CHEMICAL ASSOCIATION IN SIMPLE MODELS OF MOLECULAR AND IONIC FLUIDS: II. THERMODYNAMIC PROPERTIES

Yaoqi Zhou[1,*] and George Stell[2]

[1] *Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794.*

[2] *Departments of Chemistry and Mechanical Engineering, State University of New York at Stony Brook, Stony Brook, NY 11794.*

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ABSTRACT

A simple interpolation scheme (SIS) suggested in an earlier paper is used to obtain the excess Helmholtz free energy and the equation of state for the sticky-shell model and the shielded sticky-point model of associative fluids. It is found that the equation of state under the SIS for a fully associated homonuclear dumbbell fluid is quite accurate as long as $L^* = L/\sigma \geq 0.8$. For ionic association, the excess Helmholtz free energy in this work reduces to that of Bjerrum's theory in the ideal limit. An analytical equation of state for associative ions is evaluated.

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* Present address: Applied Phys. & Chem. Lab, 4066, E. Mission Blvd. Pomona, CA91766

I. INTRODUCTION

In an earlier paper[1], we presented a simple interpolation scheme (SIS) that yields approximation for various sticky-shell models[2–5] and shielded sticky-point models.[1] The latter extend Wertheim's sticky-point model.[6] The approximation, which we found to be equivalent to Wertheim's first-order thermodynamic perturbation theory (TPT)[7] for the sticky-point model, is obtained from simple interpolation between the law of mass action in the low concentration limit and the complete dissociation result in the high-temperature limit.

In ref. [1] we focused almost exclusively on the association constant of our models. In this extension of our work, we consider the more general thermodynamic properties of the models through their Helmholtz free energies.

Under the TPT, Wertheim showed that the excess Helmholtz free energy (over the complete dissociated fluid system) of his sticky-point model has a simple relation with the association degree α[6,7]

$$\beta A^{ex}/N = \frac{\alpha}{2} + \ln(1-\alpha) \tag{1.1}$$

where N is the total number of atomic particles (both bound and not bound), $\beta = 1/k_BT$ with T the absolute temperature, and $\alpha = \rho_{AB}/\rho_{A0}$ with the number density of dimers ρ_{AB} and $\rho_{A0} = \rho_{B0} = \rho_0 = N/2V$. In Section II of this paper we shall show that this simple expression holds in the SIS even when the stickiness is shielded inside a repulsive core. The pressure obtained from the excess free energy (1.1) becomes less accurate as the bounding length $L \to 0$ (Section III). Nevertheless, at the complete hard-sphere association limit, $\alpha = 1$, the pressure derived from (1.1) for the reduced density $\rho\sigma^3 < 0.5$ is within 3% of the accurate TS equation of state[8] for the hard-dumbbell fluid for a reduced bond length $L^* = L/\sigma \geq 0.8$. We also investigate ionic association. We show that eq. (1.1) is very closely related to the expression of the excess free energy of Bjerrum's theory.[9,10] Finally, we give some results of an analytical equation of state for associative ions.

II. THE APPROXIMATION

We refer the reader to ref. [1] for a full discussion of the models we treat here. Our terminology and notation follow that of ref. [1] and we give only a condensed summary to make the paper notationally self-contained.

We consider an equal-association reaction

	A	+	B	$\rightleftharpoons$	AB
pre-reaction densities	ρ_0		ρ_0		0
post-reaction densities	$\rho_0(1-\alpha)$		$\rho_0(1-\alpha)$		$\alpha\rho_0(=\rho_{AB})$

In the sticky-shell models, devoted to both non-ionic[2,3] and ionic[3,4] association, the Mayer f function is given by[4]

$$f_{ij}(r) = \begin{cases} -1 + L(1-\delta_{ij})\delta(r-L)/(12\tau), & r < \sigma, \\ \exp[-\beta z_i z_j e^2/(\epsilon r)] - 1, & r > \sigma\ . \end{cases} \tag{2.1}$$

This results in a pair correlation $h_{ij}(r)$ inside the hard core given by

$$h_{ij}(r) = -1 + \lambda(1-\delta_{ij})L\delta(r-L)/12, \quad r < \sigma \tag{2.2}$$

with

$$\rho_{AB} = \rho_0 \int_{L^-}^{L^+} d\mathbf{r}(1 + h_{AB}), \quad \alpha = \eta\lambda(\frac{L}{\sigma})^3 = \frac{\rho_{AB}}{\rho_0} \tag{2.3}$$

where δ_{ij} is a Kronecker delta, $\delta(r-L)$ is a delta function, and $z_i e$ and σ are the charge and diameter of particles of species i, with $z_A = -z_B$. Here ϵ is the dielectric constant of the solvent, τ^{-1} is a "bare" association (stickness) parameter[11], λ is the mean association parameter[2-5] for the system at arbitrary density, $i = A$, or B, $\eta = \pi\rho_0\sigma^3/3$, and $L \leq \sigma/2$. If the charges are turned off, one obtains the Mayer f function for a simple non-ionic association model.

The excess Helmholtz free energy for the sticky-shell model can be obtained from[4a,c]

$$\beta A^{ex}/N = -\frac{1}{2}\eta(\frac{L}{\sigma})^3 \int_0^{\xi} y_{AB}(L,\tilde{\xi})d\tilde{\xi} \tag{2.4}$$

where $\xi = 1/\tau$, and $y_{ij} = e^{\beta u_{ij}}g_{ij}$ with the pair potential u_{ij} and the radial distribution function g_{ij}. Since [cf. (2.1) and (2.2)]

$$\lambda = \xi y_{AB}(L), \tag{2.5}$$

(2.4) can be rewritten as [cf.(2.3)]

$$\beta A^{ex}/N = -\frac{1}{2}\int_0^{\alpha}(1-\tilde{\alpha}\frac{d\ln y_{AB}}{d\tilde{\alpha}})d\tilde{\alpha} \tag{2.6}$$

Using the SIS approximation introduced earlier,[1]

$$y_{AB} = (1-\alpha)^2 y_{AB}^{ref} \tag{2.7}$$

where $y_{AB}^{ref}(r)$ is the cavity function of a reference system, which is full dissociated fluid system ($\alpha = 0$). we have immediately

$$\beta A^{ex}/N = \frac{\alpha}{2} + \ln(1-\alpha) \tag{2.8}$$

For shielded sticky point models, similar results can also be obtained. We shall omit derivations here. (When $L \geq \sigma/2$ the shielded sticky-point model rather than the shedded sticky-shell model must be used to avoid the formation of trimers, tetramers etc., as noted in ref. [1].)

Under the approximation (2.7), we have[1]

$$\frac{\alpha}{\rho_0(1-\alpha)^2} = K_0 y_{AB}^{ref}(L) \tag{2.9}$$

where K_0 is the ideal gas limit of the association constant K

$$K \equiv \frac{\rho_{AB}}{\rho_A\rho_B} \stackrel{\rho_0\to 0}{\longrightarrow} K_0(T) \tag{2.10}$$

$$K_0(T) = \int_{L^-}^{L^+} (1 + f_{AB}) d\mathbf{r} = \frac{\pi L^3}{3\tau} \tag{2.11}$$

From the expression for the excess free energy (2.8), we can obtain the excess pressure [cf.(2.9)]

$$\beta(p - p^{ref}) = -\alpha\rho_0[1 + \rho_0 \frac{d\ln y_{AB}^{ref}(L)}{d\rho_0}] \tag{2.12}$$

Again, this equation extends Wertheim's results[6] for $L = \sigma$ to the case $L < \sigma$.

III. LIMITING CASES AND APPLICATIONS

A. Hard-Sphere Association: The Limiting Case of $L = 0$

For equal-size hard-sphere association with zero bonding length, the pressure for "associated hard-sphere dumbbells" in the full association limit is the same as the hard-sphere pressure but with half number density

$$p = p^{ref}(\rho_0) = p^{hs}(\rho_0), \quad \text{when } L = 0,\ \alpha = 1. \tag{3.1}$$

Here the reference system is a pure hard-sphere fluid with number density $2\rho_0$. Then Eq.(2.12) becomes

$$\beta[p^{hs}(\rho_0) - p^{hs}(2\rho_0)] = -\rho_0[1 + \rho_0 \frac{d\ln y^{hs}(0)}{d\rho_0}] \tag{3.2}$$

From the first zeroth-separation theorem,[12] we can rewrite (3.2) as

$$\beta[p^{hs}(\rho_0) - p^{hs}(2\rho_0)] = -\beta\rho_0 \frac{dp^{hs}}{d\rho}|_{\rho=2\rho_0} \tag{3.3}$$

It is obvious that eq.(3.3) is only exact through the first order in the density ρ_0. It has been already shown that at $L/\sigma = 1$ and $\alpha = 1$ (2.12) gives an accurate equation of state for hard dumbbells;[6] we see that one can expect the equation of state predicted by eq.(2.12) to become worse as L gets smaller. However numerical calculation shows that for the density $2\rho_0\sigma^3 \leq 0.5$ the difference between the accurate Tildesley, Streett (TS) equation of state[8] for hard dumbbells and eq.(2.12) at $\alpha = 1$ is less than 3% as long as $L/\sigma \geq 0.8$.

B. Ionic Association: The Ideal Limit and an Accurate Equation of State

1. As early as 1926, Bjerrum used an association theory to understand the behaviour of strong electrolytes. His theory gives as an expression for the excess Helmoltz free energy

$$\beta A^{ex}/N = \frac{\alpha}{2} + \ln(1-\alpha) + \alpha(\phi^{ref} - 1) \tag{3.4}$$

where $\phi^{ref} = \beta p^{ref}/\rho, \quad \rho = 2\rho_0$. If $\phi^{ref} \approx 1$, (2.8) reduces to Bjerrum's result.

2. In Fig.1 we show the equation of state for associative ions with the bonding length $L = \sigma$ where $y_{+-}^{ref}(\sigma)$ is calculated in the $T\Gamma 2 - EXP$ approximation, which was shown in earlier work to be an accurate approximation for charged hard spheres.[13,14] For the closed-form analytic expression for the charged-sphere $y_{+-}(\sigma)$, we refer to reader to ref. [13] or [14].

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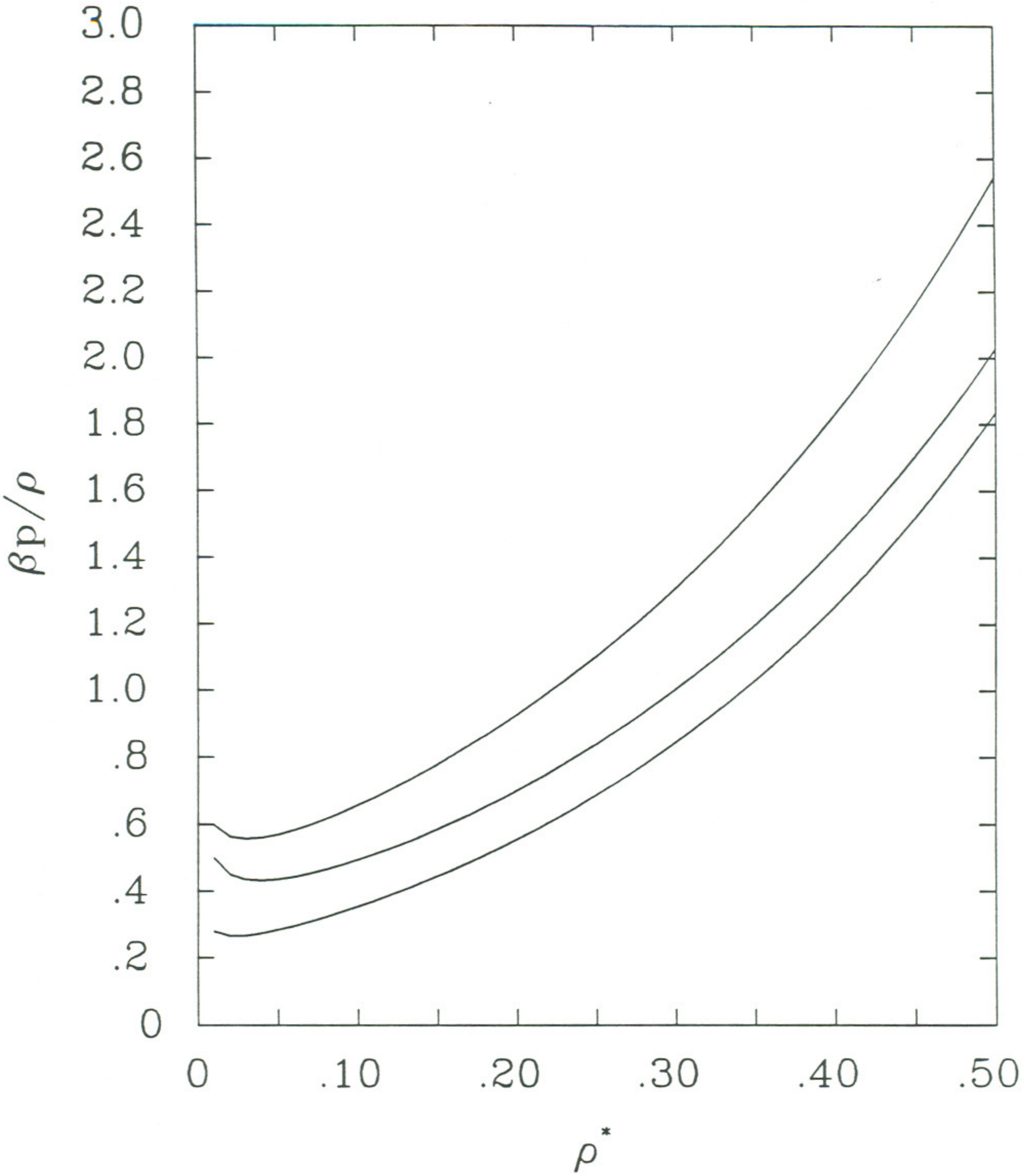
FIGURE CAPTION

Fig.1 $\beta p/\rho$ for associative ions as a function of the reduced density $\rho^* = 2\rho_0\sigma^3$. From top to below, fully associated ions ($\alpha = 1$, dipolar dumbbell), partially associated ions ($\tau = 100$), and fully dissociated ions ($\alpha = 0$). All at the reduced temperature $T^* = 0.15$ ($T^* = 1/\beta^*$, $\beta^* = \beta z_1 z_2 e^2/\epsilon\sigma$).


3.0
2.8
2.6
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.2
0
βp/ρ
0
.10
.20
.30
.40
.50
ρ*