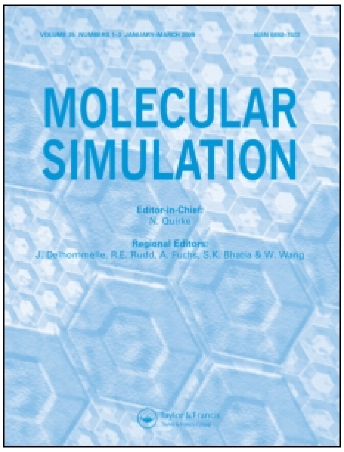

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Qin, Yuan , Zhao, Kai , Liu, Honglai and Hu, Ying(2003) 'Molecular Thermodynamics of Size Asymmetrical Charged Hard-dumbbell Fluids', Molecular Simulation, 29: 12, 743 — 748

To link to this Article: DOI: 10.1080/0892702031000122599

URL: http://dx.doi.org/10.1080/0892702031000122599

Molecular Simulation, Vol. 29 (12), December 2003, pp. 743–748

Molecular Thermodynamics of Size Asymmetrical Charged Hard-dumbbell Fluids

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(Received November 2002; In final form January 2003)

A molecular thermodynamic model of size asymmetrical charged hard dumbbell fluids is proposed, which consists of two parts: one is the reference electrolyte solution contribution and the other is the positive and negative ions association contribution. For the former we use MSA result of primitive model electrolyte and the latter is a function of the cavity correlation function of the positive and the negative ions. To test the theory, Monte Carlo simulations are performed to calculate the thermodynamic properties at high temperature. We find that if the original MSA solution is used, the variations of thermodynamic properties with the asymmetry of the ions size is qualitatively wrong. If we take the size asymmetrical ions mixtures as symmetrical ones with effective diameter σ_{12} ($\sigma_{12} = (\sigma_1 + \sigma_2)/2$ is the mean diameter of the positive and negative ions.) not only the formula is greatly simplified but also the agreement between theory and simulation is greatly improved.

Keywords: Charged hard-dumbbell; Monte Carlo simulation; Molecular thermodynamics; Mean spherical approximation

INTRODUCTION

The criticality of the electrolyte solution has recently been the focus of considerable attention [1–7]. At low temperature the ions tend to form various kinds of clusters, and to model the thermodynamic properties correctly, this phenomena must be accounted. For instance, in the theory of Fisher and Levin [2], neutral ion pairs are introduced to reduce the effective concentration of charged species. Zhou *et al.* [3] gave a theory which includes ion pairs and takes more accurate account of the ion–dumbbell interactions. Shelley and Patey [5] have simulated coexistence curves for both the restricted primitive model electrolyte and charged hard-dumbbell fluids by grand canonical Monte Carlo simulations. They found that the phase behavior of both models is very similar. They thus reached the conclusion that it might prove more useful to view these ionic systems as charged hard-dumbbell fluids perturbed by free ions rather than the reverse. So the study of charged hard-dumbbell fluids may help us understanding the properties of electrolyte solution at low temperature. Kalyuzhnyi [8] has derived expressions for the Helmholtz function and other thermodynamic properties for charged hard-dumbbell fluids through the Chandler–Silbey–Ladanyi integral equation closed by the mean-spherical-approximation closure. In a preliminary work [11], we have used Zhou and Stell's method [9–10] to develop a simple thermodynamic model of the charged hard-dumbbell fluids and simulated thermodynamic properties at high temperatures, and the agreement between the theory and the simulation is fairly good. Independently, Jiang *et al.* [12] also get a similar theory. All these theories [8,11,12] of charged hard dumbbell fluids are restricted to the size symmetrical cases. Recently, Romero-Enrique *et al.* [6] found that the variation of the criticality parameters with the size asymmetry of the positive and the negative ions, as predicted by current theories, contradicts the simulation result. This inspires us to extend our previous work on size symmetrical charged hard dumbbell fluids to the size asymmetrical cases.

MOLECULAR THERMODYNAMIC MODEL

We consider a charged hard-dumbbell fluid with molecule number N and number density ρ.

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ISSN 0892-7022 print/ISSN 1029-0435 online
DOI: 10.1080/0892702031000122599

All molecules are embedded in a continuum medium with permittivity ε. A charged hard-dumbbell molecule consists of two freely tangent-jointed and oppositely charged hard spheres. The diameters and the charges of the hard spheres are σ_i and $z_i e$ respectively. The charges of the hard spheres are identical but with opposite sign, i.e. $z_1 e = -z_2 e = ze$ (e is the elementary charge). $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ is the bond length of the dumbbell molecules and the parameter $\lambda = \sigma_1/\sigma_2$ is used to characterize the size asymmetry of the hard spheres. The Bjerrum length is $l_{\mathrm{B}} = z^2 e^2 \beta/\varepsilon$, where $\beta = 1/kT$, k is the Boltzmann constant and T the temperature. The bond length σ_{12} provided the basic length scale, which can be used to define reduced temperature and the reduced density via $T^* = \sigma_{12}/l_{\mathrm{B}}$ and $\rho^* = 2\rho\sigma_{12}^3$.

We use Zhou and Stell's method [9,10] to construct the molecular thermodynamic model for the charged hard-dumbbell fluids. Here the primitive model electrolyte is used as the reference system and the number densities of the ions are identical with that of the charged hard-dumbbell molecules, i.e. $\rho_1 = \rho_2 = \rho$. Then, the positive and negative hard ions are pairwise associated to form charged hard dumbbell fluids. Similar to the previous work [11,12], the residual Helmholtz function can be expressed as:

$$\frac{\beta A^{\mathrm{r}}}{N} = \frac{\beta A^{\mathrm{r(ref)}}}{N} + \frac{\beta \Delta A^{\mathrm{ass}}}{N} = \frac{\beta A^{\mathrm{r(ref)}}}{N} - \ln y_{12}^{\mathrm{ref}}(\sigma_{12}) \quad (1)$$

where $A^{\mathrm{r(ref)}}$ and A^{ass} are the residual Helmholtz function of the reference system and the Helmholtz function due to the association of the positive and the negative ions, respectively. $y_{12}(\sigma_{12})$ is the cavity correlation function of positive and negative ions in the reference system, which is defined by

$$y_{12}(\sigma_{12}) = \exp[\beta\varepsilon(\sigma_{12})]g_{12}(\sigma_{12}) \quad (2)$$

where $\varepsilon(\sigma_{12})$ and $g_{12}(\sigma_{12})$ are the interaction energy and the radial distribution function of the ionic pair in the reference system, respectively.

The residual internal energy, compressibility and residual chemical potential can be obtained from the Helmholtz function by using thermodynamic relations:

$$E^{\mathrm{r}} = \left(\frac{\partial \beta A^{\mathrm{r}}}{\partial \beta}\right)_{N,V}, \quad \frac{\beta p}{\rho} = \rho\left(\frac{\partial \beta A/N}{\partial \rho}\right)_{N,T}, \quad \mu^{\mathrm{r}} = \left(\frac{\partial A^{\mathrm{r}}}{\partial N}\right)_{T,V} \quad (3)$$

Thermodynamic Properties of the Reference System

The Helmholtz function of the reference primitive model electrolyte can be expressed as:

$$A^{\mathrm{ref}} = A^{\mathrm{hs}} + A^{\mathrm{ele}} \quad (4)$$

A^{hs} and A^{ass} are the hard spheres mixture and electrical contribution to the Helmholtz function, respectively. For the hard spheres contribution, the Mansoori–Carnahan–Starling–Leland equation is used:

$$\frac{\beta A^{\mathrm{hs}}}{N_0} = \left(\frac{\zeta_2^3}{\zeta_0 \zeta_3^2} - 1\right)\ln \Delta + \frac{\pi \zeta_1 \zeta_2}{2\zeta_0 \Delta} + \frac{\pi \zeta_2^3}{6\zeta_0 \zeta_3 \Delta^2} \quad (5)$$

where $\zeta_i = \sum_{j=1}^{2} \rho_j \sigma_j^i$ and $\Delta = 1 - \pi\zeta_3/6$, N_0 is the total number of the ions.

For the electrical contribution, Blum's MSA (Mean Spherical Approximation) analytical solution [13] is used:

$$\frac{\beta A^{\mathrm{ele}}}{N_0} = -\frac{\alpha_0^2}{4\pi\rho_0}\sum_{i=1}^{2}\frac{\rho_i z_i}{1+\sigma_i \Gamma}\left(z_i \Gamma + \frac{\pi \sigma_i P_n}{2\Delta}\right) + \frac{\Gamma^3}{3\pi\rho_0}. \quad (6)$$

where ρ_0 is the number density of both positive and negative ions, P_n and Γ can be solved from the following two coupling equations:

$$P_n = \sum_{i=1}^{2}\frac{\rho_i z_i \sigma_i}{1+\sigma_i \Gamma} \Bigg/ \left[1 + \frac{\pi}{2\Delta}\sum_{i=1}^{2}\frac{\rho_i \sigma_i^3}{1+\sigma_i \Gamma}\right] \quad (7)$$

$$4\Gamma^2 = \alpha_0^2 \sum_{i=1}^{2}\frac{\rho_i}{(1+\sigma_i\Gamma)^2}(z_i - \pi\sigma_i^2 P_n/2\Delta)^2 \quad (8)$$

If the diameters of the positive and the negative ions are identical, the equation can by simplified as:

$$\frac{\beta A^{\mathrm{ele}}}{N_0} = -\frac{l_{\mathrm{B}}\Gamma}{(1+\sigma\Gamma)} + \frac{\Gamma^3}{3\pi\rho_0} \quad (9)$$

and Γ is calculated by

$$\Gamma = ((1+2\sigma\kappa)^{1/2} - 1)/2\sigma \quad (10)$$

where $\kappa^2 = 8\pi\rho_0 l_{\mathrm{B}}$.

Cavity Correlation Function between Positive and Negative Ions

As in previous work, we use the EXP approximation for $g_{12}^{\mathrm{ref}}(\sigma_{12})$, the radial distribution function of the reference system. Thus the cavity correlation function of positive and the negative ions becomes:

$$y_{12}^{\mathrm{ref}}(\sigma_{12}) = g_{12}^{\mathrm{hs}}(\sigma_{12})\exp[\Delta g(\sigma_{12})]\exp(-l_{\mathrm{B}}/\sigma_{12}) \quad (11)$$

where $g_{12}^{\mathrm{hs}}(\sigma_{12})$ radial distribution function of the hard spheres mixture, for which we use the Mansoori–Carnahan–Starling–Leland result:

$$g_{12}^{\mathrm{hs}}(\sigma_{12}) = \frac{1}{\Delta} + \frac{3}{2}\frac{K_{12}}{\Delta^2} + \frac{1}{2}\frac{K_{12}^2}{\Delta^3} \quad (12)$$

with

$$K_{12} = \frac{\pi}{6}\frac{\sigma_1\sigma_2}{\sigma_{12}}\xi_{12}.$$

$\Delta g_{12}(\sigma_{12})$ is defined as [13]:

$$\Delta g_{12}(\sigma_{12}) = -\frac{\Gamma^2 a_1 a_2}{\pi\sigma_{12}\alpha_0^2} \tag{13}$$

with

$$\alpha_i = \frac{\alpha_0^2}{2\Gamma(1+\sigma_i\Gamma)}\left(z_i - \frac{\pi\sigma_i^2 P_n}{2\Delta}\right). \tag{14}$$

For the case of identical diameter the $\Delta g_{12}(\sigma_{12})$ is simplified as:

$$\Delta g_{12}(\sigma_{12}) = \frac{l_B}{\sigma_{12}(1+\sigma_{12}\Gamma)^2}. \tag{15}$$

Thermodynamic Properties of the Charged Hard Dumbbell Fluid

Substitute Eqs. (4) and (11) into Eq. (1) we get the Helmholtz function of the charged hard dumbbell fluids:

$$\begin{aligned}\frac{\beta A^{\mathrm{r}}}{N} &= 2\left(\frac{\zeta_2^3}{\zeta_0\zeta_3^2} - 1\right)\ln\Delta + \frac{\pi\zeta_1\zeta_2}{\zeta_0\Delta} + \frac{\pi\zeta_2^3}{3\zeta_0\zeta_3\Delta^2}\\ &\quad - \ln\left(\frac{1}{\Delta} + \frac{\pi\sigma_1\sigma_2\zeta_2}{4\sigma_{12}\Delta^2}\right)\\ &\quad - \frac{\alpha_0^2}{4\pi\rho}\sum_{i=1}^{2}\frac{\rho_i z_i}{1+\sigma_i\Gamma}\left(z_i\Gamma + \frac{\pi\sigma_i P_n}{2\Delta}\right)\\ &\quad + \frac{\Gamma^3}{3\pi\rho} + \frac{\Gamma^2 a_1 a_2}{\pi\sigma_{12}\alpha_0^2} + \frac{l_{\mathrm{B}}}{\sigma_{12}}.\end{aligned} \tag{16}$$

As P_n and Γ should be solved explicitly from Eqs. (7) and (8), the expressions of the other thermodynamic functions got from Eq. (16) will be very complex. Even more, as will be shown in part 4, the thermodynamic properties predicted by Eq. (16) is qualitatively wrong. After some study, we find a measure to solve this problem. For the hard sphere contribution to the Helmholtz function we still use the result of Eq. (16), but for the electrical contribution we take the size asymmetrical ions mixture as size symmetrical one with σ_{12} as the effective ion diameter. By this way, not only Eq. (16) is greatly simplified, but also the agreement between theory and simulation is greatly improved. The revised Helmholtz function of the charged hard dumbbell fluids is as follows:

$$\begin{aligned}\frac{\beta A^{\mathrm{r}}}{N} &= 2\left(\frac{\zeta_2^3}{\zeta_0\zeta_3^2} - 1\right)\ln\Delta + \frac{\pi\zeta_1\zeta_2}{\zeta_0\Delta} + \frac{\pi\zeta_2^3}{3\zeta_0\zeta_3\Delta^2}\\ &\quad - \ln\left(\frac{1}{\Delta} + \frac{\pi\sigma_1\sigma_2\zeta_2}{4\sigma_{12}\Delta^2}\right) - \frac{2l_B/\Gamma}{1+\sigma_{12}\Gamma} + \frac{\Gamma^3}{3\pi\rho}\\ &\quad + \frac{l_{\mathrm{B}}}{\sigma_{12}}\left(1 - \frac{1}{(1+\sigma_{12}\Gamma)^2}\right).\end{aligned} \tag{17}$$

The residual internal energy, compressibility and the residual chemical potential calculated from Eq. (17) are:

$$\begin{aligned}\frac{\beta E^{\mathrm{r}}}{N} &= -\frac{2l_B/\Gamma}{1+\sigma_{12}\Gamma}\\ &\quad + \frac{l_{\mathrm{B}}}{\sigma_{12}}\left(1 - \frac{1}{(1+\sigma_{12}\Gamma)(1+2\sigma_{12}\Gamma)}\right)\end{aligned} \tag{18}$$

$$\begin{aligned}\frac{\beta p}{\rho} &= \frac{2-\Delta}{\Delta} + \frac{18\pi\zeta_1\zeta_2 + \pi^2\zeta_2^3}{18\zeta_0\Delta^2} + \frac{\pi^2\zeta_2^3}{9\zeta_0\Delta^3}\\ &\quad - \frac{4\sigma_{12}\Delta(1-\Delta) + \pi\sigma_1\sigma_2\zeta_2(2-\Delta)}{4\sigma_{12}\Delta + \pi\sigma_1\sigma_2\zeta_2} - \frac{\Gamma^3}{3\pi\rho}\\ &\quad + \frac{l_B/\Gamma}{(1+\sigma_{12}\Gamma)^2(1+2\sigma_{12}\Gamma)}\end{aligned} \tag{19}$$

$$\beta\mu^{\mathrm{r}} = \frac{\beta A^{\mathrm{r}}}{N_0} + \frac{\beta p}{\rho_0}. \tag{20}$$

MONTE CARLO SIMULATION

To test the molecular thermodynamic model we simulated the thermodynamics properties of this model fluid at high temperatures by Monte Carlo method. The simulation is performed in a canonical ensemble with 256 charged hard-dumbbell molecules. The electrical energies are calculated by the Ewald's summation method [14]. A trial move of the Monte Carlo step consists of random translation and rotation of the dumbbell molecules. The maximum displacement is adjusted so as the acceptance ratio is about 40–50%. The α-f.c.c. lattices of the dumbbell molecules are used as the initial configurations and 1000–10,000 cycles are used to equilibrate the system; here by one cycle we mean each molecule is moved once. After equilibration, 3000–50,000 cycles are used to calculate the energies and chemical potentials. Widom's test particle method is used to calculate the chemical potentials and 500 test molecules are used in each sample configuration. The energy increase by a test molecule, u_t, is

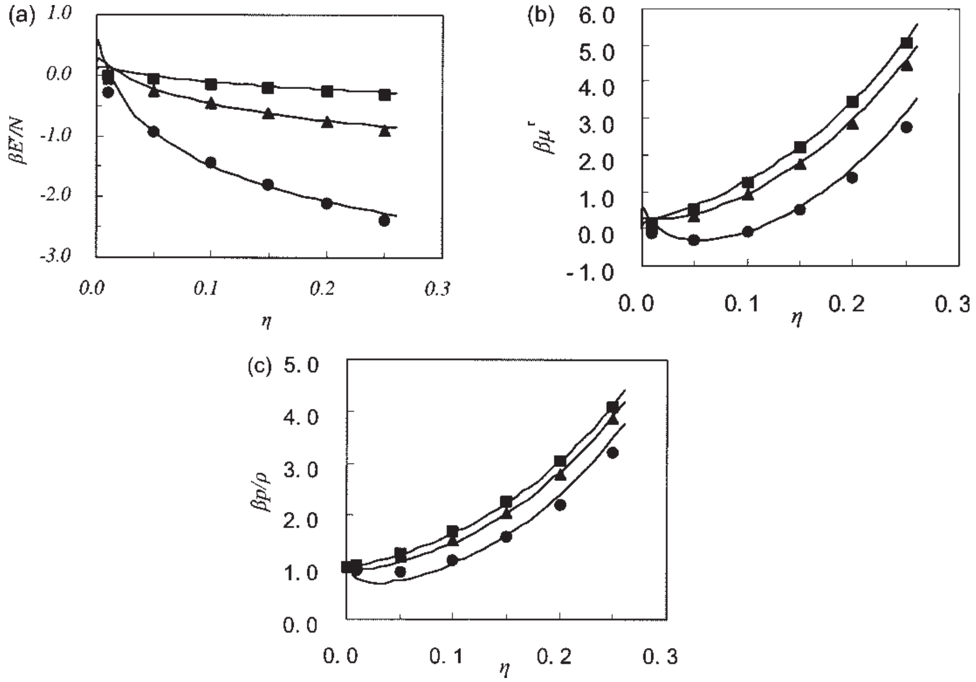

FIGURE 1 Thermodynamic properties of charged hard-dumbbell fluids for size symmetrical cases. η is the packing fraction. Monte Carlo results: squares, $T^* = 0.5$; triangles, $T^* = 0.25$; circles, $T^* = 0.125$. Theory: solid lines.

also calculated by Ewald's summation method. The residual chemical potential is simply calculated by

$$\mu^{\mathrm{r}} = -kT\ln\langle\exp(-u_t/kT)\rangle \tag{21}$$

where $\langle\ldots\rangle$ means ensemble average. The pressures are calculated indirectly by integration of the chemical potentials at different densities. For convenience, residual chemistry potential are fitted by truncated virial equation,

$$\mu^{\mathrm{r}} = \sum_{i=2}^{K} \frac{i}{i-1} B_i \rho^{i-1}. \tag{22}$$

Correspondingly, the compressibility can be expressed as:

$$\beta p/\rho = 1 + \sum_{i=2}^{K} B_i \rho^{i-1}. \tag{23}$$

It is found that $K = 5$ is sufficient for the current situation.

RESULTS AND DISCUSSIONS

First we test the size symmetrical cases. Figure 1(a–c) shows the comparisons of theory with simulation for residual internal energy, residual chemical potential

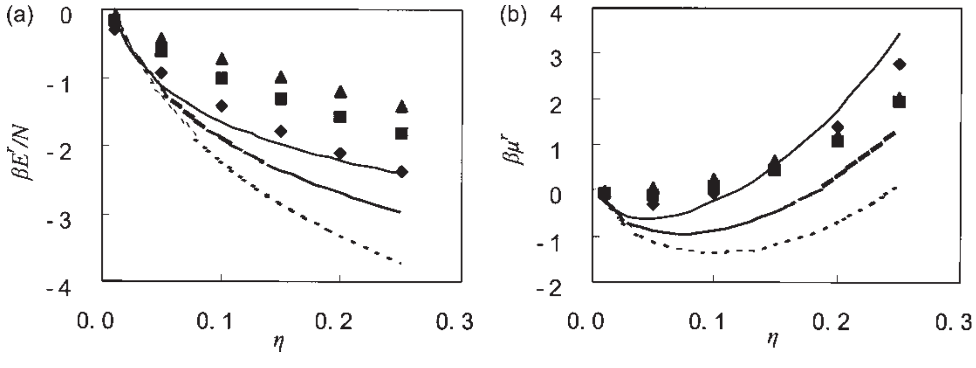

FIGURE 2 Thermodynamic properties of size asymmetrical charged hard dumbbell fluid calculated by Eq. (16), $T^* = 0.125$, η is the packing fraction. Monte Carlo simulation result: diamond, $\lambda = 1$; square, $\lambda = 3$; triangle, $\lambda = 5.67$. Theory: solid line, $\lambda = 1$; dotted and dashed line, $\lambda = 3$; dashed line, $\lambda = 5.67$.

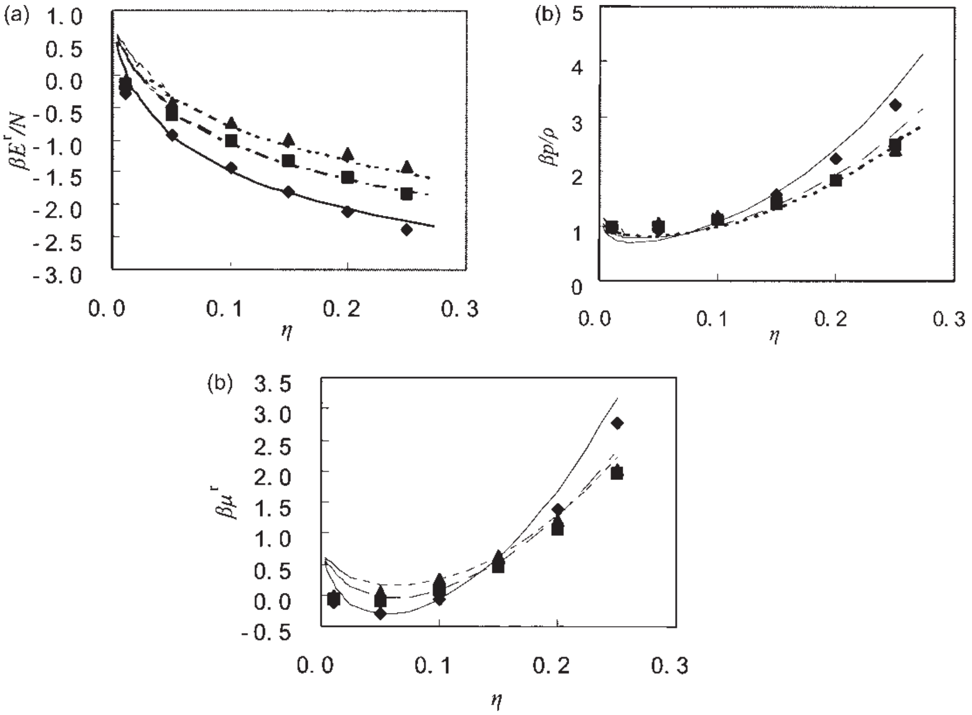

FIGURE 3 Thermodynamic properties of size asymmetrical charged hard dumbbell fluid calculated by Eq. (17), $T^* = 0.125$, η is the packing fraction. Monte Carlo simulation result: diamond, $\lambda = 1$; square, $\lambda = 3$; triangle, $\lambda = 5.67$. Theory: solid line, $\lambda = 1$; dotted and dashed line, $\lambda = 3$; dashed line, $\lambda = 5.67$.

and compressibility, respectively. Three reduced temperatures, $T^* = 0.5$, 0.25 and 0.125 are shown. Generally, the theory fits the simulation well in the region studied except at extremely low densities. At extremely low densities, the residual internal energies are positive. This is unphysical. This defect may be due to the fact that the MSA analytical solution of electrolyte is not accurate enough at low densities.

It may seem straightforward to extend the size symmetrical cases to the size asymmetrical ones. Figure 2(a,b) shows the residual energy and the residual chemical potential at different size asymmetries calculated from Eq. (16). Strikingly, the dependences of the thermodynamic properties on the size asymmetry parameter λ are qualitatively wrong. At the same packing fraction, the residual internal energies predicted by the theory decrease when λ increases, which is in contradiction with the simulation results. For the residual chemical potential, the discrepancies between the theory and the simulation increase when λ increases. These results are rather unexpected. Fortunately, if we use the revised theory of Eqs. (17)–(20) to calculate the thermodynamic properties, satisfactory results are obtained as shown in Fig. 3(a–c). The nature of this revised theory is that when calculating the electrical contribution to the Helmholtz function, the size asymmetrical electrolyte is equivalent to a symmetrical one with the effective ion diameter σ_{12}.

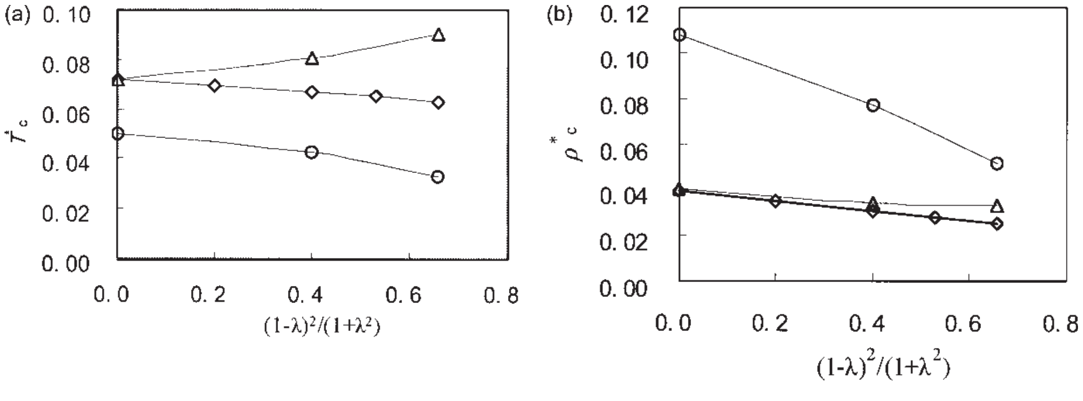

FIGURE 4 Reduced criticality parameters of size asymmetrical charged hard dumbbell fluids as a function of asymmetry parameter $(1-\lambda)^2/(1+\lambda^2)$. Open diamond: the revised MSA theory calculation for charged hard dumbbell fluid; open triangle: the original MSA theory calculation for charged hard dumbbell fluid; open cycle: MC simulation result for charged hard dumbbell fluid [6].

It should be mentioned that Harvey *et al.* [15] have pointed out that if this method is used to calculate the thermodynamic properties of the electrolyte solution little error is introduced.

It is interesting to calculate the critical parameters using the original and the revised theory, respectively. Figure 4(a,b) shows the calculated reduced critical temperature T_c^* and reduced critical density ρ_c^*. Also shown in Fig. 4 is the fine-discretization Monte Carlo simulation result of Romero-Enrique *et al.* [6]. T_c^* calculated by the original MSA theory tend upwards as λ increases while the simulation tends downwards, and T_c^* calculated by the revised theory is in consistent with the simulation. ρ_c^* calculated by the original MSA theory and the simulation result are consistent in trend, but the curve of the original theory is too flat in comparison with that of the simulation, and the revised theory is improved in that ρ_c^* decreases with λ more rapidly.

In summary, using the original MSA analytical solution of the size asymmetrical electrolyte to calculate the thermodynamic properties of the charged hard dumbbell fluid results in some severe qualitative problems. If we take the asymmetrical electrolyte as the symmetrical one with effective diameter σ_{12}, not only is the formula greatly simplified but also the theory prediction is greatly improved.

Acknowledgements

This work was supported by National Science Foundation of China (Project No. 20025618), the Doctoral Research Foundation by Ministry of Education of China (Project No. 1999025103) and the Education committee of Shanghai City of China.

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