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Solution of the polymer MSA for the polymerizing primitive model of electrolytes

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An analytical solution of the polymer MSA (mean spherical approximation) for the polymerizing primitive model of electrolytes is obtained. The approximation is an extension of the associative MSA proposed recently [M.Holovko and Yu.Kalyuzhnyi, Mol.Phys., **73**, 1145(1991)] to study the effects of association in ionic systems. The model is defined by adding charges to the totally-flexible sticky two-point model of associating monomers introduced by Wertheim. In the limiting case of an uncharged system, our solution reduces to the solution of the Wertheim polymer PY approximation solved recently [J.Chang and S.I.Sandler, J.Chem.Phys., **102**, 437(1995)].

I. INTRODUCTION

In the last decade a number of studies of model polymer fluids using integral-equation theory have been initiated. These include the polymer RISM theory of Curro and Schweizer [1] and its applications [2] and extensions [3,4], and the Percus-Yevick (PY) theory extended to polymer fluids by Chiew [5]. Recently the Wertheim integral-equation theory for associating fluids [6] and our extension of this theory have also [7] been applied. In [8] the OZ-like equation developed by Wertheim was solved analytically using the polymer PY (PPY) approximation [6] for his totally flexible two-site model [10]. This model is defined by a hard-sphere system with two sticky points placed randomly on a surface of each hard sphere. Concurrently in [9] an analytical solution of the PPY type of the closure [7] for the shielded sticky shell (SSS) model of a polymerizing fluid [11] has been obtained. The method of solution developed in [9] is quite general and is immediately applicable to a number of other models of polymerizing fluids, including the extension of the totally flexible two-site model proposed in [9]. In this extension each sticky point is randomly placed on an attractive shell of diameter $L < 1$ with the latter shielded by a repulsive core of unit diameter. We refer to this model as to the shielded sticky two-point (SS2P) model, the limiting version of which, the sticky two-point (S2P) model, coincides with the totally flexible two-site model of Wertheim [10].

In the present study we find an analytical solution of the mean spherical-like approximation for a model of a polymerizing ionic fluid. The approximation is an extension of the associative mean spherical approximation (AMSA) earlier proposed for the description of the effects of dimerization in the ionic fluids [12,13]. We refer to this extension as to the polymer MSA (PMSA). The model is a polymerizing version of the primitive model of electrolytes that is rather straightforward generalization of the S2P model to ionic systems. It consists of an n-component mixture of charged hard spheres of species $1, ..., a, ..., n$ with number density ρ_a and charge Z_a. The mixture is electroneutral, so that the following condition is satisfied

$$\sum_{a=1}^{n} \rho_a Z_a = 0 \tag{1}$$

As in the case of S2P model, each hard sphere has two sticky points A and B, (regarded as being distinguishable) randomly positioned on its surface. Unlike the version of the S2P model considered in [8] we preserve here the possibility of bonding between any of the two sites which belong to the two particles of any species. Further generalization along the same lines that yield the SS2P generalization of the S2P model is possible; however it is not considered here. For the sake of simplicity we choose an equal diameter for each of the hard-sphere species, although the extension of our theoretical treatment to the more general case with arbitrary diameters is rather straightforward.

Our extension of the AMSA to the case of polymerizing ionic fluids is discussed in Section II of this paper. An anlytical solution of the PMSA is obtained via the Baxter factorization technique [14] in Section III. In Section IV the simplified restricted primitive version of the model, in which the association is allowed only between sites of different species belonging to the oppositelly charged ions, is considered. It is also demonstrated that in the case of the zero charges on the ions our solution reduces to that obtained in [8] via the single bonding approximation, if the stickiness parameter in our model is chosen to be half of that used in [8]. (This factor of 1/2 is a consequence of the positive and negative ions representing two distinct species, even when they are discharged, whereas in [8] a single-species system is considered.)

II. POLYMER MSA

The pair potential of our primitive model of a polymerizing electrolyte solution is given by

$$U_{ab}(12) = U_{h.sp.}(r) + U_{ab}^{(C)}(r) + \sum_{K,L} U_{KL}^{ab}(12) \tag{2}$$

where 1 and 2 stand for the spatial and orientational coordinates of two ions, a and b are the indexes for the ionic species, $U_{h.sp.}(r)$ is the hard-sphere potential, $U_{ab}^{(C)}(r)$ is the Coulomb

potential, and $U^{ab}_{KL}(12)$ is the short-ranged site-site potential responsible for association. Here K and L take the values A and B and denote the type of site. As usual, the Coulomb interaction has the form

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

where e is the elementary charge, Z_a is the charge of the ion of a species in electron units, and ϵ is the dielectric constant of the continuum.

Due to the site-site interaction $U^{ab}_{KL}(r)$ the total pair potential is strongly dependent on the orientation of the ions. However, as was already noted in [15,9] the type of the model considered here can be described by an orientationally-averaged version of the Wertheim theory. The latter in conjunction with the S2P model has been discussed in [8]. Its extension to the case of a multicomponent system is rather obvious, and therefore in what follows we shall omit any details, refering the readers to the original publications.

For the present model the Wertheim OZ equation can be written in terms of the orientationally-averaged partial correlation functions $h^{ab}_{\alpha\beta}(r)$ and $c^{ab}_{\alpha\beta}(r)$ in the form

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

where $[\boldsymbol{\sigma}]_{ab} = \delta_{ab}\boldsymbol{\sigma}_a$ and the matrices $\hat{\mathbf{H}}(k)$ and $\hat{\mathbf{C}}(k)$ contain the elements which are the Fourier transform of the elements of the matrices $\mathbf{H}(r)$ and $\mathbf{C}(r)$, respectivly. Here $[\mathbf{H}(r)]_{ab} = \mathbf{h}_{ab}(r)$ and $[\mathbf{C}(r)]_{ab} = \mathbf{c}_{ab}(r)$. In turn $\mathbf{h}_{ab}(r)$, $\mathbf{c}_{ab}(r)$, and $\boldsymbol{\sigma}_a$ are the matrices which take the form

$$\mathbf{h}_{ab}(r) = \begin{pmatrix} h^{ab}_{00}(r) & h^{ab}_{0A}(r) & h^{ab}_{0B}(r) & h^{ab}_{0\Gamma}(r) \\ h^{ab}_{A0}(r) & h^{ab}_{AA}(r) & h^{ab}_{AB}(r) & h^{ab}_{A\Gamma}(r) \\ h^{ab}_{B0}(r) & h^{ab}_{BA}(r) & h^{ab}_{BB}(r) & h^{ab}_{B\Gamma}(r) \\ h^{ab}_{\Gamma 0}(r) & h^{ab}_{\Gamma A}(r) & h^{ab}_{\Gamma B}(r) & h^{ab}_{\Gamma\Gamma}(r) \end{pmatrix}, \qquad \boldsymbol{\sigma}_a = \begin{pmatrix} \sigma^a_\Gamma & \sigma^a_B & \sigma^a_A & \sigma^a_0 \\ \sigma^a_B & 0 & \sigma^a_0 & 0 \\ \sigma^a_A & \sigma^a_0 & 0 & 0 \\ \sigma^a_0 & 0 & 0 & 0 \end{pmatrix}$$

where the lower indices α and β in σ^a_α and in the correlation functions $h^{ab}_{\alpha\beta}(r)$ and $h^{ab}_{\alpha\beta}(r)$ denote the bonded states of the correspondent particle. The case of $\alpha = 0$ corresponds to

unbonded particle, $\alpha = A$ or $\alpha = B$ to the particle with bonded site A or B, and $\alpha = \Gamma$ to the particle with both sites, A and B, bonded. The density parameters σ_α^a are related to the densities ρ_α^a of α-bonded particles by

$$\sigma_0^a = \rho_0^a, \quad \sigma_A^a = \rho_0^a + \rho_A^a, \quad \sigma_B^a = \rho_0^a + \rho_B^a,$$

$$\sigma_\Gamma^a = \rho_a = \rho_0^a + \rho_A^a + \rho_B^a + \rho_\Gamma^a \tag{5}$$

In our study we are using the MSA-like closure conditions [12,13] which for the present model reads

$$h_{\alpha\beta}^{ab}(r) = -\delta_{\alpha 0}\delta_{\beta 0}, \qquad for \quad r < 1$$

$$c_{\alpha\beta}^{ab}(r) = -\delta_{\alpha 0}\delta_{\beta 0}\beta U_{ab}^{(C)}(r) + (1-\delta_{\alpha 0})(1-\delta_{\beta 0})B_{\alpha\beta}^{ab}\delta(r-1), \quad for \quad r > 1 \tag{6}$$

where $\beta = \frac{1}{kT}$ and hereafter we assume the unit diameter for the hard-spheres.

Here, as in [8], the site-site potential is choosed to be infinitesimally short-ranged so that its averaged Mayer function $f_{KL}^{ab}(r)$ takes the form

$$f_{KL}^{ab}(r) = K_{KL}^{ab}\delta(1-r)$$

where δ is the Dirac delta-function and K_{KL}^{ab} is the parameter describing the strength of the stickiness. The constants $B_{\alpha\beta}^{ab}$ are related to the stickiness parametes K_{KL}^{ab} by

$$B_{KL}^{ab} = y_{00}^{ab}K_{KL}^{ab}, \quad B_{\Gamma A}^{ab} = K_{AA}^{ab}y_{B0}^{ab} + K_{BA}^{ab}y_{A0}^{ab}, \quad B_{\Gamma B}^{ab} = K_{BB}^{ab}y_{A0}^{ab} + K_{AB}^{ab}y_{B0}^{ab},$$

$$B_{\Gamma\Gamma}^{ab} = K_{AA}^{ab}y_{BB}^{ab} + K_{AB}^{ab}y_{BA}^{ab} + K_{BA}^{ab}y_{AB}^{ab} + K_{BB}^{ab}y_{AA}^{ab} \tag{7}$$

where $y_{\alpha\beta}^{ab}$ is the contact value of the function defined by

$$g_{\alpha\beta}^{ab}(r) = e_{h.sp.}(r)[y_{\alpha\beta}^{ab}(r) + B_{\alpha\beta}^{ab}(1-\delta_{\alpha 0})(1-\delta_{\beta 0})\delta(r-1)] \tag{8}$$

and $e_{h.sp.}(r) = \exp(-\beta U_{h.sp.}(r))$ and $g_{\alpha\beta}^{ab}(r) = h_{\alpha\beta}^{ab}(r) + \delta_{\alpha 0}\delta_{\beta 0}$.

Finally the relation between the densities ρ_α^a and parameters $B_{\alpha\beta}^{ab}$ are found to be [6,8]

$$\rho_A^a = 4\pi\rho_0^a \sum_b [B_{AA}^{ab}(\rho_0^b + \rho_B^b) + B_{AB}^{ab}(\rho_0^b + \rho_A^b) + B_{A\Gamma}^{ab}\rho_0^b]$$

$$\rho_B^a = 4\pi\rho_0^a \sum_b [B_{BB}^{ab}(\rho_0^b + \rho_A^b) + B_{BA}^{ab}(\rho_0^b + \rho_B^b) + B_{B\Gamma}^{ab}\rho_0^b]$$

$$\rho_\Gamma^a = \rho_0^a [\frac{\rho_A^a \rho_B^a}{(\rho_0^a)^2} + 2\pi \sum_b \rho_0^b B_{\Gamma\Gamma}^{ab}] \tag{9}$$

This completes our PMSA closure conditions for the primitive model of polymerizing electrolytes. Here, in contrast to [8], we do not restrict ourselves to the single-bonding approximation. The latter can be easily introduced into the theory as in [8].

III. SOLUTION OF THE PMSA FOR THE PRIMITIVE MODEL OF POLYMERIZING ELECTROLYTES

Our solution of the OZ equation (4) together with the set of equations (6), which specify the closure conditions and relation between the densities (9) is based upon the Baxter factorization tecknique [14] and is similar to that developed in [12,13]. We begin by presenting the OZ equation (4) in the form

$$[\boldsymbol{\sigma}^{-1} - \hat{\mathbf{C}}(k)][\mathbf{1} + \boldsymbol{\sigma}\hat{\mathbf{H}}(k)] = \boldsymbol{\sigma}^{-1} \tag{10}$$

suitable for factorization

$$\boldsymbol{\sigma}^{-1} - \hat{\mathbf{C}}(k) = \hat{\mathbf{q}}^T(-k)\boldsymbol{\sigma}\hat{\mathbf{q}}(k) \tag{11}$$

$$\hat{\mathbf{q}}(k)[\mathbf{1} + \boldsymbol{\sigma}\hat{\mathbf{H}}(k)] = [\boldsymbol{\sigma}\hat{\mathbf{q}}^T(-k)\boldsymbol{\sigma}]^{-1} \tag{12}$$

In real r-space this set of equations can be written as

$$-rc_{\alpha\beta}^{ab}(r) = [q_{\alpha\beta}^{ab}(r)]' - 2\pi \sum_c \sum_{\gamma\delta} \sigma_{\gamma\delta}^c \partial/\partial r \int_0^\infty q_{\gamma\alpha}^{ca}(t) q_{\delta\beta}^{cb}(r+t)dt \tag{13}$$

$$-rh_{\alpha\beta}^{ab}(r) = [q_{\alpha\beta}^{ab}(r)]' - 2\pi \sum_c \sum_{\gamma\delta} \sigma_{\gamma\delta}^c \int_0^\infty q_{\alpha\gamma}^{ac}(t)(r-t)h_{\delta\beta}^{cb}(|r-t|)dt \tag{14}$$

where $\sigma^c_{\gamma\delta}$ is the correspondent element of the matrix $\boldsymbol{\sigma}_c$ and

$$4\pi^2 q^{ab}_{\alpha\beta} = \int_{-\infty}^{\infty} \{[\boldsymbol{\sigma}^{-1}]^{ab}_{\alpha\beta} - \hat{q}^{ab}_{\alpha\beta}(k)\} \exp[-ikr]\, dk \tag{15}$$

Making use of the analytical properties of the function $\hat{q}^{ab}_{\alpha\beta}(k)$ together with the closure conditions (6) yield the following long-range behaviour of the function $q^{ab}_{\alpha\beta}(r)$ defined by (15)

$$2\pi q^{ab}_{\alpha\beta}(r) = -\alpha^{ab}_{\alpha}\delta_{0\beta} \exp[-\mu r] \quad (\mu \rightarrow 0), \qquad for \quad r > 1 \tag{16}$$

where α^{ab}_{α} is an unknown constant, which satisfies the set of algebraic equations

$$\sum_c \sum_{\gamma\delta} \alpha^{ca}_{\gamma} \sigma^c_{\gamma\delta} \alpha^{cb}_{\delta} = \frac{4\pi\beta e^2 Z_a Z_b}{\epsilon} \tag{17}$$

obtained by substituting (16) into (13) and studing its long-range asymptotic behaviour. Using the symmetry property of (17) and following [16] we have

$$\alpha^{ab}_{\alpha} = Z_b \omega^a_{\alpha} \tag{18}$$

where the constants ω^a_{α} satisfy the following set of equations

$$\sum_c \sum_{\gamma\delta} \omega^c_{\gamma} \sigma^c_{\gamma\delta} \omega^c_{\delta} = \frac{4\pi\beta e^2}{\epsilon} \tag{19}$$

Next, considering equation (14) in the range $0 < r < 1$ and making use of the electroneutrality condition (1) and relation (18), we arrive at the second order polynomial for the q-function

$$q^{ab}_{\alpha\beta}(r) = \frac{1}{2}\delta_{0\beta} a^a_{\alpha}\, r^2 + (\delta_{0\beta} b^a_{\alpha} + \omega^a_{\alpha} J^b_{\beta})\, r + c^{ab}_{\alpha\beta}, \qquad for \;\; 0 < r < 1 \tag{20}$$

Here

$$a^a_{\alpha} = \delta_{0\alpha} - 2\pi \sum_c \sum_{\gamma} \sigma^c_{\gamma 0} \int_0^1 q^{ac}_{\alpha\gamma}(t)\, dt \tag{21}$$

$$b^a_{\alpha} = 2\pi \sum_c \sum_{\gamma} \sigma^c_{\gamma 0} \int_0^1 q^{ac}_{\alpha\gamma}(t) t\, dt \tag{22}$$

$$J^a_{\alpha} = \sum_c \sum_{\gamma} \sigma^c_{0\gamma} J^{ca}_{\gamma\alpha} Z_c \qquad\qquad J^{ab}_{\alpha\beta} = \int_{1^-}^{\infty} t h^{ab}_{\alpha\beta}(t)\, dt \tag{23}$$

and the constants $c_{\alpha\beta}^{ab}$ follow from the boundary conditions imposed on the function $q_{\alpha\beta}^{ab}(r)$

$$q_{\alpha\beta}^{ab}(1^+) - q_{\alpha\beta}^{ab}(1^-) = -(1-\delta_{\alpha 0})(1-\delta_{\beta 0})B_{\alpha\beta}^{ab} \tag{24}$$

After some simple algebraic manipulations the set of equations (21), (22) and (24), which define the unknowns a_α^a, b_α^a and $c_{\alpha\beta}^{ab}$ can be written explicitly as

$$(1+\frac{1}{3}\pi\rho_T)a_\alpha^a + \pi\rho_T b_\alpha^a + 2\pi\sum_c\sum_\gamma \sigma_{\gamma 0}^c c_{\alpha\gamma}^{ac} = \delta_{0\alpha} - \pi\omega_\alpha^a\sum_c\sum_\gamma \sigma_{\gamma 0}^c J_\gamma^c \tag{25}$$

$$\frac{1}{4}\pi\rho_T a_\alpha^a + (\frac{2}{3}\pi\rho_T - 1)b_\alpha^a + \pi\sum_c\sum_\gamma \sigma_{\gamma 0}^c c_{\alpha\gamma}^{ac} = -\frac{2}{3}\pi\omega_\alpha^a\sum_c\sum_\gamma \sigma_{\gamma 0}^c J_\gamma^c \tag{26}$$

$$\frac{1}{2}a_\alpha^a\delta_{0\beta} + b_\alpha^a\delta_{0\beta} + c_{\alpha\beta}^{ab} = -\frac{1}{2\pi}\omega_\alpha^a Z_b\delta_{0\beta} - \omega_\alpha^a J_\beta^b + (1-\delta_{\alpha 0})(1-\delta_{\beta 0})B_{\alpha\beta}^{ab} \tag{27}$$

where $\rho_T = \sum_a \rho_a$.

The rest of the $8n-1$ equations for the unknown parameters ω_α^a and J_α^a can be obtained from (13) considered at $r = 0$. Since the direct correlation functions $c_{\alpha\beta}^{ab}(r)$ are finite at $r = 0$, we have

$$b_\alpha^a\delta_{\alpha 0} + \omega_\alpha^a J_\alpha^a + \pi\sum_c\sum_{\gamma\delta}\sigma_{\gamma\delta}^c c_{\gamma\alpha}^{ca}c_{\delta\alpha}^{ca} = (1-\delta_{\alpha 0})\pi\sum_c\sum_{\gamma\delta}\sigma_{\gamma\delta}^c(1-\delta_{\gamma 0})(1-\delta_{\delta 0})B_{\gamma\alpha}^{ca}B_{\delta\alpha}^{ca} \tag{28}$$

$$\begin{aligned} &b_\alpha^a + b_0^b\delta_{\alpha 0} + \omega_\alpha^a J_0^b + \omega_0^b J_\alpha^a + 2\pi\sum_c\sum_{\gamma\delta}\sigma_{\gamma\delta}^c c_{\gamma\alpha}^{ca}c_{\delta 0}^{cb} + \\ &+(1-\delta_{\alpha 0})\sum_c\sum_{\gamma\delta}(1-\delta_{\gamma 0})\sigma_{\gamma\delta}^c Z_c\omega_\delta^c B_{\gamma\alpha}^{ca} = 0 \end{aligned} \tag{29}$$

The contact values of $y_{\alpha\beta}^{ab}(r)$, which appear in the expression (7) for $B_{\alpha\beta}^{ab}$, follow from (14) at $r \to 1^+$

$$y_{\alpha\beta}^{ab} = \delta_{0\beta}(a_\alpha^a + b_\alpha^a) + \omega_\alpha^a J_\beta^b - 2\pi(1-\delta_{0\beta})\sum_c\sum_{\gamma\delta}(1-\delta_{\delta 0})\sigma_{\gamma\delta}^c c_{\alpha\gamma}^{ac}B_{\delta\beta}^{cb} \tag{30}$$

Thus the solution of the PMSA for the primitive model of polymerizing electrolyte solution reduces to the solution of the set of algebraic equations (9) and (25)-(30).

IV. SOLUTION OF THE PMSA FOR THE RESTRICTED PRIMITIVE MODEL OF POLYMERIZING ELECTROLYTES

Substantial simplification occurs in the final equations of the previous section if for the ionic system the restricted primitive model of particles with equal sized cores is used. In addition, if one assume that bonding is taking place only between the sites of different species belonging to the oppositly charged ions,

$$K_{KL}^{aa} = K_{KK}^{ab} = 0, \qquad K_{AB}^{+-} = K_{AB}^{-+} \neq 0 \tag{31}$$

where + and − denote positively and negatively charged ions, the set of equations (25)-(30) can be presented formally as two independent sets of equations. One of these sets of equations involves the quantities related to the correspondent polymerizing uncharged hard-sphere system, while the other describes the parameters related to the additional effects of the electrostatic interaction. These two sets of equations, as in the case of a dimerizing ionic system [12], are coupled via the relation between the densities (9).

Because of the symmetry of the present model and due to (19) parameters α_α^{ab}, which defined the long-range behaviour of the Baxter q-functions, we have

$$\alpha_\alpha^{++} = \alpha_\alpha^{--} = -\alpha_\alpha^{+-} = -\alpha_\alpha^{-+} = \alpha_\alpha, \quad and \quad \alpha_A = \alpha_B \tag{32}$$

For the density parameters we have also

$$\sigma_\alpha^{+} = \sigma_\alpha^{-} = \sigma_\alpha, \qquad and \qquad \sigma_A = \sigma_B \tag{33}$$

Now equation (19) for α_α takes the form

$$\sigma_\Gamma \omega_0^2 + \sigma_K \omega_0 \omega_K + 2\sigma_0 \omega_0 \omega_\Gamma + 2\sigma_0 \omega_K^2 = \frac{4\pi\beta e^2}{\epsilon} \tag{34}$$

where $\omega_\alpha^{+} = -\omega_\alpha^{-} = \omega_\alpha$.

The set of equations (25)-(30) can be simplified by introducing instead of $c_{\alpha\beta}^{ab}$ a new set of the unknown parameters $c_{\alpha\beta}^{(S)}$ and $c_{\alpha\beta}^{(D)}$ defined by

$$c_{\alpha\beta}^{(S)} = \frac{1}{2}(c_{\alpha\beta}^{++} + c_{\alpha\beta}^{+-}), \quad c_{\alpha\beta}^{(D)} = \frac{1}{2}(c_{\alpha\beta}^{++} - c_{\alpha\beta}^{+-}). \tag{35}$$

In terms of these parameters the set of equations (25)-(27) can be written as

$$(1 + \frac{1}{3}\pi\rho_T)a_\alpha + \pi\rho_T b_\alpha + 4\pi\sum_\gamma \sigma_{\gamma 0} c_{\alpha\gamma}^{(S)} = \delta_{0\alpha}$$

$$\frac{1}{4}\pi\rho_T a_\alpha + (\frac{2}{3}\pi\rho_T - 1)b_\alpha + 2\pi\sum_\gamma \sigma_{\gamma 0} c_{\alpha\gamma}^{(S)} = 0$$

$$\frac{1}{2}a_\alpha\delta_{0\beta} + b_\alpha\delta_{0\beta} + c_{\alpha\beta}^{(S)} = \frac{1}{2}(1-\delta_{\alpha 0})(1-\delta_{\beta 0})B_{\alpha\beta}^{+-} \tag{36}$$

where $a_\alpha = a_\alpha^+ = a_\alpha^-$, $b_\alpha = b_\alpha^+ = b_\alpha^-$.

Solution of this set of linear equation gives the following expressions for a_α, b_α, $c_{\alpha\beta}^{(S)}$ and the contact values of $y_{\alpha\beta}^{(S)}(r) = \frac{1}{2}(y_{\alpha\beta}^{++}(r) + y_{\alpha\beta}^{+-}(r))$

$$a_0 = \frac{1+2\eta_T}{(1-\eta_T)^2}, \quad b_0 = \frac{-3\eta_T}{2(1-\eta_T)^2}, \quad c_{00}^{(S)} = \frac{-1}{2(1-\eta_T)^2}, \tag{37}$$

$$a_\alpha = \frac{R_\alpha}{1-\eta_T}, \quad b_\alpha = \frac{-R_\alpha}{2(1-\eta_T)}, \quad c_{\alpha 0}^{(S)} = 0, \quad for \;\; \alpha \neq 0,$$

$$c_{\alpha\beta}^{(S)} = \frac{1}{2}(1-\delta_{\alpha 0})B_{\alpha\beta}^{+-}, \qquad for \;\; \beta \neq 0 \tag{38}$$

$$y_{00}^{(S)} = \frac{2+\eta_T}{2(1-\eta_T)^2}, \quad y_{\alpha 0}^{(S)} = y_{0\alpha}^{(S)} = \frac{R_\alpha}{2(1-\eta_T)}, \tag{39}$$

$$y_{\alpha\beta}^{(S)} = \pi\sigma_0\{(1-\delta_{\alpha A})(1-\delta_{\beta B})B_{\alpha A}^{+-}B_{B\beta}^{+-} + (1-\delta_{\alpha B})(1-\delta_{\beta A})B_{\alpha B}^{+-}B_{A\beta}^{+-}\}, \tag{40}$$

$$for \;\; \alpha \neq 0 \;\; and \;\; \beta \neq 0$$

where $\eta_T = \frac{\pi}{6}\rho_T$ and

$$R_K = -2\pi(\sigma_K B_{KK'}^{+-} + \sigma_0 B_{K\Gamma}^{+-}), \quad R_\Gamma = -2\pi(2\sigma_K B_{\Gamma K'}^{+-} + \sigma_0 B_{\Gamma\Gamma}^{+-})$$

Here we are using similar notation as that of [6,8], where K and K' denote sites of a different type, i.e. if $K = A$ then $K' = B$ and vice versa.

One can easily see that the above expressions essentially reduce to those obtained in the PPY approximation in [8] if $Z_a = 0$, $K_{AB}^{(PPY)} = 2K_{AB}^{+-}$ and the single bonding approximation is utilized. The only difference is due to the fact that even in the uncharged case we still have here a two-component system in the terminology we are using.

For the set of equations (28), (29) and contact values of the functions $y_{\alpha\beta}^{(D)}(r) = \frac{1}{2}(y_{\alpha\beta}^{++}(r) - y_{\alpha\beta}^{+-}(r))$ we have

$$\alpha_0 J_0^{(D)} + 2\pi^2(\frac{1}{2\pi} + 2J_0^{(D)})^2 = 0$$

$$2(\alpha_0 J_K^{(D)} + \alpha_K J_0^{(D)}) + 2\pi(\frac{1}{2\pi} + 2J_0^{(D)})[8\pi\beta^* J_K^{(D)} + (\sigma_K B_{K'K}^{+-} + \sigma_0 B_{\Gamma K}^{+-})\alpha_0 + \sigma_0 B_{K'K}^{+-}\alpha_K] -$$

$$-\sigma_0 B_{K'K}^{+-}\alpha_K - (\sigma_K B_{K'K}^{+-} + \sigma_0 B_{\Gamma K}^{+-})\alpha_0 = 0$$

$$2(\alpha_0 J_\Gamma^{(D)} + \alpha_\Gamma J_0^{(D)}) + 2\pi(\frac{1}{2\pi} + 2J_0^{(D)}[8\pi\beta^* J_\Gamma^{(D)}) + (\sigma_K B_{K'K}^{+-} + \sigma_0 B_{\Gamma\Gamma}^{+-})\alpha_0 + \sigma_0 B_{K'\Gamma}^{+-}\alpha_K] -$$

$$-2\sigma_0\alpha_K B_{K'\Gamma}^{+-} - (2\sigma_K B_{K'\Gamma}^{+-} + \sigma_0 B_{\Gamma\Gamma}^{+-})\alpha_0 = 0$$

$$\alpha_K J_K^{(D)} + 2\pi J_K^{(D)}[4\pi\beta^* J_K^{(D)} + (\sigma_K B_{K'K}^{+-} + \sigma_0 B_{\Gamma K}^{+-})\alpha_0 + \sigma_0 B_{K'K}^{+-}\alpha_K] = 0$$

$$2\alpha_\Gamma J_\Gamma^{(D)} + 4\pi J_\Gamma^{(D)}[4\pi\beta^* J_\Gamma^{(D)} + (2\sigma_K B_{K'\Gamma}^{+-} + \sigma_0 B_{\Gamma\Gamma}^{+-})\alpha_0 + 2\sigma_0 B_{K'\Gamma}^{+-}\alpha_K] = \pi\sigma_0 B_{K\Gamma}^{+-} B_{K'\Gamma}^{+-} \quad (41)$$

$$y_{\alpha\beta}^{(D)} = 2\alpha_\alpha J_\beta^{(D)} +$$

$$+4\pi(1-\delta_{\beta 0})\{\alpha_\alpha(\frac{1}{2\pi} + 2J_0^{(D)})[(1-\delta_{A\beta})B_{A\beta}^{+-}\sigma_B + (1-\delta_{B\beta})B_{B\beta}^{+-}\sigma_A + B_{\Gamma\beta}^{+-}\sigma_0] +$$

$$+[2\alpha_\alpha J_A^{(D)} + \frac{1}{2}(1-\delta_{\alpha 0})(1-\delta_{\alpha A})B_{\alpha A}^{+-}](1-\delta_{\beta B})B_{B\beta}^{+-}\sigma_0 +$$

$$+[2\alpha_\alpha J_B^{(D)} + \frac{1}{2}(1-\delta_{\alpha 0})(1-\delta_{\alpha B})B_{\alpha B}^{+-}](1-\delta_{\beta A})B_{A\beta}^{+-}\sigma_0\} \quad (42)$$

where $\beta^* = \frac{Z_+^2 e^2}{\epsilon}\beta$ and $J_\beta^{(D)} = \frac{1}{2}\sum_\gamma \sigma_{0\gamma}(J_{\gamma\beta}^{++} - J_{\gamma\beta}^{+-})$

Finally the relation between the densities (9) will takes the form

$$4\pi(B_{KK'}^{+-} + B_{K\Gamma}^{+-})\rho_0^2 + 4\pi B_{KK'}^{+-}\rho_0\rho_K - \rho_K = 0 \quad (43)$$

$$2\pi B_{\Gamma\Gamma}^{+-}\rho_0^3 + \rho_0^2 + (2\rho_K - \rho)\rho_0 + \rho_K^2 = 0 \quad (44)$$

where $\rho = \rho_+ = \rho_-$, $\rho_\alpha = \rho_\alpha^+ = \rho_\alpha^-$.

V. CONCLUDING REMARKS

In this paper we present an analytical solution of the mean spherical-like approximation [12,13] for a polymerizing primitive model of electrolytes. The model considered here is an extension of the totally flexible sticky two-point model of Wertheim [10] to the case of systems with ~~associating~~ that can interpenetrate upon association ionic monomers. In our version of the model bonding is allowed between any of two sites which belong to ~~the~~ two particles of any species. By choosing different types of site-site interaction a number of different submodels with different distributions of charge along the polymer chain formed due to the site-site interaction can be generated. The uncharged version of the model with site-site bonding allowed only between the sites of different types reduces to the totally flexible sticky two-site model considered in [8]. The restricted primitive version of the model with sticky interaction possible only between one pair of sites of the same type which belong to two particles of different species, reduces to the dimerizing model studied in [12]. Both cases can be treated as special cases to which the solution presented here applies.

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