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A Model for Polyelectrolytes

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We have solved a polymerizing version of the mean spherical approximation (MSA) for polyelectrolytes. The polyelectrolytes are modeled as tangentially bonded hard-sphere segments interacting via the Coulombic potential in a continuous medium with dielectric constant. Analytical solutions for thermodynamic properties and radial distribution functions at contact are obtained for some specific systems (negatively charged chains and counterions) studied in the literature via computer simulations, with which good agreement is found for the osmotic pressure.

KEY WORDS: Polyelectrolyte; integral equation theory; mean spherical approximation.

1. INTRODUCTION

The combination of long range Coulombic forces with the constraints of chain connectivity results in the unique and fascinating behavior of polyelectrolytes while also presenting a serious challenge to their study.$^{(1)}$ Nevertheless a number of different statistical mechanical methods have been applied to the study of polyelectrolytes.

Liquid state theories which have been used to treat both chain molecules and electrolytes include the Percus–Yevick,$^{(2)}$ Hypernetted chain$^{(3)}$ and MSA theories for monomers,$^{(4)}$ dimers$^{(5)}$ and longer chains.$^{(6)}$ In particular Blum and coworkers$^{(6)}$ have provided a general theoretical framework which provides for the formation of chains consisting of segments of different size and charge, although no specific results for thermodynamic properties are presented. The formalism followed in this work

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is based largely on that presented by Kalyuzhnyi and Stell(12) and may be considered as a particular case of the general formalism of Blum and coworkers.

The theoretical framework employed in this work to model chain formation is the powerful multi-density Ornstein–Zernike (MDOZ) developed by Wertheim(7) and Baxter(8) details of which can be found in those works.

It is also appropriate to mention here the work of Stell and coworkers in connection with the cavity correlation function(9) which applies polymerizing potentials involving segments with multiple bonding sites to form chains. In addition concepts from chemical association coupled with various integral equation theories have been employed.(10) A number of systems have been studied by this group,(11) notably that examined by Kalyuzhnyi and Stell(12) which provides a general framework and much notation for this work.

Finally, mention should be made of the use of perturbation theories to predict the thermodynamic properties of some polyelectrolyte systems,(13) results which agree well with available simulation data.(14)

In this paper we shall provide a theoretical framework in which we briefly provide a general solution for the MSA model of polyelectrolytes followed by a more detailed solution for a specific case (fully charged negative chain and counterions of equal diameter and equal and opposite charge with no added salt). We show some results for selected thermodynamic and structural properties followed by concluding remarks.

2. THEORETICAL FRAMEWORK

The solution of the specific systems considered here is based on the generalized model of equal sized hard-sphere segments possessing different charges and short-ranged sticky interactions. More detail can be found in the work of Kalyuzhnyi and Stell(12) and von Solms and Chiew.(15)

The segment pair potential is given generally as:

$$U_{ab}(12) = U_{HS}(r) + U^{C}_{ab}(r) + \sum_{KL} U^{ab}_{KL}(12) \tag{1}$$

where a and b are the segment indices (in our case either $+$ or $-$ only, i.e., no uncharged segments are included in the analysis, although the inclusion of neutral species either in the form of added salts or as neutral chain segments is quite straightforward). K and L are the segment site indices for short range (bonding) attraction and take on the values A or B. Thus each segment has two sites at which bonding can occur. By specifying which sites on which segments may form bonds we can specify the creation of specific types of chains. A further point is that the relative location of the two sites on a segment is not specified so that flexible chains can form, within the constraints of steric hindrance. $U_{HS}(r)$ is the hard-sphere potential and $U^{ab}_{KL}(12)$ is the short-range sticky potential defined through its Mayer function as:

$$f^{ab}_{KL} = K^{ab}_{KL}\delta(1-r) \tag{2}$$

where as usual $f = e^{-\beta U} - 1$ and K^{ab}_{KL} is the strength of the sticky interaction. $U^{C}_{ab}(r)$ is the Coulombic potential and is given by

$$U^{C}_{ab}(r) = \frac{e^2 Z_a Z_b}{\varepsilon r} \tag{3}$$

The problem now entails solution of the MDOZ equation which in Fourier space is

$$\hat{\mathbf{H}}(k) = \hat{\mathbf{C}}(k) + \hat{\mathbf{C}}(k)\,\boldsymbol{\sigma}\hat{\mathbf{H}}(k) \tag{4}$$

Here, $\hat{\mathbf{H}}(k)$ and $\hat{\mathbf{C}}(k)$ are Fourier transforms of the following matrices for the untransformed functions $h(r)$, $c(r)$ and the density elements $\boldsymbol{\sigma}$:

$$\mathbf{h}_{ab}(r) = \begin{pmatrix} h^{ab}_{00}(r) & h^{ab}_{0A}(r) & h^{ab}_{0B}(r) & h^{ab}_{0\Gamma}(r) \\ h^{ab}_{A0}(r) & h^{ab}_{AA}(r) & h^{ab}_{AB}(r) & h^{ab}_{A\Gamma}(r) \\ h^{ab}_{B0}(r) & h^{ab}_{BA}(r) & h^{ab}_{BB}(r) & h^{ab}_{B\Gamma}(r) \\ h^{ab}_{\Gamma 0}(r) & h^{ab}_{\Gamma A}(r) & h^{ab}_{\Gamma B}(r) & h^{ab}_{\Gamma\Gamma}(r) \end{pmatrix}$$

$$\mathbf{c}_{ab} = \begin{pmatrix} c^{ab}_{00}(r) & c^{ab}_{0A}(r) & c^{ab}_{0B}(r) & c^{ab}_{0\Gamma}(r) \\ c^{ab}_{A0}(r) & c^{ab}_{AA}(r) & c^{ab}_{AB}(r) & c^{ab}_{A\Gamma}(r) \\ c^{ab}_{B0}(r) & c^{ab}_{BA}(r) & c^{ab}_{BB}(r) & c^{ab}_{B\Gamma}(r) \\ c^{ab}_{\Gamma 0}(r) & c^{ab}_{\Gamma A}(r) & c^{ab}_{\Gamma B}(r) & c^{ab}_{\Gamma\Gamma}(r) \end{pmatrix}$$

and

$$\boldsymbol{\sigma}_a = \begin{pmatrix} \sigma^a_{00} & \sigma^a_{0A} & \sigma^a_{0B} & \sigma^a_{0\Gamma} \\ \sigma^a_{A0} & \sigma^a_{AA} & \sigma^a_{AB} & \sigma^a_{A\Gamma} \\ \sigma^a_{B0} & \sigma^a_{BA} & \sigma^a_{BB} & \sigma^a_{B\Gamma} \\ \sigma^a_{\Gamma 0} & \sigma^a_{\Gamma A} & \sigma^a_{\Gamma B} & \sigma^a_{\Gamma\Gamma} \end{pmatrix} = \begin{pmatrix} \sigma^a_{\Gamma} & \sigma^a_{B} & \sigma^a_{A} & \sigma^a_{0} \\ \sigma^a_{B} & 0 & \sigma^a_{0} & 0 \\ \sigma^a_{A} & \sigma^a_{0} & 0 & 0 \\ \sigma^a_{0} & 0 & 0 & 0 \end{pmatrix}$$

In the above definitions the superscripts a and b refer to species of individual particles ($+$ or $-$) and the subscripts 0, A, B or Γ refer to the bonded state of the particle (0 refers to an unbonded particle, A to a particle bonded only at site A, B to a particle bonded only at site B and Γ to a particle bonded at both sites). The MDOZ equation is solved with the use of appropriate closures. We use the PY-MSA like closure:(5)

$$
\begin{aligned}
&h^{ab}_{\alpha\beta}(r) = -\delta_{\alpha 0}\delta_{\beta 0} \qquad \text{for} \quad r<1 \\
&\quad c^{ab}_{\alpha\beta} = -\delta_{\alpha 0}\delta_{\beta 0}\beta U^{C}_{ab}(r) + (1-\delta_{\alpha 0})(1-\delta_{\beta 0})\, B^{ab}_{\alpha\beta}\delta(r-1) \qquad \text{for} \quad r>1
\end{aligned}
\tag{5}
$$

where the segment diameter is equal to unity. The parameters $B^{ab}_{\alpha\beta}$ are stickiness parameters and can be related to the values K^{ab}_{KL} via the method of cluster integrals. The contact values for the various partial radial distribution functions are also found this way. The detailed analysis will not be presented here but can be found in our previous work.(15) An excellent discussion of the use of these methods can be found in the works of Stell(16) and McQuarrie.(17) In order only to allow the formation of linear negatively charged chains and counterions, we specify that bonding only occurs between unlike sites of negative segments. We could also form linear chains by allowing bonding only between unlike segments, but employ the conventional prescription used previously.(18) Hence the only non-zero stickiness constants are K^{--}_{AB} and K^{--}_{BA} which are equal.

The relationship between the densities in terms of the stickiness parameters in the Wertheim(7) multi-density formalism for our system is given by(18)

$$
\begin{aligned}
\rho^{-}_{A} &= 4\pi\rho^{-}_{0}\,(B^{--}_{AB}\,\sigma^{-}_{A} + B^{--}_{A\Gamma}\,\sigma^{-}_{0}) \\
\rho^{-}_{B} &= 4\pi\rho^{-}_{0}\,(B^{--}_{BA}\,\sigma^{-}_{B} + B^{--}_{B\Gamma}\,\sigma^{-}_{0}) \\
\rho^{-}_{\Gamma} &= \rho^{-}_{0}\left(\frac{\rho^{-}_{A}\,\rho^{-}_{B}}{(\rho^{-}_{0})^{2}} + 4\pi(B^{--}_{\Gamma\Gamma}\,\sigma^{-}_{0} + B^{--}_{\Gamma A}\,\sigma^{-}_{B} + B^{--}_{\Gamma B}\,\sigma^{-}_{A})\right)
\end{aligned}
\tag{6}
$$

We define the average chain length m for the negatively charged chains as the ratio of number of segments to number of chains (analogous to the number average molecular weight for polymers). In terms of the parameters of our system we then have:

$$
m \equiv \frac{\sigma^{-}_{\Gamma}}{\sigma^{-}_{K}} \tag{7}
$$

from which we have

$$
\sigma^{-}_{K} = \frac{\rho_{T}}{2m} \tag{8}
$$

We shall make the additional assumption that

$$\frac{\sigma_K^-}{\sigma_0^-} = m \tag{9}$$

which is similar to the so-called ideal-chain assumption of Chang and Sandler$^{(18)}$ for neutral chains. We can now rewrite the density relations (6)

$$\begin{aligned} B_{KK'}^{--} + \frac{B_{K\Gamma}^{--}}{m} &= \frac{m(m-1)}{12\eta} \\ B_{\Gamma\Gamma}^{--} &= -2mB_{\Gamma K}^{--} \end{aligned} \tag{10}$$

where K and K' represent either A or B.

The MDOZ equation (4) can be written in terms of Baxter q-functions as$^{(8, 12, 15)}$

$$-rc_{\alpha\beta}^{ab}(r) = [q_{\alpha\beta}^{ab}(r)]' - 2\pi \sum_c \sum_{\gamma\delta} \sigma_{\gamma\delta}^c \frac{\partial}{\partial r} \int_0^\infty q_{\gamma\alpha}^{ca}(t)\, q_{\delta\beta}^{cb}(r+t)\, dt \tag{11}$$

$$-rh_{\alpha\beta}^{ab}(r) = [q_{\alpha\beta}^{ab}(r)]' - 2\pi \sum_c \sum_{\gamma\delta} \sigma_{\gamma\delta}^c \int_0^\infty q_{\alpha\gamma}^{ac}(t)(r-t)\, h_{\delta\beta}^{cb}(|r-t|)\, dt \tag{12}$$

Solution of these equations gives

$$q_{\alpha\beta}^{ab}(r) = \tfrac{1}{2}\delta_{0\beta} a_\alpha^a r^2 + (\delta_{0\beta} b_\alpha^a + \omega_\alpha^a J_\beta^b)\, r + c_{\alpha\beta}^{ab} \tag{13}$$

where the parameters J_α^a account for long-range forces

$$J_{\alpha\beta}^{ab} = \int_{1^-}^\infty t h_{\alpha\beta}^{ab}(t)\, dt \tag{14}$$

$$J_\alpha^a = \sum_c \sum_{\gamma\delta} \sigma_{0\gamma}^c J_{\gamma\alpha}^{ca} Z_c \tag{15}$$

and the parameters ω_α^a arise from the electroneutrality condition

$$\sum_c \sum_{\gamma\delta} \omega_\gamma^c \sigma_{\gamma\delta}^c \omega_\delta^c = \frac{4\pi\beta e^2}{\varepsilon} \tag{16}$$

a_α^a and b_α^a arise from conditions inside the core and the constants $c_{\alpha\beta}^{ab}$ which incorporate both hard-core and long-range parameters can be solved using the discontinuities in the q-functions at $r = 1$:

$$\frac{1}{2}\delta_{0\beta} a_\alpha^a + \delta_{0\beta} b_\alpha^a + c_{\alpha\beta}^{ab} = -\frac{1}{2\pi}\omega_\alpha^a Z_b \delta_{0\beta} - \omega_\alpha^a J_\beta^b + (1-\delta_{0\alpha})(1-\delta_{0\beta})\, B_{\alpha\beta}^{ab} \tag{17}$$

Detailed solution of (11) at $r=0$ gives the following two equations(12, 15)

$$b^a_\alpha \delta_{\alpha 0} + \omega^a_\alpha J^a_\alpha + \pi \sum_c \sum_{\gamma\delta} \sigma^c_{\gamma\delta} c^{ca}_{\gamma\alpha} c^{ca}_{\delta\alpha} = (1-\delta_{\alpha 0})\, \pi \sum_c \sum_{\gamma\delta} \sigma^c_{\gamma\delta} (1-\delta_{\gamma 0})(1-\delta_{\delta 0})\, B^{ca}_{\gamma\alpha} B^{ca}_{\delta\alpha} \tag{18}$$

$$b^a_\alpha + b^b_0 \delta_{\alpha 0} + \omega^a_\alpha J^b_0 + \omega^b_0 J^a_\alpha + 2\pi \sum_c \sum_{\gamma\delta} \sigma^c_{\gamma\delta} c^{ca}_{\gamma\alpha} c^{cb}_{\delta 0} + (1-\delta_{\gamma 0}) \sum_c \sum_{\gamma\delta} \sigma^c_{\gamma\delta} Z_c \omega^c_\delta B^{ca}_{\gamma\alpha} = 0 \tag{19}$$

3. SOLUTION FOR FULLY CHARGED CHAIN AND COUNTERIONS

The density relations (10) are already written for the specific system under consideration. We now solve for the specific parameters of our problem. Setting $\alpha=0$, $a=-$ and $\alpha=0$, $a=+$ in Eq. (18) and combining the resulting equations, after a good deal of algebra we obtain the simple relations:

$$\begin{aligned} \omega_\Gamma &= -2m\omega_K \\ J_\Gamma &= -2mJ_K \end{aligned} \tag{20}$$

Setting $\alpha=K$ and $\alpha=\Gamma$ in Eq. (18) and combining the results, after similarly tedious algebra we obtain the expression

$$\frac{m(m-1)}{12\eta}\left(\omega_0 - \frac{\omega_K}{m}\right) = 0 \tag{21}$$

from which we have either $m=1$ (the monomer case) or for general m

$$\omega_K = m\omega_0 \tag{22}$$

We can substitute these values into Eq. (16) to solve for ω_0 in terms of the known physical parameters of the system. The result is

$$\omega_0^2 = \frac{\alpha^2}{2\rho_T} \tag{23}$$

This solution differs from the monomer solution[(4)] only by a factor of two. The value of J_0 is then

$$J_0 = \frac{-1-2\omega_0\rho_T + \sqrt{1+4\omega_0\rho_T}}{4\pi\omega_0\rho_T} \tag{24}$$

Setting $\alpha = K$ or $\alpha = \Gamma$ and $b = +$ or $b = -$ in (19) and using (10) we obtain for the remaining charge parameter J_K:

$$J_K = m\left(\frac{1}{2\pi} + J_0\right) \tag{25}$$

and the stickiness parameters:

$$B_{KK'}^{--} = \frac{m(m-1)}{12\eta} - \frac{m^2}{6\eta(1+2\pi J_0)}\left(\frac{\omega_0(1-\eta)}{\pi} - 1\right) \tag{26}$$

$$B_{K\Gamma}^{--} = \frac{m^3}{6\eta(1+2\pi J_0)}\left(\frac{\omega_0(1-\eta)}{\pi} - 1\right) \tag{27}$$

$$B_{\Gamma K}^{--} = -\frac{m^3}{6\eta(1+2\pi J_0)} \tag{28}$$

$$B_{\Gamma\Gamma}^{--} = \frac{m^4}{3\eta(1+2\pi J_0)} \tag{29}$$

The hard-sphere parameters are found to be:

$$a_0 = \frac{1+2\eta}{(1-\eta)^2} \tag{30}$$

$$b_0 = -\frac{3\eta}{2(1-\eta)^2} \tag{31}$$

$$a_K = -\frac{m-1}{2(1-\eta)} \tag{32}$$

$$b_K = \frac{m-1}{4(1-\eta)} \tag{33}$$

$$a_\Gamma = b_\Gamma = 0 \tag{34}$$

We have tacitly assumed the conventions: $a_0^+ = a_0^- = a_0$; $b_0^+ = b_0^- = b_0$; $\omega_0^+ = -\omega_0^- = \omega_0$; $J_0^+ = -J_0^- = J_0$; $\omega_K = \omega_K^-$; $\omega_\Gamma = \omega_\Gamma^-$; $J_K = J_K^-$ and $J_\Gamma = J_\Gamma^-$.

4. THERMODYNAMIC AND STRUCTURAL PROPERTIES

Although there are a number of ways of deriving thermodynamic properties[(19)] from knowledge of the radial distribution function, a successful and simple method for electrolytes is the energy route[(4)] which however suffers from the drawback of requiring the properties of a reference system—in our case a hard-sphere chain/hard-sphere mixture.[(2, 15, 20)]

The electrostatic energy ΔE given by:[(4)]

$$\Delta E = 2\pi\rho \sum_{ij} X_i X_j \int_0^\infty g_{ij} u_{ij} r^2 \, dr \tag{35}$$

Using Eqs. (14) and (15) we have:

$$\Delta E = 2\pi \left(\frac{e^2}{\varepsilon}\right) \sum_{i\gamma} Z_i \sigma_{0\gamma}^i J_\gamma^i \tag{36}$$

Expanding the summation gives:

$$\Delta E = 2\pi \left(\frac{e^2}{\varepsilon}\right) \rho_T \left[J_0 - \frac{J_K}{m} - \frac{J_\Gamma}{2m^2} \right] \tag{37}$$

which simplifies to

$$\Delta E = 2\pi \left(\frac{e^2}{\varepsilon}\right) \rho_T J_0 \tag{38}$$

the Helmholtz energy

$$\beta \Delta A^{\text{elec}} = \frac{1}{2\pi} \left[-\frac{\kappa}{\sqrt{2}} - \frac{\kappa^2}{2} + \frac{1}{6}(1 + 2\sqrt{2}\,\kappa)^{3/2} - \frac{1}{6} \right] \tag{39}$$

and the osmotic pressure:

$$\frac{\beta \Delta P^{\text{elec}}}{\rho_T} = \frac{1}{4\pi\rho_T} \left[\frac{\kappa}{\sqrt{2}} + \frac{\kappa}{\sqrt{2}}(1 + 2\sqrt{2}\,\kappa)^{1/2} - \frac{1}{3}(1 + 2\sqrt{2}\,\kappa)^{3/2} + \frac{1}{3} \right] \tag{40}$$

where

$$\kappa^2 = \frac{4\pi\beta e^2}{\varepsilon} \rho_T \tag{41}$$

Osmotic pressure vs density results are shown in Fig. 1 for chain lengths of 16, 32 and 64 and compared with the simulation data of Stevens and

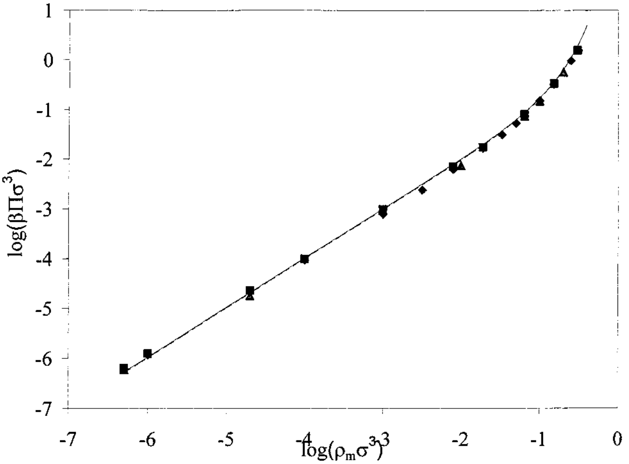

Fig. 1. Osmotic pressure as a function of density for 16 (squares), 32 (diamonds) and 64-mer (triangles) chains and counterions. The Bjerrum length $\lambda_B = 0.833$. The lines are predictions from the theory and the points are simulation data of Stevens and Kremer.$^{(14)}$

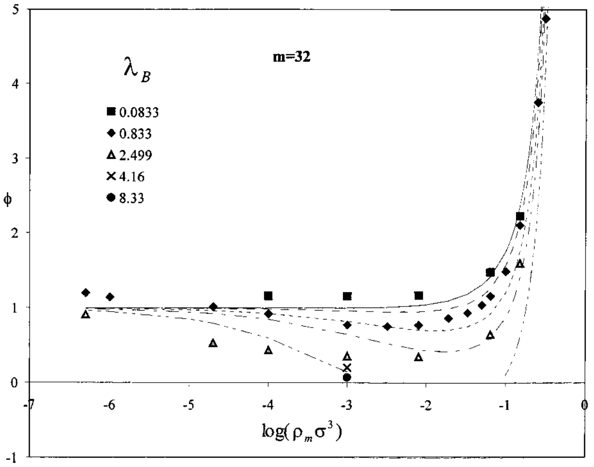

Fig. 2. Osmotic coefficient as a function of density for 32-mer chains at different Bjerrum lengths. The lines are predictions from the theory and the open squares are simulation data of Stevens and Kremer.$^{(14)}$

Kremer.(14) Osmotic coefficient data for 32-mers at different Bjerrum lengths are shown in Fig. 2. As can be seen, the theory is in good agreement with the simulation and captures the correct low- and high density scaling behavior. Finally, we give the results for the overall (total) radial distribution functions at contact:

$$g_{++}(1^+) = \frac{1+\eta/2}{(1-\eta)^2} + \omega_0 J_0 \tag{42}$$

$$g_{-+}(1^+) = g_{+-}(1^+) = \frac{1+\eta/2}{(1-\eta)^2} - \frac{m-1}{2m(1-\eta)} - \omega_0 J_0 \tag{43}$$

$$g_{--}(1^+) = \frac{1+\eta/2}{(1-\eta)^2} - \frac{m-1}{m(1-\eta)} + \omega_0 J_0 + \left(\frac{m-1}{m}\right)^2 \frac{1}{12\eta} - \left(\frac{m-1}{m}\right) \frac{\omega_0(1-\eta)}{6\eta\pi(1+2\pi J_0)} \tag{44}$$

5. CONCLUSIONS

We have solved analytically the mean spherical approximation for the thermodynamic properties and contact radial distribution functions of polyelectrolytes and counterions in solution, where the polyelectrolyte is considered to be a chain of hard spheres each carrying a unit negative charge and counterions are equal sized hard spheres carrying equal and opposite charge. Analytical expressions for the electrostatic internal energy, Helmholtz energy, and osmotic pressure are given. The osmotic pressure predicted by the theory agrees well with available simulation results. Contact values are found for the three radial distribution functions.

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