$ is the full interaction potential between the two molecules, and the average is over the orientations (Ω_1 and Ω_2) of both molecules. We calculate this function exactly using a Monte Carlo scheme and approximately using the integral equation theory described above. Figure 1 compares theoretical predictions to the Monte Carlo results for $N = 20$ and $\Gamma = 0.2$. $g(r)$ increases monotonically from a small value at short distances and eventually goes to 1 for large r. Asymptotically, $g(r) \sim \exp(-\Gamma N^2/r)$ for large r. The theory is extremely accurate at all distances, in fact almost indistinguishable from the exact simulations. Since we are primarily interested in the behavior at low concentrations, the accuracy of the theory at infinite dilution suggests that the theory will be quantitatively accurate for the cases that we consider.

Figure 2 depicts the site-site pair correlation function for $N = 20$, $d = \sigma$, $\Gamma = 1$, and several volume fractions ϕ ($\equiv \pi c_p \sigma^3/6$). For $\phi = 10^{-5}$ $g(r)$ displays a peak at distances of the order of the length of the molecules. As ϕ is increased from 10^{-5} to 10^{-3} the peak becomes more pronounced and some liquidlike layering is evident from the oscillations in $g(r)$. At a higher con-
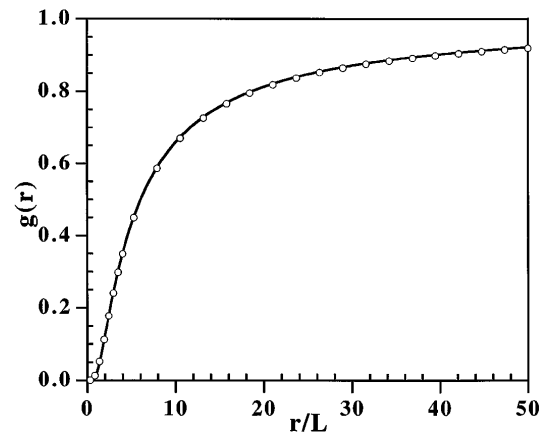

FIG. 1. Comparison of theoretical predictions (lines) for the pair correlation function at infinite dilution to exact Monte Carlo calculations (symbols) for $N = 20$ and $\Gamma = 0.2$.

centration ($\phi = 0.01$) the peak disappears. Since the potential of mean force is given by $-kT \ln g(r)$ the theory predicts an attractive well in the potential of mean force at very low but nonzero concentrations. This attractive well disappears at higher concentrations.

A physical picture emerges from these results. At low concentrations the highly charged particles prefer to remain widely separated. One could imagine each rod being confined to a sphere with a diameter of the order of the length of the rods. These spheres "pack" amongst each other in a manner similar to simple liquids of hard spheres. In the hard sphere analogy, the effective volume fraction of these spheres is larger than that of the rods by a factor of N^2 and high enough to show liquidlike order. This explains the peak in $g(r)$ at low concentrations. At higher concentrations the rods begin to interpenetrate and this causes the layering to disappear. Interpenetration of the rods becomes possible because the mean separation of the rods and the range of the Coulombic repulsion (recall $\kappa \sim c_p^{1/2}$)
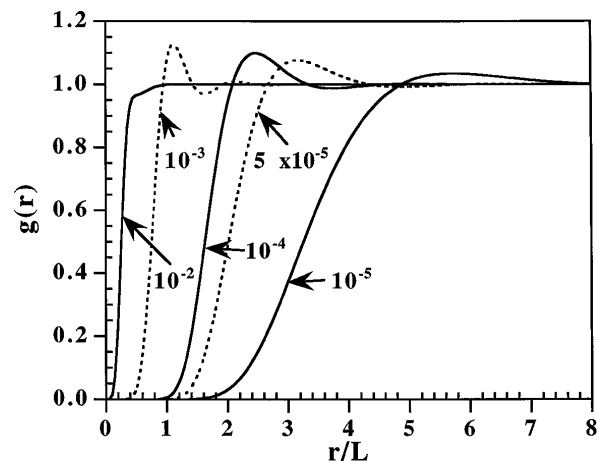

FIG. 2. Site-site pair correlation function between the virus particles for $N = 20$, $\Gamma = 1$, and various volume fractions (as marked).

become smaller as the concentration is increased. This interpenetration is possible only because the actual volume fraction of molecules inside the "spheres" referred to above is very small. In suspensions of spherical colloidal particles, for example, the magnitude of liquidlike layering will monotonically increase with increasing concentration. At much higher concentrations steric interactions can become important and one might observe strong liquidlike ordering on a length scale of σ or (for long enough rods) nematic and other liquid crystalline phases. These steric effects are not expected to be important at the concentrations considered in this work. If c^* is the overlap threshold concentration ($c^* = 1/N^2$ in the theory and $c^* \approx 2.45$ mg/ml in the TMV experiments) the isotropic to nematic transition in TMV solutions occurs at about $c_p = 10c^*$ [10]. At the concentrations of interest no orientational order is observed in birefringence measurements [3].

Figure 3 compares theoretical predictions for the dependence of q_{max} on concentration to experimental data for TMV and fd-virus solutions [3]. The theoretical calculations are for $N = 500$ and $\Gamma = 0.2$, but very similar results are obtained for other values of N or Γ. Note that there are no adjustable parameters in this comparison. The theory is in very good agreement with the experiments. If we fit a straight line to the theoretical predictions at the extremes of the concentration regime in Fig. 3 we obtain exponents of $\nu = 0.32 \pm 0.01$ and 0.5 ± 0.01, respectively. The theory shows a very large crossover regime where effective exponents in between $1/3$ and $1/2$ can be obtained.

To compare the theory to experiments for $S(q)$, we need estimates for the various parameters in the model. We find that the theoretical predictions are not sensitive to the number of interaction sites as long as the length and total charge are kept constant. We set $N = 200$, and fix $\sigma = 18$ nm and $L \equiv (N - 1)d + \sigma = 300$ nm in accordance with the accepted size of TMV particles. The screening length is obtained from the simple Debye-

Hückel expression $\kappa = q \sqrt{4\pi l_B c_p}$. The only unknown parameter is the total charge on the molecule Q. Since the charge for our purposes is unknown, we use this as an adjustable parameter and vary it to reproduce the height of the first peak in the structure factor.

The theory predicts all the features in $S(q)$ observed in experiments: At low concentrations there is a strong peak and a secondary peak in $S(q)$. As the concentration is increased, the primary peak broadens and moves to higher wave vectors while the second peak disappears. Figures 4(a) and 4(b) compare theoretical predictions to experimental data [2] for $c = 0.11c^*$ ($Q = 195e$) and $0.854c^*$ ($Q = 124e$), respectively. The theory is in excellent agreement with the experiments for the shape of the structure factor. Similarly good agreement is observed at other concentrations. At the lowest concentration the theoretical predictions appear shifted a little to the right when compared to experiment. It is possible that this is due to slight uncertainties (about 3%–5%) in the value of the concentration obtained from experiment.

In summary, a theory is presented for the scattering from polyelectrolyte solutions. The theory predicts liquidlike layering on long length scales in dilute solution, which is diminished in the semidilute regime. One consequence of

FIG. 4. Comparison of theoretical prediction for the structure factor to experimental data for (a) $c = 0.11c^*$ and (b) $c = 0.845c^*$.
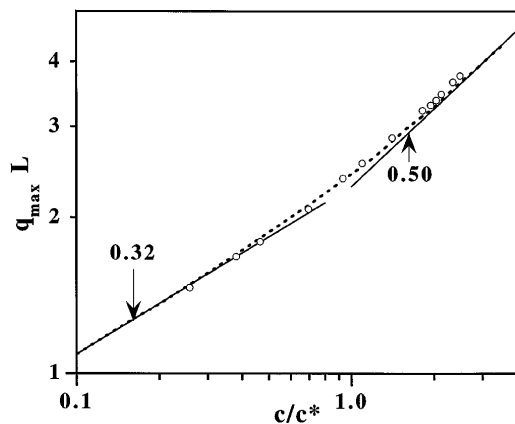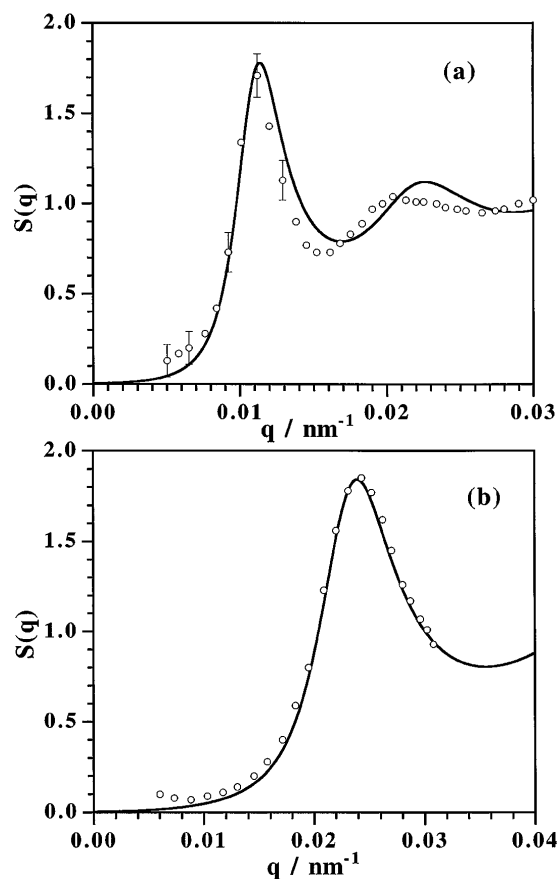

FIG. 3. Scaling of position of peak in structure factor with concentration. Symbols are experimental data and the dashed line is the theoretical prediction with no adjustable parameters. The solid lines are linear least squares fit to the theory in the low and high concentration regimes with slopes as marked.

this layering is that an attractive potential of mean force is observed at very low but nonzero concentrations. The theoretical predictions for the static structure factor are in very good agreement with experimental data. Only rigid molecules were considered in this work, but the theory is easily extended to solutions of flexible polyelectrolytes. The present work treats the salt and counterion distribution in a very crude fashion, and appears sufficient to obtain the qualitative features of the structure factor. A more rigorous treatment would model the solution as a ternary mixture containing polymer, counterion, and co-ion molecules, with corresponding increase in the complexity of the theory.

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