Multicomponent mixture of charged hard-sphere chain molecules in the polymer mean-spherical approximation

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The analytical solution of the recently proposed ideal chain polymer mean-spherical approximation [Kalyuzhnyi, Mol. Phys. 94, 735 (1998)] is presented for the multicomponent mixture of charged hard-sphere linear chain flexible molecules. The solution applies to any mixture of chain molecules with arbitrary distribution of the charge and size of the beads along the molecular backbone. Closed form analytical expressions for the internal energy, Helmholtz free energy, chemical potentials, and pressure are derived. By way of illustration thermodynamical properties of several versions of the fluid of charged chain molecules of different length, including the molecules with uniform, diblock, and alternating distribution of the charge, are studied. Theoretical predictions are in reasonable agreement with available computer simulation predictions. We also present the liquid–gas phase diagrams for systems with diblock and alternating distribution of the charge. © 2001 American Institute of Physics. [DOI: 10.1063/1.1376426]

I. INTRODUCTION

In recent years a substantial amount of effort has been focused on the development of theoretical approaches predicting the equilibrium structure and thermodynamical properties of charged polymer solutions. This information enables one to establish the stability limits and to build the phase diagrams of such fundamentally and technologically important systems as polyelectrolyte solutions (e.g., DNA, polyacrylic acid) and polynamphotye solutions (e.g., proteins). One of the simplest continuum models of charged polymer solutions is represented by the fluid of charged hard-sphere linear chain flexible molecules. In spite of its simplicity this model incorporates several essential features of charged polymer fluids, such as excluded volume effects, chain connectivity and flexibility, distribution of the charge along the chain backbone, and Coulomb interaction. Recently several off-lattice theories for the fluid of flexible charged chain molecules, based on the integral-equation techniques developed for the fluids of small molecules, have been proposed. These include extension of the polymer reference interaction site model (RISM) integral equation theory of Schweizer and Curro, extension of the simple interpolation scheme of Stell and Zhou, and extensions of the multidensity integral equation theory of Wertheim for associating fluids. The latter studies are based on the analytical solution of the mean spherical approximation (MSA) version of multidensity theory, the so-called polymer MSA (PMSA). In the case of an uncharged system, direct application of Wertheim’s original formulation by Chang and Sandler gave rise to a polydispersed fluid of chains with a prescribed mean number of beads. A subsequent extension by Kalyuzhnyi and Cummings yielded a model that polymerizes to a fluid of chains of fixed length in the complete association limit. In that limit, Wertheim’s two-density Ornstein–Zernike (OZ) equation becomes identical to the Rossky–Chiles version of the “proper” site–site integral equations ("proper RISM") as first noted by Kalyuzhnyi and Stell and later discussed in more detail by Stell and Kalyuzhnyi and Cummings. Using the extension proposed by Kalyuzhnyi and Cummings the so-called product-reactant OZ approach (PROZA) has been formulated and applied for the description of a number of different versions of uncharged flexible chain molecular systems. The PROZA, based on earlier work of Wertheim, is a general statistical-mechanical theory of reacting mixtures in which the product molecules and the reacting molecules are treated on the same footing. When applied to polymerizing monomers, PROZA yields the mean monomer–monomer pair correlation function, from which the thermodynamics of a fluid of polymerizing particles can be obtained directly. In the complete association limit, the theory becomes the theory for the structure and thermodynamics of a fluid of fully polymerized chains and it is such a fluid that we are concerned with here. Unlike the version of the PRISM theory utilized by Dymitrowska and Belloni, PROZA provides a self-contained description of both intramolecular and intermolecular correlations and is able to predict the conformational properties of the flexible chain molecules.

More recently, PROZA was combined with the ideal chain approximation and generalized for systems with arbitrary long-range potential outside the hard-core region. As a result the corresponding version of the PMSA was for-
mulated and the Høye–Stell scheme\textsuperscript{27} of calculating the simple fluids’ thermodynamical properties was extended in the frames of the PMSA.\textsuperscript{9} Subsequently von Solms and Chiew\textsuperscript{10} combined PMSA and ideal chain approximation in a manner similar to that proposed by Chang and Sandler.\textsuperscript{13} The resulting polydisperse chain mixture was used to describe thermodynamical properties of the two-component mixture of fixed-length chain molecules with equally charged beads and oppositely charged monomer counterions. Results of the theory appear to be in reasonable agreement with computer simulation results.\textsuperscript{26} We note in passing that the ideal chain approximation utilized by von Solms and Chiew is somewhat different from the original one.\textsuperscript{11,13} In the corresponding Wertheim OZ equation the authors take into account all partial correlation functions, while due to the original ideal chain approximation\textsuperscript{11,13} correlations involving at least one doubly bonded particle are neglected. Recently a general solution of the PMSA\textsuperscript{7,8} for polymerizing charged hard spheres, supplemented by the ideal chain approximation, was used to derive closed form analytical expressions for thermodynamical properties of charged chain fluid with certain restrictions imposed on the sizes of the chain beads.\textsuperscript{29} In the latter study the authors propose an improved version of the ideal chain approximation, which satisfies the Debye–Hückel limiting law. PROZA, supplemented by the so-called polymer Percus–Yevick approximation, appears to be quite successful in predicting thermodynamical properties of the fluid of hard-sphere chain molecules of chain length up to 200 monomer units.\textsuperscript{24,25} In general the agreement between the results of the theory and computer simulation results is better at higher densities and shorter chain lengths. One may expect a similar tendency in the case of the present PMSA approach, which would be in agreement with earlier applications of the MSA-based theories.\textsuperscript{2–4,10}

The goal of this paper is to develop the theory for thermodynamical properties of the fluid of charged chain molecules. We present an analytical solution of the ideal chain PMSA\textsuperscript{9} for the multicomponent mixture of charged hard-sphere flexible chain molecules. Unlike previous studies the proposed version of the PMSA is quite general and applies for any mixture of chain molecules with arbitrary distribution of the charge and size of the beads along the molecular backbone. Our solution represents a complete association limit of the general solution obtained earlier\textsuperscript{7,8} for the fluid of polymerizing charged hard spheres. Similar to the case of the primitive electrolyte model\textsuperscript{25} this solution reduces to the solution of only one algebraic equation for the MSA-like screening parameter $\Gamma$. We also generalize a recently developed method of calculating PMSA thermodynamics via the energy route\textsuperscript{9} for the multicomponent case and derived closed form analytical expressions for internal energy, Helmholtz free energy, chemical potentials, and pressure in terms of the present solution. By way of illustration we consider several different versions of the fluid of charged hard-sphere chain molecules, including the molecules with uniform, diblock, and alternating distribution of the charge along the chain backbone.

The paper is organized as follows. In Sec. II we discuss details of the model to be studied and formulate ideal chain PMSA theory. Section III gives a solution of the ideal chain PMSA and Sec. IV contains expressions for thermodynamic and structure properties of the system. Theoretical results, their comparison with available computer simulation results, and a discussion can be found in Sec. V and in Sec. VI we present our conclusions.

II. THE MODEL AND IDEAL CHAIN PMSA THEORY

The model fluid we consider consists of the $M$-component mixture of freely jointed tangent hard-sphere chain molecules with each molecule of species $a$ represented by $m_a$ charged hard-sphere sites of sizes $\sigma^a_0$ and charges $e\varepsilon^a_0$. The total number density of the system is $\rho = \sum \rho_a$, where $\rho_a$ is the number density of species $a$, and we assume charged neutrality conditions

$$\sum_a \rho_a \varepsilon^a = 0. \quad (1)$$

We denote the molecular species by the lower-case letters $a, b, c, \ldots$ taking the values $1, 2, \ldots, M$ and the site type in a given molecule $a$ by lower-case greek letters $\alpha, \beta, \gamma, \ldots$, which take the values $1, 2, \ldots, m_a$. Thus the site has two indices, one denoting the species of the molecule and the other the site type in the molecule. For example the hard-sphere diameter of the site of type $a$ belonging to the molecule of the species $a$ is denoted by $\sigma^a_0$.

The site–site pair potential $U_{ab}(r)$ between the sites of types $a$ and $\beta$ belonging to the molecules of species $a$ and $b$ can be written in the form

$$U_{ab}(r) = U_{ab}^{st}(r) + U_{ab}^{\text{Coul}}(r), \quad (2)$$

where $U_{ab}^{st}(r)$ is the hard-sphere potential and $U_{ab}^{\text{Coul}}(r)$ is the Coulomb potential

$$U_{ab}^{\text{Coul}}(r) = \frac{e^2 \varepsilon^a \varepsilon^b}{\varepsilon_0 r}. \quad (3)$$

with $\varepsilon_0$ being the dielectric constant of the continuum.

In this study we are using the multidensity version of the mean spherical approximation (MSA)\textsuperscript{11,12,6,9} [or polymer MSA (PMSA)] supplemented by the so-called ideal chain approximation.\textsuperscript{11,13,23,9} Both PMSA and the ideal chain approximation have been discussed at length earlier and therefore we will omit any details and present only the final expressions. The theory consists of the Ornstein–Zernike-type integral equation

$$\hat{h}_{ab}(k) = \hat{c}_{ab}(k) + \sum \rho_c \sum \delta(k-r) \hat{h}_{cb}(k) \quad (4)$$

and PMSA boundary conditions

$$c_{ab}(r) = -E \beta U_{ab}^{\text{Coul}}(r) + \frac{e^2 \varepsilon^a \varepsilon^b}{2 \pi \sigma_{ab}} \delta(r-\sigma_{ab}), \quad r > \sigma_{ab} + \frac{1}{2} (\sigma^a_0 + \sigma^b_0),$$

$$h_{ab}(r) = - E, \quad r < \sigma_{ab}. \quad (5)$$
where \( \hat{h}_{ab}(k) \) and \( \hat{c}_{ab}(k) \) are the matrices with the elements being the Fourier transforms of the elements of the matrices \( h_{ab}(r) \) and \( c_{ab}(r) \).

\[
\begin{align*}
\hat{h}_{ab}(r), \hat{c}_{ab}(r) &= (c_{a_0b_0}^{ab}(r) \ c_{a_0b_1}^{ab}(r) \ c_{a_1b_0}^{ab}(r)) \ c_{a_1b_1}^{ab}(r) \ .
\end{align*}
\]

Here \( t_{ij} \), \( \alpha \), and \( E \) are the following matrices:

\[
\begin{align*}
t_{ij}^{ab} &= 2 \beta_{ij} [ \delta_{ij} \delta_{ab}^{\alpha+1} + \delta_{ij} \delta_{ab}^{\alpha-1}], \\
\alpha_{ij} &= 1 - \delta_{ij}, \ E_{ij} = \delta_{ij}.
\end{align*}
\]

The general solution was obtained using Baxter’s technique, which factorizes the initial OZ equation (4) into a set of two equations

\[
\begin{align}
S_{ab}^h(|r|) &= Q_{ab}^h(r) - \sum_c \rho_c \sum_y T \int dr' Q_{ab}^{hc}(r') \\
& \times \alpha (Q_{ab}^{hc}(r') - r')^T, \\
J_{ab}^{cb}(r') &= \int dr' \ J_{ab}^{hc}(r' - r) \\
& \times \alpha Q_{ab}^{hc}(r'),
\end{align}
\]

where \( T \) denotes the transpose matrix. The projections \( S_{ab}^h(r) \) and \( J_{ab}^{cb}(r') \) satisfy the following boundary conditions:

\[
\begin{align}
J_{ab}^{cb}(r) &= \pi r^2 E + J_{ab}^{cb}, \quad r \equiv \sigma_{ab}, \\
S_{ab}^h(r) &= - \beta e^{-2 \sigma_{ab}} \mu E, \quad r > \sigma_{ab},
\end{align}
\]

obtained from Eq. (5). Here \( J_{ab}^{cb}(0) = \sigma_{ab} \) and the limit \( \mu \to 0 \) is to be taken at the end of the calculations.

From the analysis of Eqs. (7) and (8) we get the following expression for the factor function \( Q_{ab}^b(r) \):

\[
Q_{ab}^b(r) = \theta(\sigma_{ab} - r)[Q_{ab}^b(r) + \mu \alpha_b] - (\alpha_a^b) E_{ab}^b,
\]

where \( \lambda_{ba} = (\sigma_{ab} - \sigma_{ba})/2 \) and the function \( \alpha_{ab} \) is defined in the range \( \lambda_{ba} < r < \sigma_{ab} \).

\[
Q_{ab}^b(r) = \frac{1}{E} J_{ab}^{cb}(r - \sigma_{ab}) (r - \lambda_{ba} + \beta_{ab}(r - \sigma_{ab}).
\]

The set of OZ equations (4) together with the PMSA closure conditions (5) represent our ideal chain PMSA theory for the fluid of charged linear chain hard-sphere molecules.

### III. SOLUTION OF THE IDEAL CHAIN PMSA FOR THE FLUID OF CHARGED CHAIN MOLECULES

Recently a general solution of the PMSA for the multicomponent mixture of polymerizing charged hard spheres was published.7,8 Here we elaborate on this general solution by utilizing additionally the ideal chain approximation11,13,9 and specializing it for the case of the model at hand.

The general solution was used using Baxter’s technique, which factorizes the initial OZ equation (4) into a set of two equations

\[
\begin{align}
S_{ab}^h(|r|) &= Q_{ab}^h(r) - \sum \rho \sum \gamma \ T \int dr' Q_{ab}^{hc}(r') \\
& \times \alpha (Q_{ab}^{hc}(r') - r')^T, \\
J_{ab}^{cb}(r) &= \int dr' \ J_{ab}^{hc}(r' - r) \\
& \times \alpha Q_{ab}^{hc}(r'),
\end{align}
\]

where \( T \) denotes the transpose matrix. The projections \( S_{ab}^h(r) \) and \( J_{ab}^{cb}(r') \) satisfy the following boundary conditions:
\[ \tau_{a\beta}^a(y) = \frac{1}{2} \sum_{\gamma=1}^{m_{a\gamma}-1} \Gamma_{\gamma\alpha} \sum_{\delta=1}^{\gamma_{\alpha\beta}+1} \prod_{\gamma+1}^{\gamma} \delta_{a\gamma} \left( 2^\gamma - 1 \delta_{a\alpha} \right) \frac{\delta_{a\beta}}{\sigma_{a\alpha} + 1} \delta_{a\gamma} \right) (1 - \delta_{a\beta}). \]  

(20)

Here \( \Gamma \) satisfies the following equation:

\[ \Gamma^2 = \pi \beta \sum \rho_a \sum \mathbf{X}_a \alpha (\mathbf{X}_a)^T, \]  

(21)

where \( \mathbf{X}_a \) is the row vector \( \mathbf{X}_a = (X_{a1}, X_{a2}, X_{a3}) \).

Thus solution of the PMSA for the present model reduces to the solution of the algebraic equation (21) for the screening parameter \( \Gamma \).

\[ T_{a\beta}^{ab} = \delta_{ab} \left[ \frac{(1 - \delta_{a\alpha})(1 - \delta_{a\beta})}{4 \rho_a \sigma_{a\alpha} \sigma_{a\beta} + 1} \right] + \frac{1}{2} \left[ \frac{(1 - \delta_{a\alpha})(1 - \delta_{a\beta})}{4 \rho_a \sigma_{a\alpha} \sigma_{a\beta} + 1} \right] \times \left[ \frac{(1 - \delta_{a\alpha}) \delta_{a\beta} \sigma_{a\alpha} + (1 - \delta_{a\alpha}) \delta_{a\beta} \sigma_{a\beta}}{2 \Delta \delta_{a\alpha} \delta_{a\beta}} \right] + \frac{1}{\pi} \right] \]  

(23)

The values of \( g_{a\beta}^{ab}(r) \) for \( r > \sigma_{a\beta} \) can be calculated using the following relation:

\[ g_{a\beta}^{ab}(r) = \delta_{a\alpha} \delta_{a\beta} \rho_a \alpha \left[ \hat{\varphi}_a^{ab}(k) \right] k \sin(kr) dk, \]  

(24)

where \( \hat{\varphi}_a^{ab}(k) \) is the Fourier transform of the Coulomb potential \( \hat{U}_{a\beta}^{ab}(r) \) and expression for the function \( \hat{\varphi}_a^{ab}(k) = \hat{h}_{a\beta}^{ab}(k) - \hat{c}_{a\beta}^{ab}(k) \) follows from the set of equations (7) and (8), written in the Fourier k-space,

\[ \rho^{-1} - \hat{c}(k) = \hat{Q}(k) \rho \hat{Q}^T(-k), \]  

(25)

\[ \rho^{-1} + \hat{h}(k) = \left[ \rho \hat{Q}(k) \rho \hat{Q}^T(-k) \rho \right]^{-1}, \]

which gives

\[ \hat{\varphi}(k) = \hat{Q}(k) \rho \hat{Q}^T(-k) + \left[ \rho \hat{Q}(k) \rho \hat{Q}^T(-k) \rho \right]^{-1} - 2 \rho^{-1}. \]  

(26)

Here \( \rho, \hat{h}(k), \hat{c}(k) \), and \( Q(k) \) are the matrices with the elements \( \rho_{a\beta}^{ab} = \delta_{a\alpha} \delta_{a\beta} \alpha \rho_a \), \( \hat{h}_{a\beta}^{ab}(k) \), \( \hat{c}_{a\beta}^{ab}(k) \), and

**IV. STRUCTURE AND THERMODYNAMICS**

**A. Structure properties**

The contact values of the regular part of the partial pair distribution functions \( g_{a\beta}^{ab}(\sigma_{a\beta} + ) \) follow from relation (8) after differentiating it with respect to \( r \) and taking the limit of \( r - \sigma_{a\beta}^{-} \)

\[ 2 \pi \sigma_{a\beta}^{ab} g_{a\beta}^{ab}(\sigma_{a\beta} + ) = 2 \pi \delta_{a\alpha} \delta_{a\beta} \sigma_{a\alpha} \sigma_{a\beta}^{(a\beta)} \]  

\[ - 2 \pi \beta \sigma_{a\beta} X_{a\beta} X_{a\beta}^{b} + T_{a\beta}^{ab}, \]  

(22)

where \( \sigma_{a\beta}^{(a\beta)}(\sigma_{a\beta} + ) \) is the hard-sphere contact values and

\[ \hat{Q}(k) = \rho^{-1} g_{a\beta}^{ab}(\sigma_{a\beta} + ) \]  

(27)

respectively. Substituting the expression for the function \( Q_{a\beta}^{ab}(r) \) (11) into the right-hand side of the Fourier transformation (27) we find that

\[ Q_{a\beta}^{ab}(k) = \delta_{a\alpha} \delta_{a\beta} \rho_a \alpha \left[ \frac{\pi}{\rho_a \sigma_{a\alpha} + 1} \right] \hat{\varphi}_a^{ab}(k, \sigma_a) \]  

\[ + \left( \beta_{a\beta}^{ab} - \frac{1}{\rho_a \sigma_{a\alpha} + 1} \right) \hat{\varphi}_a^{ab}(k, \sigma_a) \]  

(28)

where

**FIG. 1.** Schematic diagrams of the models with uniform distribution of the charge (M1), diblock distribution of the charge (M2), and alternating distribution of the charge.
This result allows us to derive the expression for the structure factor

\[ S_{\alpha\beta}^{ab}(k) = \delta_{\alpha\beta} \delta_{a'b'} + \sqrt{\rho_a \rho_b} \delta_{a'b'}(k). \]

Using the second equation of (25) we have

\[ S_{\alpha\beta}^{ab}(k) = \frac{1}{\sqrt{\rho_a \rho_b}} [\hat{Q}(k) \rho \hat{Q}^T(-k)]^{-1} \delta_{a'b'}. \]
B. Thermodynamic properties

The expression for the excess internal energy $\Delta E$ follows from the standard relation

$$\frac{\Delta E}{V} = 2 \pi \sum_{ab} \rho_a \rho_b \sum_{\alpha \beta} \int_0^\infty dr \ r^2 \xi_{\alpha \beta}^{ab}(r) g_{\alpha \beta}^{ab}(r),$$

which after some calculations gives

$$\beta \frac{\Delta E}{V} = \beta^* \sum_{\alpha} \rho_a \sum_{\alpha} \sigma_{\alpha}^a N_a,$$

where $\sigma_{\alpha}^a N_a = \sum_{i=0}^{B} X_{\alpha}^a - \zeta_{\alpha}^a$. 

The other thermodynamical properties of the system in question can be calculated following the method developed earlier. This method generalizes the Høye–Stell MSA energy route to thermodynamics in the frames of the present PMSA approach. Originally this generalization was developed for the one-component case. Extension of the method in the multicomponent case is rather straightforward and yields the following expressions for the Helmholtz free energy $A$, pressure $P$, and chemical potential $\mu_a^{ex}$ in excess of their reference system values:

$$-\beta \frac{A^{(ref)}}{V} = J - \frac{1}{2} \sum_{ab} \rho_a \rho_b \sum_{\alpha \beta} \left[ \alpha \left[ \hat{c}_{\alpha \beta}^{ab} - \hat{c}_{\alpha \beta}^{(0)ab} \right] \alpha \right]_{00} - \beta \frac{\Delta E}{V} + \frac{1}{3} \sum_{ab} \rho_a \rho_b \sum_{\alpha \beta} \left( \sigma_{\alpha \beta}^{ab} \right)^2 \text{Tr} \left[ \tilde{g}_{\alpha \beta}^{ab} \phi_{\beta \alpha}^{ab} \alpha \right]$$

$$- \phi_{\alpha \beta}^{(0)ab} \alpha \phi_{\beta \alpha}^{(0)ba} \alpha \right] - \frac{1}{3} \sum_{ab} \rho_a \rho_b \sum_{\alpha \beta} \left( \sigma_{\alpha \beta}^{ab} \right)^2 \text{Tr} \left[ \tilde{g}_{\alpha \beta}^{ab} \phi_{\beta \alpha}^{ab} \alpha \right],$$

where $\phi_{\alpha \beta}^{(0)ab}$ is the osmotic pressure $P^* = \beta P \sigma^3$ (a) and osmotic coefficient $\phi = PV/NkT$ (b) as a function of packing fraction $\eta = \pi \rho_s \sigma^3 / 6 \ (\rho_s = \sum_m m_i \rho_i)$ for model M1 from the present theory at $\lambda_B = 2.499$ (solid lines), $\lambda_B = 0.833$ (dashed lines), and $\lambda_B = 0$ (dashed-dotted lines). For each set of lines from the top to the bottom at $\log \eta = -2$, $m_p = 8, 16, 32, 64$. Symbols are computer simulation predictions (Ref. 28) for $\lambda_B = 0.833$ and for $m_p = 16$ (diamonds), $m_p = 32$ (circles) and $m_p = 64$ (squares).
\[ \beta (P - P^{\text{(ref)}}) = - \beta \frac{A - A^{\text{(ref)}}}{V} - \frac{1}{2} \sum_{ab} \rho_a \rho_b \sum_{\alpha} \{ \alpha (\hat{c}^{ab})_{00} + \beta \frac{\Delta E}{V} \}, \]

\[ - \beta \rho_a (\mu_a^\alpha - \mu_a^{\text{(ref)}}) = \frac{1}{2} \rho_b \sum_{\beta} \rho_b \sum_{\beta} \{ \alpha (\hat{c}^{ab})_{00} - \beta \frac{\Delta E^{\text{(lab)}}}{V} \}, \]

where the quantities with the superscript (ref) denote the reference system quantities and the quantities with superscript (0) denote the corresponding zero charge PMSA quantities

\[ \hat{c}^{ab}_{\alpha\beta} = \hat{c}^{ab}_{\alpha\beta} (k = 0), \quad g^{ab}_{\alpha\beta} = g^{ab}_{\alpha\beta} (s a_b^+), \]

\[ \frac{\partial g^{ab}_{\alpha\beta}}{\partial r} = \frac{\partial g^{ab}_{\alpha\beta}}{\partial r} (s a_b^+) + \frac{\partial \gamma^{ab}_{\alpha\beta}}{\partial r}, \]

\[ \rho_a \sum_{\beta} \rho_b \sum_{\beta} \int_0^\infty r \gamma^{ab}_{\alpha\beta} (r) U(C)^{\text{lab}} (r) dr, \]

and

\[ J = - \beta \sum_{ab} \rho_a \rho_b \sum_{\alpha\beta} \int_{r > N_{\alpha\beta}} g^{ab}_{\alpha\beta} (r) r \nabla U(C)^{\text{lab}} (r) dr. \]

The reference system is represented by the multicomponent mixture of uncharged hard-sphere chain molecules. Expressions (34)–(36) are quite general and apply for any type of the potential outside the hard core. The quantities which enter these expressions can be written in terms of the present solution of PMSA for the model at hand. We have

\[ \frac{\Delta E^{\text{lab}}}{V} = \beta^{\text{lab}} \rho_a s a_b^+ N_{\alpha\beta}, \quad J = \frac{1}{3} \beta \frac{\Delta E^{\text{lab}}}{V}, \]

\[ \rho_a \sum_{\beta} \rho_b \sum_{\beta} \int_0^\infty r \gamma^{ab}_{\alpha\beta} (r) U(C)^{\text{lab}} (r) dr, \]

\[ \rho_a \sum_{\beta} \rho_b \sum_{\beta} \int_0^\infty r \gamma^{ab}_{\alpha\beta} (r) U(C)^{\text{lab}} (r) dr, \]

where

\[ M^{ab}_{\alpha\beta} = - \frac{1}{\pi} \sigma_a^0 \sigma_b^0 \frac{\Delta T}{a_b^0} - \frac{1}{2} \sigma_a^0 \sigma_b^0 \frac{\Delta T}{a_b^0} + \frac{1}{\pi} \sigma_a^0 \sigma_b^0 \frac{\Delta T}{a_b^0}, \]

Here expression (41) is obtained by differentiating of the equation (8) twice and considering the limit of \( r - \sigma_a^0 \), and expression (42) follows from the first equation of (25) at \( k \rightarrow 0 \).

V. RESULTS AND DISCUSSION

To illustrate the above-mentioned solution of the PMSA, in this section we present the numerical results for thermodynamical properties of several versions of charged chain fluid model. We consider a two-component mixture of chain polyelectrolytes with the beads of equal charge \( z_a^0 = z_b^0 = -1 \) and oppositely charged counterions \( z_a^0 = z_b^0 = 1 \) (model M1) and two versions of three-component mixture of chain polyelectrolytes with diblock and alternating distribution of oppositely charged beads, \( z_a^0 = z_b^0 = -1 \), and two types of counterions with opposite charges \( z_a^0 = -z_b^0 = 1 \) (models M2 and M3). The densities of the counterions of these two models were chosen to be \( \rho_c^0 = \rho_a^0 = \frac{1}{2} m_a \rho_a \). Here the indices \( a \) and \( b \) denote polyelectrolyte and counterion, respectively. We also consider the one-component version of charged chain fluid models with diblock and alternating distribution of the charge along the chain backbone. In all cases the hard-sphere diameters of the chain beads \( \sigma_a^0 \) and counterions \( \sigma_c^0 \) were chosen to be equal, \( \sigma_a^0 = \sigma_b^0 = \sigma_c = 1 \). A schematic representation of the models studied is shown in Fig. 1. Thermodynamical properties of the uncoupled versions of these models were calculated using the TPTD theory of Chang and Sandler.14

In Fig. 2 we compare osmotic coefficient results obtained using the present version of the PMSA, von Solms and Chiew’s version of PMSA10 and molecular dynamics (MD) computer simulation method28 for model M1 at a different chain length \( (m_a = 36, 64) \) and Bjerrum length \( \lambda_B = 0.833 \). In the region of the intermediate densities our theory underestimates and the theory of von Solms and Chiew overestimates the value of the osmotic coefficient \( \phi = \beta P/\rho \), where \( \rho = \sum_a \rho_a \). In the region of low densities both theories predict for the osmotic coefficient an ideal gas value of \( \phi = 1 \), while MD simulation gives a value which is slightly above 1. This disagreement could be due to the uncertainties of the MD simulation in the diluted region. In general, predictions of the present approach are more accurate than those of von Solms and Chiew’s approach.10

In Figs. 3–5 we compare the density dependence of the osmotic pressure and osmotic coefficient at different values of Bjerrum length \( (\lambda_B = 0.833, 2.499) \) for different polyelectrolyte models. In the case of low Bjerrum length \( (\lambda_B = 0.833) \) one can see the linear dependence of the osmotic pressure with respect to the density on the log–log scale [Figs. 3(a)–5(a)]. In this region the osmotic pressure is almost independent of the chain length and distribution of the charge along the chain. With the increase of \( \lambda_B \) \( (\lambda_B = 2.499) \) there is a departure from linearity, which is substantial for model M1, slightly smaller for model M2, and almost negligible for model M3. At the same time one can see the substantial chain length dependence of the osmotic...
pressure in the case of models M1 and M2. This dependence is absent for model M3 [Figs. 3(b)–5(b)]. Thus for systems with more random distribution of the charge along the chain backbone the chain length dependence is smaller. Increasing the Bjerrum length leads to more intensive attraction between counterions and polyions, which in turn increases the number of counterions ‘‘condensed’’ on the polyion, i.e., immobilized counterions, which are moving together with polyions. This effect is enhanced with the increase of the chain length due to the increase of the polyionic charge. As a result of the increase of the number of immobilized counterions, osmotic pressure decreases. With a further increase of the number of chain beads counterionic screening length becomes small in comparison with the chain length, which prevents further ‘‘condensation’’ of free counterions. It is reasonable to expect that for \( n > 64 \) and \( \lambda_p = 2.499 \) chain length dependence of the osmotic pressure will be negligible for all the models studied. This behavior is typical for the polyelectrolyte solutions.\(^{31,32}\)

In Fig. 6 the liquid–gas phase diagrams for the one-component version of the models with diblock and alternating distribution of the charge are presented. We consider the systems with molecular chain length \( m_p = 2,4,6,8,10 \). Computer simulation results are available only in the case of the chains length \( m_p = 2 \).\(^{33}\) In general, theoretical results are in qualitative agreement with computer simulation results with certain disagreement for the slope steepness of the liquid branches of the coexistence curves; the slope of the theoretical curve is steeper than that of the computer simulation curve. In addition, the position of the theoretical critical point is shifted toward lower values of the density and higher values of the temperature. According to the previous discussion the systems with diblock distribution of the charge have a larger degree of nonideality in comparison with systems with an alternating distribution of the charge. This is reflected in Fig. 6, where the critical temperature of systems with diblock chains is higher than that of systems with alternating chains of the same length. The corresponding values of the critical densities are larger in the case of systems with alternating chains. In both cases an increase of the chain length leads to an increase of the critical temperature and slight decrease (increase) of the critical density for diblock (alternating) distribution of the charge. We note in passing that due to the lack of a solution of the equation for screen-
ing parameter $\Gamma$ (21) at lower densities we were not able to determine the coexistence curve for systems with alternating chain charge of the chain length $m_p = 8,10$ below the temperatures shown in Fig. 6(b).

Finally in Fig. 7 we present the liquid–gas phase diagram for the system of trimers with the middle bead charge $z_2^p = -2z_1^p = -2z_3^p$, where $z_1^p$ and $z_3^p$ are the charges of the terminal beads, $z_2^p = z_3^p = 1$. Similar to the case of an alternating charged chain system with $m_p = 8,9$ there is no solution of Eq. (21) in the low density region, therefore we were not able to calculate the coexistence curve for temperatures lower than those shown in Fig. 7. This model can be seen as a complete association limit of the primitive 2:1 electrolyte model. Recent computer simulation studies $^{33-36}$ of the electrolyte primitive model suggest that in the vicinity of the coexistence region the system is highly associated and the fraction of charged clusters, including free ions, is negligible. Therefore the equilibrium properties of the system are determined by the presence of the neutral ionic clusters, to which the lower order clusters give the main contribution. Assuming that in the case of the electrolyte restricted primitive model (RPM) all such clusters are represented by the neutral ionic pairs, the RPM liquid–gas phase diagram has been successfully reproduced by the Monte Carlo (MC) computer simulation method $^{33}$ and theoretically. $^{9}$ Making a similar assumption in the case of the 2:1 primitive electrolyte model the corresponding liquid–gas phase diagram can be modeled using the phase diagram obtained for trimers. Unfortunately, computer simulation predictions for the entire phase diagram of the 2:1 electrolyte model currently are not available. Recently Camp and Patey $^{36}$ presented a MC estimate for the critical temperature, which appears to be $T^*_c = 0.1 \pm 0.01$. The rough estimate of the ranges for the critical density can be obtained from Fig. 5 of Ref. 36; our estimate is $\rho^*_c = 0.115 \pm 0.085$. This estimate for the critical point together with Debye–Hückel (DH) theory estimate $^{36}$ and MSA phase diagram are shown in Fig. 7. In addition, for the sake of completeness, we present the liquid–gas phase diagram for the RPM of electrolyte, obtained from the MC simulation method, $^{34,37}$ MSA, and our PMSA for neutral diatomics. $^{9}$ One can see that predictions of the PMSA are much better in comparison with the usual MSA. In both cases DH predictions for the critical temperature are close to those of the
PMSA, however the corresponding predictions for the critical density are much worse.

VI. CONCLUDING REMARKS

In this study we obtained an analytical solution of the ideal chain PMSA for the multicomponent mixture of charged hard-sphere flexible linear chain molecules. This solution applies to any mixture of chain molecules with arbitrary distribution of the charge and size of the beads along the molecular backbone. We present closed form analytical expressions for thermodynamical and structure properties of the system. These expressions are used to calculate thermodynamics of several different versions of a charged hard-sphere chain model. We consider a two-component mixture of chains with equally charged beads and oppositely charged counterions, two versions of the three-component mixture of chains with diblock and alternating distribution of the charge, and two types of oppositely charged counterions. Comparison of the theoretical predictions for the osmotic pressure of the two-component model with corresponding computer simulation predictions shows that the present version of the ideal chain PMSA theory is reasonably accurate for the model parameters studied and gives somewhat better agreement than that of the theory of von Solms and Chiew. Effects due to the difference in Bjerrum length, molecular chain length, and distribution of the charge were also studied. The largest deviation from ideal behavior was demonstrated by the system with uniform distribution of the charge; the behavior of the system with alternating distribution of the charge shows much less nonideality. This conclusion is verified by comparison of the liquid–gas phase diagrams calculated for the one-component version of the models with diblock and alternating distribution of the charge; the latter model has a substantially lower critical temperature than the former. With the increase of chain length the critical temperature for both models increases, while the corresponding critical density slightly increases for alternating charge model and decreases for the diblock charge model. Finally it was demonstrated that the liquid–gas phase diagram of the neutral trimers with a doubly charged middle bead and singly charged...
charged terminal beads of opposite sign can be used to correct MSA results for the phase diagram of the 2:1 primitive electrolyte model.

In this paper only thermodynamical properties of the fluid of charged hard-sphere flexible linear chain molecules, as predicted by the polymer mean spherical approximation (PMSA), have been studied. In a future paper we are planning to study the structural properties of the model at hand. In particular the correlation between the conformational properties of the chain molecules, like average end to end distance, and thermodynamical properties (osmotic pressure) will be investigated for various parameters of the model.

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