Statistical mechanical models of chemical reactions
Analytic solution of models of $A + B \rightarrow AB$ in the Percus–Yevick approximation

by P. T. CUMMINGS† and G. STELL

Departments of Mechanical Engineering and Chemistry,
State University of New York at Stony Brook, Stony Brook,
New York 11794, U.S.A.

(Received 13 April 1983; accepted 11 May 1983)

We introduce models for the association of spherically symmetric atoms into diatomic molecules. In the Percus–Yevick approximation, we solve analytically for the equilibrium properties of a one-parameter family of such models corresponding to $A + B \rightarrow AB$ association. We focus in detail on the behaviour of the association constant, comparing alternative definitions of that quantity. We find that our results are insensitive to the details of the repulsive core of the $AB$ potential as long as it is several times larger than $k_B T$ ($k_B =$ Boltzmann's constant, $T =$ temperature). As a result, we conclude that a limiting-case model in which the repulsive core of the $AB$ potential is a hard core is of particular interest and utility. The mathematics of the Percus–Yevick approximation simplifies considerably in this limiting-case analysis.

1. INTRODUCTION

This is the first of a series of papers in which we report the results of a study of a class of hamiltonian models of chemical association.

A fundamental quantity in the description of chemical equilibrium is the equilibrium rate constant $k$ which governs the concentrations of reacting species. For a simple chemical reaction between species $A$ and $B$ particles, given by

$$A + B \rightleftharpoons AB \quad (1.1)$$

the equilibrium rate constant is defined to be

$$k = \frac{[AB]}{[A][B]} \quad (1.2)$$

where $[X]$ denotes the concentration of species $X$ particles. This paper is concerned with the calculation of $k$ from a statistical mechanical viewpoint using a set of simple hamiltonian models that we can describe classically and that we can solve analytically in the context of an appropriate integral equation approximation (described in § 2).

† Present address: Department of Chemical Engineering, Thornton Hall, University of Virginia, Charlottesville, Virginia 22901, U.S.A.
Suppose that we have a model for the interaction of species A and B particles at the microscopic level (that is, the pair potentials $\phi_{AA}(r)$, $\phi_{AB}(r)$ and $\phi_{BB}(r)$ are prescribed) [1]. In principle, one can calculate the properties of an equimolar mixture of species A and B particles yielding the pair correlation functions $g_{AA}(r)$, $g_{AB}(r)$ and $g_{BB}(r)$. If $\rho_{A0}$ and $\rho_{B0}$ are the total densities of species A and B particles respectively, then the definition of $g_{AB}(r)$ implies that

$$\rho_{B0} \int_{R_1 < r < R_2} g_{AB}(r) \, dr = \text{the average number of type } B \text{ particles whose distance from a chosen type } A \text{ particle is between } R_1 \text{ and } R_2. \quad (1.3)$$

(In the equimolar case $\rho_{B0} = \rho_{A0}$.) Contact with $k$ may now be made as follows: we define a pair of A and B particles to be associated into a diatomic (or dimer) $AB$ if the separation $r_{AB}$ of their centres lies in a prescribed range $R_L < r_{AB} < R_U$. From (1.3) it follows that the density of dimers, $\rho_{AB}$, is given by

$$\rho_{AB} = \rho_{A0}\rho_{B0} \int_{R_5 < r < R_6} g_{AB}(r) \, dr \quad (1.4)$$

This provides one definition of the quantity $[AB]$; the quantities $[A]$ and $[B]$ are identified with the densities of unassociated type A and B particles respectively. Alternate definitions of $[AB]$ are discussed at the end of this introduction.

The models which we shall be studying have the following two properties:

(i) the hamiltonian model ensures steric saturation—that is, there is formation of $AB$ diatomics (dimerization) but no formation of $n$-mers for $n \geq 3$ (such as $ABA$, $BBA$, etc.);

(ii) the models are analytically solvable in the Percus–Yevick (PY) [3] approximation.

We are led to the models we actually solve analytically by first considering a prototypic model shown in figure 1. The $AA$ and $BB$ interactions are hard sphere interactions of diameter $\sigma$. The $AB$ interaction consists of a mound of width $\sigma$ with a deep, narrow attractive well width $w$ centred on $L$, where $L < \sigma/2$ and $L + w/2 \leq \sigma/2$. More precisely,

$$\phi_{AA}(r) = \phi_{BB}(r) = \infty, \quad r < \sigma,$$

$$= 0, \quad r > \sigma, \quad (1.5a)$$

$$\phi_{AB}(r)/k_B = \epsilon_1, \quad 0 < r < L - w/2,$$

$$= -\epsilon_2, \quad L - w/2 < r < L + w/2,$$

$$= \epsilon_1, \quad L + w/2 < r < \sigma,$$

$$= 0, \quad r > \sigma, \quad (1.5b)$$

where $k_B$ is Boltzmann's constant. If $R_U$ is chosen to be $L + w/2$ and $R_L$ to be in the range $[0, L + w/2)$, the definition (1.4) for the density of dimers is unambiguous through the prevention of polymerizations beyond the dimer level, since simple geometric considerations make it clear that once a type $A$ and type $B$ particle are separated by less than $L + w/2 \leq \sigma/2$, no other type $A$ or
type B particles may be bound to the dimer. We refer to this mechanism of excluding higher order polymerizations as steric saturation.

There are two obvious candidates for $R_L$ in this model: $R_L = 0$ and $R_L = L - w/2$. The latter version is, in many respects, the natural choice since it corresponds to an energetic definition of associated atoms. That is, two atoms are defined to be associated if their two body energy of interaction is large and negative (and, in fact, equal to $-\varepsilon_2$). In real chemical systems, an energetic definition such as this is expected to characterize associated atoms. In this paper, we shall report results for the two association constants that follow from the two choices of $R_L$.

This is an appropriate point to touch upon the question of association into $AA$ and $BB$ dimers. If we restrict ourselves to models for which (1.5 a) always holds, as we shall in this paper, and extend (1.4) to define $\rho_{AA}$ and $\rho_{BB}$ (by replacing $B$ everywhere by $A$ and $A$ everywhere by $B$ respectively), the natural $R_U$ to use is $\sigma$. The natural $R_L$ is either $\sigma$ or 0. With these choices $\rho_{AA}$ and $\rho_{BB}$ are both identically zero.

The model (1.5), while being an appropriate hamiltonian model for a reacting system, is not solvable analytically in the PY approximation. In § 2, we describe a transformation of (1.5) that yields an analytically-solvable problem. Section 3 contains the analytic solution of the PY approximation for the model defined in § 2, with some of the details being explicitly developed in the Appendices. In § 4, results for the association constant and the radial distribution functions are presented.

We return now to a discussion of (1.4) and other possible definitions of the association constant $k$. For some models (although not for ours) and for many real systems, there are a number of fundamental difficulties with an expression such as (1.4). Foremost among these is that unless $\phi_{AA}(r), \phi_{AB}(r)$ and $\phi_{BB}(r)$ are such that they preclude higher order polymerization, the $\epsilon_{AB}(r)$...
appearing in (1.4) contains contributions that come from these higher order associations. Such contributions must then be subtracted out, for example through the use of $n$-body correlation functions for $n > 2$ [4]. A second problem is that in some applications $R_L$ and $R_U$ are quite arbitrary; a good example of this is provided by the study of association of oppositely charged ions in electrolyte theory [5] where $R_L$ is chosen to be zero, but no universal consensus on $R_U$ has been reached. In an attempt to address this problem, some time ago Guggenheim [6] suggested an alternate definition for the density of dimers which we shall denote $\rho_{AB}^*$. For low densities $\rho_{AB}$ and $\rho_{BO}$ he suggested the use of

$$\rho_{AB}^* = \rho_{AB} \rho_{BO} \int f_{AB}(r) \, dr,$$

(1.6)

where the integral is over all space and $f_{AB}(r)$, the Mayer $f$-function, is defined by

$$f_{ij}(r) = \exp \left\{ -\beta \phi_{ij}(r) \right\} - 1,$$

(1.7)

where $\beta = 1/k_B T$, $T$ being the absolute temperature. The $k$ that follows from (1.6) is called by Guggenheim the sociation constant to distinguish it from the usual association constant (defined by (1.1)), while the quantity $\rho_{AB}^*$ is called by him the degree of sociation. Since $f_{AB}(r) = 0$ for an ideal (uncorrelated) system, Guggenheim argues that (1.6) gives the deviation of the degree of pairing from that obtained in the ideal case. (This same point is made by Mayer [7] as part of a more general argument concerning the physical significance of each of the coefficients in the full fugacity expansion of the pressure of a fluid.)

The natural extension of Guggenheim’s expression to a non-ionic [8] system of arbitrary density is given by [9]

$$\rho_{AB}^* = \rho_{AB} \rho_{BO} \int h_{AB}(r) \, dr,$$

(1.8)

where $h_{ij}(r)$, the total correlation function, is $g_{ij}(r) - 1$.

To discuss the relationship between the alternate definitions (1.4) and (1.8) it is instructive to first consider the various parts of the potentials $\phi_{ij}(r)$, $ij = AA, AB, BB$. In broad terms,

$$\phi_{ij}(r) = \phi_{ij}^{\text{overlap}}(r) + \phi_{ij}^{\text{rest}}(r), \quad ii = AA, BB,$$

$$\phi_{AB}(r) = \phi_{AB}^{\text{overlap}}(r) + \phi_{AB}^{\text{binding}}(r) + \phi_{AB}^{\text{rest}}(r)$$

(1.9)

The overlap parts, $\phi_{ij}^{\text{overlap}}(r)$, arise from the electronic cloud overlap and are short-ranged, positive, and well over an order of magnitude larger than $k_B T$ where $T$ is a temperature typical of the liquid state. The binding part of $\phi_{AB}(r)$ is (presumably) short ranged, and is (definitely) large in magnitude and negative. If the dissociation energy of $AB$ diatomics is of the order of 10 kcal mol$^{-1}$ (40 kJ mol$^{-1}$) at room temperature, then

$$\phi_{ij}^{\text{binding}}(r) \approx -18 k_B T.$$

By way of contrast, $\phi_{ij}^{\text{rest}}(r) \ll k_B T$ for $ij = AA, AB, BB$.

We expect that

$$g_{ij}(r) \approx 0 \quad \text{where } \phi_{ij}(r) \text{ is dominated by } \phi_{ij}^{\text{overlap}}(r),$$

$$g_{AB}(r) \gg 1 \quad \text{where } \phi_{AB}(r) \text{ is dominated by } \phi_{AB}^{\text{binding}}(r).$$
Thus, if $R_L$ and $R_U$ are defined so that $\phi_{AB}(r)$ is dominated by $\phi_{AB}^{\text{binding}}(r)$ on the range $R_L < r < R_U$, then the definitions (1.4) and (1.8) will in practice be equivalent, as pointed out by Guggenheim in the context of the low density case in which $g_{AB}(r)$ in (1.4) becomes $\int f_{AB}(r) + 1$. If there is no range of $r$ on which $\phi_{AB}(r)$ is large and negative, definitions (1.4) and (1.8) may yield substantially different answers. If (1.6) or (1.8) is used to define $\rho_{AA}^*$ (through replacement of $B$ by $A$) and $\rho_{BB}^*$ (through replacement of $A$ by $B$), one finds for $\phi_{AA}$ and $\phi_{BB}$ given by (1.5a) that $\rho_{AA}^*$ and $\rho_{BB}^*$ are negative. This is fully consistent with the notion that (1.8) yields the deviation from ideal-gas pairing (since repulsive potentials will give negative deviation). It means however that $\rho_{AA}^*$ and $\rho_{BB}^*$ cannot be regarded as physical densities.

In a recent paper, Høye and Olaussen [9] examined a model much like ours for the potentials $\phi_{ij}(r)$. The $AA$ and $BB$ potentials were assumed to be hard sphere interactions of diameter $\sigma$, so that

$$\phi_{AA}(r) = \phi_{BB}(r) = -\infty, \quad r < \frac{\sigma}{2};$$

$$\phi_{AB}(r) = 0, \quad r > \frac{\sigma}{2}. \quad (1.10)$$

The potential $\phi_{AB}(r)$ was not specified in detail, except that it was assumed to be zero for $r > \frac{\sigma}{2}$, and additionally to be characterized by

$$\phi_{AB}(r) = 1, \quad r < \frac{\sigma}{2}. \quad (1.11)$$

Høye and Olaussen [9] used definition (1.8) for the density of $AB$ dimers; from our discussion, one sees that for their hamiltonian it is equally appropriate to use (1.4) with $R_L = 0$ and $R_U = \frac{\sigma}{2}$, viz.

$$\rho_{AB} = \rho_{A0} \rho_{B0} \int_{r < \frac{\sigma}{2}} g_{AB}(r) \, dr. \quad (1.12)$$

This definition corresponds physically to assuming type $A$ and $B$ species particles are chemically bound only when the distance between the centres of the $A$ and $B$ particles is less than $\sigma/2$. This unambiguously defines the existence of a dimer since the hamiltonian models used by Høye and Olaussen exhibit steric saturation according to our definition of association. Since there is no polymerization beyond the dimer level, and since $\rho_{AA} = \rho_{BB} = 0$ in keeping with our comments following (1.5), the density $\rho_{\text{t}}$ of unassociated monomers is given by

$$\rho_{\text{t}} = \rho_{\text{i}} - \rho_{AB} \quad (1.13)$$

as it is in our model of § 2. The definition of unassociated monomer density most appropriate to (1.8), on the other hand, is somewhat less clear. Since $\rho_{AA}^*$ and $\rho_{BB}^*$ are non-zero, these as well as $\rho_{AB}^*$ must be subtracted from $\rho_{\text{i0}}$. If one again assumes no polymerization beyond the dimer level one has then

$$\rho_{\text{t}}^* = \rho_{\text{i0}} - \rho_{AB}^* - \rho_{AA}^* - \rho_{BB}^*. \quad (1.14)$$

However, the assumption of zero $n$-mer density for $n \geq 3$, which follows naturally from the definition of association that yields (1.8) and (1.12), is no longer as clearly dictated when (1.8) is used instead.

From the above discussion it would appear that the use of (1.4) and (1.13), rather than (1.8) and (1.14), provides the most convenient and unambiguous definition of $k$ for the model we develop in § 2 (except in the low $\rho_{\text{i0}}$ limit,
where both pairs of equations seem equally useful since $\rho_\gamma \approx \rho_{(0)}$. We shall therefore restrict ourselves to the former equations for the remainder of this paper.

It is worth pointing out that our PY results for $\rho_A$, $\rho_B$ and $\rho_{AB}$ are all exact through third order in monomer density $\rho_{(0)}$. Thus, not only are we assured of exact limiting behaviour as that density goes to zero, but we are assured of accurate extrapolation well into the non-ideal regime as that density is increased from zero. In light of the overall success of the PY approximation in treating similar hamiltonians at typical liquid state densities, we expect our results to be of use even at such densities.

In a sequel to this paper, we consider the homogeneous association problem

$$A + A \rightleftharpoons A_2$$

(1.15)

In addition to our interest in this model as a one component fluid of associating $A$ particles (for which we are able to solve the PY approximation analytically), we find that one limit of our analysis corresponds to a fluid of fused hard sphere diatomic molecules. In this limit, we recover the zero pole approximation for a one component fluid of such hard diatomics arrived at from an entirely different viewpoint by Morriss and Cummings [10]. As such, the analysis represents an explicit construction of the ‘particle–particle’ viewpoint of polyatomic fluids discussed in great detail by Cummings and Stell [11].

In the third paper in this series, we consider both the association reactions (1.1) and (1.15) in the presence of a hard sphere solvent (species $C$). Again, we are able to solve the PY approximation analytically, recovering (in appropriate form) certain formally exact results predicted some time ago by Stell [12] in the case of identical solute–solvent and solvent–solvent interactions, as well as subsequent formally exact results of Chandler and Pratt [13]. One limit of this analysis is found to correspond to the zero pole approximation for a mixture of fused hard sphere diatomic molecules and hard spheres, a model fluid of considerable interest in its own right.

2. DEVELOPMENT OF THE HAMILTONIAN MODEL

Consider the Mayer $f$-functions for the potentials given in (1.5): $f_{AA}(r)$ and $f_{BB}(r)$ are given by (1.10), while $f_{AB}(r)$ is given by

$$f_{AB}(r) = \begin{cases} \exp [-\beta \epsilon_1] - 1, & 0 < r < L - w/2, \\ \exp [\beta \epsilon_2] - 1, & L - w/2 < r < L + w/2, \\ \exp [-\beta \epsilon_1] - 1, & L + w/2 < r < \sigma, \\ 0, & r > \sigma. \end{cases}$$

We find, for technical reasons, that the PY approximation is not explicitly analytically solvable with $f_{AB}(r)$ given by (2.1). We follow a procedure introduced by Baxter [14] for modelling a deep and narrow square well by a more analytically tractable form. We replace the attractive well in (2.1) by an infinitely deep, infinitesimally wide attractive well so that the second virial coefficient, $B_2$, given by

$$B_2 = \int f_{AB}(r) \, dr$$

(2.2)
is unchanged. We thus obtain (in the limit \( w \to 0, \epsilon_2 \to \infty \)) a new Mayer \( f \)-function \( f_{AB}^*(r) \) given by (where \( \delta(x) \) is the one dimensional Dirac delta function)

\[
f_{AB}^*(r) = D_0 + \frac{L}{12\tau} \delta(r - L), \quad 0 < r < \sigma, \\
= 0, \quad r > \sigma,
\]

with a corresponding second virial coefficient \( B_2^* \). The parameter \( D_0 \) is given by

\[
D_0 = 1 - \exp (-\beta\epsilon_1).
\]

The parameter \( \tau \) is a dimensionless measure of the temperature. The requirement \( B_2 = B_2^* \) yields the following expression for \( \tau \):

\[
\tau = \frac{L^3}{(12L^3 w + w^2)} \frac{1}{\exp (\beta\epsilon_2) - \exp (-\beta\epsilon_1)}.
\]

In this limit, we are now free to choose

\[
0 < L \leq \sigma/2
\]

since at \( L = \sigma/2 \) steric saturation effectively operates. This is because the set of configurations of three spheres labelled 1, 2, 3 where \( r_{12} = r_{23} = \sigma/2 \) (\( r_{ij} \) is the distance between the centres of spheres labelled \( i \) and \( j \)) is a set of measure zero. Thus, there are effectively no polymerizations beyond the dimer level for \( L \) in the range (2.6) and with \( f_{AB}(r) \) given by (2.3).

The two obvious choices for \( R_L \) and \( R_U \), discussed in \( \S \) 1, now become \( (R_L, R_U) = (0, L^+) \) and \( (L^-, L^+) \), where by \( L^+ \) and \( L^- \) we specifically mean the limits

\[
L^\pm = \lim_{\alpha \to 0} L \pm \alpha, \quad \alpha \geq 0.
\]

It turns out that the model defined by (1.10) and (2.3) is still not yet analytically solvable in the PY approximation. However, a closely related model that is analytically solvable is defined by conditions on the \( h_{ij}(r) \) and the direct correlation functions \( c_{ij}(r) \). The latter functions are defined by the OZ equation

\[
h_{ij}(r) = c_{ij}(r) + \sum_{k=A,B} \rho_{k0} \int c_{ik}(s) h_{kj}(|r - s|) \, ds,
\]

where the integral is over all space, \( s = |s| \) and \( \rho_{k0} \) is the number density of species \( k \) particles, \( k=A, B \). (For our model, these densities are assumed to be equal.) In terms of these functions, the model that we solve analytically is given by

\[
h_{AA}(r) = h_{BB}(r) = -1, \quad r < \sigma, \\
c_{AA}(r) = c_{BB}(r) = 0, \quad r > \sigma,
\]

\[
h_{AB}(r) = -D + \frac{\lambda L}{12} \delta(r - L), \quad r < \sigma, \\
c_{AB}(r) = 0, \quad r > \sigma,
\]
where \( \lambda \) and \( D \) are (as yet undefined) constants. These conditions correspond to the PY approximation for a fluid interacting with potentials having Mayer \( f \)-functions given by (1.10) and

\[
f_{AB}^s(r) = f_{\text{soft}}(r) + \frac{L}{12\tau} \delta(r - L),
\]

(2.10)

where \( f_{\text{soft}}(r) \) is the Mayer \( f \)-function for a soft potential that is state dependent. From the PY approximation,

\[
f_{\text{soft}}(r) = \frac{e_{AB}(r)}{1 - D - e_{AB}(r)}, \quad r \neq L.
\]

(2.11)

We determine the parameter \( D \) by requiring that

\[
B_2^s = B_2^* = B_2.
\]

(2.12)

Thus, in the limit of low density, where \( h_{AB}(r) \rightarrow f_{AB}(r) \)

\[
D \rightarrow D_0, \quad \lambda \rightarrow \frac{1}{\tau}
\]

(2.13)

as inspection of (2.3) and (2.9) shows.

The procedure we have outlined above will be useful (in the sense that conclusions regarding systems interacting via the state-independent potential (2.3) can be drawn) only if the state dependence of \( f_{AB}(r) \) is weak. As we shall show, this is indeed the case.

In figure 2, we plot the behaviour of the parameter \( \tau \) as a function of \( T \) for \( L = \sigma/3 \) and various cases of \( \epsilon_1 \) and \( \epsilon_2 \). Our main aim in displaying this figure is to emphasize that, except at very low temperature, \( \tau \) is an almost

![Figure 2. The parameter \( \tau \) as a function of absolute temperature \( T \) for various values of \( \epsilon_1 = 1000, \epsilon_2 = 500 \) (---), \( \epsilon_1 = 400, \epsilon_2 = 800 \) (---) and \( \epsilon_1 = \epsilon_2 = 1000 \) (-----). These results follow from equation (2.5) with \( L = \sigma/3 \).](image-url)
linear function of $T$ and can, for all purposes, be regarded as synonymous with $T$. Further, we note that low temperatures (or, equivalently, large $\varepsilon_2$) are associated with $\tau$ typically in the vicinity of $10^{-2}$ to $10^{-1}$.

Before continuing, we note that $D_0$ will, in general, be close to unity. For $\beta\varepsilon_1 \approx 5$ (that is, $\phi_{\text{overlap}}(r) \approx 5 k_B T$), $D_0 \approx 0.99$, and indeed $D_0 \geq 0.6$ for $\beta\varepsilon_1 \geq 1$. This suggests that only values of $D_0$ close to 1 merit consideration.

An interesting hamiltonian model that can be solved directly with the $f_{\text{AB}}(r)$ of (2.3) and (2.4) is obtained by taking the limit $\varepsilon_1 \to \infty$ (equivalently, $D_0 = 1$). The model for the $AB$ interaction is then a hard sphere interaction with a shell of infinite stickiness located at $r = L$. At first sight, this limiting model appears to have features that render it suspect as a model for association. How can pairs of particles penetrate the two body, hard sphere core to ‘feel’ the stickiness in the first place? (If they cannot, the mechanism for association is lost.) The answer is twofold. First, it is not hard to see that according to a direct evaluation of the equilibrium ensemble averages, via the canonical or grand canonical partition functions, the particles do feel the stickiness—the entirety of phase space sampled includes the configurations for which $A$ and $B$ spheres overlap, and the adhesive potential assigns a non-zero probability to the overlap configurations corresponding to the formation of $AB$ dimers. From the standpoint of equilibrium ensemble averaging, then, the $D_0 = 1$ limit defines a perfectly reasonable model of associating species. The remaining question involves the nature of the dynamics that correspond to this equilibrium result. Here the answer lies in regarding the model as a limiting case of a process that takes place over substantial time, while the particles are interacting. At $t = \to \infty$, one starts with a finite value of $\varepsilon_1$ and raises $\varepsilon_1$ adiabatically, i.e., so slowly that the particles are able to maintain thermal equilibrium over the whole limiting process as $\varepsilon_1 \to \infty$ (and $D_0 \to 1$). To stay arbitrarily close to equilibrium requires arbitrarily long time; only at $t = 0$ has $D_0$ reached its limiting value of 1. Throughout this process $p_{\text{AB}}$ and $p_{\text{AB}*}$ will indeed have the values given by (1.4) and (1.8), respectively, as they will have in the limit $D_0 = 1$ at $t = 0$.

Our quantitative results in § 4 (see especially figure 9 and the accompanying discussion) show that the values of $k$ obtained by use of (1.4) are nearly insensitive to the value of $D_0$ as soon as $D_0$ is close to 1, which occurs as soon as $\varepsilon_1$ is a few times larger than $k_B T$. The values for $D_0 = 1$ are thus quantitatively representative of values for $D_0$ near 1. As a consequence, we use the model with $D_0 = 1$ (and analogous models of the reaction $A + A \to A_2$) in future studies to characterize the whole regime of $\varepsilon_1 \gg k_B T$.

It must be emphasized that although we find $p_{\text{AB}}$ to be virtually insensitive to the precise value of $D_0$ when $D_0$ is near 1, one can not expect the true rates of association to share this insensitivity. In dealing with such time-dependent quantities, one expects to encounter great differences as one considers values of $D_0$ closer and closer to 1 (unless one introduces appropriate scaling factors to renormalize the time scale in taking the $D_0 \to 1$ limit).

3. Analytic solution of the PY approximation

Consider the problem of solving the mixture $OZ$ equation (2.7) subject to closures (2.8) and (2.9). (From this point on, we find it convenient to denote species $A$ and species $B$ quantities by subscripts 1 and 2 respectively, so that
Since the \( c_{ij}(r) \) are finite ranged (in fact, all are zero for \( r \geq \sigma \)) we may use the factorized form of the mixture OZ equation due to Baxter [15]. For the special case where each of the \( c_{ij}(r) \) have the same range \( \sigma \), these equations are given by

\[
hr_{ij}(r) = -q'_{ij}(r) + 2\pi \sum_{k=1}^{2} \rho_{k0} \int_0^{\sigma} q_{ik}(t)(r-t)h_{kj}(|r-t|) \, dt, \quad r \geq 0, \quad (3.1a)
\]

\[
rc_{ij}(r) = -q'_{ij}(r) + 2\pi \sum_{k=1}^{2} \rho_{k0} \int_{0}^{\sigma-r} q_{ik}(t)q'_{kj}(r+t) \, dt, \quad 0 < r < \sigma. \quad (3.1b)
\]

For the problem defined by (2.8) and (2.9), we have the special symmetry

\[
h_{11}(r) = h_{22}(r),
\]

in addition to the usual symmetry \( h_{12}(r) = h_{21}(r) \). As a consequence of this, (3.1a) then yields

\[
q_{21}(r) = q_{12}(r), \quad q_{11}(r) = q_{22}(r) \quad (3.2)
\]

We need only, therefore, consider the equations for \( h_{11}(r) \) and \( h_{12}(r) \), which explicitly are given by

\[
hr_{11}(r) = -q'_{11}(r) + 2\pi \rho \int_0^{\sigma} dt (r-t)[q_{11}(t)h_{11}(|r-t|) + q_{12}(t)h_{12}(|r-t|)], \quad (3.3a)
\]

\[
hr_{12}(r) = -q'_{12}(r) + 2\pi \rho \int_0^{\sigma} dt (r-t)[q_{11}(t)h_{11}(|r-t|) + q_{12}(t)h_{11}(|r-t|)], \quad (3.3b)
\]

Note that in (3.3) we have specialized to the equimolar mixture \( (\rho_{A0} = \rho_{B0} = \rho) \).

One further result from the Baxter analysis is required: the functions \( q_{11}(r) \) and \( q_{12}(r) \) satisfy the following conditions

\[
q_{11}(r), q_{12}(r) = 0, \quad r \geq \sigma. \quad (3.4)
\]

Substituting (2.8) and (2.9) into (3.3), we obtain the following equations for \( q_{11}(r) \) and \( q_{12}(r) \):

\[
q'_{11}(r) + p[q_{12}(r + L) - q_{12}(r - L)] = (a_{11} + Da_{12})r + b_{11} + Db_{12}, \quad (3.5a)
\]

\[
q'_{12}(r) + p[q_{11}(r + L) - q_{11}(r - L)] + \frac{\lambda L^2}{12} \delta(r - L) = (Da_{11} + a_{12})r + Db_{11} + b_{12}, \quad (3.5b)
\]

where

\[
p = \frac{\pi \rho \lambda L^2}{6} \quad (3.6)
\]

and

\[
a_{ij} = \delta_{ij} - 2\pi \rho \int_0^{\sigma} dt q_{ij}(t), \quad (3.7a)
\]

\[
b_{ij} = 2\pi \rho \int_0^{\sigma} dt t q_{ij}(t). \quad (3.7b)
\]

The \( q_{ij}(r) \) satisfy the boundary conditions

\[
\begin{align*}
q_{11}(\sigma), q_{12}(\sigma) &= 0, \\
q_{12}(L^-) &= q_{12}(L^+) + \frac{\lambda L^2}{12}
\end{align*}
\]

\[
q_{12}(L^-) = q_{12}(L^+) + \frac{\lambda L^2}{12} \quad (3.8)
\]

The latter condition arises as a result of the delta function in (3.5b).
Consider the functions $q_+ (r)$ and $q_- (r)$ defined by

$$q_+ (r) = q_{11} (r) + q_{12} (r),$$

$$q_- (r) = q_{11} (r) - q_{12} (r).$$

(3.9a)  (3.9b)

Hence,

$$q_{11} (r) = \frac{1}{2} [q_+ (r) + q_- (r)],$$

(3.10a)

$$q_{12} (r) = \frac{1}{2} [q_+ (r) - q_- (r)].$$

(3.10b)

It follows from (3.5) that the functions $q_+ (r)$ and $q_- (r)$ satisfy the equations

$$q_+ ^\prime (r) + p [q_+ (r + L) - q_+ (r - L)] + \frac{\lambda L^2}{12} \delta (r - L) = a_+ r + b_+,$$

(3.11a)

$$q_- ^\prime (r) - p [q_- (r + L) - q_- (r - L)] - \frac{\lambda L^2}{12} \delta (r - L) = a_- r + b_-,$$

(3.11b)

where

$$a_\pm = (1 \pm D) \left[ 1 - 2 \pi \rho \int_0^\sigma dt q_\pm (t) \right],$$

(3.12a)

$$b_\pm = (1 \pm D) 2 \pi \rho \int_0^\sigma dt t q_\pm (t),$$

(3.12b)

with the additional boundary conditions

$$q_\pm (\sigma) = 0, \quad q_\pm (L-) = q_\pm (L+) + \frac{\lambda L^2}{12}.$$

(3.13)

Suppose we now consider the general problem of determining the function $q (r)$ satisfying the equation

$$q_\prime (r) + p [q (r + L) - q (r - L)] + \frac{\lambda L^2}{12} \delta (r - L) = a r + b$$

(3.14)

with

$$a = \int \left[ 1 - 2 \pi \rho \int_0^\sigma dt q (t) \right],$$

(3.15a)

$$b = 2 \pi \rho \int_0^\sigma dt t q (t)$$

(3.15b)

and

$$q (\sigma) = 0, \quad q (L-) = q (L+) + \frac{\lambda L^2}{12}.$$

(3.16)

If we denote the solution of (3.14)-(3.16) by $q (\eta, \lambda, \rho; r)$, where

$$\eta = \frac{\pi}{6} \rho \sigma^3$$

(3.17)

is the dimensionless density, then it is clear that

$$q_+ (r) = q (\eta, \lambda, 1 + D; r),$$

(3.18a)

$$q_- (r) = q (\eta, - \lambda, 1 - D; r).$$

(3.18b)
Before continuing on to consider specific values of $L$, we introduce the dimensionless quantity $\nu$ related to $p$ (see (3.6)) as

$$\nu = p\sigma = \eta \lambda \left( \frac{L}{\sigma} \right)^2. \tag{3.19}$$

We now consider two specific values of $L$ as representative of the general behaviour expected for $0 < L \leq \sigma/2$. We will give details of our analysis for $L = \sigma/2$, and give results only for the analysis for $L = \sigma/3$. Once the problem is cast into the form (3.14)–(3.16), it is very similar mathematically to that arising in the analytic solution of integral equations for polyatomic fluids (for a discussion of the corresponding polyatomic fluid problem, see [10]).

3.1. Analysis for the $L = \sigma/2$ case

To find $q(r)$ requires the solution of (3.14) as a difference–differential equation [16]. Define two functions $q_1(r)$ and $q_2(r)$ with the properties that

$$q_1(r) = \begin{cases} q(r) & 0 < r < \sigma/2, \\ 0 & \text{elsewhere,} \end{cases}$$

$$q_2(r) = \begin{cases} q(r) & \sigma/2 < r < \sigma, \\ 0 & \text{elsewhere.} \end{cases} \tag{3.20}$$

so that

$$q(r) = q_1(r) + q_2(r). \tag{3.21}$$

On the two ranges of $r$, $[0, \sigma/2]$ and $[\sigma/2, \sigma]$, (3.14) becomes

$$q_1'(r) + pq_2(r + \sigma/2) = ar + b, \quad 0 < r < \sigma/2, \tag{3.22a}$$

$$q_2'(r) - pq_1(r - \sigma/2) = ar + b, \quad \sigma/2 < r < \sigma. \tag{3.22b}$$

For $0 < r < \sigma/2$, we can write (3.22 b) as

$$q_2'(r + \sigma/2) - pq_1(r) = a(r + \sigma/2) + b, \quad 0 < r < \sigma/2. \tag{3.23}$$

Differentiating (3.22 a) once and substituting for the $q_2$ term using (3.23) we obtain

$$q_1''(r) + p^2 q_1(r) = -apr + (1 - \nu/2)a - bp \tag{3.24}$$

the solution of which is

$$q_1(r) = \frac{a}{p} r + \frac{a}{p^2} (1 - \nu/2) - \frac{b}{p} + A \cos pr + B \sin pr, \quad 0 < r < \sigma/2. \tag{3.25}$$

From (3.25) and (3.22), $q_2(r)$ follows immediately. Thus, combining these results with (3.21) we find that

$$q(r) = \begin{cases} -a r + \frac{a}{p^2} (1 - \nu/2) - \frac{b}{p} + A \cos pr + \sin pr, & 0 < r < \sigma/2, \\ -a r + \frac{a}{p^2} (1 - \nu/2) + \frac{b}{p} + A \sin p(r - \sigma/2) - B \cos p(r - \sigma/2), & \sigma/2 < r < \sigma. \end{cases} \tag{3.26}$$
To determine the parameters $a$, $b$, $A$ and $B$, we substitute (3.26) into (3.15) (with $L = a/2$) and (3.15), obtaining the following equations:

\[ \frac{1}{\nu} a + \frac{2}{\nu} \frac{b}{\sigma^2} c - \frac{A}{\sigma^2} (1 + s) = -\frac{\lambda}{48}, \]  
\[ (3.27 \ a) \]

\[ \frac{1}{\nu^2} (1 + \nu/2) a + \frac{1}{\nu} \frac{b}{\sigma^2} s - \frac{B}{\sigma^2} c = 0, \]  
\[ (3.27 \ b) \]

\[ a \left( 1 + \frac{12\eta f}{\nu^2} (1 - \nu/4) \right) + \frac{A}{\sigma^2} \frac{12\eta f}{\nu} [1 - c + s] + \frac{B}{\sigma^2} \frac{12\eta f}{\nu} [1 - c - s] = f, \]  
\[ (3.27 \ c) \]

\[ a \left( -\frac{6\eta f}{\nu^2} \right) + \frac{b}{\sigma} \left( 1 - \frac{3\eta f}{\nu} \right) + \frac{A}{\sigma^2} \cdot \frac{-12\eta f}{\nu^2} \left[ -1 + \nu/2 + (1 - \nu)c + (1 + \nu) s \right] + \frac{B}{\sigma^2} \cdot \frac{-12\eta f}{\nu^2} \left[ 1 - (1 + \nu/2)c + (1 - \nu)s \right], \]  
\[ (3.27 \ d) \]

where

\[ c = \cos \nu/2, \quad s = \sin \nu/2. \]  
\[ (3.28) \]

These equations are linear in the parameters $a$, $b/\sigma$, $A/\sigma^2$ and $B/\sigma^2$. Consequently, they can be written as a matrix equation

\[ \begin{bmatrix} a \\ b/\sigma \\ A/\sigma^2 \\ B/\sigma^2 \end{bmatrix} = \begin{bmatrix} -\lambda/48 \\ 0 \\ f \\ 0 \end{bmatrix}, \]  
\[ (3.29) \]

where the elements of the matrix $M$ are defined obviously by referring to (3.27). Analytic expressions for $a$, $b/\sigma$, $A/\sigma^2$ and $B/\sigma^2$ are given in Appendix A. These solution parameters are, in fact, functions of the parameters $\eta$, $\lambda$ and $f$ defined at (3.17) above. Thus, we may write $a = a(\eta, \lambda, f)$ and similarly for $b/\sigma$, $A/\sigma^2$ and $B/\sigma^2$. Recalling (3.18) and (3.10), we find that $q_{11}(r)$ and $q_{12}(r)$ are given by

\[ q_{11}(r) = -\frac{a_D}{p} r + \frac{a_S}{p^2} - \frac{a_{D\sigma}}{2p} - \frac{b_D}{p} + A_s \cos pr + B_s \sin pr, \quad 0 < r < \sigma/2, \]
\[ = \frac{a_D}{p} r + \frac{a_S}{p^2} - \frac{a_{D\sigma}}{2p} + \frac{b_D}{p} + A_s \sin pr - B_s \cos pr, \quad \sigma/2 < r < \sigma, \]  
\[ (3.30) \]

\[ q_{12}(r) = -\frac{a_D}{p} r + \frac{a_S}{p^2} - \frac{a_{D\sigma}}{2p} + \frac{b_S}{p} + A_s \cos pr + B_s \sin pr, \quad 0 < r < \sigma/2, \]
\[ = \frac{a_D}{p} r + \frac{a_S}{p^2} - \frac{a_{D\sigma}}{2p} - \frac{b_S}{p} + A_s \sin pr - B_s \cos pr, \quad \sigma/2 < r < \sigma, \]  
\[ (3.31) \]
where
\[
\begin{align*}
\alpha_s &= \frac{1}{2}[a(\eta, \lambda, 1 + D) + a(\eta, -\lambda, 1 - D)], \\
\alpha_D &= \frac{1}{2}[a(\eta, \lambda, 1 + D) - a(\eta, -\lambda, 1 - D)], \\
\beta_s &= \frac{1}{2}[b(\eta, \lambda, 1 + D) + b(\eta, -\lambda, 1 - D)], \\
\beta_D &= \frac{1}{2}[b(\eta, \lambda, 1 + D) - b(\eta, -\lambda, 1 - D)], \\
\lambda_s &= \frac{1}{2}[A(\eta, \lambda, 1 + D) + A(\eta, -\lambda, 1 - D)], \\
\lambda_D &= \frac{1}{2}[A(\eta, \lambda, 1 + D) - A(\eta, -\lambda, 1 - D)], \\
\beta_s' &= \frac{b_s}{\sigma}, \\
\beta_D' &= \frac{b_D}{\sigma}, \\
\lambda_s' &= \frac{A_s}{\sigma^2}, \\
\lambda_D' &= \frac{A_D}{\sigma^2}, \\
\beta_s' &= \frac{b_s}{\sigma^2}, \\
\beta_D' &= \frac{b_D}{\sigma^2}.
\end{align*}
\] (3.32)

The primed quantities are clearly dimensionless.

The final step in completing the analytic solution is to derive an equation relating \( \lambda \) to \( \tau \). This comes from imposition of the PY closure, which may be written in the form
\[
1 + h_{ij}(r) = [1 + f_{ij}(r)] y_{ij}(r), \tag{3.36}
\]
where
\[
y_{ij}(r) = 1 + h_{ij}(r) - c_{ij}(r). \tag{3.37}
\]

From (3.1) and (3.7), for \( y_{12}(r) \) we find
\[
ry_{12}(r) = r(1 - D + Da_{11} + a_{12}) + Db_{11} + b_{12} + 2\pi \rho \int_0^r dt \frac{L}{12} \delta(|r-t|-L) - 2\pi \rho \int_0^r dt [q_{11}(t)q'_{12}(r+t) + q_{12}(t)q'_{11}(r+t)]. \tag{3.38}
\]

Although \( h_{12}(r) \) and \( c_{12}(r) \) are discontinuous at \( r = L \), careful examination of (3.38) reveals that \( y_{12}(r) \) is not discontinuous there. Explicitly, we find that, for \( L = \sigma/2 \), (3.38) becomes
\[
\sigma^2/2y_{12}(\sigma/2) = \sigma^2/2(1 - D + Da_{11} + a_{12}) + Db_{11} + b_{12} + \frac{\pi \rho \lambda \sigma^2}{24} q_{11}(0) - 2\pi \rho \int_0^{\sigma/2} dt [q_{11}(t)q'_{12,c}(\sigma/2 + t) + q_{12}(t)q'_{11}(\sigma/2 + t)]. \tag{3.39}
\]

where \( q'_{12,c}(r) \) is the continuous part of \( q'_{12}(r) \); that is, the delta function part has been subtracted out. From (3.36) and (2.9), we see that the PY approximation implies that
\[
\lambda \tau = y_{12}(\sigma/2). \tag{3.40}
\]
After evaluating the terms on the right hand side of (3.39), we find that (3.40) becomes

\[ 1 - D + D a_{11} + a_{12} + 2 \left( D \frac{b_1}{\sigma} + \frac{b_2}{\sigma} \right) + 2 \nu \left[ a_s - \frac{a_D}{2\nu} - b'_D \frac{1}{\nu} + A'_s \right] = -\lambda \sigma \]

\[ -24 \eta \left\{ \left( a_s^2 + a_D^3 \right) \frac{1}{2\nu^3} - a_s a_D \frac{3}{4\nu^2} - (b'_D a_s + b'_S a_D) \frac{1}{2\nu^3} \right\} \]

\[ + (b'_D A'_S + b'_S A'_D) \frac{s}{\nu} - (b'_D B'_D + b'_S B'_S) \frac{(1 - c)}{\nu} \]

\[ + (a'_S a_S + a'_D a_D) \frac{2s}{\nu^2} + (a'_D a'_S + a_S a'_D) \frac{(1 - c) - \nu k}{\nu^2} \]

\[ + (a'_D B'_D + a_S B'_S) \left[ (1 - 2) + v^2 - s \right] / \nu^2 + (a'_S B'_D + a_D B'_S) (1 - c) / \nu^2 \]

\[ + (A'_s^2 + A'_D^2 + B'_D^2 + B'_S^2) \nu / 4 + (A'_s^2 + A'_D^2 - B'_D^2 - B'_S^2) (\sin \nu) / 4 \]

\[ + (B'_D A'_S + B'_S A'_D) (1 - \cos \nu) / 2 \right\} = 0. \]

(3.41)

Using (3.7), (3.30) and (3.31), the parameters \( a_{11}, a_{12} \) and \( b_{12} \) are given by

\[ a_{11} = 1 - 12 \eta \left\{ - \frac{a_D}{4\nu} + \frac{a_S}{\nu^2} + (A'_S - B'_S) \frac{s}{\nu} + (A'_D + B'_D) (1 - c) / \nu \right\}, \]

(3.42 a)

\[ a_{12} = -12 \eta \left\{ \frac{a_S}{4\nu} + \frac{a_D}{\nu^2} + (A'_D - B'_D) \frac{s}{\nu} + (A'_S + B'_S) (1 - c) / \nu \right\}, \]

(3.42 b)

\[ \frac{b_{12}^2}{\sigma} = 12 \eta \left\{ \frac{a_D}{2\nu^3} + \frac{b'_S}{4\nu} + A'_D \left[ c - 1 + (v/2)s \right] / \nu^2 + A'_S \left[ (v/2) - vc + s \right] / \nu^2 \right\} \]

\[ + B'_S \left[ s - (v/2)c \right] / \nu^2 + B'_D (1 - c - vs) / \nu^2 \right\}. \]

(3.43)

(By replacing \( S \) with \( D \) and vice versa in (3.43), the expression for \( b_{11}/\sigma \) is obtained.) Given the analytic expressions that follow from the results given in Appendix A, (3.41) is a non-linear equation for the parameter \( \lambda \), the solution of which is discussed in § 3.3 below. This completes the analysis for the \( L = \sigma/2 \) case.

3.2. Analysis for the \( L = \sigma/3 \) case

Using similar methods to those used above for \( L = \sigma/2 \), we find that for \( L = \sigma/3 \) the functions \( q_{11}(r) \) and \( q_{12}(r) \) are given by

\[ q_{11}(r) = \frac{a_S}{2} r^2 + \left[ \frac{-a_D}{2p} + \frac{1}{3} a_S \sigma + b_S \right] r + A_S + B_S \cos \sqrt{2p} r \]

\[ + C_D \sin \sqrt{2p} r, \quad 0 < r < \sigma/3, \]

(3.44)
\[ q_{12}(r) = \frac{a_D}{2} r^2 + \left[ -\frac{a_S}{2p} + \frac{3}{2} a_D \sigma + b_D \right] r + A_D + B_D \cos \sqrt{2pr} + C_S \sin \sqrt{2pr}, \quad 0 < r < \alpha/3, \]
\[ = \frac{a_D}{2p^3} - \frac{a_S \sigma}{3p} + B_S \sqrt{2} \sin \sqrt{2p(r - \alpha/3)} \\
- C_D \sqrt{2} \cos \sqrt{2p(r - \alpha/3)}, \quad \alpha/3 < r < 2\alpha/3, \]
\[ = \frac{a_D}{2} r^2 + \left[ \frac{a_S - a_D \sigma}{3p} + b_D \right] r + \frac{b_S}{p} - \frac{3}{8} b_D \sigma + A_D \\
- B_D \cos \sqrt{2p(r - 2\alpha/3)} - C_S \sin \sqrt{2p(r - 2\alpha/3)}, \quad 2\alpha/3 < r < \alpha. \]

As in the \( L = \alpha/2 \) case,
\[ a_S = \frac{1}{6} [a(\eta, \lambda, 1 + D) + a(\eta, -\lambda, 1 - D)], \]
\[ a_D = \frac{1}{6} [a(\eta, \lambda, 1 + D) - a(\eta, -\lambda, 1 - D)], \]
with similar expressions holding for the other parameters. The parameters \( a(\eta, \lambda, f), \ldots, C(\eta, \lambda, f) \) satisfy five linear equations which can be summarized in matrix form as
\[
\begin{bmatrix}
    a \\
    b/\sigma \\
    A/\sigma^2 \\
    B/\sigma^2 \\
    C/\sigma^2
\end{bmatrix} =
\begin{bmatrix}
    \lambda/108 \\
    0 \\
    0 \\
    f \\
    0
\end{bmatrix}
\]
the explicit elements of \( M \) being given in Appendix B. This Appendix also contains the analytic expressions for the parameters \( a, \ldots, C/\sigma^2 \) that satisfy (3.47). The five equations that yield (3.47) consist of the four equations given in (3.15) and (3.16), plus an additional continuity condition
\[ q \left( \eta, \lambda, f; \frac{2\sigma^-}{3} \right) = q \left( \eta, \lambda, f; \frac{2\sigma^+}{3} \right). \] (3.48)

An analogous equation to (3.41) can be derived and is given in Appendix B as equation (B 23). This completes the analysis for the \( L = \alpha/3 \) case.

### 3.3. Determination of \( \lambda \) and \( D \)

In implementing the solution given above it is necessary to solve the non-linear equation that follows from (3.36) (given as (3.41) for \( L = \alpha/2 \), (B 23) for \( L = \alpha/3 \)). For fixed \( D \), as in the model discussed in § 2 above with \( \epsilon_1 \to \infty \) (for which \( D = 1 \)), we have only this one non-linear equation which we solve numerically using the method of false position [17]. For given \( \tau \), we begin at zero density (where \( \lambda \to 1/\tau \)) and increment the density \( \eta \) in small steps, solving for \( \lambda \) at each density value.
For the case of finite $\epsilon_1$, as discussed in § 2 we determine $D=D(\eta, \tau)$ by the requirement (2.12) that the second virial coefficient remain fixed. Conceptually, it is useful to regard (2.12) and the equation that follows from (3.36) as two simultaneous non-linear equations for the two solution parameters $\lambda$ and $D$. We solve these equations numerically using the hybrid Newton’s-method steepest-descent algorithm developed by Powell [18], again starting at zero density ($\eta=0$) where $\lambda \to 1/\tau$, $D \to D_0$, and incrementing $\eta$ by small amounts.

3.4. Expressions for the association constant

We derive expressions for the association constant $k$ that follow from the definition of the density of $AB$ dimers (1.4) for the two choices of $(R_L, R_U)$ given by $(O, L^+)$ and $(L^-, L^+)$. We begin by noting that each of the two quantities $\langle N_1 \rangle$ and $\langle N_2 \rangle$ defined by

$$\langle N_1 \rangle = \rho 4\pi \int_L^{L^+} g_{12}(r)r^2 dr = 2\eta \lambda \left( \frac{L}{\sigma} \right)^3,$$  
$$\langle N_2 \rangle = \rho 4\pi \int_0^{L^+} g_{12}(r)r^2 dr = [8(1 - D) + 2A] \left( \frac{L}{\sigma} \right)^3,$$  

corresponds to the average number of $B$ particles chemically bonded to a chosen $A$ particle. The two formulae reflect two different definitions for the existence of a chemical bond: (3.49) corresponds to the definition that an $A$ particle and a $B$ particle are chemically bonded when the distance between their centres is equal to $L$; (3.50) corresponds to the definition that a chemical bond exists when this distance is less than or equal to $L$.

The density $\rho_{AB}$ of $AB$ dimers is given by (1.4). For the two definitions of a chemical bond described above, we have two corresponding expressions for $\rho_{AB}$ which we denote as $\rho_{AB,i}$; they are given by

$$\rho_{AB,i} = \rho \langle N_i \rangle, \quad i=1, 2. \quad (3.51)$$

The density of $A$ and $B$ monomers (cf. (1.13)) is given by

$$\rho_A = \rho_B = \rho - \rho_{AB}. \quad (3.52)$$

Thus, the expressions for the association constants $k_1$ and $k_2$ can be derived using (3.50)–(3.52) and the definition of $k$

$$k = \frac{\rho_{AB}}{\rho_A \rho_B}. \quad (3.53)$$

The subscript $i$ on $k_i$, $i=1, 2$, will refer to the two different definitions of $\rho_{AB}$ given in (3.51).

In this paper, we report dimensionless association constants $K_1$ and $K_2$, related to $k_1$ and $k_2$ by $K_i = k_i/\sigma^3$, $i=1, 2$. Combining (3.50)–(3.53), it is easily verified that

$$K_1 = \frac{\pi \lambda (L/\sigma)^3}{3(1 - \langle N_1 \rangle)^2}, \quad (3.54)$$
$$K_2 = \frac{\pi(\lambda + 4(1 - D))(L/\sigma)^3}{3(1 - \langle N_2 \rangle)^2}. \quad (3.55)$$
At zero density, we find that
\[ K_1^0 = K_1(\eta = 0) = \frac{\pi}{3\tau} (L/\sigma)^3, \quad (3.56) \]
\[ K_2^0 = K_2(\eta = 0) = \frac{\pi}{3} [1/\tau + 4(1 - D_0)](L/\sigma)^3. \quad (3.57) \]

Note that if \( \epsilon_1 \to \infty \) \( (D = D_0 = 1) \), then \( K_1 = K_2 \)—that is, the two definitions of the association constant are consistent. This is because for \( D = 1 \) particles are completely excluded from the range of interparticle separation \( r < L \).

As one final point, we note that in an exact solution of the hamiltonian mode defined by (1.5a) and (2.3) we have the restriction
\[ \langle N_1 \rangle \leq 1. \quad (3.58) \]

This follows from steric saturation. In addition, we have the inequality
\[ \langle N_1 \rangle \leq \langle N_2 \rangle. \quad (3.59) \]

As we shall see, the PY approximation violates (3.58) at high density, indicating that it is unphysical in this regime. However, this unphysical aspect of the PY approximation is reminiscent of the failure of the PY approximation to predict a fluid–solid transition for the hard sphere fluid. For the latter case, the PY approximation yields analytic results for thermodynamics and structure up to a volume fraction of unity, corresponding to the spheres overlapping (which is clearly unphysical). Similarly, the violation of (3.58) corresponds to the overlap of hard cores, and so is perhaps not unexpected. This unphysical characteristic of the PY approximation does not prevent it from being quantitatively accurate at low to moderate densities, and qualitatively accurate to high density. Consequently, we regard the high-density anomaly of the PY approximation as a feature of our results that does not detract significantly from their overall usefulness.

4. RESULTS

We shall report results for three values of \( D_0 \) (0.8, 0.95 and 1.0) and three values of \( \tau \) (0.02, 0.1 and 0.2) all for \( L* = L/\sigma = 1/2 \). The most complete results presented are for \( D_0 = 1 \), and for this value we include some results for \( L* = 1/3 \). The results for \( D_0 = 0.95 \) are quite limited in scope, and their main purpose is to demonstrate that results for this value of \( D_0 \) are qualitatively—and to a large extent quantitatively—indistinguishable from those for \( D_0 = 1 \). The limit \( D_0 = 1 \), discussed in §2, corresponds to the limit \( \beta_1 \to \infty \); on the basis of the results presented in this section, we find that there is little practical difference between \( D_0 \geq 0.95 \) (\( \beta_1 \geq 3 \)) and \( D_0 = 1 \), and in future work we restrict our attention to the limiting value, \( D_0 = 1 \).

In figures 3 and 4, we plot the behaviour of the solution parameter \( \lambda \) as a function of density \( \eta \) for \( D_0 = 0.8 \) (figure 3) and \( D_0 = 1 \) (figure 4) for three values of \( \tau \); figure 4 also contains results for \( L* = 1/3 \). The locus of points for which \( \langle N_1 \rangle = 1 \) is also shown on the figures and can be regarded as the upper limit of physically feasible solutions. There is a great similarity between the \( D_0 = 0.8 \) and \( D_0 = 1 \) results, although as \( \tau \) increases the limit \( \langle N_1 \rangle = 1 \) is reached at much
Statistical mechanical models of chemical reactions

Figure 3. The parameter \( \lambda \) as a function of density \( \eta \) for \( D_0 = 0.8 \). Three isotherms are shown: \( T = 0.02 \) (---), 0.1 (-----) and 0.2 (----). The locus of points at which \( \langle N_L \rangle = 1 \) is shown as a dotted curve.

Figure 4. The parameter \( \lambda \) as a function of density \( \eta \) for \( D_0 = 1 \). Three isotherms are shown: \( T = 0.02 \) (---), 0.1 (-----) and 0.2 (----). The locus of points at which \( \langle N \rangle = 1 \) is shown as a dotted curve. For each value of density and temperature, there are two values of \( \lambda \) plotted: the smaller of these is for the \( L = \sigma/2 \), the larger for \( L = \sigma/3 \).
Figure 5. The expected number of nearest neighbours $\langle N \rangle$ for $D_0=0.8$ and $\tau=0.02$ (---), 0.1 (-----) and 0.2 (--------). For each value of density and temperature, $\langle N_1 \rangle$ is the smaller of the two values of $\langle N \rangle$ shown, $\langle N_2 \rangle$ the larger.

Figure 6. The expected number of nearest neighbours $\langle N \rangle$ for $D_0=1$ and $\tau=0.02$ (---), 0.1 (-----) and 0.2 (--------). For each value of density and temperature, the smaller of the two values of $\langle N \rangle$ shown corresponds to $L^*=1/3$, the larger to $L^*=1/2$. 
higher densities in the $D_0=0.8$ case. We believe that this is physically sensible since the volume effectively available to the soft particles ($D_0=0.8$) is considerably larger than that available to the hard particles ($D_0=1$). Thus, as the density increases, steric effects are destined to play a somewhat diminished role in the soft particle case compared to the hard particle case. Although in general $\lambda$ is a decreasing function of $\eta$ (at least for high enough $\tau$), the expected number of nearest neighbours, given either by $\langle N_1 \rangle$ or $\langle N_2 \rangle$ depending on the definition used (see § 2), is not (since it is proportional to the product of $\lambda$ and $\eta$) as shown in figures 5 ($D_0=0.8$) and 6 ($D_0=1$). We see here the effect of density in that $\langle N_i \rangle$ increases with density along isotherms. We can picture this as follows: as density increases, the particles are pushed closer together so that the probability of two particles overlapping (with the result they become associated) is increased.

There is an interesting dichotomy in the behaviour of $\langle N_i \rangle$ isotherms as a function of density. For low temperature ($\tau=0.02$), the isotherms have a slope greater than unity, while for high temperature ($\tau=0.2$) their slope is less than one. At zero density, the slope of $\langle N_i \rangle$ is simply a constant times $K_i^0$ (refer to § 3.4), so that the behaviour we are observing has its origin in the relative effective strength of the attraction at the two temperatures. At lower temperatures, the effect of the $\phi^{\text{binding}}(r)$ is strong enough to ‘trap’ unlike particles in the vicinity of the bonding region and become associated; at higher temperature, the mechanism is more dependent on the increasing density ‘pushing’ unlike atoms together into a bonding situation, and the difference in

![Figure 7. The reduced association constant $K/K^0$ for $D_0=0.8$ and $\tau=0.02$ (———), 0.1 (— — —) and 0.2 (— — ——). For each value of density and temperature, the smaller value of $K/K^0$ corresponds to $K_1/K_1^0$, the larger to $K_2/K_2^0$. Note that $K_1/K_1^0$ at $\tau=0.1$ and $K_2/K_2^0$ at $\tau=0.2$ are indistinguishable on the scale of this graph.](image)
the slope of $<N_i>$ at low density is a reflection of this. The low density behaviour of $K_i$ does not reflect this dichotomy (that is, as we shall see, there is no qualitative difference in the low density behaviour of $K_i$ for widely differing temperatures), except in the magnitude of $K_i$ at zero density.

In figures 7 and 8, $K_i/K_i^0$ isotherms are shown for $D_0=0.8$ (figure 7) and $D_0=1$ (figure 8); the latter figure includes results for $L^*=1/3$. We begin by noting that there is a considerable range of density, $\eta \leq 0.1$, where $K_i/K_i^0$ shows no strong $\eta$ dependence and no $\tau$ dependence (at least on the scale of these figures). As the density increases beyond this value, $K_i/K_i^0$ rapidly escalates in value and ultimately diverges at the point at which $<N_i>=1$. It was noted in §3.4 that $<N_1> \leq <N_2>$ at the same state conditions; moreover, the density dependence of $<N_1>$ and $<N_2>$ is such that $K_2$ is expected to increase more rapidly than $K_1$ as a function of $\eta$. We see this reflected in the fact that $K_i/K_i^0 < K_2/K_2^0$ in figure 7. It is useful to keep in mind that $K_i^0$ is nearly linear in $\tau$ (exactly linear for $i=1$) so that the fact that $K_i/K_i^0$ exhibits only weak temperature dependence lends support to our contention that the primary effect on $K_i$ is steric. Figure 8 verifies that $L^*=1/2$ and $L^*=1/3$ results are qualitatively the same.

In figure 9, $K_i$ isotherms are shown for $D_0=1$ and $D_0=0.95$. We present these results with a twofold purpose: the temperature dependence of $K_i$ (rather than $K_i/K_i^0$) is made explicit; secondly, we wish to draw attention to the fact that $K_i$ for $D_0=0.95$ ($\beta\varepsilon_i=2.998$) exhibits the same qualitative features as $K (=K_1=K_2)$ for $D_0=1$ ($\beta\varepsilon_i\to\infty$). We believe that these results justify our concentration on the limit $\beta\varepsilon_i\to\infty$ in future papers in this series.
As discussed in §2, the validity of our results for $D_0 < 1$ depends to some extent on the degree of state dependence exhibited by the pair potential implied by (2.11). That is, let us consider the pair potential

$$\beta \phi_{12}(\eta, \lambda; r) = -\log \left[ \frac{e_{12}(r)}{1 - D - e_{12}(r)} \right], \quad r \neq L, \quad 0 < r < \sigma, \quad (4.1)$$

where the dependence of $\phi$ on $\eta$ and $\tau$ is brought out explicitly in the notation adopted here. In figure 10, this potential is shown for $D_0 = 0.8$ ($\beta \epsilon_1 = 1.609$) and $\tau = 0.02$ and 0.1. As the density is increased along an isotherm, the potential becomes more repulsive near the origin and less so in the vicinity of $r = L$. However, it remains repulsive for all physically accessible states and we regard its state dependence as fairly weak. The larger $D_0$ is, the less the degree of state dependence in $\beta \phi_{12}(\eta, \tau; r)$, although we have not included results here for any larger values of $D_0$. We conclude, then, that provided $D_0$ is sufficiently close to unity (i.e. $D_0 \gtrsim 0.8$) the pair potential between the reacting species is reasonably state-independent.

The behaviour of the solution parameter $D$ along isotherms is shown in figure 11 for $D_0 = 0.95$ and $D_0 = 0.8$. In line with the comments made above, we note that $D$ is less state-dependent for the higher value of $D_0$.

We now turn to consideration of the structure of the associating fluid. Our most complete results are for $D_0 = 1$, so we shall discuss these first. Figures 12 and 13 show $g_{11}(r)$ and $g_{12}(r)$ for $D_0 = 1$ and the three usual values of temperature at densities $\eta = 0.1$ (figure 12) and 0.2 (figure 13). The first noteworthy
Figure 10. The state dependent pair potential \( \beta \phi_{12}(\eta, \tau; r) \) for \( D_0 = 0.8 \) and \( \tau = 0.02 \) (---) and 0.1 (--.--). The potential is shown at two densities, \( \eta = 0.1 \) and 0.2. For both values of \( \tau \), the higher density curve has the larger value at \( r = 0 \). The zero density form of the pair potential is shown as the dotted line (\( \beta \epsilon_1 = 1.609 \)).

Figure 11. The parameter \( D \) as a function of density \( \eta \) for \( D_0 = 0.8 \) and 0.95. Three isotherms are shown: \( \tau = 0.02 \) (---), 0.1 (--.--), and 0.2 (--.--.--). At each density and temperature, the larger value of \( D \) clearly corresponds to \( D_0 = 0.95 \).
Figure 12. The radial distribution functions $g_{11}(r)$ and $g_{12}(r)$ for $D_0=1$ and $\eta=0.1$ at temperatures $\tau=0.02$ (---), 0.1 (----) and 0.2 (--------). For each value of the temperature, the radial distribution function with the larger contact value ($g(\sigma^*)$) is $g_{11}(r)$. Note that for $\tau=0.2$ $g_{11}(r)$ and $g_{12}(r)$ are indistinguishable on the scale of this plot.

Figure 13. The radial distribution functions $g_{11}(r)$ and $g_{12}(r)$ for $D_0=1$ and $\eta=0.2$ at temperatures $\tau=0.02$ (---), 0.1 (----) and 0.2 (--------). For each value of the temperature, the radial distribution function with the larger contact value ($g(\sigma^*)$) is $g_{11}(r)$. 
aspect is that as the temperature increases, the differences between $g_{11}(r)$ and $g_{12}(r)$ diminish. (In fact, in the limit of infinite temperature, $g_{11}(r)$ and $g_{12}(r)$ must of course become equal to $g_{11}(2\eta; r)$, the PY approximation for the radial distribution function for a hard sphere fluid at density $2\eta$.)

The second point to note is that, quite generally, for all the results obtained $g_{11}(\alpha+) \geq g_{12}(\alpha+)$, but $g_{11}(\alpha + L) \approx g_{12}(\alpha + L)$. The first observation is intuitively clear since a substantial fraction (essentially $\langle N_i \rangle$) of the species 1 and species 2 particles are associated and thus separated by distances $r \leq L$; because of steric saturation, this necessarily implies that unlike particles will tend to be excluded from the range $L < r \leq \sigma + L$. (In the hard-particle case being considered here, the range of exclusion is $\sigma \leq r \leq \sigma + L$.) Thus, one expects $g_{11}(r) > g_{12}(r)$ for $r \approx \sigma$ as a reflection of this fact. On the other hand, the distance $\sigma + L$, while certainly being a distinguished distance for like particle separations, should be a region of reduced population of like particles due to the preponderance of like particles at $r \approx \sigma$; moreover, $\sigma + L$ should be a separation at which it is increasingly likely to find unlike particles, since the exclusion alluded to earlier ceases to operate beyond this distance. In light of this, the observation that $g_{11}(\sigma + L) \approx g_{12}(\sigma + L)$ should not be surprising.

One interesting overall feature of the correlation functions is the presence of a cusp at $r = \sigma + L$ in both $g_{11}(r)$ and $g_{12}(r)$. This is a reflection of the delta function at $r = L$. For $L^*$ greater than $1/2$, $g_{11}(r)$ and $g_{12}(r)$ are discontinuous at $r = 2\sigma$; for example, the adhesive hard sphere fluid of Baxter [14] can be thought of as a specific value of $L$, namely $\sigma^-$, and for this model the correlation functions are discontinuous at $r = \sigma + L = 2\sigma$ [19]. We presume this discontinuity reflects higher order polymerization (i.e., beyond the dimer level).

![Figure 14. The radial distribution functions $g_{11}(r)$ and $g_{12}(r)$ at complete association ($\langle N_i \rangle = 1$) for $D_0 = 1$ and temperatures $\tau = 0.02$ (---), $\eta = 0.203$ and $0.2$ (-----) ($\eta = 0.270$). For each value of the temperature, the radial distribution function with the larger contact value ($g(\sigma^+)$) is $g_{11}(r)$.](image-url)
which must occur for $L^* > 1/2$ with the Hamiltonian models considered in this paper.

For the hard-particle model, at the point at which $\langle N \rangle = 1$, we should have $g_{11}(r) = g_{12}(r)$, $r \neq L$, since in this limit each atom is part of a homonuclear diatomic molecule. Thus, apart from the delta function at $r = L$ in $g_{12}(r)$ (reflecting the presence of an unlike atom in the same molecule), $g_{11}(r)$ and $g_{12}(r)$ should be identical since each of the two atoms in a different molecule are indistinguishable to the atom at the origin. In figure 14 we exhibit $g_{ij}(r)$ at complete association ($\langle N \rangle = 1$) for $\tau = 0.02$ and 0.2. They are clearly not equal. This emphasizes the inadequacy of the PY approximation in the vicinity of complete association.

That $g_{11}(r)$ and $g_{12}(r)$ are different at all densities is perhaps not surprising in view of the fact that the closure relations (2.8) and (2.9) to the OZ equation are asymmetric in the $h_{ij}(r)$ while being symmetric in the $c_{ij}(r)$. As a consequence, one expects quite generally that $g_{11}(r) \neq g_{12}(r)$. A natural question to ask is what asymmetry in the closure for the $c_{ij}(r)$ is necessary to make $g_{11}(r) = g_{12}(r)$ except at $r = L$. That is, if we write

$$c_{ij}(r) = c_{ij}(r) + \Delta c_{ij}(r),$$  \hspace{1cm} (4.2)

where $c_{ij}(r)$ ($\Delta c_{ij}(r)$) is the part of $c_{ij}(r)$ independent of (dependent on) the species indices $i$ and $j$, we seek the functional form of $\Delta c_{ij}(r)$ consistent with

$$g_{12}(r) = \frac{\lambda L}{12} \delta(r - L) + g_{11}(r).$$  \hspace{1cm} (4.3)

Substitution of (4.3) into the OZ equation (2.7) yields

$$\Delta c_{11}(k) = \frac{-1}{\rho(1 - \omega^2)},$$  \hspace{1cm} (4.4a)

$$\Delta c_{12}(k) = \frac{\omega}{\rho(1 - \omega^2)},$$  \hspace{1cm} (4.4b)

where

$$\omega = \omega(k) = \frac{\rho \tau \lambda L \delta \sin kL}{3kL} = 2 \eta \lambda \left( \frac{L}{\sigma} \right)^2 \sin \frac{kL}{kL}.$$  \hspace{1cm} (4.5)

Note that (4.4) is both a necessary and sufficient condition for (4.3) to hold, and, as expected, $c_{11}(r) \neq c_{12}(r)$ for $r > \sigma$.

Now, on physical grounds, (4.3) is expected to hold only at saturation, at which point (4.5) becomes

$$\omega = \frac{\sin kL}{kL}$$  \hspace{1cm} (4.6)

and, as a consequence, (4.4) implies that $c_{11}(r)$ and $c_{12}(r)$ are long ranged. In this limit of complete association, the mixture OZ equation with closures (2.8), (2.9), (4.2) and (4.4) becomes equivalent to the site-site Ornstein–Zernike (SSOZ) equation introduced by Chandler and Andersen [20] for a diatomic molecular fluid. We have discussed this connection in considerable detail in an earlier publication [11] and do not repeat our arguments here. However, we wish to point out that the inadequacy of the PY approximation to describe the complete association limit is directly attributable to its failure to predict a
Figure 15. The radial distribution functions $g_{11}(r)$ and $g_{12}(r)$ for $L^* = 1/3$, $D_0 = 1$ and $\tau = 0.02$ at densities $\eta = 0.1$ (-----), 0.2 (- - -) and 0.3 (-----). For each value of the density, the radial distribution function with the larger contact value ($g(\sigma^+)$) is $g_{11}(r)$.

Figure 16. The radial distribution functions $g_{11}(r)$ and $g_{22}(r)$ for $L^* = 1/2$, $D_0 = 0.8$ and $\tau = 0.1$ at densities $\eta = 0.1$ (-----), 0.2 (- - -) and 0.3 (-----). For each value of the density, the radial distribution function with the larger contact value ($g(\sigma^+)$) is $g_{11}(r)$.
long ranged, asymmetric $c_{ij}(r)$ at this limit. In the sequel to this paper, we shall consider a model for which the PY approximation makes no obvious errors at the complete association limit.

Formally, one can ask, for a given value of $\eta$, what value of $\tau$ yields $\langle N_1 \rangle = 1$ (i.e., the complete association limit). (This is obtained by setting $\lambda$ to its complete association value in (3.40) and trivially obtaining $\tau$.) For $\eta$ large enough, $\tau$ is small and positive; for small $\eta$, however, $\tau$ is negative and this result is clearly not physically sensible. We regard this unphysical behaviour as an indicator of the inadequacy of the closure for $c_{ij}(r)$ in (2.8) and (2.9) compared with (4.2) and (4.4), the latter clearly becoming singular as $\eta \to 0$.

In figure 15, results for $L^* = 1/3$ and $D_0 = 1$ at the low temperature state $\tau = 0.02$ are shown. The overall similarity between these results and the $L^* = 1/2$ results is obvious. Figure 15 also shows clearly the trend in both $g_{11}(r)$ and $g_{12}(r)$ toward well-defined liquid-like oscillations as the density is increased.

Finally, in figure 16, we show $g_{ij}(r)$ results for $D_0 = 0.8$ and $\tau = 0.1$. They are similar qualitatively to those for $D = 1$, with one added feature: the non-zero value of $g_{12}(r)$ inside the core. As density increases, $g_{12}(r)$ inside the core increases (a reflection of the decrease in $D$ along this isotherm—compare with figure 11). This is in line with our intuition in that it simply reflects the fact that as the particles are pushed together, there is an increased tendency to overlap on the range $0 < r < \alpha$. Note from figure 11 that as temperature decreases, there is a low density range over which $D$ initially increases ($g_{12}(r)$ decreases, $0 < r < \alpha$) before decreasing monotonically. Presumably, this corresponds to the density regime where temperature effects initially dominate steric effects (see the discussion above concerning figures 5 and 6).

The authors wish to acknowledge the National Science Foundation for support of this research. The authors take pleasure in thanking Harold Friedman for many useful discussions and suggestions and Song Hi Lee for his valuable comments after a careful reading of the manuscript.

APPENDIX A

Details of the solution for $L = \alpha/2$

In this Appendix, we give expressions for the dimensionless quantities $a(\eta, \lambda, f)$, $b(\eta, \lambda, f)/\sigma$, $A(\eta, \lambda, f)/\sigma^2$ and $B(\eta, \lambda, f)/\sigma^2$ that arise in the analytic solution of the PY approximation described in § 3.1 of the text. The determinant $\Delta(\eta, \lambda, f)$ of the matrix $\mathbf{M}$ in (3.29) is given by

$$\Delta = \Delta(\eta, \lambda, f) = \frac{1}{1 + s} \left\{ \frac{3\eta f}{\nu^4} \left[ (-8 + 4v - v^2)(1 + s) + 8c + (1 + s) \right] \right\}^2,$$

(A 1)

where $c$ and $s$ are given by (3.28). Letting $T_{ij}$ denote the $ij$th cofactor of the matrix $\mathbf{M}$, we find (where $\xi = \eta f$)

$$T_{11} = -\frac{12 \xi}{\nu} \left( 1 - \frac{3 \xi}{\nu} \right) (1 - s - c) - \frac{144 \xi^2}{\nu^4} \left[ 4 - v + (-4 + v)c - vs \right],$$

(A 2)

$$T_{12} = -\frac{6 \xi}{\nu^2} \left[ 2 - 2v - (2 - v)c + 2s \right] - \frac{18 \xi^2}{\nu^4} \left[ 2 + 2v - (2 + v)c - 6s \right] + \frac{72 \xi^2}{\nu^4} \left[ 2 + v - 2c - (2 + v)s \right] + \frac{144 \xi^2}{\nu^4} \left[ 4 - v + (-4 + v)c - vs \right],$$

(A 3)
The solution of (3.29) is then given by

\[ a(\eta, \lambda, f) = \frac{1}{\Delta} \left( -\frac{\lambda}{48} T_{11} + f T_{31} \right), \tag{A10} \]

\[ b(\eta, \lambda, f) = \frac{1}{\Delta} \left( -\frac{\lambda}{48} T_{12} + f T_{32} \right), \tag{A11} \]

\[ A(\eta, \lambda, f) = \frac{1}{\Delta} \left( -\frac{\lambda}{48} T_{13} + f T_{33} \right), \tag{A12} \]

\[ B(\eta, \lambda, f) = \frac{1}{\Delta} \left( -\frac{\lambda}{48} T_{14} + f T_{34} \right), \tag{A13} \]

**APPENDIX B**

**Details of the solution for \( L = a/3 \)**

In this Appendix, we give further details of the analysis for the \( L = a/3 \) solution discussed in § 3.2 of the text.

The solution parameters \( a(\eta, \lambda, f), b/\sigma, A/\sigma^2, B/\sigma^2 \) and \( C/\sigma^2 \) for the \( L = a/3 \) case are found to satisfy five simultaneous linear equations given by

\[
\frac{1}{6v^2} (-3 + v + v^2)a + \frac{b}{\sigma} + \frac{A}{\sigma^2} + c \frac{B}{\sigma^2} + (\sqrt{2} + s) \frac{C}{\sigma^2} = \frac{\lambda}{108}. \tag{B1} \]
Statistical mechanical models of chemical reactions

\[ \frac{1}{6v} (3 + \nu) a + \frac{1}{3v} (3 + \nu) \frac{b}{\sigma} + \frac{A}{\alpha^2} - \frac{c}{\alpha^2} - \frac{2}{\sigma} - \frac{C}{\alpha^2} = 0, \quad (B2) \]

\[ \frac{1}{6\nu^2} (3 - 4\nu) a - \frac{1}{\nu} \frac{b}{\sigma^2} + \frac{A}{\sigma^2} - \frac{(1 + \sqrt{2}s) B}{\sigma^2} - \sqrt{2}c \frac{C}{\sigma^2} = 0, \quad (B3) \]

\[ \left[ 1 + \frac{2\xi}{2\nu^2} (27 + 8\nu^2) \right] a + \frac{4\xi}{3\nu} (3 + \nu) \frac{b}{\sigma} + \frac{8\xi}{\sigma^2} + \frac{12\xi}{\nu} (1 - c) \frac{B}{\sigma^2} \]
\[ - \frac{12\xi}{\nu} \frac{C}{\sigma^2} = f, \quad (B4) \]

\[ \frac{\xi}{5\nu^2} (3 + 2\nu + \nu^2) a + \left[ -1 + \frac{10\xi}{27\nu^2} (2\nu + 9) \right] \frac{b}{\sigma} + \frac{4\xi}{\sigma^2} \]
\[ + \frac{6\xi}{\nu^2} \left[ \frac{2\nu}{3} - \frac{4\nu}{3} \frac{c}{\sigma^2} + \left( \sqrt{2} - \frac{2\nu^2}{3} \right) s \right] \frac{B}{\sigma^2} \]
\[ + \frac{6\xi}{\nu^2} \left[ \sqrt{2} - \frac{2\nu^2}{3} + \left( - \sqrt{2} + \frac{2\nu^2}{3} \right) e - \frac{4\nu}{3} \right] s \frac{C}{\sigma^2} = 0, \quad (B5) \]

where again \( \xi = \eta f \) and

\[ c = \cos \left( \frac{\sqrt{2}\nu}{3} \right), \quad s = \sin \left( \frac{\sqrt{2}\nu}{3} \right). \quad (B6) \]

The elements of the matrix \( \mathbf{M} \) in (3.47) are determined straightforwardly by comparing (B1)-(B5) with (3.47).

The determinant \( \Delta = \Delta(\eta, \lambda, f) \) of the matrix \( \mathbf{M} \) in (3.47) is given by

\[ \Delta = \frac{1}{(-3\sqrt{2} - 4s + \sqrt{2}c)} \left[ \frac{2\eta f}{27\nu^2} [(162 - 189\nu + 99\nu^2 + 3\nu^3)\sqrt{2} \right. \]
\[ + (-162 + 135\nu - 45\nu^2 - \nu^3)c + (162 - 216\nu + 126\nu^2 + 4\nu^3)s] \]
\[ \left. - 3\sqrt{2} - 4s + \sqrt{2}c \right)^2. \quad (B7) \]

The cofactors \( T_{ij} \) of the matrix \( \mathbf{M} \) have been determined and are given by

\[ T_{11} = \frac{4\xi}{\nu} \left[ (-3 + 2\nu + 3\nu^2)\sqrt{2} + 2\nu s \right] + \frac{8\xi^2}{27\nu^3} \left[ (-324 + 297\nu - 24\nu^2 - 2\nu^3)\sqrt{2} \right. \]
\[ + (324 - 243\nu + 6\nu^2)\sqrt{2}c + (-162 + 162\nu - 2\nu^3)s], \quad (B8) \]

\[ T_{12} = \frac{4\xi}{\nu} \left[ (-3 + 4\nu - \nu^2)\sqrt{2} + (3 - 3\nu)\sqrt{2}c + (-3 + 3\nu - \nu^2)s \right] \]
\[ + \frac{4\xi^2}{27\nu^3} \left[ (486 - 810\nu + 891\nu^2 - 462\nu^3 + 19\nu^4 + 2\nu^5)\sqrt{2} \right. \]
\[ + (486 + 810\nu - 837\nu^2 + 354\nu^3 - 3\nu^4)\sqrt{2}c \]
\[ + (-324\nu + 594\nu^2 - 336\nu^3 - 6\nu^4 + 2\nu^5)s], \quad (B9) \]
\[ T_{13} = -\sqrt{2} - s + \frac{2\xi}{27 \nu^3} \left[ (162 - 135\nu + 18\nu^2 + 2\nu^3)\sqrt{2} 
+ (-162 + 54\nu + 9\nu^2)\sqrt{2c} + (243 - 162\nu + 2\nu^3)s \right] 
+ \frac{4\xi^2}{729 \nu^6} \left[ (-13122 + 15309\nu - 7290\nu^2 + 1296\nu^3 + 540\nu^4 - 18\nu^5 
- \nu^6)\sqrt{2} + (13122 - 15309\nu + 5832\nu^2 + 162\nu^3 - 459\nu^4 - 9\nu^5)\sqrt{2c} 
+ (8748\nu - 9477\nu^2 + 1944\nu^3 + 972\nu^4 - \nu^5)s \right], \quad (B\ 10) \]

\[ T_{14} = -s - \sqrt{2c} + \frac{2\xi}{27 \nu^3} \left[ (27\nu - 18\nu^2)\sqrt{2} + (-54\nu + 63\nu^2 + 2\nu^3)\sqrt{2c} 
+ (81 - 108\nu + 54\nu^2 + 2\nu^3)s \right] + \frac{4\xi^2}{729 \nu^6} \left[ (2187 - 729\nu - 1458\nu^2 + 81 - 108\nu - 54\nu^2 - 2\nu^3)c \n+ (-54\nu + 63\nu^2 + 2\nu^3)\sqrt{2c} + (-2187 + 729\nu + 1944\nu^2 - 1080\nu^3 - 63\nu^4 - \nu^5)s \right], \quad (B\ 11) \]

\[ T_{15} = -1 + c - \sqrt{2s} + \frac{2\xi}{27 \nu^3} \left[ 81 - 54\nu + 54\nu^2 + 2\nu^3 + (-81 + 108\nu - 54\nu^2 - 2\nu^3)c \n- (54\nu + 63\nu^2 + 2\nu^3)\sqrt{2c} \right] + \frac{4\xi^2}{729 \nu^6} \left[ -729\nu \n+ 1134\nu^2 - 756\nu^3 - 54\nu^4 - \nu^5 + (2187\nu - 1620\nu^2 + 378\nu^3 \n+ 54\nu^4 + \nu^5)c + (-2187 + 729\nu + 1944\nu^2 - 1080\nu^3 - 63\nu^4 - \nu^5)\sqrt{2s} \right], \quad (B\ 12) \]

\[ T_{41} = (-3 + c)\sqrt{2} - 4s + \frac{2\xi}{27 \nu^3} \left[ (162 - 270\nu + 45\nu^2 - 24\nu^3)\sqrt{2} 
+ (-162 + 216\nu + 9\nu^2 - 10\nu^3)\sqrt{2c} + (162 - 216\nu + 18\nu^2 - 32\nu^3)s \right], \quad (B\ 13) \]

\[ T_{42} = \frac{\xi}{3 \nu^2} \left[ (9 + 6\nu + 3\nu^2)\sqrt{2} + (-9 - 6\nu + \nu^2)\sqrt{2c} + (12\nu + 4\nu^2)s \right], \quad (B\ 14) \]

\[ T_{43} = \frac{\xi}{6 \nu^2} \left[ (-3 + 7\nu + 3\nu^2)\sqrt{2} + (3 - 4\nu)\sqrt{2c} + (-3 + 10\nu + 4\nu^2)s \right] 
+ \frac{\xi}{81 \nu^5} \left[ (243 - 810\nu + 432\nu^2 - 60\nu^3 - 97\nu^4 - 3\nu^5)\sqrt{2} 
+ (-243 + 810\nu - 351\nu^2 + 60\nu^3 + 13\nu^4)\sqrt{2c} \n+ (-324\nu + 270\nu^2 - 78\nu^3 - 127\nu^4 - 4\nu^5)s \right], \quad (B\ 15) \]

\[ T_{44} = \frac{\xi}{6 \nu^2} \left[ (3 - \nu + \nu^2)\sqrt{2} - (3 + 2\nu)\sqrt{2c} + (3 - 4\nu + 2\nu^2)s \right] 
+ \frac{\xi}{81 \nu^5} \left[ (-243 + 324\nu - 108\nu^2 + 60\nu^3 - 35\nu^4 - \nu^5)\sqrt{2} 
+ (243 - 324\nu + 27\nu^2 + 48\nu^3 + 11\nu^4)\sqrt{2c} \n+ (324\nu - 432\nu^2 + 294\nu^3 - 77\nu^4 - 2\nu^5)s \right], \quad (B\ 16) \]
\[ T_{45} = \frac{1}{6v^a} \left[ -3 - 2\nu + (-3 + 4\nu - 2\nu^2)c + (-3 - 2\nu)\sqrt{2s} \right] \]

\[ + \frac{\xi}{81v^b} \left[ 162\nu - 216\nu^2 + 84\nu^3 + 11\nu^4 \right. \]

\[ + (-324\nu + 432\nu^2 - 294\nu^3 + 77\nu^4 + 2\nu^5)c \]

\[ \left. + (243 - 324\nu + 27\nu^2 + 48\nu^3 + 11\nu^4)\sqrt{2s} \right]. \quad (B\ 17) \]

The parameters \( a, b/a, A/a^2, B/a^2, C/a^2 \) are given by

\[ a(\eta, \lambda, f) = \frac{1}{\Delta} \left( \frac{\lambda}{108} T_{11} + fT_{41} \right), \quad (B\ 18) \]

\[ \frac{b}{\sigma}(\eta, \lambda, f) = \frac{1}{\Delta} \left( \frac{\lambda}{108} T_{12} + fT_{42} \right), \quad (B\ 19) \]

\[ \frac{A}{\sigma^2}(\eta, \lambda, f) = \frac{1}{\Delta} \left( \frac{\lambda}{108} T_{13} + fT_{43} \right), \quad (B\ 20) \]

\[ \frac{B}{\sigma^2}(\eta, \lambda, f) = \frac{1}{\Delta} \left( \frac{\lambda}{108} T_{14} + fT_{44} \right), \quad (B\ 21) \]

\[ \frac{C}{\sigma^2}(\eta, \lambda, f) = \frac{1}{\Delta} \left( \frac{\lambda}{108} T_{15} + fT_{45} \right). \quad (B\ 22) \]

The equation for \( L = \sigma/3 \) that is analogous to (3.41) in the \( L = \sigma/2 \) case is given by

\[ 1 - D + (Da_{11} + a_{12}) + 3 \left( D \frac{b_{11}}{\sigma} + \frac{b_{12}}{\sigma} \right) + 3\nu \left[ 2B'S - a_D - b'D' \frac{1}{\nu} \right] \]

\[ - \lambda\tau - 36\eta(S_4 + S_5) = 0, \quad (B\ 23) \]

where

\[ a_{11} = 1 - 12\eta \left[ \left( \frac{4}{81} + \frac{1}{6\nu^2} \right) a_S + \frac{1}{3}\nu b'_S + \frac{1}{3}\nu b'_D + \frac{1}{3}A'_S \right. \]

\[ + \frac{(1-c)}{\nu} B'_S - \frac{s}{\nu} C'_S \], \quad (B\ 24) \]

\[ a_{12} = -12\eta \left[ \left( \frac{4}{81} + \frac{1}{6\nu^2} \right) a_D + \frac{1}{3}\nu b'_D + \frac{1}{3}\nu b'_S + \frac{1}{3}A'_D \right. \]

\[ + \frac{(1-c)}{\nu} B'_S - \frac{s}{\nu} C'_D \], \quad (B\ 25) \]

\[ \frac{b_{11}}{\sigma} = 12\eta \left[ \left( \frac{1}{36} + \frac{1}{12\nu^2} \right) a_S + \frac{1}{18\nu} (a_D + 5b'_D) + \frac{5}{81} b'_S + \frac{1}{3}A'_S - \frac{\sqrt{2s}}{3\nu} B'_S \right. \]

\[ + \frac{\sqrt{2}}{3\nu} (1 + c) C'_D + \frac{1}{2\nu^2} \left( \frac{2\nu}{3} (1 - 2c) + \sqrt{2s} \right) B'_D \]

\[ \left. + \frac{1}{2\nu^2} \left[ \sqrt{2(1-c)} - \frac{4\nu s}{3} \right] C'_S \right], \quad (B\ 26) \]
\[
\frac{b_{12}}{\sigma} = 12\eta \left\{ \frac{1}{36} + \frac{1}{12\nu^2} \right\} a_D + \frac{1}{18\nu} \left( a_S + S b' s \right) + \frac{5}{81} b'D + \frac{1}{3\nu} A'D - \frac{\sqrt{2}s}{3\nu} B'D \\
+ \frac{\sqrt{2}}{3\nu} (-1 + c) C'S + \frac{1}{2\nu^2} \left[ \frac{2\nu}{3} - (1 - 2c) + \sqrt{2}s \right] B'S \\
+ \frac{1}{2\nu^2} \left[ \sqrt{2}(1 - c) - \frac{4\nu_s}{3} \right] C'D, \tag{B 27}
\]

\[
S_1 = \left\{ \frac{1}{12\nu^2} a_D^2 + \frac{1}{36\nu^2} a_D a_S - \frac{1}{18\nu} a_S^2 + \frac{1}{6\nu^2} a_D b' s - \frac{1}{9\nu} a_S b' s \\
+ \frac{1}{2\nu^2} \left[ 3 - \frac{\sqrt{2}}{3} \nu s - 3c \right] a_D B'S + \frac{1}{6\nu} \left[ -2 + \sqrt{2}\nu s + 2c \right] a_S B'S \\
+ \frac{1}{2\nu^2} \left[ -3s - \frac{\sqrt{2}\nu}{3} c \right] a_D C'D + \frac{1}{6\nu} \left[ 2s - \sqrt{2}\nu c \right] a_S C'D \\
+ \frac{\sqrt{2}s}{3} b' s B'S - \frac{\sqrt{2}s}{3} b' s C'D + \sqrt{2}s A'S B'S + \sqrt{2}(1 - c) A'S C'D \\
+ \frac{2\nu}{3} \left[ (B'S)^2 + (C'D)^2 \right] \right\} \tag{B 28}
\]

and \(S_2\) is given by (B 28) after each occurrence of the \(S\) subscript is changed to \(D\) and vice versa. The primed quantities are defined in the same way that the corresponding quantities are defined in § 3.1 (see (3.32) to (3.35)).

References

[1] Strictly speaking, the potential giving rise to the association between \(A\) and \(B\) particles must be quantum mechanical in nature. However, using effective pair potentials for input to a classical statistical mechanical formalism which yields the required degree of association has a long history. (See, for example, BOLTZMANN, L., 1898, Lectures on Gas Theory, Part II (translated by S. G. Brush (University of California Press, 1964), Chap. 6.) As another more recent example, the Central Force Model (CFM) for liquid water proposed by Lemberg and Stillinger [2] is precisely of this form. The CFM potentials are characterized by Coulomb interactions (between \(H^+\) and \(O^{2-}\) ions) at large separations, and by rapidly varying forces at short range that, in concert, act to impose the correct geometry and stoichiometry on the water molecules formed. Note that the complicated nature of the CFM potential precludes its analytic solution.


[4] A quite different definition of association for electrolyte systems that precludes higher order polymerizations is suggested by POIRIER, J. C., and De LAP, J. H., 1961, J. chem. Phys., 35, 213. However, the relationship between the association constants so defined to experimental results is quite obscure.


[8] In the ionic case, Guggenheim introduces the notion of supersociation which essentially corresponds to subtracting from \(h_A B(r)\) the large-\(r\) asymptotic form of that function to obtain an integrand replacing \(h_A B(r)\) in (1.8). Since we shall not deal with ionic solutions in this paper, we shall not discuss the rationale for this choice compared to (1.7).
    particle’ idea was first introduced by Høyæ, J. S., and Stell, G., 1977, S.U.N.Y.
    College of Engineering and Applied Sciences Report No. 307. See also § IV.A.2
    Press).
    Equations, edited by P. Rabinowitz (Gordon & Breach).