

The perturbed-hard sphere-chain theory(PHSC)모델과 the mean spherical approximation theory(MSA)모델의 비교

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The comparison between the mean spherical approximation theory and the perturbed-hard sphere-chain theory

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Introduction

Recently, remarkable advances have been achieved in the application of the perturbation theory, integral equation theory and molecular simulation for the thermodynamical functions of polar, electrolyte fluids including polymer electrolytes. A series of statistical models based on such as Barker-Henderson[1], statistical associating fluid theory (SAFT)[2] and perturbed-hard-sphere-theory (PHST) have been successfully used for nonpolar monoatomic fluids, polar associating fluids, chain-like polymers and electrolyte solutions, respectively.

The integral equation theory (IET) based on the Ornstein-Zernike(OZ) equation with analytical solvable approaches such as Percus-Yevick(PY), hypernetted chain(HYC) and mean spherical approximation(MSA) has been proved to be effective for real fluids. Due to the simplicity, the MSA among analytical solvable approximations is more attractive for chemical engineers to explain the thermodynamic properties of the real fluids.

Blum and co-workers[3] have extensively studied application of the mean-spherical approximation for symmetric and nonsymmetric electrolytes. By adopting Baxter's factorization procedure, the generalized Fourier transform of the Ornstein-Zernike equation is decomposed into two fundamental equations : one for the total correlation function and the other for the direct correlation function. The sticky-electrolyte model[4] taken into account ion pairs and other formations has been developed by several authors.

Theories for MSA and PHSC

1 Perturbed Hard Sphere Chain Theory

According to perturbation theories, the interactions of molecules can be divided into a repulsive part and a contribution due to the attractive part of the potential. To calculate the repulsive contribution, a reference fluids where no attractions are presented. The reference part is based on the generalized result of the Canahan-Starling(CS) theory for hard sphere chains. The attractive interactions are treated as a perturbation to the reference system

The PHSC equation of state (EOS) for pure fluids is given by

$$Z = \left(\frac{P}{\rho kT} \right) = Z_{ideal} + Z_{HS} + Z_{bonding} + Z_{pert} \quad (1)$$

From EOS, Helmholtz free energy can be derived

$$A = A_{ideal} + A_{HS} + A_{bonding} + A_{pert} \quad (2)$$

2. Molecular model for PHSC

In the model EOS, molecules are conceived to be chains composed of spherical segments. The pair potential for the segment of a chain is given by a modified square-well (SW) potential, which was suggested by Chen and Kreglewski

$$u(r) = \begin{cases} \infty & r < (\sigma - s_1) \\ 3\varepsilon & (\sigma - s_1) \leq r < \sigma \\ -\varepsilon & \sigma \leq r < \lambda\sigma \\ 0 & \lambda\sigma \leq r \end{cases} \quad (3)$$

where $u(r)$ is the pair potential, r is the radial distance between two segments, σ is the temperature-independent segment diameter, ε is the depth of the potential well, and λ is the reduced well width. As suggested by Chen and Kreglewski, a ratio of $s_1/\sigma = 0.12$ is assumed.

Table 1. PHSC models

	Molecular model	$Z_{HS}/(m^2 b\rho)$	$Z_{bonding}$	Z_{pert}
PHSC-Song ^a	SW ($\sigma \leq r \leq \lambda\sigma$)	$g(d^+)$ with CS	$-(m-1)[g(d^+)-1]$	$-\frac{r^2 a\rho}{k_B T}$
PHSC-Hino ^b	SW	$g(d^+)$ with CS	$-(m-1)[g(d^+)-1]$	$f(\eta, \varepsilon)$ with Chang & Sandler RDF
PHSC-Sadoski ^c	SW, equation (3)	$g(d^+)$ with CS	$-(m-1)\rho \frac{\partial \ln g(d^+)}{\partial \rho}$	$h(\eta, \varepsilon)$ with Chiew results

a) Y. Song, S. M. Lambert, J. M. Prausnitz, Chem. Eng. Sci. **49**(1994) 255

b) T. Hino, J. M. Prausnitz, Fluid Phase Equilib. **138**(1997) 105

c) J. Gross, G. Sadowski, Fluid Phase Equilib. **168**(2000) 185

The best analytical explicit form for radial distribution function of hard sphere at contact diameter d^+ is obtained from Carnahan-Starling equation as follows,

$$g(d^+)^{HS} = \frac{1-\eta/2}{(1-\eta)^3} \quad (4)$$

where $\eta = \frac{r\rho\pi\sigma^3}{6}$ is the packing fraction.

3 The mean spherical approximation theory

The Helmholtz free energy has four contributions from, respectively, the ideal gas, the hard sphere repulsion, the mass action law (MAL) and the electrostatic interactions:

$$A = A_{ideal} + A_{SHS} + A_{MAL} + A_{ele} \quad (5)$$

The mass action law (MAL) is described by the stoichiometric association constant, density and

the degree of association for ions.

4. Molecular model for MSA

The interaction potential $u(r)$ is given by

$$u(r) = \begin{cases} \infty & r < \sigma, r \neq L \\ 0 & r > \sigma, r = L \\ -\beta^{-1} \ln(L\delta(r-L)/12\tau) & \\ \frac{z_i z_j e^2}{4\pi D r} & \end{cases} \quad (6)$$

where L is the sticky distance for a pair and δ is the Delta function. $\beta = 1/k_B T$, τ is the inverse of the sticky coefficient which measures the strength of the stickiness. D is the dielectric constant.

Recently, Bernard[5] reported an analytical solution of the binding mean spherical approximation (BMSA) by solving the Wertheim Ornstein-Zernike (WOZ) [6] integral equation. Unlike the usual OZ derived from Mayer density expansion, the WOZ is derived from the activity expansion and can account properly for saturation effects in which only one bond is allowed between ions.

From the BMSA according to the restricted-primitive model (RPM), the Helmholtz free energy is given by

$$\left(\frac{A}{Nk_B T} \right)_{\text{ideal}} = 2\rho_0 \ln \rho_0 - 2\rho_0$$

where ρ_0 is the half of number density of hard spheres; half of the species have a charge $+ze$ and the other half $-ze$ ($e = 1.602 \times 10^{-19} \text{C}$)

$$\left(\frac{A}{Nk_B T} \right)_{\text{HS}} = \frac{2\rho_0 \eta (4 - 3\eta)}{(1 - \eta)^2} \quad (\eta = \rho^* \pi / 6, \rho^* = 2\rho_0 \sigma^3)$$

$$\left(\frac{A}{Nk_B T} \right)_{\text{MAL}} = 2\rho_0 \ln \alpha + \rho_0 (1 - \alpha)$$

where α is the degree of dissociation and then the number density of free ions is $\rho_+ = \rho_- = \rho_0 (1 - \alpha)$. The number density of neutral ion pairs is $\rho_P = \rho_0 \alpha$.

$$\left(\frac{A}{Nk_B T} \right)_{\text{ele}} = -2l_B \rho_0 z^2 \frac{\Gamma^B}{1 + \Gamma^B} + \frac{(\Gamma^B)^3}{3\pi}$$

where $l_B = \beta e^2 / 4\pi D$ is the Bjerrum length characterizing the dielectric property of the continuous medium. Γ^B is the screening parameter calculated by L. Blum et. al.[7]

Result and Conclusion

J. Lu explained[8] that a comprehensive study on various internal energies, pressures and chemical potentials for the pure dipolar hard sphere fluids and Stockmayer fluids was reported based on the perturbation theory(PT) from Cotterman and Henderson-Blum-Tani(HBT) theory. The PT could give more accurate results than MSA.

While the hard core contribution was important in determining the phase coexistence of electrolytes, inclusion of hard core into MSA model such Debye-Hukel-Bjerrum-Dipole-ion-Hardcore (DHBjDIHC) [7] was in poorer agreement with MC simulation results.

For electrolyte fluids, recent review shows that BIMSA is in good agreement with system but the combined model is good in the polymer electrolyte fluids

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