Journal of Statistical Physics, Vol. 100, Nos. 1/2, 2000

Highly Asymmetric Electrolytes in the Associative Mean-Spherical Approximation

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Received September 14, 1999; final November 16, 1999

The associate mean-spherical approximation (AMSA) is used to derive the closed-form expressions for the thermodynamic properties of an $(n+m)$-component mixture of sticky charged hard spheres, with m components representing polyions and n components representing counterions. The present version of the AMSA explicitly takes into account association effects due to the high asymmetry in charge and size of the ions, assuming that counterions bind to only one polyion, while the polyions can bind to an arbitrary number of counterions. Within this formalism an extension of the Ebeling–Grigo choice for the association constant is proposed. The derived equations apply to an arbitrary number of components; however, the numerical results for thermodynamic properties presented here are obtained for a system containing one counterion and one macroion $(1+1$ component) species only. In our calculation the ions are pictured as charged spheres of different sizes (primitive model) embedded in a dielectric continuum. Asymmetries in charge of $-10:+1$, $-10:+2$, $-20:+1$, and $-20:+2$ and asymmetries in diameter of $2:0.4nm$ and $3:0.4nm$ are studied. Monte Carlo simulations are performed for the same model solution. By comparison with new and existing computer simulations it is demonstrated that the present version of the AMSA provides semiquantitative or better predictions for the excess internal energy and osmotic coefficient in the range of parameters where the regular hypernetted chain (HNC) and improved (associative) HNC do not yield convergent solutions. The AMSA liquid–gas phase diagram in the limit of complete association (infinitely strong sticky interaction) is calculated for models with different degrees of asymmetry.

KEY WORDS: Highly asymmetric electrolyte; primitive model; association; mean spherical approximation; osmotic coefficient.

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I. INTRODUCTION

It is our pleasure to dedicate this paper to George Stell whose fundamental work in statistical mechanics yielded considerable progress in the theory of strongly interacting solutions.

Physico-chemical properties of charged hard spheres, embedded in a dielectric continuum to mimic electrolyte solutions, have been attracting the attention of the liquid state research community for more than three decades. The existence of a liquid–gas phase transition for a two-component mixture of charged hard spheres of equal size in a dielectric continuum has been indicated first in computer simulations.(1–3) The next important contribution toward an understanding of this phenomenon was the theoretical work of Stell and coworkers.(4, 5) Though the first computer simulations have been performed as early as in 1971,(1–3) it is only recently that reliable simulation data on the values of critical parameters became available.(6–9) Concurrently, efforts have been focused on further development of the theoretical description for a charged hard sphere system (see ref. 10 and references therein). Though substantial progress has been achieved along these lines recently,(10–12, 14, 13, 15, 16) a consistent theory describing the RPM liquid–gas phase separation with reasonable quantitative accuracy is still emerging. It is therefore no surprise that a theoretical description of related systems, characterized by strong asymmetry in charge and size, is even less developed. Highly asymmetric electrolytes, where the ions are described as charged hard spheres of different size and charge, are used as models for micellar solutions, globular proteins and colloidal dispersions.(17, 18) For these electrolytes (also called polyelectrolytes) strong attractive and repulsive Coulombic forces acting between the ions are typical. These forces are primarily responsible for the non-ideal behaviour of polyelectrolyte solutions; the mobility and activity of small ions are reduced considerably below their values in bulk simple electrolytes.

In this work an electrolyte solution is treated as a multicomponent mixture of charged hard spheres immersed in a dielectric continuum representing the solvent. A number of theoretical methods have been applied to describe the equilibrium properties of these solutions.(17, 18) Among them the hypernetted chain (HNC) theory and the MSA have been used most extensively.(19–42) In comparison with computer simulations, the HNC approximation is found to be more accurate (for a review of integral equation results see ref. 18). However, the solution of the HNC approximation has to be obtained numerically, while the MSA has a relatively simple analytical solution that provides explicit expressions for the direct correlation function and thermodynamic properties.(43) For low asymmetry in charge and size both approximate theories provide reliable results for the equilibrium properties of these systems. However, the theories become less reliable if the asymmetry in charge and size increases. Finally, there is a range of the parameters corresponding to highly charged micelles and colloids for which the HNC approximation does not yield convergent solutions.(44) The region of parameters at which both HNC approximation and MSA fail to provide descriptions of these systems is characterized by an appreciable degree of macroion–counterion association.

Both the HNC approximation and the MSA are based on the Mayer ρ-expansion. For strongly associating fluids an infinite number of terms in the density expansion should be included to reproduce the correct low-density limit.(45) It is therefore unlikely that an approximation, based on a regular one-density integral equation theory, will provide adequate results for these strongly associating systems. Recently, a multidensity integral equation theory which explicitly accounts for the association effects in ionic systems,(45, 46) and in particular for ionic systems characterized by high asymmetry in charge and size,(35, 39, 40) has been proposed. The corresponding two-density version of the HNC approximation (we refer to it as the associative HNC (AHNC) approximation), yields better agreement with Monte Carlo data than the regular HNC approximation, and moreover, the range of applicability of the theory is extended toward lower concentrations. Unfortunately, the AHNC approximation is not immune to convergency problems (as associated with the regular HNC theory), especially if divalent counterions are present in solution. In addition, the two-density HNC theory is numerically quite complex; it is not convenient for daily analysis of experimental data. In contrast the potential theories such as a modified Poisson–Boltzmann theory(47) or a simple symmetric Poisson–Boltzmann theory(48, 49) require few iterations for convergence. The accuracy of these approximations for highly asymmetric electrolytes has not yet been extensively tested, however, recent studies of the multicomponent models(50, 51) show that both theories agree quite well with the Monte Carlo simulations.

In the present work an alternative approach to the study of dilute solutions of macroions and counterions is proposed. The theory is based on a two-density version of the multidensity formalism for systems with high asymmetry in interaction(35, 39) and an MSA-type of closure condition.(41, 52, 53) We refer to this extension of the MSA as the associative MSA (AMSA).(52, 53) Within the AMSA formalism the associative effects are taken into account via an additional "sticky" term in the closure, a term which causes the formation of clusters of particles with each cluster consisting of one polyion and an arbitrary number of counterions. Within this formalism, an extension of the Ebeling–Grigo(59) choice for the association constant is proposed. An analytical solution of the AMSA for the primitive model of a highly asymmetric electrolyte solution has been derived recently.[41] Similarly, as in the case of the regular MSA,[43] the electrostatic part of the solution reduces to the solution of one nonlinear algebraic equation for the MSA-like scaling parameter Γ. In the present paper, the general solution of the AMSA[41] is used to derive the closed form analytical expressions for the Helmholtz free energy, osmotic coefficient, and chemical potential. Our derivation is based on the extension of the method proposed previously in ref. 54. While the newly derived equations apply to an arbitrary number of components, the numerical results to be presented here apply to the simplest possible system; i.e., to a solution of macroions and counterions ($1+1$ component). Asymmetries in charge of $-10:+1$, $-10:+2$, $-20:+1$, and $-20:+2$, and asymmetries in diameter of $2:0.4nm$ and $3:0.4nm$ were considered. In parallel, the Monte Carlo computer simulations were performed for the same system.

This paper is organized as follows. After the Introduction, the AMSA and its analytical solution is reviewed in Section II. In Section III, we derive the relations for thermodynamic properties in the associative mean-spherical approximation. In the next section (IV) we discuss the equations valid for the two-component system containing macroions and counterions, and in Section V the corresponding numerical results are presented. Finally, we offer a few concluding remarks in Section VI.

II. ASSOCIATIVE MSA FOR THE PRIMITIVE MODEL OF A HIGHLY ASYMMETRIC ELECTROLYTE SOLUTION

We consider a model which consists of an $(m+n)$-component mixture of charged hard spheres of species $p_1,..., p_i,..., p_m$ with diameter σ_{p_i}, number density ρ_{p_i} and charge ez_{p_i} representing the polyions, and species $c_1,..., c_i,..., c_m$ with diameter σ_{c_i}, number density ρ_{c_i} and charge ez_{c_i} representing the counterions. For convenience we shall also use the indices $a, b, d,...$ to denote all $m+n$ species. The mixture is electroneutral:

$$\sum_a \rho_a z_a = 0 \tag{1}$$

The two-density version of the associative MSA for the model at hand can be written in the following form:

$$\mathbf{c}_{ab}(r) = -\frac{\beta e^2}{\varepsilon_0}\frac{z_a z_b}{r}\mathbf{E}_{ab} \qquad \text{for} \quad r > \sigma_{ab} \tag{2}$$

$$\mathbf{h}_{ab}(r) = -\mathbf{E}_{ab} + \frac{\mathbf{t}_{ab}}{2\pi\sigma_{ab}}\delta(r-\sigma_{ab}) \qquad \text{for} \quad r \leqslant \sigma_{ab} \tag{3}$$

where $\sigma_{ab}=\frac{1}{2}(\sigma_a+\sigma_b)$, ε_0 is the dielectric constant of the continuum, $\beta=1/k_BT$, and $\mathbf{E}_{ab}$ is the matrix with the elements $[\mathbf{E}_{ab}]^{\alpha\beta}=E_{ab}^{\alpha\beta}=\delta_{\alpha 0}\delta_{\beta 0}$. Further, $\mathbf{h}_{ab}(r)$ and $\mathbf{c}_{ab}(r)$ are the matrices with the elements being the partial total $h_{ab}^{\alpha\beta}(r)$ and direct $c_{ab}^{\alpha\beta}(r)$ correlation functions

$$\mathbf{h}_{ab}(r)=\begin{pmatrix} h_{ab}^{00}(r) & h_{ab}^{01}(r) \\ h_{ab}^{10}(r) & h_{ab}^{11}(r) \end{pmatrix}, \qquad \mathbf{c}_{ab}(r)=\begin{pmatrix} c_{ab}^{00}(r) & c_{ab}^{01}(r) \\ c_{ab}^{10}(r) & c_{ab}^{11}(r) \end{pmatrix} \tag{4}$$

The superscripts α and β assume the values 0 and 1 and denote the bonded ($\alpha=1$) and unbonded ($\alpha=0$) states of the corresponding particle, and $\mathbf{t}_{ab}$ is the matrix with the elements

$$\mathbf{t}_{ab}=\delta_{ap_i}\delta_{bc_j}\begin{pmatrix} 0 & t_{p_ic_j} \\ 0 & 0 \end{pmatrix}+\delta_{ac_i}\delta_{bp_j}\begin{pmatrix} 0 & 0 \\ t_{c_ip_j} & 0 \end{pmatrix} \tag{5}$$

where $t_{p_ic_j}=K_{p_ic_j}g_{p_ic_j}^{00}$, $g_{p_ic_j}^{00}(\sigma_{p_ic_j}+\ )$ and $K_{p_ic_j}$ describes the strength of the associative interaction.

The total and direct correlation functions satisfy the following Ornstein–Zernike (OZ) equation

$$\mathbf{h}_{ab}(r)=\mathbf{c}_{ab}(r)+\sum_d \rho_d\int d\mathbf{r}_1\,\mathbf{c}_{ad}(|\mathbf{r}_1-\mathbf{r}|)\,\boldsymbol{\alpha}_d\mathbf{h}_{db}(\mathbf{r}_1) \tag{6}$$

where

$$\boldsymbol{\alpha}_a=\begin{pmatrix} 1 & \alpha_a \\ \alpha_a & 0 \end{pmatrix} \tag{7}$$

$\alpha_a=\rho_a^0/\rho_a$ ($\alpha_{p_i}=1$) and ρ_a^0 is the "density" of the unbonded counterions, which is defined by

$$\rho_{c_i}=\rho_{c_i}^0\left[1+2\sum_k^m \rho_{p_k}\sigma_{c_ip_k}t_{c_ip_k}\right] \tag{8}$$

Recently, a general solution of the AMSA for a multicomponent mixture of polyions and counterions was published.$^{(41)}$ The derivation will be very briefly repeated here; the interested readers are referred to the original publication for more details.

The solution was obtained by utilizing Baxter's technique, which factorizes the initial OZ equation (6) into the two parts

$$\mathbf{S}_{ab}(r)=\mathcal{Q}_{ab}(r)-\sum_d \rho_d\int dr_1\,\mathcal{Q}_{ad}(r_1)\,\boldsymbol{\alpha}_d\mathcal{Q}_{bd}^T(r_1-r) \tag{9}$$

and

$$\mathbf{J}_{ab}(r) = \mathcal{Q}_{ab}(r) + \sum_{d} \rho_d \int dr_1\, \mathbf{J}_{ad}(|r_1 - r|)\, \boldsymbol{\alpha}_d \mathcal{Q}_{db}(r_1) \tag{10}$$

where T denotes the transpose matrix. The projections $\mathbf{S}_{ab}(r)$ and $\mathbf{J}_{ab}(r)$

$$\mathbf{J}_{ab}(r) = 2\pi \int_r^\infty ds\, s\, \mathbf{h}_{ab}(s) \tag{11}$$

$$\mathbf{S}_{ab}(r) = 2\pi \int_r^\infty ds\, s\mathbf{c}_{ab}(s) \tag{12}$$

satisfy the boundary conditions

$$\mathbf{J}_{ab}(r) = \pi r^2 \mathbf{E}_{ab} + \mathbf{J}_{ab} \qquad \text{for} \quad r \leqslant \sigma_{ab} \tag{13}$$

$$\mathbf{S}_{ab}(r) = -\frac{\beta e^2}{\varepsilon_0} \frac{z_b z_a e^{-\mu |r|}}{\mu} \mathbf{E}_{ab} \qquad \text{for} \quad r > \sigma_{ab} \tag{14}$$

obtained from (2) and (3). Here $\mathbf{J}_{ab} = \mathbf{J}_{ab}(0)$ and the limit $\mu = 0$ is to be taken at the end of the calculation.

From the analysis of Eqs. (9) and (10) for $\mathcal{Q}_{ab}(r)$ we have

$$\mathcal{Q}_{ab}(r) = [\mathbf{Q}_{ab}(r) + \mathbf{t}_{ab}]\, \theta(\sigma_{ab} - r) - \hat{\mathbf{z}}_a \hat{\mathbf{a}}_b \qquad \text{for} \quad \lambda_{ab} < r \tag{15}$$

where $\lambda_{ba} = \frac{1}{2}(\sigma_b - \sigma_a)$ and the function $\mathbf{Q}_{ab}(r)$ is defined in the range $\lambda_{ba} < r < \sigma_{ab}$ by

$$\mathbf{Q}_{ab}(r) = \tfrac{1}{2} \mathbf{A}_b (r - \sigma_{ab})(r - \lambda_{ba}) + \boldsymbol{\beta}_{ab}(r - \sigma_{ab}) \tag{16}$$

Here $\hat{\mathbf{a}}_a$ and $\hat{\mathbf{z}}_a$ are the row and column vectors, respectively

$$\hat{\mathbf{a}}_a = (a_a^0, a_a^1), \qquad \hat{\mathbf{z}}_a = \begin{pmatrix} z_a \\ 0 \end{pmatrix}$$

Coefficients of the Baxter $\mathcal{Q}$-function $\mathbf{A}_b$, $\boldsymbol{\beta}_{ab}$ and $\hat{\mathbf{a}}_b$ can be expressed in terms of two parameters, i.e., the fraction of the free particles α_a and the screening AMSA parameter Γ.(41, 43, 55) We obtain

$$\beta_{ab}^{\alpha\beta} = \delta_{\alpha 0}\left[\frac{\pi\sigma_b}{\mathit{\Delta}}\,\delta_{\beta 0} + M_a^0 a_b^\beta\right] + (1-\delta_{\alpha 0})\, B_a^\alpha a_b^\beta \tag{17}$$

$$A_b^{\alpha\beta} = 2\delta_{\alpha 0} a_b^\beta \eta^B + \delta_{\alpha 0}\delta_{\beta 0}\,\frac{2\pi}{\mathit{\Delta}}\left[1+\zeta_2\,\frac{\pi\sigma_b}{2\mathit{\Delta}}\right] - \frac{2\pi}{\mathit{\Delta}}\,\delta_{\alpha 0} t_b^\beta \tag{18}$$

$$a_a^0 = \frac{1}{\mathscr{D}}\left[-2M_a^0 - 2\sigma_a\eta^B + 2\sum_d \rho_d \alpha_d t_{ad}^{01}(M_d^0\sigma_d + z_d)\right] \tag{19}$$

$$a_a^1 = \frac{1}{\mathscr{D}}\left[2\sum_d \rho_d t_{ad}^{10}(\sigma_d N_d^T + z_d)\right] \tag{20}$$

where

$$\sigma_a M_a^0 = X_a^0 - z_a, \qquad B_a^0 = N_a^T - \alpha_a B_a^1 - \frac{\pi}{6}\sum_d \rho_d \sigma_d^3 N_d^T + \chi_2 \mathit{\Delta}, \qquad \sigma_a B_a^1 = X_a^1 \tag{21}$$

$$\sigma_a N_a^T = X_a^T - z_a, \qquad X_a^T = X_a^0 + \alpha_a X_a^1 \tag{22}$$

$$\mathscr{D} = \sum_d \rho_d(\sigma_d N_d^T + z_d)^2 - \sum_d \rho_d(\sigma_d\alpha_d B_d^1)^2 \tag{23}$$

$$\chi_2 = \sum_d \rho_d z_d \sigma_d^2, \qquad \mathit{\Delta} = 1 - \tfrac{1}{6}\pi\zeta_3, \qquad \zeta_k = \sum_d \rho_d \sigma_d^k \tag{24}$$

and unknowns X_a^0 and X_a^1 satisfy the following set of linear equations:

$$\sum_d \mathscr{M}_{ad}\hat{\mathbf{X}}_d = \hat{\mathbf{z}}_a \tag{25}$$

In this equation $\hat{\mathbf{X}}_a$ is a column vector $\hat{\mathbf{X}}_a = \binom{X_a^0}{X_a^1}$ and $\mathscr{M}_{ab}$ is the following matrix

$$\mathscr{M}_{ab} = (1+\mathit{\Gamma}^T\sigma_b)\,\delta_{ab} + \rho_b\sigma_a\left[\frac{\pi}{2\mathit{\Delta}}\,\sigma_b\sigma_a\mathbf{E}_{ab} - \mathbf{t}_{ab}\right]\boldsymbol{\alpha}_b \tag{26}$$

By taking into account the structure of matrix $\mathbf{t}_{ab}$ for the model at hand, we can obtain the solution for this set of equations in a closed form. As a result we get

$$X_{x_i}^\alpha = \frac{\tau_{x_i}^\alpha(z) - \eta^B\tau_{x_i}^\alpha(\sigma^2)}{1+\sigma_{x_i}\mathit{\Gamma}} \qquad (\alpha = 0, 1;\ x = p, c) \tag{27}$$

where

$$\eta^B = \frac{(\pi/2\Delta)[\tau_p(z) + \tau_c(z)]}{1 + (\pi/2\Delta)[\tau_p(\sigma^2) + \tau_c(\sigma^2)]} \tag{28}$$

$$\tau_x(v) = \sum_k \rho_{x_k}\sigma_{x_k} \frac{\tau^0_{x_k}(v) + \alpha_{x_k}\tau^1_{x_k}(v)}{1 + \sigma_{x_k}\Gamma} \qquad (v = z, \sigma^2) \tag{29}$$

$$\tau^0_{p_i}(v) = v_{p_i} + \sigma_{p_i} \sum_k \rho_{c_k}\alpha_{c_k} \frac{t_{p_i c_k} v_{c_k}}{1 + \sigma_{c_k}\Gamma} \tag{30}$$

$$\tau^1_{p_i}(v) = 0 \tag{31}$$

$$\frac{\tau^1_{c_i}(v)}{\sigma_{c_i}} = \sum_k^m \rho_{p_k} \frac{t_{c_i p_k} v_{p_k}}{1 + \sigma_{p_k}\Gamma} + \sum_k^m \rho_{p_k}\sigma_{p_k} \frac{t_{c_i p_k}}{1 + \sigma_{p_k}\Gamma} \sum_l^m \rho_{c_l}\alpha_{c_l} \frac{t_{p_k c_l} v_{c_l}}{1 + \sigma_{c_l}\Gamma} \tag{32}$$

Finally, the screening parameter Γ follows from the solution of the nonlinear algebraic equation

$$\Gamma^2 = \pi \frac{\beta e^2}{\varepsilon_0} \left\{ \sum_k^m \rho_{p_k}(X^0_{p_k})^2 + \sum_k^n \rho_{c_k}[(X^0_{c_k})^2 + 2\alpha_{c_k} X^1_{c_k} X^0_{c_k}] \right\} \tag{33}$$

where the fraction of monomers α_{c_i} satisfies Eq. (8). This equation contains the contact value of the partial pair correlation function $g^{00}_{c_i p_j}(r)$

$$2\pi\sigma_{c_i p_j} g^{00}_{c_i p_j}(\sigma^+_{c_i p_j}) = 2\pi\sigma_{c_i p_j} g^{hs}_{c_i p_j}(\sigma^+_{c_i p_j}) - 2\pi \frac{\beta e^2}{\varepsilon_0} X^0_{c_i} X^0_{p_j} - \frac{\pi}{\Delta}\sigma_{c_i} t_{p_j} \tag{34}$$

Here, $g^{hs}_{c_i p_j}(\sigma^+_{c_i p_j})$ is the corresponding hard-sphere contact value and

$$t_{p_j} = \sum_l \rho_{c_l}\sigma_{c_l}\alpha_{c_l} t_{c_l p_j}$$

III. THERMODYNAMIC PROPERTIES

Thermodynamic properties will be obtained through the energy route by generalization of the method developed for a fluid of dimerizing charged hard spheres.(54) From the standard expression for the excess internal energy per unit volume,(43)

$$\Delta E = 2\pi \sum_{ab} \rho_a \rho_b \int_0^\infty dr\, r^2 U^{(C)}_{ab}(r)\, g_{ab}(r) \tag{35}$$

we get

$$\beta \Delta E = \frac{e^2}{\varepsilon} \sum_a \rho_a z_a N_a^T \tag{36}$$

where N_a^T is defined by Eq. (22).

The excess Helmholtz free energy per unit volume is then$^{(43, 56)}$

$$\beta \Delta A = \beta \Delta E - \int_0^{\Gamma} d\Gamma' \, \beta' \, \frac{\partial}{\partial \Gamma'} \Delta E \tag{37}$$

The internal energy depends on screening parameter Γ explicitly, and also through the fraction of monomers α_{c_i} and parameter $t_{c_i p_j}$. Since these two quantities appear only in the form of the product $\alpha_{c_i} \rho_{c_i} t_{c_i p_j}$, the expression for the Helmholtz free energy (37) can be written as follows

$$\beta \Delta A = \beta \Delta E - \int_0^{\Gamma} d\Gamma' \, \beta' \left(\frac{\partial \Delta E}{\partial \Gamma'} \right)_{\rho_d} - \int_0^{\Gamma} d\Gamma' \, \beta' \sum_{ik} \left(\frac{\partial \Delta E}{\partial \alpha_{c_i} \rho_{c_i} t_{c_i p_k}} \right)_{\Gamma} \frac{\partial \alpha_{c_i} \rho_{c_i} t_{c_i p_k}}{\partial \Gamma'} \tag{38}$$

where subscripts ρ_d and Γ indicate that differentiation is carried out at constant values of the product $\alpha_{c_i} \rho_{c_i} t_{c_i p_k}$ and screening parameter Γ. From (36) and (22) we obtain

$$\beta \left(\frac{\partial \Delta E}{\partial \Gamma} \right)_{\rho_d} = \beta^* \sum_a \frac{\rho_a z_a}{\sigma_a} \left(\frac{\partial X_a^T}{\partial \Gamma} \right)_{\rho_d} \tag{39}$$

where $\beta^* = \beta e^2/\varepsilon_0$. The expression for $(\partial X_a^T/\partial \Gamma)_{\rho_d}$ can be derived from the set of equations (25). In this respect it is convenient to rewrite this set in a form which involves the sum of X_a^0 and X_a^1, i.e., $X_a^T = X_a^0 + \alpha_a X_a^1$. We obtain

$$\sum_b M_{ab} X_b^T = z_a + \sigma_a T_a^0(z) \tag{40}$$

where

$$M_{ab} = \delta_{ab}(1 + \sigma_a \Gamma) + \frac{\pi}{2\Delta} \sigma_a \rho_b \sigma_b [T_a^0(\sigma^2) + \sigma_a] \tag{41}$$

and

$$T_a^0(x) = \sum_b \rho_b \frac{\alpha_b t_{ab}^{01} + \alpha_a t_{ab}^{10}}{1 + \sigma_b \Gamma} \tau_b^0(x) \tag{42}$$

By differentiation of Eq. (40) with respect to Γ at constant $\alpha_{c_i}\rho_{c_i}t_{c_ip_j}$ we get the following expression for $\partial X_a^T/\partial\Gamma$

$$\begin{aligned} -\left(\frac{\partial X_a^T}{\partial \Gamma}\right)_{\rho_d} = {} & \sum_j \sigma_{p_j} M^{-1}_{ap_j}\left[X^T_{p_j} + \sum_k \rho_{c_k}\frac{\alpha_{c_k}\sigma_{c_k}X^0_{c_k}t_{p_jc_k}}{1+\sigma_{c_k}\Gamma}\right] \\ & + \sum_j \sigma_{c_j} M^{-1}_{ac_j}\left[X^T_{c_j} + \alpha_{c_j}\sum_k \rho_{p_k}\frac{\sigma_{p_k}X^0_{p_k}t_{c_jp_k}}{1+\sigma_{p_k}\Gamma}\right. \\ & \left. + \alpha_{c_j}\sum_k\sum_l \rho_{p_k}\rho_{c_l}\frac{\alpha_{c_l}\sigma_{p_k}\sigma_{c_l}X^0_{c_l}t_{c_jp_k}t_{p_kc_l}}{(1+\sigma_{p_k}\Gamma)(1+\sigma_{c_l}\Gamma)}\right] \end{aligned} \tag{43}$$

By substituting this expression into (39) and using (41) to calculate the inverse of matrix M_{ab} we arrive finally at the following relation$^{(42)}$

$$\beta\left(\frac{\partial \Delta E}{\partial \Gamma}\right)_{\rho_d} = -\frac{\Gamma^2}{\pi} \tag{44}$$

which gives us the possibility to calculate the first integral in (38)

$$\begin{aligned} \beta\Delta A = {} & \beta\Delta E + \frac{\Gamma^3}{3\pi} - 2\beta^* \sum_{ik} \rho_{p_k}\alpha_{c_i}\rho_{c_i}t_{c_ip_k}X^0_{p_k}X^0_{c_i} \\ & + 2\sum_{ik}\int_0^{\Gamma} d\Gamma'\, \beta'\alpha_{c_i}\rho_{c_i}\rho_{p_k}t_{c_ip_k}\frac{\partial \beta^* X^0_{p_k}X^0_{c_i}}{\partial\Gamma} \end{aligned} \tag{45}$$

In this expression (45), the last two terms on the right hand side appear as a result of the modification of the second integral in Eq.(38), by using the equality

$$\beta\sum_{ik}\left(\frac{\partial \Delta E}{\partial \alpha_{c_i}\rho_{c_i}t_{c_ip_k}}\right)_{\Gamma}\frac{\partial \alpha_{c_i}\rho_{c_i}t_{c_ip_k}}{\partial \Gamma} = 2\beta^*\sum_{ik}\rho_{p_k}X^0_{p_k}X^0_{c_i}\frac{\partial\alpha_{c_i}\rho_{c_i}t_{c_ip_k}}{\partial\Gamma} \tag{46}$$

This relation can be obtained after straightforward but tedious algebra by a direct differentiation of the equation (36) for the excess internal energy.

To evaluate the second integral in (38) we will follow ref. 54 and introduce the following quantity

$$\beta\Delta A_{\mathrm{MAL}} = \sum_i \rho_{c_i}\ln\alpha_{c_i} \tag{47}$$

which after differentiation gives

$$\frac{\partial \beta \Delta A_{\mathrm{MAL}}}{\partial \Gamma} = -2 \sum_{ij} \alpha_{c_i} \rho_{c_i} \rho_{p_j} \sigma_{c_i p_j} t_{c_i p_j} \frac{\partial \ln g^{00}_{c_i p_j}}{\partial \Gamma} \tag{48}$$

Here the relation between the densities (8) has been used. Now, assuming the exponential approximation for the contact value $g^{00}_{c_i p_j}$, i.e.,

$$g^{00}_{c_i p_j} = \left(g^{(\mathrm{hs})}_{c_i p_j} - \frac{\sigma_{c_i}}{2\Delta \sigma_{c_i p_j}} r^{(\mathrm{ref})}_{p_j} \right) \exp \left\{ -\frac{\beta^*}{\sigma_{c_i p_j}} X^0_{c_i} X^0_{p_j} - \frac{\sigma_{c_i}}{2\Delta \sigma_{c_i p_j}} (t_{p_j} - t^{(\mathrm{ref})}_{p_j}) \right\} \tag{49}$$

and substituting it into Eq. (48) we obtain

$$\frac{\partial \beta \Delta A_{\mathrm{MAL}}}{\partial \Gamma} = 2 \sum_{ij} \alpha_{c_i} \rho_{c_i} \rho_{p_j} t_{c_i p_j} \frac{\partial \beta^* X^0_{c_i} X^0_{p_j}}{\partial \Gamma} + \frac{1}{2\Delta} \sum_j \rho_{p_j} \frac{\partial t^2_{p_j}}{\partial \Gamma} \tag{50}$$

This result allows us to write the final expression for the difference in the Helmholtz free energy between the original and reference system

$$\beta \Delta A = \beta \Delta E + \frac{\Gamma^3}{3\pi} - 2\beta^* \sum_{ik} \rho_{p_k} \alpha_{c_i} \rho_{c_i} t_{c_i p_k} X^0_{p_k} X^0_{c_i} + \beta(\Delta A_{\mathrm{MAL}} - \Delta A^{(\mathrm{ref})}_{\mathrm{MAL}})$$
$$- \frac{1}{2\Delta} \sum_j \rho_{p_j} [(t_{p_j})^2 - (t^{(\mathrm{ref})}_{p_j})^2] \tag{51}$$

Here, the reference system is chosen to be equal to the original system but with zero charges ($z_a = 0$) on the ions. The values of $K_{c_i p_j}$ remain unchanged. In (49) and (51) $t^{(\mathrm{ref})}_{p_j}$ and $\Delta A^{(\mathrm{ref})}_{\mathrm{MAL}}$ correspond to t_{p_j} and ΔA_{MAL} for such a reference system.

Application of expression (51) for the Helmholtz free energy requires a thermodynamic description of the reference system; the properties of the latter can be obtained as described before.$^{(57)}$ The virial expansion for the Helmholtz free energy of the system with uncharged particles (ions stripped of their charge) $A^{(\mathrm{ref})}$ in excess to that of the hard-sphere system A_{hs} is given by

$$\beta(A^{(\mathrm{ref})} - A_{\mathrm{hs}}) = \sum_i \rho_{c_i} \ln \alpha^{(\mathrm{ref})}_{c_i} - \rho_{c_i} \alpha^{(\mathrm{ref})}_{c_i} + \rho_{c_i} - \frac{1}{V} (c^{(0)}_{\mathrm{ref}} - c^{(0)}_{\mathrm{hs}}) \tag{52}$$

where

$$\frac{1}{V} (c^{(0)}_{\mathrm{ref}} - c^{(0)}_{\mathrm{hs}}) = 2 \sum_{ij} \rho_{p_j} \alpha^{(\mathrm{ref})}_{c_i} \rho_{c_i} \sigma_{c_i p_j} t^{(\mathrm{ref})}_{c_i p_j} \tag{53}$$

and $\alpha_{c_i}^{(\mathrm{ref})}$ is the fraction of unbonded counterions of the reference system. Taking into account the relation between the densities (8) we have

$$\beta(A^{(\mathrm{ref})} - A_{\mathrm{hs}}) = \sum_i \rho_{c_i} \ln \alpha_{c_i}^{(\mathrm{ref})} = \beta \Delta A_{\mathrm{MAL}}^{(\mathrm{ref})} \tag{54}$$

Finally the expression for the Helmholtz free energy of the system in excess to that of the hard-sphere system is:

$$\begin{aligned}\beta\Delta A = \beta\Delta E + \frac{\Gamma^3}{3\pi} - 2\beta^* \sum_{ik} \rho_{p_k} \alpha_{c_i} \rho_{c_i} t_{c_i p_k} X_{p_k}^0 X_{c_i}^0 + \beta\Delta A_{\mathrm{MAL}} \\ - \frac{1}{2\Delta} \sum_j \rho_{p_j} [(t_{p_j})^2 - (t_{p_j}^{(\mathrm{ref})})^2]\end{aligned} \tag{55}$$

Another important thermodynamic quantity is the osmotic coefficient φ. To derive this property we use the standard thermodynamic relation

$$\Delta\varphi = \rho \left[\frac{\partial}{\partial\rho} \left(\frac{\Delta A}{\rho} \right) \right]_{\Gamma} \tag{56}$$

where $\rho = \sum_a \rho_a$. By using (36), (47), and 8 we get

$$\left(\frac{\partial\beta\Delta E}{\partial\rho} \right)_{\Gamma} = \left(\frac{\partial\beta\Delta E}{\partial\rho} \right)_{\Gamma, \rho_d} + 2\beta^* \sum_{ik} X_{p_k}^0 X_{c_i}^0 \rho_{p_k} \left(\frac{\partial \rho_{c_i} \alpha_{c_i} t_{c_i p_k}}{\partial\rho} \right)_{\Gamma} \tag{57}$$

$$\begin{aligned}\left(\frac{\partial\beta\Delta A_{\mathrm{MAL}}}{\partial\rho} \right)_{\Gamma} &= \sum_i x_{c_i} \ln \alpha_{c_i} - 2 \sum_{ij} x_{p_j} \alpha_{c_i} \rho_{c_i} \sigma_{c_i p_j} t_{c_i p_j} \\ &\quad - 2 \sum_{ij} \rho_{p_j} \alpha_{c_i} \rho_{c_i} \sigma_{c_i p_j} t_{c_i p_j} \frac{\partial}{\partial\rho} \left[\ln \left(g_{c_i p_j}^{(\mathrm{hs})} - \frac{\sigma_{c_i}}{2\Delta\sigma_{c_i p_j}} t_{p_j}^{(\mathrm{ref})} \right) \right. \\ &\quad \left. - \frac{\beta^*}{\sigma_{c_i p_j}} X_{c_i}^0 X_{p_j}^0 - \frac{\sigma_{c_i}}{2\Delta\sigma_{c_i p_j}} (t_{p_j} - t_{p_j}^{(\mathrm{ref})}) \right]\end{aligned} \tag{58}$$

where $x_a = \rho_a / \rho$. By substituting (55), (57), and (58) into (56) we obtain the expression for the excess osmotic coefficient

$$\begin{aligned}\Delta\varphi = & -\frac{\Gamma^3}{3\pi\rho} - \beta^* \frac{2}{\pi\rho} (\eta^B)^2 - 2 \sum_{ij} x_{p_j} \alpha_{c_i} \rho_{c_i} \sigma_{c_i p_j} t_{c_i p_j} \\ & \times \left[1 + \rho \frac{\partial}{\rho} \ln \left(g_{c_i p_j}^{(\mathrm{hs})} - \frac{\sigma_{c_i}}{2\Delta\sigma_{c_i p_j}} t_{p_j}^{(\mathrm{ref})} \right) \right] \\ & + \frac{1 - \Delta}{2\rho\Delta^2} \sum_j \rho_{p_j} (t_{p_j} - t_{p_j}^{(\mathrm{ref})})^2 - \frac{1}{\Delta} \sum_j \rho_{p_j} (t_{p_j} - t_{p_j}^{(\mathrm{ref})}) \frac{\partial t_{p_j}^{(\mathrm{ref})}}{\partial\rho}\end{aligned} \tag{59}$$

Knowing the Helmholtz free energy and the osmotic coefficient enables us to write down the expression for the mean activity coefficient. It follows directly from the thermodynamic relation

$$\Delta \ln \gamma_{+-} = \beta \frac{\Delta A}{\rho} + \Delta \varphi \tag{60}$$

IV. TWO-COMPONENT CASE: A SOLUTION OF MACROIONS AND COUNTERIONS

To illustrate the general results obtained in the previous sections we consider a system which consists of one species representing polyions and another species representing counterions. The system as whole is electroneutral.

A. Solution of the AMSA for the 2-Component Case

The set of nonlinear algebraic equations representing solution of the AMSA will be reduced now to a set of two equations, i.e.,

$$\Gamma^2 = \pi\beta^* \{\rho_p (X_p^0)^2 + \rho_c[(X_c^0)^2 + 2X_c^0 \alpha_c X_c^1]\} \tag{61}$$

and

$$\alpha_c + 2\rho_p K_{cp} \alpha_c \left[\sigma_{cp} g_{cp}^{(\mathrm{hs})} - \frac{\sigma_c^2 (1-\alpha_c^{(\mathrm{ref})})\, \rho_c}{4\rho_p \sigma_{cp} \Delta} \right] \\ \times \exp\left\{ -\frac{\beta^*}{\sigma_{cp}} X_c^0 X_p^0 - \frac{\sigma_c^2 \rho_c}{4\rho_p \sigma_{cp}^2 \Delta} (\alpha_c^{(\mathrm{ref})} + \alpha_c) \right\} - 1 = 0 \tag{62}$$

where $g_{cp}^{(\mathrm{hs})} = g_{cp}^{(\mathrm{hs})}(\sigma_{cp}^{+})$. The first equation (61) follows from the expression for Γ (33) and the second one (62) is obtained from Eq. (8), in which the exponential approximation for the contact value g_{pc}^{00} is used. Both equations contain X_p^0, X_c^0 and X_c^1 as parameters. These quantities are related to α_c and Γ via Eq. (27). For the two-component case we have

$$X_p^0 = \Gamma_p \left[(z_p - \sigma_p^2 \eta^B) + \frac{\rho_c \sigma_p}{2\rho_p \sigma_{cp}} (1-\alpha_c)(z_c - \sigma_c^2 \eta^B)\, \Gamma_c \right] \tag{63}$$

$$X_c^0 = \Gamma_c (z_c - \sigma_c^2 \eta^B) \tag{64}$$

$$\alpha_c X_c^1 = \frac{\sigma_c (1-\alpha_c)}{2\sigma_{cp}} \Gamma_c X_p^0 \tag{65}$$

where $\Gamma_a = (1+\sigma_a\Gamma)^{-1}$, and

$$\eta^B = \frac{\begin{array}{c}\rho_p\sigma_p z_p\Gamma_p + \rho_c\sigma_c z_c\Gamma_c + ((1-\alpha_c)/2\sigma_{cp})\,\rho_c(\sigma_p^2 e_c + \sigma_c^2 z_p)\,\Gamma_p\Gamma_c \\ + ((1-\alpha_c)^2/4\sigma_{cp}^2\rho_p)\,\rho_c^2\sigma_c^2\sigma_p z_c\Gamma_c^2\Gamma_p\end{array}}{\begin{array}{c}(2\Delta/\pi) + \rho_p\sigma_p^3\Gamma_p + \rho_c\sigma_c^3\Gamma_c + ((1-\alpha_c)/\sigma_{cp})\,\rho_c\sigma_p^2\sigma_c^2\Gamma_p\Gamma_c \\ + ((1-\alpha_c)^2/4\sigma_{cp}^2\rho_p)\,\rho_c^2\sigma_c^4\sigma_p\Gamma_c^2\Gamma_p\end{array}} \tag{66}$$

The fraction of unbonded counterions for the uncharged system $\alpha_c^{(\mathrm{ref})}$ is given by

$$\alpha_c^{(\mathrm{ref})} = \frac{\Delta\sigma_{cp}}{\sigma_c^2\rho_c K_{cp}}\left[\sqrt{B^2 + \frac{2\sigma_c^2\rho_c K_{cp}}{\Delta\sigma_{cp}}} - B\right] \tag{67}$$

where

$$B = 1 + \left(2\rho_p\sigma_{cp}\,g_{cp}^{(\mathrm{hs})} - \frac{\sigma_c^2\rho_c}{2\Delta\sigma_{cp}}\right)K_{cp} \tag{68}$$

B. Thermodynamic Quantities

The expressions for the internal energy (36), Helmholtz free energy (55) and osmotic coefficient (59) reduce for the two-component system to the following form:

$$\beta\Delta E = \frac{e^2}{\varepsilon_0}\left[\frac{\rho_c z_c}{\sigma_c}(X_c^0 + z_c + \alpha_c X_c^1) + \frac{\rho_p z_p}{\sigma_p}(X_p^0 + z_p)\right] \tag{69}$$

$$\begin{aligned}\beta\Delta A = {} & \beta\Delta E + \frac{\Gamma^3}{3\pi} - \beta^*\,\frac{1-\alpha_c}{\sigma_{cp}}\,\rho_c X_p^0 X_c^0 + \beta\rho_c\ln\alpha_c \\ & - \frac{1}{2\Delta}\,\frac{\sigma_c^2\rho_c^2}{4\rho_p\sigma_{cp}^2}\,(\alpha_c^{(\mathrm{ref})} - \alpha_c)(2 - \alpha_c^{(\mathrm{ref})} - \alpha_c)\end{aligned} \tag{70}$$

$$\begin{aligned}\rho\Delta\varphi = {} & -\frac{\Gamma^3}{3\pi} - \frac{2\beta^*}{\pi}(\eta^B)^2 + \frac{1}{\Delta}\,\frac{\sigma_c^2\rho_c^2}{4\rho_p\sigma_{cp}^2}\,(\alpha_c - \alpha_c^{(\mathrm{ref})}) \\ & \times\left[\frac{1-\Delta}{2\Delta}(\alpha_c^{(\mathrm{ref})} - \alpha_c) + \frac{\partial\alpha_c^{(\mathrm{ref})}}{\partial\rho}\right] \\ & - (1-\alpha_c)\,\rho_c\left[1 + \rho\left(g_{cp}^{(\mathrm{hs})} - \frac{\sigma_c^2\rho_c(1-\alpha_c)}{4\rho_p\sigma_{cp}^2\Delta}\right)^{-1}\right. \\ & \left.\times\left(\frac{\partial g_{cp}^{(\mathrm{hs})}}{\partial\rho} + \frac{\sigma_c^2\rho_c}{4\rho_p\sigma_{cp}^2\Delta}\,\frac{\partial\alpha_c^{(\mathrm{ref})}}{\partial\rho}\right)\right]\end{aligned} \tag{71}$$

where the derivative $\partial\alpha_c^{(\mathrm{ref})}/\partial\rho$ is obtained from (67).

V. NUMERICAL RESULTS

In this section the numerical results for the thermodynamic properties of a highly asymmetric electrolyte in the associated mean-spherical approximation are presented. The expressions derived above were used to calculate the excess internal energy and osmotic coefficient of the model solution where the ions are depicted as charged hard-spheres. Four different model solutions were examined: (i) $z_p=-10$, $z_c=+1$, $\sigma_p=2nm$, $\sigma_c=0.4nm$; (ii) $z_p=-10$, $z_c=+2$, $\sigma_p=2nm$, $\sigma_c=0.4nm$; (iii) $z_p=-20$, $z_c=+1$, $\sigma_p=3nm$, $\sigma_c=0.4nm$; and (iv) $z_p=-20$, $z_c=+2$, $\sigma_p=3nm$, $\sigma_c=0.4nm$. Two different values of β^* were used for the model (i), i.e., $\beta^*=0.7155nm$ and $\beta^*=1.2nm$. The latter value of β^* was used to model the electrolyte in a solvent with a dielectric constant lower than that for water. In all other examples (ii)–(iv) the value of β^* was set to $0.7155nm$ to mimic an aqueous solution at 25°C.

Application of the equations derived in previous sections requires a knowledge of the constant of the association K_{ab}. There are several ways to choose the value of association constant K_{ab}.(13, 15, 58–61) In ref. 61 a connection between K_{ab} and the Ebeling–Grigo choice of association constant was established and a corresponding scheme for its evaluation in the case of a symmetrical electrolyte developed. According to this scheme parameter K_{pc} was chosen as a part of the ionic second virial coefficient which is not taken into account by the MSA. Unfortunately, direct application of the scheme proposed in ref. 61 is not possible, since in the case of an asymmetric ionic system it leads to divergency of the constant of association K_{pc}. Therefore application of a certain resummation procedure is needed. In the present study we used a modified version of the method proposed earlier.(61) Our modification is based on the optimized cluster expansion(62) which gives the following expression for the constant of association K_{pc}

$$X_pX_c\backslash\sigma_{pc}K_{pc}=2\pi\exp[-G^{\mathrm{MSA}}_{pc}]\sum_{ab}x_ax_b\int r^2$$

$$\times\{\exp[G^{\mathrm{MSA}}_{ab}]r(]-1-G^{\mathrm{MSA}}_{ab}(r)-\tfrac{1}{2}(G^{\mathrm{MSA}}_{ab}(r))^2\}\,dr \tag{72}$$

where $G^{\mathrm{MSA}}_{ab}(r)=h^{\mathrm{MSA}}_{ab}(r)-h^{\mathrm{hs}}_{ab}(r)$ is the MSA charge–charge correlation function (screened potential in the optimized cluster expansion(62)), $G_{pc}=G_{pc}(\sigma^+_{pc})$ and $h^{\mathrm{MSA}}_{ab}(r)$ is the MSA pair correlation function for the model under investigation. In the previous study(61) G_{pc} was chosen to be equal to the contact value of the interionic interaction. In the framework of the present scheme the contribution of the second virial coefficient is taken into account exactly. For the sake of simplicity $h_{ab}^{\mathrm{MSA}}(r)$ has been approximated as follows[(63)]

$$G_{ab}^{\mathrm{MSA}}(r)=\beta^* \frac{z_a z_b}{r(1+\sigma_a \Gamma^{\mathrm{MSA}})(1+\sigma_b \Gamma^{\mathrm{MSA}})} \exp[-\kappa_{ab}(r-\sigma_{ab})] \quad (73)$$

where Γ^{MSA} is the MSA screening parameter and $\kappa_{ab}^2=4\pi\beta^* \sum_a \rho_a z_a^2$. This approximation is exact at low densities and is expected to be of reasonable accuracy for the range of parameters studied in this work.

The accuracy of the proposed associated mean-spherical approximation was tested against computer simulations. New Monte Carlo simulations were performed in a canonical ensemble with 64 macroions and an equivalent number of counterions in the system, using the standard Metropolis algorithm.[(18, 35, 39, 40, 61)] Long runs were needed to obtain reliable results: the averages were taken over 35 to 50 million configurations with at least 5 million attempted configurations spent for the equilibration. To avoid effects due to the finite size of the simulation cell the Ewald summation method was used. The relative uncertainty in Monte Carlo results is about 1% for the excess internal energies and from 2 to 4% for the osmotic coefficients.

Numerical results for the excess internal energy and osmotic coefficient are presented in Figs. 1–4. Figures 1 and 2 show the excess internal energy

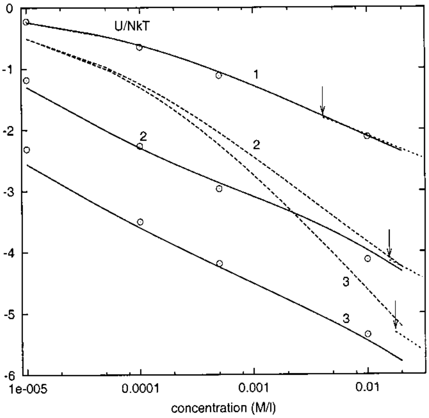

Fig. 1. Excess internal energy $\Delta E=U$ for a 10:1 electrolyte (1), 10:1 electrolyte at $\beta^*=1.2nm$ (2), and a 10:2 electrolyte (3). Simulations are presented by symbols and the lines denote theoretical results: AMSA (solid lines), MSA (long dashed lines), and HNC (short dashed lines). The Monte Carlo results for 10:1 (1) and 10:2 electrolytes (3) for macroion concentrations $c_p=0.0001$ M and $c_p=0.0005$ M, are from ref. 40.

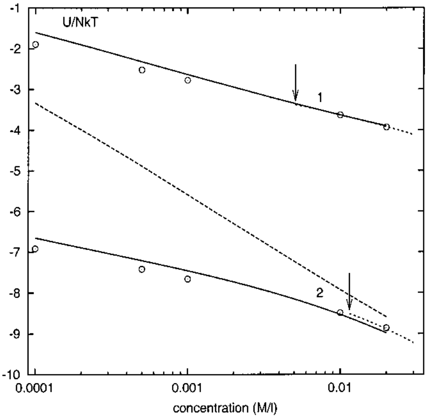

Fig. 2. Excess internal energy $\Delta E = U$ for a 20:1 electrolyte (1), and a 20:2 electrolyte (2). Simulations are presented by symbols and the lines denote theoretical results: AMSA (solid lines), MSA (long dashed lines), and HNC (short dashed lines). The Monte Carlo results for 20:1 (1) and 20:2 electrolytes (2) for macroion concentrations $c_p = 0.0001$ M and $c_p = 0.0005$ M, are from ref. 40.

for 10:1 and 10:2 electrolyte solutions and for 20:1 and 20:2 electrolyte solutions, respectively. Figures 3 and 4 present the corresponding results for the osmotic coefficient. In all figures the symbols denote the Monte Carlo results and the results of the AMSA theory are shown by the solid line. For the sake of comparison we also present the corresponding MSA

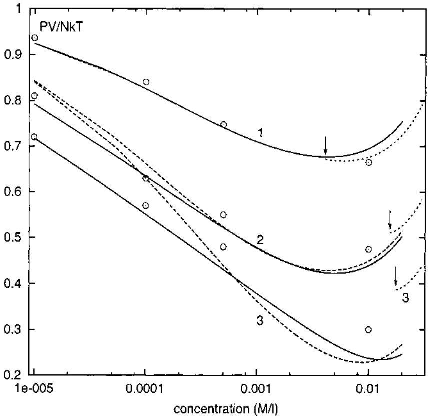

Fig. 3. Osmotic coefficient $\varphi = PV/NkT$ for a 10:1 electrolyte (1), 10:1 electrolyte at $\beta^* = 1.2nm$ (2), and a 10:2 electrolyte (3). Legend as for Fig. 1. The Monte Carlo results for 10:1 (1) and 10:2 electrolytes (3) for macroion concentrations $c_p = 0.0001$ M and $c_p = 0.0005$ M, are from ref. 40.

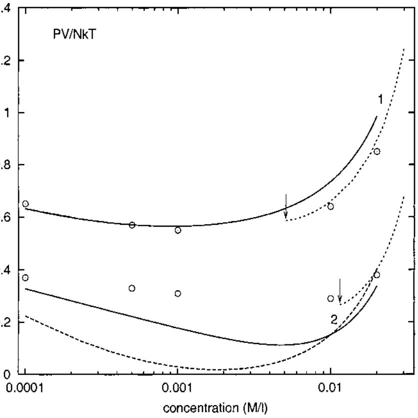

Fig. 4. Osmotic coefficient $\varphi = PV/NkT$ for a 20:1 electrolyte (1), and a 20:2 electrolyte (2). Legend as for Fig. 3. The Monte Carlo results for 20:1 (1) and 20:2 electrolytes (2) for macroion concentrations $c_p = 0.0001$ M and $c_p = 0.0005$ M, are from ref. 40.

results (long dashed lines) and HNC approximation results (short dashed lines) in the region where the convergent solution could be obtained. In the latter case, the limiting concentration below which we have not been able to obtain convergent results of the HNC approximation is pointed out by an arrow.

In all cases studied in this contribution the AMSA follows the Monte Carlo data for the excess internal energy reasonably well. Predictions of the MSA theory are in a good agreement with computer simulations for aqueous solutions with monovalent counterions ($\beta^* = 0.7155nm$). In this case the MSA results coincide with the AMSA predictions. For stronger couplings; i.e., for $\beta^* = 1.2nm$ or for solutions with divalent counterions ($z_c = 2$), the MSA breaks down. Similar tendencies are observed for the osmotic coefficient calculation. The agreement between the AMSA theory and MC simulation is quantitative or semiquantitative only for solutions with monovalent counterions and for $c \leqslant 0.001$ M. The MSA results for the osmotic coefficient coincide with those of AMSA in the case of aqueous solutions with monovalent counterions (i.e., for $\beta^* = 0.7155nm$). For 20:2 electrolyte solutions AMSA gives only qualitative correct predictions for this quantity.

The failure of the AMSA and other theories$^{(40)}$ to give an adequate description of polyelectrolyte solutions with divalent (or trivalent) counterions seem to be connected to the strong correlations between multivalent counterions. Recent computer simulations (see also ref. 18 and references therein) indicate that in solutions with monovalent counterions the macroions are distributed at larger distances from each other. In solutions with divalent counterions the macroions come closer to each other and share a layer of counterions,(64) while in solutions with trivalent counterions the macroions form clusters.(65) This explains the success of the two-density formalism in the case of solutions with monovalent counterions and also its failure for systems containing multivalent counterions.

Finally, in Fig. 5 we present the liquid–gas phase diagram for the primitive model of a highly asymmetric electrolyte solution in the limit of complete association. In this limit all the counterions are bonded; the average number of counterions bonded to a macroion is z_p/z_c and most of such polyion–counterion clusters are neutral. Theoretical investigation(66) and recent computer simulations(7, 67, 68) suggest that for the restrictive primitive model the fraction of free ions is negligible in the vicinity of the

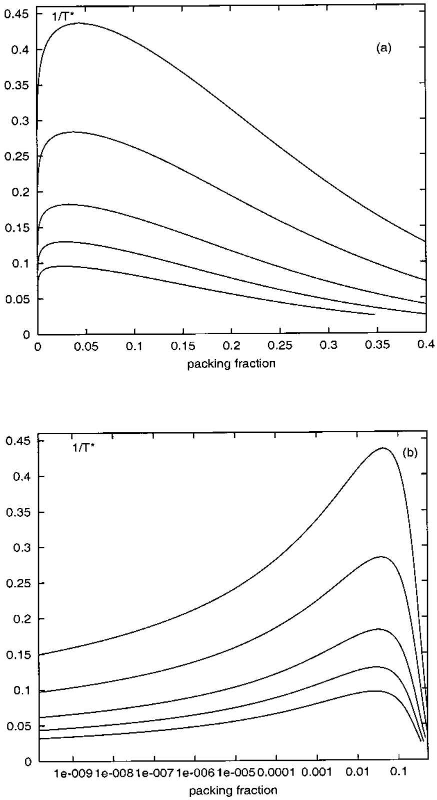

Fig. 5. Liquid–gas phase diagram in β^* versus η coordinates. From the top to the bottom at $\eta = z_p{:}z_c = 20{:}1$ ($\sigma_p{:}\sigma_c = 10{:}1$), $10{:}1(7.071{:}1)$, $5{:}1(5{:}1)$, $3{:}1(3.873{:}1)$, $2{:}1(3.333{:}1)$.

coexistence region. In this way, the equilibrium properties of the system are mostly determined by the present of the neutral ionic clusters, to which the ionic pairs give the main contribution. By assuming that in the complete association limit all the polyion–counterion clusters are neutral, it is possible to use the AMSA results to describe the liquid–gas separation for highly asymmetric electrolytes. Five different models with the charge and size ratio $z_p\!:\!z_c(\sigma_p\!:\!\sigma_c)=20\!:\!1(10\!:\!1)$, $10\!:\!1(7.071\!:\!1)$, $5\!:\!1(5\!:\!1)$, $3\!:\!1(3.873\!:\!1)$, $2\!:\!1(3.333\!:\!1)$ were studied. For the models considered here, the value of the polyion surface charge, i.e., the ratio z_p/σ_p^2 was kept constant. The results presented in Fig. 5 show that increase in the asymmetry in charge and size at constant polyion surface charge causes a decrease of the critical temperature and critical density. Unfortunately, the computer simulation data for these conditions are not available yet, and the predictions show in Fig. 5 remain to be tested.

VI. CONCLUDING REMARKS

Currently there seems to be a growing interest in extending theoretical techniques of the statistical mechanics of fluids to less simple systems such as solutions involving macroions and small ions. Knowledge of such systems is relevant to understanding the behaviour of surfactant micelles, globular proteins, and colloidal suspensions. In these systems there is a strong Coulombic interaction between the highly charged macroions and small ions (with valency one or two) in solution. These (polyelectrolyte) solutions can be reasonably well represented by a primitive model, where the ions are modelled as charged hard spheres moving in a continuous dielectric.

In this paper a closed form analytical expressions for the thermodynamic properties of the primitive model highly asymmetric electrolyte solution are derived. The derivation is based on an analytical solution for the two-density version of the associative MSA, as obtained recently. The two-density theory assumes the counterions be singly bondable; each counterion bonds to only one macroion. On the other hand, each macroion can be bonded to an arbitrary number of counterions. This is assumed to be good approximation for dilute and/or moderately charged systems; for multivalent counterions present in the solution this assumption appears to be less realistic. An extension of the Ebeling–Grigo choice for the association constant is proposed for this formalism. The equations for thermodynamic properties presented in this study are general; they apply to an arbitrary number of components. In this first study, however, we present numerical results for the simplest possible model only, i.e., for a solution of macroions and counterions. The models with asymmetry in charge of

$-20:+1$, $-20:2$, $-10:+1$ and $-10:2$, and asymmetries in size of $2:0.4nm$ and $3:0.4nm$ were examined. In parallel the Monte Carlo computer simulations were performed for the same model solutions. The comparison of the AMSA results with new and existing computer simulations revealed the usefulness of the associated mean spherical approximation. The present version of the AMSA is able to provide semi-quantitative or better predictions for the excess internal energy and osmotic coefficient in the region of parameters where the regular hypernetted chain (HNC) and improved (associative) HNC fail to give convergent solutions. By assuming complete association (infinitely strong sticky interaction), it was possible to obtain AMSA predictions for the liquid–gas phase diagram of models with different degrees of asymmetry between macroions and counterions.

ACKNOWLEDGMENT

V. Vlachy acknowledges the support of the Slovene Ministry of Science and Technology.

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