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## MODEL FLUIDS OF ASSOCIATING PARTICLES

A class of statistical-mechanical model of associating atoms or ions is described. Conditions that must hold for them in the complete-association (confinement) limit are noted. In the simplest version of the models considered, this is the pure-solvent limit, of fundamental importance in solution theory. It is shown that the confinement limit is much like a critical-point limit, at which the direct correlation function assumes a very special long-ranged form. Off-confinement (partially-associated) states are then considered and a sequence of successively simpler approximations for the pair distribution functions are proposed on the basis of an Ornstein — Zernike-type equation. Explicit expressions due to Zhou and Stell are given for the simplest of these approximations, which is relevant both when the associating atoms are uncharged or when the fully associated system is of high dielectric constant. In the complete-association limit, these expressions apply to dipolar dumbbells with interpenetrating cores over a continuous range of interpenetration.

## 1. Introduction

It is a privilege and pleasure to contribute to this festschrift. I stand in awe of the courage and perseverance that Professor Holovko has shown in continuing to lead his research group under conditions that seem almost unimaginably adverse to most American scientists. I share his scientific goals and philosophy and value his scientific integrity.

In the Spring of 1985 I prepared a contribution to the Colston Symposium on Water and Aqueous Solution, which was held at the University of Bristol, England, in April, 1985. My lecture and manuscript had the same title as this contribution. I gave the lecture, had a wonderful time at the Symposium, and deposited a draft of a manuscript to be published as part of the Symposium Proceedings. Then back in the USA I began to see some things in the manuscript that needed reassessment — an assumption here, an approximation there. When deadline time came at the end of the summer, I reluctantly withdrew the manuscript because it still seemed to me to need more thought. Time passed, and a number of the observations in the manuscript found their way into my subsequent journal articles with Y. Zhou. But not all. When I looked at the manuscript a few months ago I found somewhat to my surprise that:

- (i) the general picture given in the first three sections of the manuscript concerning «sticky» models and on integral-equation method of assessing their structure had not been reproduced comprehensively in any of my later articles, although various fragments of it had appeared;
- (ii) the general picture was still worth summarizing;
- (iii) nobody else had looked at the same integral-equation method;
- (iv) there was now available some detailed algebra that could be used to implement the integral-equation method.

In light of this, I have lifted from the manuscript its general introductory discussion, annotated here and there with additional remarks and updated references. In particular Sections 2 through 4 of this contribution follow nearly verbatim most of Section 1 through 3 of the old manuscript. Then in the Appendices here I supplemented this material with a more specific discussion

of the properties of the ionic shielded sticky shell (SSS) model (especially its ionic valence) as a function of its parameter  $R/L$ , as well as some algebra associated with the SSS model. Among other things, the algebra gives in the complete-association limit the site-site distribution functions for dipolar dumbbels with interpenetrating cores over a continuous range of interpenetration,  $R/3 \leq L \leq R$ . [Rasaiah and Lee (1985a, 1985b) and Lee and Rasaiah (1987) have already given the results for  $L/R = 1/n$ ,  $n = 1$  to 5 in an approximation that is different but shares the same mathematics as ours]. Since work I am currently doing with Yu. Kalyuzhnyi of the Lviv group directly descends from the picture described in the Bristol lecture, it seems to me especially appropriate for its revision to finally see the light of day in this volume.

## 2. The models

I shall discuss here a class of statistical-mechanical models of associating particles. Some time ago Høye and Stell (1977) observed that the interaction site model [ISM] of Chandler and Andersen (1972) can be regarded as the complete-association (confinement) limit of such a model of associating particles. Among other results, Høye and Stell found that the site-site correlation functions Chandler and his colleagues used to describe the ISM could be simply related in that limit to the usual particle-particle distribution functions of a particle mixture. Cummings and Stell (1981, 1982) then further investigated the confinement limit in detail, on the basis of the Høye—Stell observation and earlier Høye — Stell work [Høye and Stell (1976)].

The initial work by Cummings and Stell (1984, 1985) on a model of association whose particles associate into interaction-site dimers (the SSS model discussed below) was done on the basis of an approximation scheme that borrowed and extended the mathematics of Rodney Baxter's solution of the Percus — Yevick (PY) approximation applied to Baxter's adhesive-sphere model. Baxter's mathematics is elegant and seductive, as is the sticky-sphere model itself; Cummings and Stell were sufficiently engrossed in the mathematics not to dwell upon the fact that it must be embedded in a scheme that is specifically tailored to the dictates of association if it is to be faithful to the law of mass action in the limit of vanishing density. The original work of Cummings and Stell and its subsequent extensions by Lee, Rasaiah, and Cummings (1985), and by Rasaiah and Lee (1985a, 1985b) was not done in the context of a relation between the strength of the association bond and the degree of association (the parameters  $S$  and  $\Lambda$  below) that is faithful to the mass-action limit. Our work here on the structure of simple associating models shows that association gives rise to characteristic correlation length  $\mathcal{X}$  such that the direct correlation functions  $C_{ij}$  considered below in general have a different form for  $\mathcal{X}r \geq 1$  and  $\mathcal{X}r \leq 1$ , where  $r$  is the distance between particle centers. We find that only under certain rather special conditions, elucidated below, can one reasonably use  $C_{ij}$  with a single functional form for all  $r$ , as the early work did.

I shall begin by considering the representative case of a binary mixture of particles of species  $A$  and  $B$ , with pair potential  $\Phi_{ij}(1, 2)$  between particles centered at  $\mathbf{r}_1$  and  $\mathbf{r}_2$ ,  $i = A, B$ ;  $j = A, B$ . The  $\Phi_{ij}$  includes a highly repulsive core term  $\Phi_{ij}^{\text{CORE}}$  which for technical reasons I shall initially take to be of the form, with  $r = |\mathbf{r}_1 - \mathbf{r}_2|$ ,

$$\Phi_{ij}^{\text{CORE}} = \begin{cases} \infty & \text{for } r < L_{ij}, \\ \varepsilon & \text{for } L_{ij} < r < R_{ij}, \\ 0 & \text{for } r > R_{ij}. \end{cases}$$

In the ionic case we also need a Coulombic term,  $\omega_{ij}(r) = q_i q_j / r$ . For simplicity I shall restrict my attention here to the symmetric case  $q_A = -q_B = q$  with overall charge neutrality that implies  $\rho_A = \rho_B = \rho$ , where  $\rho_i$  is the expected number density of species  $i$ . In addition we shall need an associating or binding pair potential  $\Phi_{ij}^+$  (12) that is responsible for chemical or ionic

association. Here we have many choices. A simple one is to let  $\Phi_{ij}^+$  be defined by an attractive «stickiness» on an interaction shell defined by  $r = L_{ij}$  so that  $\Phi_{ij}^+ = S_{ij}\delta(r - L_{ij})/4\pi L_{ij}^2$  where  $\delta$  is a Dirac delta function and  $S_{ij}$  is a strength parameter. We are often more interested in the Boltzmann factor  $e_{ij}^+ = \exp(-\beta\Phi_{ij}^+)$  associated with  $\Phi_{ij}^+$  than in  $\Phi_{ij}^+$  itself, where  $\beta^{-1} = k_B T$ ,  $k_B =$  Boltzmann's constant and  $T =$  absolute temperature. It is therefore often more convenient to directly parameterise  $e_{ij}^+$  with a strength parameter  $S_{ij}$  such that  $e_{ij}^+ = S_{ij}\delta(r - L_{ij})/4\pi L_{ij}^2$ . I shall refer to a model that includes such a  $e_{ij}^+$  as a sticky shell (SS) model. Alternatively we can let  $\Phi_{ij}^+$  (or equivalently  $e_{ij}^+$ ) be dependent on the relative orientation  $\Omega$  of a pair of particles, so that  $\Phi_{ij}^+$  or  $e_{ij}^+$  is given by sticky areas on the interaction shell corresponding to certain relative orientations. I shall refer to a model with such  $\Phi_{ij}^+$  as a selectively sticky shell model. Analytically the  $e_{ij}^+$  can be represented as  $S_{ij}A_{ij}(\Omega)\delta(r - L_{ij})/4\pi L_{ij}^2$  in this model. (A particularly useful special case is the sticky-point limit, in which the sticky area is reduced to a single point of infinite stickiness.) For either version of the SS model, the special case in which the binding attraction is present only between different species (i. e.,  $\Phi_{AB}^+ = \Phi_{BA}^+ = 0$ ) proves a particularly interesting one to consider. I refer to this as the AB version of the model. Another special case of interest, which I shall call the AA version, arises when the A and B particles are identical (so  $\Phi_{AA}^+ = \Phi_{AB}^+ = \Phi_{BB}^+$  with  $\Phi_{AA}^+ = \Phi_{AB}^+ = \Phi_{BB}^+$ ). For  $L_{ij} = R_{ij}$  the uncharged AA version of the SS model becomes Baxter's well-known adhesive-sphere model, while the uncharged selectively SS model, which was used by Hoye and Stell (1977) as an example, is a variant of a model used by Boltzmann (1898), who introduced it as the basis for his theory of chemical association. For  $L_{ij} < R_{ij}$ , things are a bit more subtle. Consider making the repulsive core term arbitrarily repulsive by letting  $\epsilon$  become arbitrarily large. One might think that the effect of stickiness would be entirely «hidden» by the resulting hard pair-potential core of diameter  $R_{ij}$  as one takes this limit. But if one thinks about taking the limit slowly enough to have equilibrium at all times (arbitrarily or «adiabatically» slowly) then in fact one must expect a certain number of associated particles to be found stuck together in this limit. And in a purely equilibrium description, the magic of the partition function and its children (virial coefficients and the like) is such that one expects them to faithfully reflect this number when accurately evaluated. For the moment let  $R_{ij} = R$  and  $L_{ij} = L$  for all  $i, j$  for further simplicity. It is not hard to see that when  $L \leq R/2$  the hard core forces saturation or association such that only dimers can form (i. e., three or more particles stuck together is sterically impossible). In the AA case, Cummings and Stell (1985) found that only a very special class of  $n$ -mers (whose atoms form the centers of regular  $n$ -gons) is possible when  $R \leq L/2$ . On the other hand, the AA and AB versions of selectively SS model can saturate even for  $L > R/2$  (in particular, for  $R = L$ ) if one has a small enough «sticky spot». We shall refer to the uniformly sticky SS model in the  $\epsilon = \infty$  limit as the «shielded sticky shell (SSS)» model and the sticky point model in this limit as the «shielded sticky point» model.

Let us now consider one more limit, letting  $S_{ij} = S$  and  $\rho_i = \rho$  for continued simplicity. We hold  $T$  and  $\rho$  fixed and increase  $S$ , first looking at a model with saturation (say the AB model with  $L < R/2$ ) or with relatively low  $n$ -mer formation,  $n \geq 3$ . More and more particles dimerize as we increase  $S$ . At infinite  $S$  we expect to reach a point at which no free particles (monomers) are left. At this point we have confinement. [If instead we are looking at a model in which  $n$ -mers can readily form for all  $n$  (e. g., the AA or AB models with  $L > R/2$ ). As we increase  $S$  we might expect to first reach instead a value  $S_p$  at which infinite clusters of stuck-together particles appear — a gelation of polymerization point which can be regarded as a (correlated) percolation point.]

### 3. Confinement

At confinement (but only at confinement) one can unambiguously identify the molecules (i. e., dimers) to which each pair of particles belong, so that one can use not only the language of particle-particle correlation functions but, alternatively, molecule-molecule correlation functions and site-site correlation functions. But to use any of these languages, we must introduce some technical terminology. On or off confinement the Ornstein — Zernike equation in particle-particle language for our 2-species models can be written in matrix notation as

$$(1 + \rho \hat{H})(1 - \rho \hat{C}) = 1, \quad (3.1)$$

where 1 is the unit matrix with elements  $\delta_{ij}$ ,  $\rho$  is species density  $\rho = \rho_i$ ,  $i = 1, 2$ , and  $\hat{H}$  and  $\hat{C}$  are matrices, the elements of which are the Fourier transforms  $\hat{H}_{ij}(\mathbf{k})$  and  $\hat{C}_{ij}(\mathbf{k})$  of the usual pair correlation function and direct correlation function  $H_{ij}(\mathbf{r})$  and  $C_{ij}(\mathbf{r})$  between particles of species  $i$  and  $j$  in a mixture. Høye and Stell (1977) [whose «particle-mixture picture» of the ISM is reviewed in Stell, Patey and Høye (1981) and in Cummings and Stell (1982)], noted that in confinement one can relate these functions to the site-site or atom-atom pair correlation function  $h_{ij}(\mathbf{r})$  and direct correlation function  $C_{ij}(\mathbf{r})$  (that refer to the intermolecular correlation between atoms in different molecules) and the intramolecular function  $s_{ij}(\mathbf{r})$  (that refers to the pair correlation between atoms within the same molecule). One breaks up  $\rho H_{ij}$  into its intramolecular and intermolecular part

$$\rho \hat{H}_{ij}(\mathbf{k}) = \hat{s}_{ij}(\mathbf{k}) + \rho \hat{h}_{ij}(\mathbf{k}). \quad (3.2a)$$

Adding a self-correlation Kronecker- $\delta$  term  $\delta_{ij}$  to both sides, with

$$\hat{\omega}_{ij}(\mathbf{k}) = \delta_{ij} + \hat{s}_{ij}(\mathbf{k}) \quad (3.2b)$$

we have

$$\delta_{ij} + \rho \hat{H}_{ij}(\mathbf{k}) = \hat{\omega}_{ij}(\mathbf{k}) + \rho \hat{h}_{ij}(\mathbf{k}) \quad (3.2c)$$

or in matrix notation

$$\rho \hat{H} = \hat{s} + \rho \hat{h}, \quad (3.3a)$$

$$1 + \rho \hat{H} = \hat{\omega} + \rho \hat{h}, \quad (3.3b)$$

$$\hat{\omega} = 1 + \hat{s}. \quad (3.3c)$$

Suppose one then similarly introduces an intramolecular function  $\hat{c}_{ij}$  by writing

$$\delta_{ij} - \rho \hat{C}_{ij}(\mathbf{k}) = [\hat{\omega}^{-1}(\mathbf{k})]_{ij} - \rho \hat{c}_{ij}(\mathbf{k}) \quad (3.4a)$$

or in matrix notation

$$1 - \rho \hat{C} = \hat{\omega}^{-1} - \rho \hat{c}, \quad (3.4b)$$

where  $\hat{\omega}^{-1}$  is the matrix inverse of  $\hat{\omega}$ , with elements  $[\hat{\omega}^{-1}(\mathbf{k})]_{ij}$ . The  $\hat{\omega}^{-1}$  is the contribution to  $\hat{C}$  from intramolecular (and self) correlation while  $\hat{c}$  is the remaining contribution that arises because of correlation between atoms in different molecules. In our simple ABSS model, for example,

$$\begin{aligned} \omega_{11} = \omega_{22} = \delta(\mathbf{r}), \quad s_{11} = s_{22} = 0, \\ \omega_{12} = s_{12} = s = \delta(\mathbf{r} - L)/4\pi L^2, \end{aligned} \quad (3.5)$$

$$\hat{\omega}_{12} = (kL)^{-1} \sin kL, \quad \hat{\omega}_{11} = \hat{\omega}_{22} = 1,$$

and the confinement condition is

$$\int s(r) dr = 1. \quad (3.6)$$

The properties of  $\hat{\omega}^{-1}$  immediately follow from those of  $\hat{\omega}$ :

$$\begin{aligned} \hat{\omega}_{ii}^{-1} &= \frac{1}{1 - \hat{s}^2} = 1 + \hat{s}^2 + \hat{s}^4 + \dots, \\ \hat{\omega}_{12}^{-1} &= \frac{-\hat{s}}{1 - \hat{s}^2} = -\hat{s} - \hat{s}^3 - \dots \end{aligned} \quad (3.7a)$$

and one can see that

$$\begin{aligned} \omega^{-1}(r) &\text{ has a } \delta(r) \text{ contribution at } r=0 \text{ and a discontinuity of} \\ &1/8\pi L^2 r \text{ at } r=2L \text{ but is otherwise continuous. It is strictly} \\ &\text{positive, } \omega_{ii}^{-1}(r) \rightarrow 3/4\pi L^2 r \text{ as } r \rightarrow \infty; \end{aligned} \quad (3.7b)$$

$$\begin{aligned} \omega_{ij}^{-1}(r) &\text{ has a } -\delta(r-L)/4\pi L^2 \text{ contribution at } r=L \text{ but is} \\ &\text{otherwise continuous. It is strictly negative with } \omega_{12}^{-1} \rightarrow -3/4\pi L^2 r \text{ as} \\ &r \rightarrow \infty. \end{aligned} \quad (3.7c)$$

Høye and Stell (1977) noted that from (3.1), (3.3) and (3.4) it follows that

$$\hat{h} = \hat{\omega} \hat{c} [1 - \rho \hat{\omega} \hat{c}]^{-1} \hat{\omega}. \quad (3.8)$$

This is precisely the equation Chandler and Anderson (1972) introduced for the interaction site model (ISM) in conjunction with the equation

$$C_{ij}(r) = -\beta \omega_{ij}(r) + -\beta q_i q_j / r, \quad r > R_{ij} \quad (3.9a)$$

to supplement the exact core condition of that model,

$$h_{ij}(r) = -1. \quad (3.9b)$$

We see that (3.8) can be regarded as an exact equation (by definition) and (3.9a) as an approximation that we shall call the interaction site approximation (ISA). Using their exact result for a fluid of ISM molecules with dielectric constant  $\omega$  (with  $R_{ij} = R$  not necessarily imposed, but with a single  $L$ )

$$9\rho [\hat{h}_{11} - \hat{h}_{12} - \hat{h}_{21} + \hat{h}_{22}] = k^2 L^2 [(\omega - 1)(y\omega)^{-1} - 3], \quad (3.10a)$$

where

$$y = 4\pi\beta\rho (qL)^2/9, \quad (3.10b)$$

Høye and Stell (1976) had earlier shown that in any approximation in which the site-site direct correlation function has the form

$$\hat{c}_{ij}(k) = -4\pi q_i q_j / k^2 + a + bk^2 + o(k^3) \quad (3.11)$$

(as it does in the ISA), a fluid of ISM molecules will have a dielectric constant given by

$$\omega - 1 = 3y. \quad (3.12)$$

Equation (3.12) implies

$$C_{ij}(r) \rightarrow -\beta q_i q_j / r, \quad \text{as } r \rightarrow \infty \quad (3.13)$$

or through (3.4) and (3.7), as  $r \rightarrow \infty$

$$\rho C_{ij}(r) \rightarrow -\rho\beta q_i q_j / r - [\hat{\omega}^{-1}]_{ij} \rightarrow -\rho\beta q_i q_j / r - 3(-1)^{i+j} / 4\pi L^2 r. \quad (3.14)$$

As pointed out by Cummings and Stell (1981, 1982), it follows from (3.1) (and some algebra) that to be consistent with (3.10) one must instead have, for  $r \rightarrow \infty$ ,

$$\rho C_{ij} \rightarrow -\rho\beta q_i q_j / r - B_{ij} [\omega^{-1}]_{ij} \quad (3.15a)$$

where

$$B_{ij} = B = 3y/(e - 1) \quad (3.15b)$$

From (3.7) [and some trivial algebra using (3.10b)] (3.15a) can be rewritten as

$$\rho C_{ij} \rightarrow -A_{ij} \rho \beta q_i q_j / r \quad (3.16a)$$

where

$$A_{ij} = \epsilon / (\epsilon - 1) \quad (3.16b)$$

Equivalently

$$\rho C_{ij} \rightarrow -\rho \beta q_i q_j / r - \rho \beta q_i q_j / (\epsilon - 1) r \quad (3.16c)$$

These exact asymptotic results, used for all  $r > R_{ij}$ , generate interesting new approximations which to our knowledge have not been fully explored. For example

$$\rho C_{ij} = -\rho \beta q_i q_j / r - B [\omega^{-1}]_{ij} \text{ for } r > R_{ij} \quad (3.17)$$

is an approximation that reduces in the uncharged case,  $q_i = 0$ , to the RISA for homonuclear diatomics ( $R_{ij} = R$ ). In this case  $B = 1$ . For the more general case  $R_{11} \neq R_{12} \neq R_{22}$ ,  $B$  does not become 1 when  $q_i \rightarrow 0$  and the RISA is no longer asymptotically faithful to (3.15), while (3.17) is by construction. (In this case,  $\epsilon - 1 \rightarrow 3yp$ , so  $B \rightarrow p^{-1}$ , where  $p$  is given in Eq. (29) of Høye and Stell (1976) and discussed by them.) An even simpler asymptotically faithful approximation is obtained by using (3.16) for all  $r > R_{ij}$ . The equivalent expression

$$\rho C_{ij} = -\rho \beta q_i q_j / r - 3(-1)^{i+j} B / 4\pi L^2 r, \quad r > R_{ij} \quad (3.18)$$

clarifies the form of this approximation in the  $q_i = 0$  case. Eq. (3.17) and (3.18) can only be reasonably used if  $L_{ij} \leq R/2$ , because of the discontinuity in  $[\omega^{-1}(r)]_{ij}$  at  $r = 2L$ . Even then, it will only give a good approximation to  $C_{ij}$  as long as  $\rho$  is not too small, because any error in  $[\omega^{-1}]_{ij}$  will appear as an error in  $\rho C_{ij}$  rather than  $C_{ij}$  itself. This yields an error in  $C_{ij}$  that becomes unbounded as  $\rho \rightarrow 0$ .

We note the following points:

(i) Although Cummings and Stell (1982) nominally base their analysis on a somewhat different assumption than (3.15a), stronger than (3.15a) for the models we consider here, the actual assumption on which their analysis rests — their Eq. (46) — is exactly equivalent to (3.15a) for our models. The usual assumption,

$$C_{ij} \rightarrow -\beta \Phi_{ij} \quad (3.19)$$

which is consistent with known results for a wide variety of Hamiltonians off singular points is inappropriate on the basis of the consideration with which we are dealing here, Eq. (3.19) is clearly too restrictive to deal with the models with a short-ranged  $\Phi^+$  at confinement. If one stays within the class of models in which  $\Phi_{ij}^+$  is short-ranged by construction, then (3.19) is inconsistent with (3.15) or (3.16) because for large  $r$ ,  $-\beta \Phi_{ij} = -\beta q_i q_j / r$ . This is because the confinement limit is a singular point much like a critical point. One cannot reach confinement with a short-ranged  $e_{ij}^+$  except when its integral becomes infinite.

(ii) Suppose  $s$  is not  $\delta$ -like but is allowed to be smeared out (e. g., Gaussian) in the vicinity of  $r = L$  to accommodate internal degrees of molecular freedom. This generalization, considered by Høye and Stell and others in detail in the context of dielectric theory [see Stell et al. (1981) and references therein], does not change our asymptotic analysis of  $C_{ij}$  here in any basic way.

#### 4. Off confinement

In Section 2 we considered only confinement (complete dimerization) which in our ABSS model is given by the condition

$$\int s(r) dr = 1.$$

Suppose we lower the parameter  $s$  to a finite value so that the probability of  $AB$  pairs sticking at  $r = L$  is less than unity. That probability is then given by  $\Lambda$ , the amplitude of a deltashell probability density,  $s(r, \Lambda)$  where

$$\begin{aligned} s(r, \Lambda) &= \Lambda \delta(r - L)/4\pi L^2, \\ \hat{s}(k, \Lambda) &= \Lambda \sin kL/kL \end{aligned} \quad (4.1)$$

and we can regard the  $s(r)$  of Section 3 as the confinement limit,  $s(r, 1)$ , of  $s(r, \Lambda)$ . The lowering of  $\Lambda$  will occur as one lowers the stickiness parameter  $S$  from infinity, which will follow in turn raising the absolute temperature from zero for a given degree of intrinsic stickiness. We comment further on the relation between  $\Lambda$  and  $\rho$  and  $\beta$  through  $S$  in Section 5.

Since all particles can no longer be regarded as atoms unambiguously associated with molecules when  $\Lambda < 1$ , we no longer have atom-atom functions  $c_{ij}(r)$  and  $h_{ij}(r)$ , although we can easily define into existence off-confinement generalizations of these functions by using (3.1)–(3.7) with  $s(r)$  and  $s(k)$  everywhere replaced by  $s(r, \Lambda)$  and  $\hat{s}(k, \Lambda)$ . Since we still have  $C_{ij}(r)$  and  $H_{ij}(r)$  this will be unnecessary for our purposes. The replacement of  $s(r, 1)$  by  $s(r, \Lambda)$  yields a  $[\omega^{-1}(r, \Lambda)]_{ij}$  that is now damped,

$$\begin{aligned} [\omega^{-1}(r, \Lambda)]_{ii} &\rightarrow 3e^{-\mathcal{X}r}/4\pi L^2 r, \text{ as } r \rightarrow \infty, \\ [\omega^{-1}(r, \Lambda)]_{12} &\rightarrow -\Lambda e^{-\mathcal{X}r}/4\pi L^2 r, \text{ as } r \rightarrow \infty, \end{aligned} \quad (4.2)$$

where

$$\mathcal{X}^2 = 3(1 - \Lambda^2)/\Lambda^2 L^2.$$

In  $k$ -space, for  $k \rightarrow 0$

$$\begin{aligned} [\hat{\omega}^{-1}(k, \Lambda)]_{ii} &\rightarrow 3/L^2 \Lambda^2 (\mathcal{X}^2 + k^2), \\ [\hat{\omega}^{-1}(k, \Lambda)]_{12} &\rightarrow -3/L^2 \Lambda^2 (\mathcal{X}^2 + k^2). \end{aligned} \quad (4.3)$$

Thus we can expect (3.15) with  $\omega^{-1}(r, 1)$  replaced by  $\omega^{-1}(r, \Lambda)$ . This is now consistent with (3.19), which we expect to hold off confinement (as long as we are off a critical point). But the value of  $B$  in (3.15b) must be reassessed off confinement. It seems reasonable to continue to use (3.15b) if we interpret  $\epsilon$  to be  $\epsilon_V$ , the dielectric constant of the fully associated dipolar solvent of density  $\rho_V$ , which will always be less than  $\rho$  for a partly dissociated fluid of diatoms. We thus have

$$\rho C_{ij} \rightarrow -\rho \beta q_i q_j / r - B [\omega^{-1}(r, \Lambda)]_{ij}, \quad (4.4a)$$

$$B = 3y/(\epsilon_V - 1), \quad y = 4\pi \beta \rho_V (qL)^2/9. \quad (4.4b)$$

Under this assumption  $\rho C_{ij}$  looks like  $\rho \beta q_i q_j \epsilon_V / (\epsilon_V - 1) r$  for  $r\mathcal{X} \ll 1$  but goes over to  $-\rho \beta q_i q_j / r$  for  $r\mathcal{X} \gg 1$ , which provides us with a means of understanding the way in which (3.19) is lost right at confinement. The approximation that is most immediately suggested by these considerations is obtained by using for all  $r > R_{ij}$  the asymptotic form given by (4.4):

$$\rho C_{ij} = -\rho \beta q_i q_j / r - B [\omega^{-1}(r, \Lambda)]_{ij} \text{ for } r > R_{ij}. \quad (4.4c)$$

As in the confinement limit, we can either use the full  $\omega^{-1}$  here for all  $r$  or, for analytic simplicity, its asymptotic form, as long as  $L_{ij} < R_{ij}/2$  and  $\rho$  is not too low. Using (4.3), we have, for  $r \geq R_{ij}$

$$\rho C_{ii} = -\rho \beta q_i q_i / r - 3B e^{-\mathcal{X}r}/4\pi L^2 r, \quad (4.5)$$

$$\rho C_{12} = -\rho \beta q_i q_j / r + 3\Lambda B e^{-\mathcal{X}r}/4\pi L^2 r.$$

When we use (4.4b), this can be rewritten as

$$\rho C_{ii} = -\rho \beta q_i q_i / r - \rho_V \beta q_i q_i e^{-\mathcal{X}r}/(\epsilon_V - 1) r, \quad (4.6)$$

$$\rho C_{12} = -\rho \beta q_i q_j / r + \Lambda \rho_V \beta q_i q_j e^{-\mathcal{X}r}/(\epsilon_V - 1) r.$$

As they should, (4.5) and (4.6) satisfy (3.14) — (3.16) in the confinement limit  $\Lambda \rightarrow 1$ . The remarkable aspect of (4.6) — (4.7) is that they give rise to an approximation that, while highly nontrivial, appears to be manageable analytically with known techniques. Near the full association limit (where  $\mathcal{X} \ll 1$ ,  $\Lambda \approx 1$ , and  $\rho_V \approx \rho$ ). Eq. (4.7) will be only negligibly different from the much simpler approximation

$$C_{ij} = -\beta q_i q_j \epsilon / (\epsilon - 1) r, \quad r > R_{ij}, \quad (4.7)$$

where  $\epsilon$  is the pure solvent dielectric constant at density  $\rho$  rather than  $\rho_V$ . This result will in fact be close to (4.6) as well as the simpler

$$C_{ij} = -\beta q_i q_j / r \quad (4.8)$$

for all degrees of association as long as  $\epsilon \gg 1$ . For the uncharged case in which  $q_i = 0$ , the value of  $B$  in (3.4) reduces to 1.

It is useful to re-express these results in terms of the correlations associated with density-density, charge-charge, and charge-density correlations. In the symmetric case,  $R_{ij} = R$ , this is particularly convenient. The density-density term is

$$H_s = (H_{11} + H_{12})/2, \quad (4.9a)$$

the charge-charge term is

$$H_D = (H_{11} - H_{12})/2 \quad (4.9b)$$

and the cross term vanishes. We have decoupled OZ equations for  $H_s$  and  $H_D$ . Eq. (4.6) then yields

$$\rho C_D = -\rho \beta q^2 / r - (1 + \Lambda) \rho \beta q^2 e^{-\mathcal{X}r/2} (\epsilon_V - 1) r, \quad (4.10a)$$

$$\rho C_s = -(1 - \Lambda) \rho \beta q^2 e^{-\mathcal{X}r/2} (\epsilon_V - 1) r, \quad (4.10b)$$

while (3.9b) with (4.1) yields

$$H_D = \Lambda \delta (r - L) / 8\pi L^2 \rho \quad \text{for } r < R, \quad (4.11a)$$

$$H_s = -1 + \Lambda \delta (r - L) / 8\pi L^2 \rho \quad \text{for } r < R. \quad (4.11b)$$

In the uncharged case, (4.10) reduces to

$$\rho C_D = -3(1 + \Lambda) \epsilon^{-\mathcal{X}r/4} / 4\pi L^2 r, \quad (4.12a)$$

$$\rho C_s = -3(1 - \Lambda) \epsilon^{-\mathcal{X}r/4} / 4\pi L^2 r. \quad (4.12b)$$

All of these results starting with (4.5) reduce to (3.18) with (4.15b) in the confinement limit.

If we include only a  $\delta$ -shell  $e_{ij}^+$ , then any treatment in which (3.19) is satisfied will be missing the  $\omega^{-1}(r, \Lambda)$  term in (3.17). At confinement, we then satisfy (3.16) but with  $A = 1$ , so that when we evaluate  $\epsilon$  from (3.16b) we find  $\epsilon = \infty$ . All standard approximations (PY, HNC, MSA, etc.) will give (3.19) and thus will give  $\epsilon = \infty$  for short-ranged  $\Phi_{ij}^+$  at confinement. As long as we don't try to use (3.16b) as a means of computing  $\epsilon$ , this is not a serious problem in terms of the error that will result in  $H_{ij}$ . If we are dealing with model parameters that would yield a large  $\epsilon$  if  $\epsilon$  were computed correctly (say  $\epsilon \approx 80$ ) then we are really talking about a  $C_{ij}$  that is off by about 1% at confinement for large  $r$  (where  $C_{ij}$  is undetectable by direct means in the first place).

## 5. Concluding remarks

The approximations of Section IV remain to be quantitatively assessed at the time of this writing. Eq. (4.4c) requires numerical solution;  $[\omega^{-1}]$  is not a simple enough function to handle analytically. On the other hand, Eqs. (4.5) and (4.6) in principle can be handled analytically, using the same techniques recently employed by Blum and his coworkers to treat sticky-charged spheres. Zhou and Stell (1989) have already done the mathematics associated with (4.7), (4.8) and (4.12) for a wide continuous range of core interpenetration,



$R/3 < L < R$ . We give their results in our Appendices. The rest of this section will be devoted to comments concerning the meaning of the mathematics of Section IV when contemplated for  $L \gg R/2$ , for which one no longer has the steric restriction to dimerization in the SSS model.

First of all eq. (4.4c) is the result appropriate to the shielded sticky point model (not the SSS model) for the whole range  $L \leq R$ . The sticky point model is stericly restricted to dimerization over this whole range. Its complete-association limit is simply the ISM-approximation result, first proposed by Chandler and Anderson (1972), for the fused-core dipolar dumbbell model. Thus it can be regarded as the natural extension of that result into the realm of partially associated dipolar dumbbells.

Eqs. (4.5) — (4.12) have a less obvious meaning when contemplated for  $L \geq R/2$ , but they appear to be relevant to the SSS model, at least over some range of  $L/R$  values. This is an intriguing issue, especially in light of the fact that when  $q = 0$  (which leads to  $B = 1$ ) and  $L = R$  the equations have exactly the structure of the Percus — Yevick (PY) approximation as applied to the model of a hard-sphere mixture of species 1 and 2 with a «sticky» attraction only between unlike species. (This is a mixture version of Baxter's «sticky sphere» model [Baxter (1968a)].)

For  $q \neq 0$  and  $L = R$  our equations have the same form as the hybrid PY/MSA equations considered by Rasaiah and Lee (1985a, 1985b) in their investigation of the ionic version of the same mixture model. We note however that our treatment of the  $\rho$  and  $\beta$  dependence of  $\Lambda$  through our parameter  $S$  is in general different from that which comes out of a PY/MSA treatment.

In order to help illuminate the meaning of (4.7), (4.8), and (4.12) for  $2L > R$ , it is worthwhile considering briefly the expected behavior for  $L > R/2$  of the ionic SSS model that defines our dissociative dipolar dumbbell fluid when  $L \leq R/2$ . For  $L > R/2$  the model remains well defined but no longer describes particles that can only associate into dumbbells.

For all  $L$ , the model is defined by the pair potential

$$\Phi_{ij}(r) = \begin{cases} kT \ln[1 + f_{ij}(r)], & r \leq R, \\ (-1)^{(i+j)} q^2/r, & r > R, \end{cases} \quad (5.1)$$

where

$$f_{ij}(r) = f^{HS}(r) + \delta(r - L) \delta_{ij}/12\pi L^2 \tau, \quad (5.2)$$

with

$$f^{HS}(r) = \begin{cases} -1, & \text{for } r \leq R, \\ 0, & \text{for } r > 0. \end{cases} \quad (5.3)$$

Here  $f^{HS}(r)$  is the hard-sphere Mayer  $f$ -function that describes the repulsive core of the interaction, the  $\delta$ -function term of strength  $1/\tau$  describes the attractive «shielded sticky shell» and the  $q^2/r$  term describes the Coulombic interaction. Thus our stickiness parameter is here being expressed in terms of  $1/\tau$ , which it equals except for a trivial factor.

For  $L \leq R/2$  the shielding of the repulsive core prevents any association except dimerization between particles of species 1 and 2. In this regime, the recent approach of Zhou and Stell (1992b) can be expected to give a satisfactory description of the relation between  $\Lambda$  and the  $\tau$  of Eq. (5.2). From the earlier work by Cummings and Stell (1984) and Lee et al. (1985) it is clear that this is not true of the PY closure (for  $q = 0$ ) or the PY/MSA closure (for  $q \neq 0$ ). In particular, those closures violate the law of mass action at low densities. The «simple interpolation scheme» developed by Stell and Zhou (1989a) and Zhou and Stell (1992a, 1992b) satisfies the law of mass action but will not give a satisfactory quantitative description of the relation between  $R$  and  $\tau$  in this regime. For  $L$  slightly larger than  $R/2$ , the model describes particles that can associate into chains of alternating species 1 and 2. As  $L/R$  further increases, a greater variety of branched chain configurations becomes possible. In this regime the spatial decay of  $C_{ij}$  seems difficult to assess for small  $\tau$  outside the core, and (A1.4b) may well be too simple to be a

reasonable approximation. Moreover the relation between  $\Lambda$  and  $\tau$  has not been investigated in this regime. For  $L$  still larger, so that  $L/R$  is slightly less than 1, the system describes particles that can freely vulcanize into a wide variety of clusters. Here (A1.4b) may offer a useful approximate description of the model, since the special steric constraints that must be embodied in  $C_{ij}$  for smaller values of  $L/R$  in order to account for chain formation are no longer present for these larger values of  $L/R$ .

When considering the general case of (5.1) in which  $q \neq 0$  it is natural to take, in equation (A1.4b),

$$\Gamma = \beta q^2, \quad (5.4)$$

which follows from (4.8) for  $L > R/2$ , since the factor  $\epsilon/(\epsilon - 1)$  of (4.7) loses its relevance when one loses the steric constraint that assures that association only produces dipolar dimers for  $L \leq R/2$ , while (A1.4b) with (5.4) is consistent with (3.19) off the complete association limit.

With (5.4) and (4.8) instead of (4.7), one is back to the simple MSA closure for  $r \leq R$ . One must continue to choose a closure condition for  $r \leq R$  to determine  $\Lambda$  as a function of  $\tau$ . For  $L/R$  less than (and close to) unity, the PY closure

$$c_{ij}(r) = f_{ij}(r) [h_{ij}(r) + 1] / [f_{ij}(r) + 1] \quad (5.5)$$

appears to remain sensible for  $r \leq R$ .

On the mathematical side, we can continue to solve the set of equations of Appendix 1, for all  $R/2 \leq L \leq R$  and for this range we give the solution in Appendix 3. In light of our discussion here, the solution appears likely to offer a useful approximate description of the SSS model only when  $L/R$  is a bit less than 1, although further work will be necessary to elucidate this question.

As  $L$  increases from  $R/2$ , when it reaches the value  $R$ , a new complication arises, since all steric shielding effects of the hard core relative to the sticky shell at  $r = L$  are lost. This permits unbridled clustering or vulcanization of such an extent that the system will lose thermodynamic stability, as one of us has already discussed in detail elsewhere [Stell (1991)]. We have two remarks in this connection. First, the PY/MSA approximation defined by (2.17) and (2.18) may remain a reasonable description of a system in which the  $\delta(r - L)$  of (2.14) is replaced by a narrow sharply peaked function of finite height, reflecting a narrow well in the pair potential of finite depth. (This is the sense in which the Baxter sticky-sphere model and its extensions are typically used.) Second, a novel alternative way of giving thermodynamic meaning to the PY/MSA solution of the model for  $L = R$  is to regard it as an approximation to the solution for  $L$  slightly less than  $R$  (given in Appendix 3) where the model is free of the instability that sets in at  $L = R$ . Finally, we note that all the closures to the OZ equation given in Section 4 are «improper» closures in the sense of Chandler and his colleagues, in the confinement limits.

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#### Appendix 1: General Treatment of eq. (4.7) and (4.8)

Our equations using (4.7) or (4.8) can be decoupled into the sum and difference equations

$$h_s = c_s + 2\rho c_s * h_s, \quad (A1.1)$$

$$h_s(r) = -1 + \frac{\lambda L}{24} \delta(r - L), \quad r < R, \quad (A1.2a)$$

$$c_s(r) = 0, \quad r > R, \quad (A1.2b)$$

$$h_d = c_d - 2\rho c_d * h_d, \quad (A1.3)$$

$$h_d(r) = \frac{\lambda L}{24} \delta(r-L), \quad r < R, \quad (A1.4a)$$

$$c_d(r) = \frac{\Gamma}{r}, \quad r > R, \quad (A1.4b)$$

with

$$h_s = \frac{H_{12} + H_{11}}{2}, \quad c_s = \frac{C_{12} + C_{11}}{2}, \quad (A1.5a)$$

$$h_d = \frac{H_{12} - H_{11}}{2}, \quad c_d = \frac{C_{12} - C_{11}}{2}. \quad (A1.5b)$$

Applying Baxter factorization [Baxter (1968b, 1970)], we have [Stell and Zhou (1989b); Lee et al. (1985); Rasaiah and Lee (1985a, 1985b); Lee and Rasaiah (1987)]

$$rh_s(r) = -q'_s(r) + 4\pi\rho \int_0^R dt q_s(t) (r-t) h_s(|r-t|), \quad (A1.6a)$$

$$rc_s(r) = -q'_s(r) + 4\pi\rho \int_r^R dt q_s(t-r) q'_s(t), \quad (A1.6b)$$

$$rh_d(r) = [q_d^0(r)]' + 4\pi\rho \int_0^\infty dt [A_d + q_d^0(t)] (r-t) h_d(|r-t|), \quad (A1.7a)$$

$$rc_d^0(r) = [q_d^0(r)]' + 4\pi\rho A_d q_d^0(r) - 4\pi\rho \int_0^R dt q_d^0(t) [q_d^0(t+r)]', \quad (A1.7b)$$

where we have defined

$$c_d^0(r) \equiv c_d(r) - \frac{\Gamma}{r} e^{-zr}, \quad z \rightarrow 0, \quad (A1.8a)$$

$$q_d^0(r) \equiv q_d(r) - A_d e^{-zr}, \quad z \rightarrow 0 \quad (A1.8b)$$

and we also have [Stell and Zhou (1989b); Lee et al. (1985); Rasaiah and Lee (1985a, 1985b); Lee and Rasaiah (1987)]

$$q_d^0(r) = 0, \quad q_s(r) = 0, \quad r \geq R, \quad (A1.8c)$$

$$A_d \equiv -\left(\frac{\Gamma}{2\pi\rho}\right)^{1/2}. \quad (A1.9)$$

Substituting eqs. (A1.2a) and (A1.4a) into eqs. (A1.6a) and (A1.7a) respectively, we have, for  $0 \leq r \leq R$ ,

$$[q_s(r)]' + v[q_s(r+L) - q_s(r-L)] = -\frac{\lambda L^2}{24} \delta(r-L) + ar + b, \quad (A1.10a)$$

$$[q_d^0(r)]' + v[q_d^0(r-L) - q_d^0(r+L)] = \frac{\lambda L^2}{24} \delta(r-L) + H + vA_d[1 - \theta(r-L)], \quad (A1.10b)$$

where

$$v = \frac{\pi\rho\lambda L^2}{6}, \quad (A1.11)$$

$$a = 1 - 4\pi\rho \int_0^R q_s(r) dr, \quad (A1.12)$$

$$b = 4\pi\rho \int_0^R r q_s(r) dr, \quad (A1.13)$$

$$H = 4\pi\rho A_d J_d(R), \quad (A1.14)$$

$$J_d(r) \equiv \int_r^\infty rh_d(r) dr, \quad (A1.15)$$

and  $\theta(r) = 0, r < 0; = 1, r > 0$ . Both  $q_s(r)$  and  $q_d^0(r)$  are continuous anywhere except at  $r = L$ :

$$q_s(L+) = q_s(L-) - \frac{\lambda L^2}{24}, \quad (\text{A1.16a})$$

$$q_d^0(L+) = q_d^0(L-) + \frac{\lambda L^2}{24}. \quad (\text{A1.16b})$$

Integration of eq. (A1.7a) yields

$$J_d(r) = -q_d(r) + 4\pi\rho \int_0^R dt q_d^0(t) J_d(|r-t|) + 4\pi\rho A_d \int_0^r J_d(y) dy + A_d/2, \quad (\text{A1.17})$$

where the condition  $8\mu\rho \int_0^\infty J_d(r) dr = 1$  is used. At  $r = 0$ , we have [cf. (A1.15), (A1.4a)]

$$J_d(R) + \frac{\lambda L^2}{24} = -q_d^0(0) + \nu \int_0^L dt q_d^0(t) - \frac{1}{2} A_d + \left[ 4\pi\rho \int_0^R dt q_d^0(t) \right] J_d(R). \quad (\text{A1.18})$$

These equations have been analytically solved for  $q_s(r)$  and  $q_d(r)$  for the case  $L = R/n, n = 1, 2, 3, 4, 5$ . Analytical solution for  $R/3 \leq L \leq R$  is obtained in Sections 4 and 5 below.

Before closing this section, we point out that the parameter  $\nu$  is closely related to the average relative concentration of dumbbells (i. e. degree of dumbbell association), which in fact is given by  $\Lambda$  of our eq. (2.5):

$$\frac{\pi\rho\lambda L^3}{3} = 2\nu L = \Lambda. \quad (\text{A1.19})$$

When  $\nu = 0$ , we have completely dissociated dumbbells (charged hard-sphere fluids). When  $\nu = 1/(2L)$ , so that  $\Lambda = 1$ , we have the complete-association limit (dipolar dumbbell fluids).

## Appendix 2: solutions for $R/3 \leq L \leq R/2$

### A. The Difference Equation

The mathematical method for solving eq. (3.10) for arbitrary  $L$  can be found in ref. 13 and is similar to the one used for the case of  $L = R/n$ . For  $R/3 \leq L \leq R/2$ , we need to divide the hard-core region  $(0, 1)$  into the five intervals  $(0, 1-2L)$ ,  $(1-2L, L)$ ,  $(L, 1-L)$ ,  $(1-L, 2L)$ , and  $(2L, 1)$ . Here and below, we shall use  $R = 1$  for convenience. Following the method of Baxter (1968b, 1970), the solution of eq. (A1.10b) is

$$q_d(r) = \begin{cases} A_1 \sin(\sqrt{2}\nu r) + A_2 \cos(\sqrt{2}\nu r) + \left(H + \frac{\nu}{2} A_d\right) r + A_3, & 0 \leq r \leq 1-2L, \\ B_1 \sin[\nu(r-1+2L)] + B_2 \cos[\nu(r-1+2L)] + \frac{H}{\nu}, & 1-2L \leq r \leq L, \\ \sqrt{2} A_1 \cos[\sqrt{2}\nu(r-L)] - \sqrt{2} A_2 \sin[\sqrt{2}\nu(r-L)] + A_d/2, & L \leq r \leq 1-L, \\ B_1 \cos[\nu(r-1+L)] - B_2 \sin[\nu(r-1+L)] - \frac{H}{\nu} A_d, & 1-L \leq r \leq 2L, \\ -A_1 \sin[\sqrt{2}\nu(r-2L)] - A_2 \cos[\sqrt{2}\nu(r-2L)] + \left(H + \frac{\nu}{2} A_d\right) (r-2L) + A_3 - H/\nu, & 2L \leq r \leq 1. \end{cases} \quad (\text{A2.1})$$

Coefficients  $A_1$ ,  $A_2$ ,  $A_3$ ,  $B_1$ , and  $B_2$  can be obtained from eq. (A1.16b) and the continuity condition of  $q_d^0(r)$  at  $r = 1 - 2L$ ,  $1 - L$ ,  $2L$ , and  $1$ . After some algebra, we obtain

$$A_1 = \frac{1}{\Delta} \left\{ \frac{H}{v} [-1 + 2c_2 - s_1 + \sqrt{2} s_1 s_2 + 3s_1 c_2 + \sqrt{2} s_2 c_1 - 2c_1 c_2 - v(1 - 2L)(\sqrt{2} s_1 s_2 - 2c_1 c_2)] + \frac{A_d}{2} [-1 + 3c_2 - s_1 + 3c_2 s_1 + \sqrt{2} s_2 c_1 + 2\sqrt{2} s_1 s_2 - 4c_1 c_2 - v(1 - 2L)\sqrt{2} s_1 s_2 - 2c_1 c_2] + \frac{v}{12\eta} [-1 + c_2 + 2c_2 s_1 + \sqrt{2} s_2 c_1] \right\}; \quad (\text{A2.2})$$

$$A_2 = \frac{1}{\Delta} \left\{ \frac{H}{v} [-\sqrt{2} + 3s_2 + \sqrt{2} c_1 + 2s_2 c_1 + \sqrt{2} c_2 s_1 - 3s_2 s_1 + \sqrt{2} c_2 c_1 + v(1 - 2L)(\sqrt{2} - 2s_2 c_1 - \sqrt{2} s_1 c_2)] + \frac{A_d}{2} [-2\sqrt{2} + \sqrt{2} c_1 - 3s_2 + 4s_2 c_1 + 2\sqrt{2} c_2 s_1 - 3s_2 s_1 + \sqrt{2} c_1 c_2 + v(1 - 2L)(\sqrt{2} - \sqrt{2} s_1 c_2 - 2c_1 s_2)] - \frac{v}{12\eta} [s_2 + 2s_2 s_1 - \sqrt{2} c_1 c_2] \right\}; \quad (\text{A2.3})$$

$$A_3 = \frac{1}{\Delta} \left\{ \frac{H}{v} [-3\sqrt{2} - s_2 + \sqrt{2} c_1 + \sqrt{2} c_1 c_2 - s_1 s_2 + 3\sqrt{2} s_1 c_2 + 4c_1 s_2 + v(1 - 2L)(3\sqrt{2} - 3\sqrt{2} c_2 s_1 - 4s_2 c_1)] + \frac{A_d}{2} [-s_2 + \sqrt{2} c_1 - 2\sqrt{2} c_2 + 2\sqrt{2} s_1 - s_1 s_2 + \sqrt{2} c_1 c_2 + v(1 - 2L)(3\sqrt{2} - 3\sqrt{2} c_2 s_1 - 4s_2 c_1)] + \frac{v}{12\eta} [-s_2 + \sqrt{2} c_1] \right\}; \quad (\text{A2.4})$$

$$B_1 = \frac{1}{\Delta} \left\{ \frac{2H}{v} [s_2 + \sqrt{2} s_1 - \sqrt{2} c_1 + \sqrt{2} c_2 s_1 + s_2 c_1 - v(1 - 2L) \times (s_2 - \sqrt{2} c_1)] + A_d [2s_2 + \sqrt{2} s_1 - 2\sqrt{2} c_1 + \sqrt{2} c_2 s_1 + s_2 c_1 - v(1 - 2L)(s_2 - \sqrt{2} c_1)] + \frac{\sqrt{2}v}{12\eta} [1 - c_2 - 2s_1] \right\}; \quad (\text{A2.5})$$

$$B_2 = \frac{1}{\Delta} \left\{ \frac{2H}{v} [-s_2 - \sqrt{2} c_2 + \sqrt{2} s_1 + \sqrt{2} c_1 + \sqrt{2} c_1 c_2 - s_1 s_2 - v(1 - 2L)(\sqrt{2} s_1 - \sqrt{2} c_2)] + A_d [-s_2 + 2\sqrt{2} s_1 + \sqrt{2} c_1 - 2\sqrt{2} c_2 - s_1 s_2 + \sqrt{2} c_1 c_2 - v(1 - 2L)(\sqrt{2} s_1 - \sqrt{2} c_2)] + \frac{v}{6\eta} [-s_2 + \sqrt{2} c_1] \right\}, \quad (\text{A2.6})$$

where

$$\Delta = -3\sqrt{2} + \sqrt{2} c_2 - \sqrt{2} s_1 + 3\sqrt{2} c_2 s_1 + 4s_2 c_1, \quad (\text{A2.7})$$

$$c_1 = \cos[v(3L - 1)], \quad s_1 = \sin[v(3L - 1)], \quad (\text{A2.8})$$

$$c_2 = \cos[\sqrt{2}v(1 - 2L)], \quad s_2 = \sin[\sqrt{2}v(1 - 2L)], \quad (\text{A2.9})$$

$$\eta = \frac{\pi\rho}{3}. \quad (\text{A2.10})$$

Substituting eqs. (A2.1), (A2.2), (A2.3), (A2.4), (A2.5) and (A2.6) into eq. (A1.18) we can solve for  $H$  [cf. (A1.14)]

$$H = \frac{a_1 + \alpha a_2 + \sqrt{a_1^2 + 2\alpha a_3}}{24a_4\eta} \quad (\text{A2.11})$$

with  $\alpha = -4\pi\rho A_d$  and

$$a_1 = -6\sqrt{2} - 2s_2 + 2\sqrt{2}c_2 - 4\sqrt{2}s_1 + 2\sqrt{2}c_1 + 6c_1s_2 + 4\sqrt{2}s_1c_2 + (2s_2 - 2\sqrt{2}c_1)Y; \quad (\text{A2.12})$$

$$a_2 = -\frac{\sqrt{2}}{\nu} [-8 + 6c_1 - 4c_2 - 3\sqrt{2}s_2 + 6c_1c_2 + 4s_1c_2 + 4\sqrt{2}c_1s_2 - 3\sqrt{2}s_1s_2 + (9 - 4c_1 - 3s_1 + 3c_2 + 2\sqrt{2}s_2 - 4c_1c_2 - 9s_1c_2 - 6\sqrt{2}c_1s_2 + 2\sqrt{2}s_1s_2)Y + (-3 + s_1 - c_2 + 3s_1c_2 + 2\sqrt{2}c_1s_2)Y^2]; \quad (\text{A2.13})$$

$$a_3 = -\frac{1}{\nu} \{[(4s_1 - 24c_1^2)s_2^2 + (-24s_1^2 - 4s_1)c_2^2 - 34\sqrt{2}c_1s_2s_1c_2 - 6\sqrt{2}c_1c_2s_2 + 6\sqrt{2}c_1s_1s_2 + 34\sqrt{2}c_1s_2 + 16s_1^2c_2 + 48s_1c_2 + 8c_1^2c_2 - 12s_1 - 24]Y + [(-12c_1 - 4)s_1 + 24c_1^2 - 12c_1]s_2^2 + [24s_1^2 + 16c_1s_1 + 4s_1 + 8c_1]c_2^2 + (34\sqrt{2}c_1 - 16\sqrt{2})s_1 + 12\sqrt{2}c_1^2 - 8\sqrt{2}s_1^2 + 6\sqrt{2}c_1 - 8\sqrt{2}]c_2s_2 + 8\sqrt{2}s_2^2s_2 + 16\sqrt{2}s_1s_2 - 6\sqrt{2}c_1s_1s_2 + 12\sqrt{2}c_1^2s_2 - 34\sqrt{2}c_1s_2 + 8\sqrt{2}s_2 - 16s_1^2c_2 + 8c_1s_1c_2 - 48s_1c_2 - 8c_1^2c_2 - 8c_1c_2 + 12s_1 - 8c_1s_1 - 16c_1 + 24\}; \quad (\text{A2.14})$$

$$a_4 = \frac{1}{\nu^2} \{(3\sqrt{2} - \sqrt{2}s_1 + \sqrt{2}c_2 - 3\sqrt{2}s_1c_2 - 4c_1s_2)Y^2 + [-6\sqrt{2} + 4\sqrt{2}c_1 + 2\sqrt{2}s_1 - 2\sqrt{2}c_2 - 4s_2 + 4\sqrt{2}c_1c_2 + 6\sqrt{2}s_1c_2 + 8c_1s_2 - 4s_1s_2]Y + (4s_1 - 4c_1 + 4)s_2 + (-\sqrt{2}s_1 - 4\sqrt{2}c_1 + 3\sqrt{2})c_2 + \sqrt{2}s_1 - 4\sqrt{2}c_1 + 5\sqrt{2}\}; \quad (\text{A2.15})$$

where  $Y = \nu(1 - 2L)$ . It is worth noting that the excess energy satisfies  $\beta E^{ex} = \alpha H/2$  [Lee et al. (1985)]. ( $H$  used here is equal to  $-H$  used by Lee et al. (1985), Rasaiah and Lee (1985a, 1985b), and Lee and Rasaiah (1987).

### B. The Sum Equation

The sum equation (I.10a) can be solved in a similar way. Results are shown below

$$q_s(r) =$$

$$= \left\{ \begin{array}{ll} \frac{1}{2}ar^2 + \left[ b - \frac{a}{2\nu}(1 - 2\nu L) \right] r + c + \nu \sin(\sqrt{2}\nu r) + u \cos(\sqrt{2}\nu r), & 0 \leq r \leq 1 - 2L, \\ -\frac{1}{\nu}a(r - L) - \frac{b}{\nu} + \frac{a}{\nu^2}(1 - 2\nu L) + q \sin[\nu(r - 1 + 2L)] + p \cos[\nu(r - 1 + 2L)], & 1 - 2L \leq r \leq L, \\ \frac{a}{2\nu^2}(1 - 2\nu L) - \sqrt{2}\nu \cos[\sqrt{2}\nu(r - L)] + \sqrt{2}u \sin[\sqrt{2}\nu(r - L)], & L \leq r \leq 1 - L, \\ \frac{a}{\nu}(r + L) + \frac{b}{\nu} + \frac{a}{\nu^2}(1 - 2\nu L) - q \cos[\nu(r - 1 + L)] + p \sin[\nu(r - 1 + L)], & 1 - L \leq r \leq 2L, \\ \frac{1}{2}ar^2 + \left[ b + \frac{a}{2\nu}(1 - 2\nu L) \right] r + (1 - 2\nu L)\frac{b}{\nu} + c - \nu \sin[\sqrt{2}\nu(r - 2L)] - u \cos[\sqrt{2}\nu(r - 2L)], & 2L \leq r \leq 1. \end{array} \right. \quad (\text{A2.16})$$

The coefficients  $a$ ,  $b$ ,  $c$ ,  $u$ ,  $v$ ,  $p$ , and  $q$  can be obtained from eq. (I.16a), the continuity condition of  $q(r)$  at  $r = 1 - L$ ,  $1 - 2L$ ,  $2L$ ,  $1$ , and equations (1.12) and (1.13):

$$\left(\frac{1}{2} + \frac{1-2vL}{2v}\right)a + \left(1 + \frac{1-2vL}{v}\right)b + c - c_2u - s_2v = 0; \quad (\text{A2.17})$$

$$\frac{a}{v^2} - c + u + s_1p - c_1q = 0; \quad (\text{A2.18})$$

$$\left[\frac{1-2vL}{2v^2} + \frac{1}{v}\right]a + \frac{b}{v} - \sqrt{2}s_2u + \sqrt{2}c_2v - q = 0; \quad (\text{A2.19})$$

$$\frac{(1-2vL)}{2v^2}a - \frac{b}{v} + \sqrt{2}v + c_1p + s_1q = \frac{\lambda L^2}{24}; \quad (\text{A2.20})$$

$$\left(\frac{1}{2} - L + \frac{1}{2v} - \frac{1}{v^2}\right)a + \left(1 - 2L + \frac{1}{v}\right)b + c + c_2u + s_2v - p = 0; \quad (\text{A2.21})$$

$$\begin{aligned} & -3\frac{\eta^2}{v^2}[(2L-1)^2v^2 + 2L(1-2L)v + 10L-3]a + \\ & + \left\{1 + \frac{2\eta}{v}[(8L^3 - 24L^2 + 18L - 4)v - 6L^2 + 6L - 3]\right\}b - \\ & - 12\eta(1-2L)c - \frac{6\eta}{v^2}[-(2\sqrt{2}Lv - \sqrt{2})s_2 + (2L-2)vc_2 + 2Lv]u + \\ & + \frac{6\eta}{v^2}[-(2L-2)vs_2 + (-2\sqrt{2}Lv + \sqrt{2})c_2 + 2\sqrt{2}Lv - \sqrt{2}]v - \\ & - \frac{12\eta}{v^2}[(1+Lv)s_1 + (1-2Lv)c_1 + (1-L)v - 1]p + \\ & + \frac{12\eta}{v^2}[(2Lv-1)s_1 + (Lv+1)c_1 + (2L-1)v - 1]q = 0; \quad (\text{A2.22}) \\ & \left\{1 + \frac{2\eta}{v^2}[(8L^3 - 6L + 2)v^2 + (-18L^2 + 6L)v + 30L - 9]\right\}a + \\ & + \frac{12\eta}{v}[2L-1][(2L-1)v-1]b + 24\eta(1-2L)c + \frac{12\eta}{v}(1-c_2)u - \\ & - \frac{12\eta}{v}s_2v + \frac{12\eta}{v}(1+s_1-c_1)p + \frac{12\eta}{v}(1-s_1-c_1)q = 1. \quad (\text{A2.23}) \end{aligned}$$

These seven linear equations can be solved by using matrix transformation. When  $L = 1/2$ ,  $c_2 = 1$  and  $s_2 = 0$ . When  $l = 1/3$ ,  $c_1 = 1$ ,  $s_1 = 0$ . At these values of  $L$ , all results presented here reduce correctly to results obtained in earlier work by Lee et al. (1985), Rasaiah and Lee (1985a, 1985b), and Lee and Rasaiah (1987).

### Appendix 3: solutions for $R/2 \leq L \leq R$

When  $1/2 \leq L \leq 1$ , the hard core region  $(0, 1)$  is divided into  $(0, 1-L)$ ,  $(1-L, L)$ , and  $(L, 1)$ . Analytical solution is shown below:

$$\begin{aligned} & q_d^0(r) = \\ & = \begin{cases} \frac{H}{v} + B_1 \sin(vr) + B_2 \cos(vr), & 0 \leq r \leq 1-L, \\ (H + vA_d)(r-1+L) + A_1, & 1-L \leq r \leq L, \\ -\frac{H}{v} - A_d + B_1 \cos[v(r-L)] - B_2 \sin[v(r-L)], & L \leq r \leq 1; \end{cases} \quad (\text{A3.1}) \end{aligned}$$

$$\begin{aligned} B_1 & = \frac{1}{1-s_1} \left\{ \frac{H}{v} [c_1 - 2s_1 - v(2L-1)s_1] + \right. \\ & \left. + A_d [c_1 - s_1 - v(2L-1)s_1] - \frac{v}{12\eta} s_1 \right\}; \quad (\text{A3.2}) \end{aligned}$$

$$B_2 = \frac{1}{1-s_1} \left\{ \frac{H}{v} [1 - s_1 - 2c_1 - v(2L-1)c_1] + \right. \\ \left. + A_d [1 - s_1 - c_1 - v(2L-1)c_1] - \frac{v}{12\eta} c_1 \right\}; \quad (\text{A3.3})$$

$$A_1 = \frac{1}{1-s_1} \left\{ \frac{H}{v} [-1 - s_1 + c_1 - v(2L-1)] + \right. \\ \left. + A_d [-1 + c_1 - v(2L-1)] - \frac{v}{12\eta} \right\}, \quad (\text{A3.4})$$

where  $c_1 = \cos [v(1-L)]$ ,  $s_1 = \sin [v(1-L)]$ , and  $v$ ,  $A_d$ , and  $\eta$  satisfy equations (A1.11), (A1.9) and (A2.10) respectively. Besides,  $H$  still satisfies eq. (4.11) but with

$$a_1 = -2 + c_1 - Y; \quad (\text{A3.5})$$

$$a_2 = \frac{1}{v} [(1 + s_1) Y^2 - (3s_1 - 4c_1 + 3) Y - 2s_1 - 6c_1 + 6]; \quad (\text{A3.6})$$

$$a_3 = -\frac{1}{v} [-(c_1 s_1 - c_1) Y + 2c_1 s_1 - 4s_1 - 2c_1^2 - 2c_1 + 4]; \quad (\text{A3.7})$$

$$a_4 = \frac{1}{2v^2} [(1 + s_1) Y^2 - (4s_1 - 4c_1 + 4) Y - 8c_1 + 8], \quad (\text{A3.8})$$

where  $Y = v(1-2L)$ .

For the sum equation, we have

$$q_s(r) = \begin{cases} -\frac{a}{v} r + \frac{a}{v^2} [1 - vL] - \frac{b}{v} + p \cos(vr) + q \sin(vr), & 0 \leq r \leq 1-L, \\ \frac{1}{2} ar^2 + br + u, & 1-L \leq r \leq L, \\ \frac{a}{v} r + \frac{a}{v^2} [1 - vL] + \frac{b}{v} + p \sin[v(r-L)] - q \cos[v(r-L)], & L \leq r \leq 1, \end{cases} \quad (\text{A3.9})$$

where  $a$ ,  $b$ ,  $u$ ,  $p$ ,  $q$  satisfies 5 linear equations:

$$\left[ \frac{1}{v} + \frac{1}{v^2} (1 - vL) \right] a + \frac{1}{v} b + s_1 p - c_1 q = 0; \quad (\text{A3.10})$$

$$\left[ \frac{1}{v^2} - \frac{L^2}{2} \right] a + \left( \frac{1}{v} - L \right) b - u - q = -\frac{\lambda L^2}{24}; \quad (\text{A3.11})$$

$$\left[ \frac{v-1}{v^2} + \frac{(1-L)^2}{2} \right] a + \left[ (1-L) + \frac{1}{v} \right] b + u - c_1 p - s_1 q = 0; \quad (\text{A3.12})$$

$$-\frac{3\eta}{2v^3} \{ (4L^3 - 6L^2 + 4L - 1) v^2 - 8L + 8 \} a + \\ + \left\{ 1 - \frac{4\eta}{v} [(2L^3 - 3L^2 + 3L - 1) v - 3L^2 + 3L] \right\} b + \\ + 6\eta [1 - 2L] u - \frac{12\eta}{v^2} \{ -[(L-1)v - 1] s_1 + (1-v)c_1 + Lv - 1 \} p - \\ - \frac{12\eta}{v^2} \{ [(L-1)v - 1] c_1 + (1-v)s_1 + 1 \} q = 0; \quad (\text{A3.13})$$

$$\left\{ 1 + \frac{2v}{v^2} [(2L^3 - 3L^2 + 3L - 1) v^2 + 6L(L-1)v - 12L + 12] \right\} a + \\ + 6\eta (2L-1) b + 12\eta [2L-1] u - \frac{12\eta}{v} [-s_1 + c_1 - 1] p + \\ + \frac{12\eta}{v} [-s_1 - c_1 + 1] q = 1. \quad (\text{A3.14})$$



When  $L = 1$ , and  $L = 1/2$ , our results reduce to the results obtained in earlier work by Stell and Zhou (1989a); Zhou and Stell (1992a, 1992b); Lee and Rasaiah (1987); Baxter (1968a).

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## ANALYTIC SOLUTION OF THE WERTHEIM'S PY APPROXIMATION FOR THE SHIELDED STICKY-POINT MODEL OF ASSOCIATING LIQUID

The analytical solution of the Wertheim's Ornstein — Zernike equation closed by the Percus — Yevick (PY)-like approximation for the shielded sticky-point model of associating liquid is presented. This model generalizes the one-site dimerizing Wertheim model for the case of associating liquids in which the bonding radius may be less than the core radius. Our numerical analysis leads to the conclusion that the present PY-like approximation provides satisfactory description of the system if the formation of associates does not change substantially an excluded volume of the system. In addition a simple approximation which relates the fraction of monomers (undimerized particles) and the strength of associative interaction is proposed. The predictions of this scheme agree well with nearly exact results of Zhou and Stell for all values of bonding radius.

### 1. Introduction

There has been considerable progress in the statistical — mechanical theory of associating liquids during the last decade [1—8]. Much of the effort has been focused on the development and application of the integral equation theory of associating systems. Two alternative versions of the integral equations theory have been proposed. In the series of papers by Cummings and Stell [1] the theory based on the Ornstein — Zernike (OZ) equation supplemented by common closure conditions, i. e., PY approximation, mixed PY and mean

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