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# Virial expansion for ionic mixtures: Point-counterion model

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A binary mixture of hard-sphere polyions and monovalent point counterions is studied using the virial expansion (VEX) of the Ornstein-Zernike equation. The zero-order VEX term, which coincides with the symmetrized Poisson-Boltzmann equation (SPB), exhibits an attraction among polyions at sufficiently high temperatures and densities where the VEX convergence is fast. The linear VEX term intensifies this effect that may be explained using the suggestion that polyions interact via a screened potential of Jukawa type. A general solution of the linearized SPB (LSPB) is not represented by a single Debye-Hückel exponent and also exhibits an attraction. Within the SPB applicability region the LSPB and SPB provide similar results.

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## I. INTRODUCTION

The classical description of the infinitely diluted ionic mixtures is based on the Debye-Hückel (DH) approach [1,2]. In this theory, the dimensionless electrical potential $\psi_{\alpha\alpha}=ez_\alpha\psi_\alpha/kT$ around an ion of species $\alpha$ is determined by the Poisson equation

$$\Delta\psi_{\alpha\alpha}=-\kappa_0^2\sum_\beta \lambda_{\alpha\beta}g_{\alpha\beta}\ , \tag{1}$$

where $e$ is the elementary charge, $z_\alpha$ is the valency of ion $\alpha$, $kT$ is the temperature in energetic units, the distance is measured in units of $R$, $\kappa_0=[4\pi ne^2R^2I/(\epsilon kT)]^{1/2}$ is the Debye parameter, $n=\sum_\alpha n_\alpha$ is the total concentration of charged species in a mixture, the summation is performed over $\alpha=1,2,\ldots,M$ ion species, $I=\sum_\alpha v_\alpha z_\alpha^2$ is the dimensionless ionic strength, $v_\alpha=n_\alpha/n$, $\epsilon$ is the dielectric constant of a solvent, and $\lambda_{\alpha\beta}=z_\alpha z_\beta/I$. The pair-correlation functions $g_{\alpha\beta}$ that characterize the distribution of ions of species $\beta$ around the central ion $\alpha$ have the Boltzmann form

$$g_{\alpha\beta}=\exp(-z_\beta\psi_{\alpha\alpha}/z_\alpha)\ . \tag{2}$$

The combination of (1) and (2) provides the nonlinear Poisson-Boltzmann (PB) equation which does not have an analytical solution.

For a binary mixture of hard spheres with equal diameters $R$ and charges $\pm Ze$ in a solvent with the same dielectric constant [so-called restricted primitive model (RPM) [3]], the solution of the linearized PB (DH) equation is given by

$$\psi_{\alpha\alpha}=\frac{X_0Z^2}{1+\kappa_0}\exp[-\kappa_0(r-1)]/r\ , \tag{3}$$

where $X_0=e^2/(\epsilon kTR)$ is the Bjerrum parameter. Obviously, the DH theory describes an attraction among opposite charges ($g_{\alpha\beta}>1$) and repulsion ($g_{\alpha\alpha}<1$) among equally charged ions.

The PB solution does not satisfy the Onsager identity

$$g_{\alpha\beta}\equiv g_{\beta\alpha} \tag{4}$$

in the case of unequal sizes or valencies of ions [2]. If the ions have unequal sizes, DH theory also violates (4). Therefore unsymmetrical ionic mixtures are generally studied using the different closures of the Ornstein-Zernike (OZ) equation (see for references [4]).

In principle, the theoretical analysis of mixtures can be performed using the diagram-ordering technique [5] which leads to the conclusion that the asymptotic correlations may have a non-DH form in the general case [6]. Another approach is based on the OZ virial expansion (VEX) [7]. Its zero-order term coincides with the symmetrized Poisson-Boltzmann (SPB) equation, which was introduced by Feat and Levine in order to preserve the condition (4) [8]. The linear VEX term outlines the region of the SPB applicability [9]. For RPM, SPB coincides with PB but in contrast to the latter it always satisfies (4). VEX convergence for RPM has been systematically examined in [10]. The analysis of different electrolyte and plasma models [9–11] shows that VEX rapidly converges if $X_0I<5$. It should be noted that $I=Z^2$ for RPM while $I=Z$ for $Z$:1 mixtures. The SPB accuracy in the parameter region related to the water electrolytes ($X_0=1.7$) was studied in [12,13]. In particular, the SPB results are close to that of the OZ hypernetted-chain (HNC) closure at $\kappa_0<1$ and $\kappa_0<0.2$ for 1:2 and 1:3 valent mixtures, respectively [9].

SPB exhibits a possibility of an attraction among polyions in electrolyte solutions [14–17]. This effect was forecasted by Oosawa [18]. An attraction in a binary mixture of hard-sphere polyions and point counterions [point-counterion model (PCM)] was noticed in computer simulations [19]. Recently this effect was demonstrated using HNC closure [20] for a mixture of polyions and a binary electrolyte with parameters similar to those in [16,17]. In this communication, we outline the region of the SPB applicability for PCM with the linear VEX term that allows to avoid possible SPB artifacts regarding the attraction phenomenon. The VEX theory is given in Sec. II and its results for PCM are presented in Sec. III. A semianalytic solution of the linearized SPB (LSPB), which also exhibits an attraction, is discussed in Sec. IV.

## II. VIRIAL EXPANSION FOR COULOMB FLUIDS

The conventional form of the OZ equation is given by [3]

$$h_{\alpha\beta}=c_{\alpha\beta}+n\sum_{\gamma}\nu_\gamma\int c_{\alpha\gamma}(r_{\alpha\gamma})h_{\beta\gamma}(r_{\beta\gamma})d\mathbf{r}_\gamma\ , \tag{5}$$

where $h_{\alpha\beta}=g_{\alpha\beta}-1$ is the total correlation function. If one presents $g_{\alpha\beta}$ in the form

$$g_{\alpha\beta}=\gamma_{\alpha\beta}\exp(w_{\alpha\beta}),\quad \gamma_{\alpha\beta}=\exp(-\phi_{\alpha\beta})\ , \tag{6}$$

where $\phi_{\alpha\beta}$ is a pair potential in $kT$ units, then the direct correlation function $c_{\alpha\beta}$ equals

$$c_{\alpha\beta}=h_{\alpha\beta}-w_{\alpha\beta}+B_{\alpha\beta}\ , \tag{7}$$

where $B_{\alpha\beta}$ is the bridge functional that represents an infinite series of integrals whose integrands are the products of the total correlation functions multiplied by increasing powers of the concentration starting with $n^2$ [21]. In HNC approximation, the bridge functional is neglected. The combination of (5) and (7) provides

$$w_{\alpha\beta}=\rho\sum_{\gamma}\nu_\gamma\int(h_{\alpha\gamma}-w_{\alpha\gamma})h_{\beta\gamma}d\mathbf{r}_\gamma+O(\rho^2)\ , \tag{8}$$

where distance is measured in units of $R$, $\rho=nR^3$ is the dimensionless density, and all terms having factors $\rho^2$ or higher powers of the density are denoted by $O(\rho^2)$. Equation (8) can be symmetrized using the identity $w_{\alpha\beta}\equiv 0.5(w_{\alpha\beta}+w_{\beta\alpha})$. Then

$$w_{\alpha\beta}=0.5\rho\sum_{\gamma}\nu_\gamma\int[(h_{\alpha\gamma}-w_{\alpha\gamma})h_{\beta\gamma}+(h_{\beta\gamma}-w_{\beta\gamma})h_{\alpha\gamma}]d\mathbf{r}_\gamma+O(\rho^2)\ . \tag{9}$$

In ionic systems, the pair potential consists of the Coulomb $[\phi^C_{\alpha\beta}=ez_\alpha z_\beta/(\epsilon kTr)]$ and short-range $[\phi^S_{\alpha\beta}]$ components. In terms of $W_{\alpha\beta}=w_{\alpha\beta}-\phi^C_{\alpha\beta}$, Eq. (9) acquires the form

$$W_{\alpha\beta}=-\psi_{\alpha\beta}+0.5\rho\sum_{\gamma}\nu_\gamma\int[(h_{\alpha\gamma}-W_{\alpha\gamma})h_{\beta\gamma}+(h_{\beta\gamma}-W_{\beta\gamma})h_{\alpha\gamma}]d\mathbf{r}_\gamma+O(\rho^2)\ , \tag{10}$$

where

$$\psi_{\alpha\beta}=\phi^C_{\alpha\beta}+0.5\rho\sum_{\gamma}\nu_\gamma\int(h_{\alpha\gamma}\phi^C_{\beta\gamma}+h_{\beta\gamma}\phi^C_{\alpha\gamma})d\mathbf{r}_\gamma\ . \tag{11}$$

Applying the Laplacian operator to Eq. (11), one obtains

$$\Delta\psi_{\alpha\beta}=-X_0z_\alpha z_\beta\delta(r)-0.5\kappa_0^2\sum_{\gamma}\nu_\gamma(\lambda_{\alpha\gamma}h_{\beta\gamma}+\lambda_{\beta\gamma}h_{\alpha\gamma})\ , \tag{12}$$

where $\delta(r)$ is the Dirac function that plays a role of a boundary condition and will be omitted further. Owing to the electroneutrality condition $\sum_\alpha n_\alpha z_\alpha=\sum_\gamma\nu_\gamma\lambda_{\alpha\gamma}=0$, Eq. (12) for $\alpha=\beta$ has the form

$$\Delta\psi_{\alpha\alpha}=-\kappa_0^2\sum_{\gamma}\nu_\gamma\lambda_{\alpha\gamma}g_{\alpha\gamma} \tag{13}$$

that coincides with the Poisson equation (1) postulated in the DH theory. It is clear from (12) that

$$\psi_{\alpha\beta}=0.5\lambda_{\alpha\beta}\left[\frac{\psi_{\alpha\alpha}}{\lambda_{\alpha\alpha}}+\frac{\psi_{\beta\beta}}{\lambda_{\beta\beta}}\right]\ . \tag{14}$$

Thus the number of the independent equations in (12) coincides with the number of charged species in a mixture $M$ and the functions $\psi_{\alpha\alpha}$ are the dimensionless electric potentials around ions $\alpha$.

The charge density around an ion $\alpha$ of radius $R_\alpha$ differs from zero at distance larger than the sum of $R_\alpha$ and the radius of the smallest ion present in a mixture, i.e., at $r>R_{\alpha m}$ where

$$R_{\alpha m}=\min{}_\beta[R_\alpha+R_\beta]\ . \tag{15}$$

Therefore the Gauss electrostatic law leads to the boundary condition

$$r^2\frac{d\psi_{\alpha\alpha}}{dr}=-X_0z_\alpha^2\quad\text{for } r=R_{\alpha m}\ . \tag{16}$$

The Poisson equation (13) should also satisfy the boundary condition at infinity,

$$\psi_{\alpha\beta}(\infty)=0\ . \tag{17}$$

The system of equations (10),(13)–(17) is equivalent to the original OZ equation (5).

The idea of VEX [10] is to expand all OZ variables in the series of the dimensionless density powers:

$$\begin{aligned}W_{\alpha\beta}&=\sum_k\rho^kW^{(k)}_{\alpha\beta},\quad \psi_{\alpha\beta}=\sum_k\rho^k\psi^{(k)}_{\alpha\beta}\ ,\\ h_{\alpha\beta}&=\sum_k\rho^kh^{(k)}_{\alpha\beta},\quad g_{\alpha\beta}=\sum_k\rho^kg^{(k)}_{\alpha\beta}\ ,\end{aligned} \tag{18}$$

while the Debye parameter $\kappa_0$ is supposed to be independent of $\rho$. The latter condition is necessary in order to preserve the Debye-type decay already in a zero-order term that ensures the convergence of the thermodynamical integrals. It should be noted that the DH exponent (3) already contains all powers of $\kappa_0\sim n^{1/2}$ and the Debye length $L_D\sim\kappa_0^{-1}$ tends to infinity if $n\rightarrow 0$. Therefore an "honest" VEX for the correlation functions of the Coulomb systems diverges [22]. After substitution of (18) into (6) and (10), the zero VEX term acquires the form

$$W^{(0)}_{\alpha\beta}=-\psi^{(0)}_{\alpha\beta},\quad g^{(0)}_{\alpha\beta}=\gamma_{\alpha\beta}\exp(-\psi^{(0)}_{\alpha\beta})\ . \tag{19}$$

In turn, the substitution of (19) into Eq. (13) leads to the SPB equation

$$\Delta\psi^{(0)}_{\alpha\alpha}=-\kappa_0^2\sum\nu_\gamma\lambda_{\alpha\gamma}\gamma_{\alpha\gamma}\exp(-\psi^{(0)}_{\alpha\gamma})\ . \tag{20}$$

The analogous procedure provides the linear VEX term

$$g^{(1)}_{\alpha\beta}=W^{(1)}_{\alpha\beta}\ , \tag{21}$$

$$W_{\alpha\beta}^{(1)} = -\psi_{\alpha\beta}^{(1)} + 0.5\sum_{\gamma} \nu_\gamma \int [(h_{\alpha\gamma}^{(0)} + \psi_{\alpha\gamma}^{(0)})h_{\beta\gamma}^{(0)} + (h_{\beta\gamma}^{(0)} + \psi_{\beta\gamma}^{(0)})h_{\alpha\gamma}^{(0)}]d\mathbf{r}_\gamma ,$$

$$\Delta\psi_{\alpha\alpha}^{(1)} = -\kappa_0^2 \sum_{\gamma} \nu_\gamma \lambda_{\alpha\gamma} g_{\alpha\gamma}^{(1)} . \tag{22}$$

For the linear and higher-order VEX terms, the boundary condition (16) is reduced to

$$r^2 \frac{d\psi_{\alpha\alpha}^{(k)}}{dr} = 0 \quad \text{for } r = R_{\alpha m} \quad \text{and } k > 0 . \tag{23}$$

The zero and linear VEX terms of the OZ and HNC approximation coincidence while the quadratic VEX term of OZ involves the bridge functional absent in HNC approximation. The quadratic VEX term for RPM was estimated in [10].

## III. ZERO AND LINEAR VEX TERMS FOR PCM

Let us consider a mixture of hard-sphere polyions ($p$) of radius $R$ and valency $Z$ and monovalent point counterions ($c$). If distance is measured in units of $R$, then

$$\gamma_{pp} = \begin{cases} 0 & \text{for } r < 2 \\ 1 & \text{for } r \geq 2 , \end{cases}$$

$$\gamma_{pc} = \begin{cases} 0 & \text{for } r < 1 \\ 1 & \text{for } r \geq 1 , \end{cases} \tag{24}$$

$$\gamma_{cc} = 1 ,$$

and SPD (20) has the form

$$\Delta\psi_{pp}^{(0)} = \frac{\kappa_0^2 Z}{Z+1} \times \begin{cases} 0, & r \leq 1 \\ \exp(-\psi_{pc}^{(0)}), & 1 \leq r \leq 2 \\ \exp(-\psi_{pc}^{(0)}) - \exp(-\psi_{pp}^{(0)}), & r \geq 2 , \end{cases}$$

$$\Delta\psi_{cc}^{(0)} = \frac{\kappa_0^2}{Z+1} \times \begin{cases} -\exp(-\psi_{cc}^{(0)}), & r \leq 1 \\ \exp(-\psi_{pc}^{(0)}) - \exp(-\psi_{cc}^{(0)}), & r \geq 1 . \end{cases} \tag{25}$$

The results of the calculations are given in Table I where $g_{\alpha\beta}^L$ is the LSPB solution, $g_{\alpha\beta} = g_{\alpha\beta}^{(0)} + \rho g_{\alpha\beta}^{(1)}$. The dimensionless pressure equals

$$p = \frac{P}{nkT} = p^{(0)} + \rho p^{(1)}$$

$$= 1 + \frac{u}{3} + 2\rho \frac{2Zg_{pc}^{(0)}(1) + g_{pp}^{(0)}(2)}{Z+1} . \tag{26}$$

The specific electrostatic energy in units of $kT$ $u = u^{(0)} + \rho u^{(1)}$ is calculated using the expression [21]

$$u = 0.5 \sum_{\alpha} \nu_\alpha \lim_{r \to 0} \left[ \frac{d}{dr} \left[ r \frac{d\psi_{\alpha\alpha}}{dr} \right] \right] . \tag{27}$$

PCM is determined by the three dimensionless parameters $X_0$, $\kappa_0$, and $Z$. For RPM, which is defined with two parameters ($X_0Z^2$ and $\kappa_0$), the parameter region of the SPB applicability has a bell shape [10] because of the slow convergence either at high values of $X_0Z^2$ or high densities $\rho = 0.25\kappa_0^2/(X_0Z^2)$. Similar convergence behavior, though complicated by the independent parameters $X_0$ and $Z$, appears for PCM. It is clear, however, that at least in the region $1 \leq X_0Z^2 \leq 4$ and $\kappa_0 < 1$, the VEX convergence is fast and the PCM thermodynamics is determined basically by SPB theory.

TABLE I. Thermodynamical data for PCM.

| $\kappa_0$ | $g_{pp}^L(2)$ | $g_{pp}^{(0)}(2)$ | $g_{pp}(2)$ | $g_{pc}^L(1)$ | $g_{pc}^{(0)}(1)$ | $g_{pc}(1)$ | $p^{(0)}$ | $p$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $X_0=0.1$, $Z=1$ | | | | |
| 0.1 | 0.96 | 0.96 | 1.00 | 1.09 | 1.09 | 1.11 | 1.00 | 1.01 |
| 0.25 | 0.99 | 0.99 | 1.23 | 1.06 | 1.07 | 1.11 | 1.00 | 1.08 |
| | | | | $X_0=0.1$, $Z=2$ | | | | |
| 0.1 | 0.85 | 0.85 | 0.86 | 1.25 | 1.20 | 1.20 | 1.00 | 1.00 |
| 0.25 | 0.91 | 0.91 | 0.97 | 1.12 | 1.17 | 1.20 | 0.99 | 1.02 |
| 0.5 | 1.01 | 1.01 | 1.28 | 1.11 | 1.13 | 1.25 | 0.99 | 1.02 |
| | | | | $X_0=0.1$, $Z=3$ | | | | |
| 0.25 | 0.77 | 0.77 | 0.79 | 1.56 | 1.27 | 1.28 | 0.99 | 1.00 |
| 0.5 | 0.91 | 0.91 | 0.99 | 1.24 | 1.22 | 1.27 | 0.98 | 1.04 |
| 1.0 | 1.20 | 1.19 | 1.75 | 1.31 | 1.17 | 1.39 | 0.97 | 1.19 |
| | | | | $X_0=1$, $Z=1$ | | | | |
| 0.25 | 0.74 | 0.75 | 0.75 | 2.19 | 2.20 | 2.20 | 0.97 | 0.98 |
| 0.75 | 0.97 | 0.97 | 1.11 | 1.66 | 1.67 | 1.73 | 0.92 | 1.06 |
| 1.0 | 1.07 | 1.07 | 1.37 | 1.47 | 1.50 | 1.63 | 0.90 | 1.14 |
| | | | | $X_0=1$, $Z=2$ | | | | |
| 0.5 | 0.43 | 0.44 | 0.42 | 3.71 | 3.74 | 3.78 | 0.89 | 0.93 |
| 1.0 | 0.72 | 0.75 | 0.72 | 2.66 | 2.67 | 2.64 | 0.89 | 0.93 |
| 1.5 | 1.00 | 1.07 | 1.10 | 2.40 | 2.16 | 2.11 | 0.79 | 1.04 |
| 2.0 | 1.36 | 1.37 | 1.67 | 1.62 | 1.84 | 1.81 | 0.76 | 1.17 |
| | | | | $X_0=2$, $Z=1$ | | | | |
| 0.5 | 0.68 | 0.70 | 0.71 | 3.67 | 3.65 | 3.64 | 0.88 | 0.93 |
| 1.0 | 0.93 | 0.96 | 1.03 | 2.43 | 2.49 | 2.48 | 0.82 | 0.99 |
| 1.25 | 1.04 | 1.07 | 1.22 | 2.08 | 2.17 | 2.18 | 0.80 | 1.05 |

The SPB values of $g_{pp}^{(0)}$ (2) increase with rise of $\kappa_0$ and become more than unity at sufficiently high densities, i.e., they exhibit an attraction. The linear VEX term intensifies this effect. Since the parameter $X_0Z^2$ plays a role of the polyion dimensionless inverse temperature [11], an attraction among ions of the same charge appears at high temperatures and high densities where the short-range potentials dominate over the electrostatic interactions. In particular, HNC approximation shows such an attraction at very high densities ($\kappa_0 > 3$) and high temperatures ($X_0Z^2 = 1.7$) even for RPM [23]. The mechanism of this effect was suggested in [14]. Namely, the screening of the charges is carried out at distance, $L_D \sim \kappa_0^{-1} \sim n^{-1/2}$, while the average distance among ions, $L_R$, is about $n^{-1/3}$. At sufficiently high densities, $L_R > L_D$ and ions interact via fully screened electrical potential. This potential having the Jukawa form similar to (3) can provide an effective attraction [24] as well as any other short-range repulsion (e.g., the hard-sphere pair potential [25]). Obviously, such screening is performed more effectively by the "small" counterions approaching the polyions at short distance ($1 \leq r < 2$ for PCM), which is inaccessible for other polyions.

One may suggest that an attraction between two plates immersed in an electrolyte, which was observed in com-

TABLE II. General LSPB solution for PCM.

| $r$ | $\psi_1$ | $\psi_2$ |
|---|---|---|
| $r \le 1$ | $A_1 + X_0 Z^2/r$ | $1 + A_2 \exp(-\alpha r)/r + (X_0 - A_2)\exp(\alpha r)/r$ |
| $1 \le r \le 2$ | $\sum_i B_i \delta_i \exp(\beta_i r)/r - Z(Z+2)$ | $1 + \sum_i B_i \exp(\beta_i r)/r$ |
| $r \ge 2$ | $C_1 Z^2 \exp(-\kappa_0 r)/r + C_2 Z \exp(-\alpha r)/r$ | $C_1 \exp(-\kappa_0 r)/r - C_2 \exp(-\alpha r)/r$ |

$\alpha = \kappa_0/\sqrt{2}$, $i = 1-4$, $\beta_{1,3} = 0.5\kappa_0\{[(3+Z) \pm [(3+Z)^2 - 8]^{1/2}\}^{1/2}/(Z+1)$, $\beta_2 = -\beta_1$, $\beta_4 = -\beta_3$, $\delta_i = 2Z(Z+1)\beta_i^2/\kappa_0^2 - Z(Z+2)$

puter simulations [26,27], represents the similar effect for the limit case of the polyions of infinite size. Also, the theory [28] can exhibit an attraction between the charged walls in an electrolyte [29].

Examples of the pair-correlation functions for PCM without (a) and with (b) attraction polyions are given in Fig. 1.

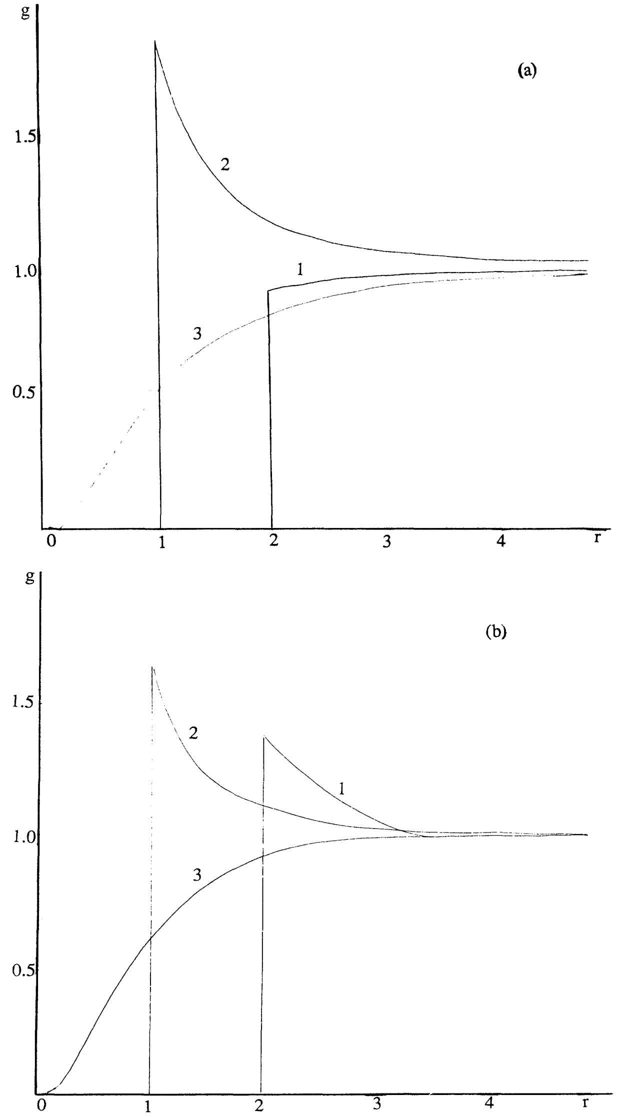

FIG. 1. Pair-correlation functions of PCM at $X_0 = 1$ and $Z = 2$ calculated with the zero and linear VEX terms. (a) $\kappa_0 = 0.5$, (b) $\kappa_0 = 1.0$; 1: $g_{pp}(r)$, 2: $g_{pc}(r)$, 3: $g_{cc}(r)$.

## IV. LINEAR SPB (LSPB) SOLUTION FOR PCM

Retaining only linear terms in the expansion of exponents in SPB (20) $[\exp(-\psi_{\alpha\beta}^{(0)}) \simeq 1 - \psi_{\alpha\beta}^{(0)}]$, one obtains a LSPB solution for PCM,

$$\Delta\psi_1 = \frac{\kappa_{b0}^2 Z}{Z+1} \times \begin{cases} 0, & r \le 1 \\ 1 + 0.5(\psi_1/Z + Z\psi_2), & 1 \le r \le 2 \\ (1 + 0.5/Z)\psi_1 + 0.5Z\psi_2, & r \ge 2 \,, \end{cases}$$

$$\Delta\psi_2 = \frac{\kappa_0^2}{Z+1} \times \begin{cases} \psi_2 - 1, & r \le 1 \\ (1 + 0.5Z)\psi_2 + 0.5\psi_1/Z, & r \ge 1 \,, \end{cases} \tag{28}$$

where $\psi_1 = \psi_{pp}^{(0)}$ and $\psi_2 = \psi_{cc}^{(0)}$. A general LSPB solution for a binary mixture with finite ion sizes was obtained in [11,13]. A general LSPB solution for PCM is presented in Table II. For $r \ge 2$, it contains two exponents. One of them is similar to the DH expression (3) and another one exhibits an attraction if $C_2 = 0$.

The partial solution of the LSPB can be obtained using the continuity conditions of the functions $\psi_i$ and $d\psi_i/dr$ for $i = 1,2$ at distances $r = 1$ and $r = 2$, i.e., via a system of eight linear algebraic equations. The coefficients of the partial LSPB solution for PCM were obtained by the numerical solution of the mentioned algebraic equations and are listed in the Table III.

At small densities ($\kappa_0 < 0.1$), $C_1 \simeq X_0$ and $C_2 \ll C_1$ [cf. with (3)]. At high temperatures ($X_0 Z^2 \sim 1$), there is always an attractive component in the polyion interactions

TABLE III. The coefficients of the LSPB partial solution for PCM.

| $\kappa_0$ | $A_1$ | $A_2$ | $B_1$ | $B_2$ | $B_3$ | $B_4$ | $C_1$ | $C_2$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $X_0 = 0.1$, $Z = 1$ | | | | |
| 0.1 | −0.02 | 7.17 | 1.10 | −0.98 | −15.7 | 15.7 | 0.10 | −0.01 |
| 0.25 | −0.05 | 2.90 | 0.41 | −0.28 | −6.21 | −6.18 | 0.07 | −0.04 |
| 0.5 | −0.15 | 1.44 | 0.17 | 0.00 | −2.99 | 2.96 | −0.05 | −0.19 |
| 1.0 | −0.39 | 0.67 | 0.05 | 0.29 | −1.33 | 1.27 | −0.93 | −1.01 |
| | | | | $X_0 = 1$, $Z = 1$ | | | | |
| 0.1 | −0.09 | 8.23 | 1.07 | 0.14 | −15.6 | 15.4 | 1.00 | −0.00 |
| 0.25 | −0.22 | 3.93 | 0.39 | 0.84 | −6.13 | 5.91 | 1.00 | −0.02 |
| 0.5 | −0.41 | 2.43 | 0.17 | 1.15 | −2.94 | 2.72 | 0.97 | −0.11 |
| 1.0 | −0.76 | 1.62 | 0.05 | 1.56 | −1.31 | 1.04 | 0.41 | −0.78 |
| | | | | $X_0 = 1$, $Z = 2$ | | | | |
| 0.1 | −0.35 | 8.23 | 0.53 | 0.82 | −20.1 | 19.7 | 1.01 | 0.00 |
| 0.5 | −1.26 | 2.44 | 0.08 | 1.37 | −3.82 | 3.46 | 1.12 | 0.03 |
| 0.85 | −1.82 | 1.79 | 0.04 | 1.60 | −2.15 | 1.78 | 1.22 | −0.03 |
| 1.0 | −2.04 | 1.64 | 0.03 | 1.71 | −1.80 | 1.41 | 1.21 | −0.11 |

since $C_2 < 0$. Moreover, even $C_1$ becomes less than zero with increase of density, i.e., polyion interactions acquire a "pure" attractive character.

At lower temperatures (see data for $X_0 = 1$, $Z = 2$), $C_2 < 0$ only at rather high values of $\kappa_0$. Positive values of $C_2$ mean an attraction among point counterions that is presumably an artifact of the linear theory. Since $C_2 \ll C_1$ in the parameter region considered, this effect is apparent only at very long distance where the potentials $\psi_i$ are close to zero. Therefore the non-DH term plays a negligible role within the region of the LSPB applicability where LSPB and SPB provide similar results.

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