Statistical mechanical models of chemical reactions

III. Solvent effects

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The statistical mechanical study of chemically reactive fluids via the analytic solution of integral equation approximations for such fluids (Cummings, P. T., and Stell, G., 1984, Molec. Phys., 51, 253; 1985, Ibid., 55, 33) is extended to a consideration of solvent effects. This is achieved by studying mixtures of molecular species some of which can undergo reaction (the solute(s)) and one of which is inert (the solvent). The results obtained near infinite dilution of the reacting solute in the inert solvent are similar in magnitude to those observed in experiments on the dissociation equilibrium of dinitrogen tetroxide.

1. INTRODUCTION

This paper further pursues the analytic study of chemically reacting systems initiated by the authors in [1] (hereafter referred to as I with equation (i.j) of I denoted (I.i,j)). In this paper, the association reaction between species $A$ and species $B$ molecules,

$$A + B \rightleftharpoons AB,$$

was studied by considering a mixture of $A$ and $B$ atoms in which the pair interactions gave rise to chemical association. In [2], the reaction

$$2A \rightleftharpoons A_2,$$

between like species molecules was modelled by using a pair potential between $A$ atoms similar to the potential between $A$ and $B$ species used in I. In this paper, we consider the effect of a solvent on both reacting systems (1.1) and (1.2).

Solvent effects on chemical equilibria are well-known [3] and can be quite dramatic [3, 4]. For example, consider the association equilibrium of nitrogen dioxide with dinitrogen tetroxide

$$2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4.$$
The ratio of the association constant $K$ (defined in equation (1.4)) to its gas phase value in various liquid solvents at 293'16 K [3].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$K/K_{gas}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCl$_4$</td>
<td>21.5</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>28.7</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>47.5</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>69.1</td>
</tr>
<tr>
<td>C$_2$H$_4$Br</td>
<td>79.7</td>
</tr>
<tr>
<td>C$_6$H$_5$Br</td>
<td>103.2</td>
</tr>
<tr>
<td>C$_6$H$_5$Cl</td>
<td>103.2</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>171.3</td>
</tr>
</tbody>
</table>

As shown by the table, in a liquid solvent it is found experimentally that the equilibrium mass action association constant

$$K = \frac{\rho_{N_2O_4}}{\rho_{N_2O_2}}$$

is between 10 and 200 times its value for the same gas phase reaction in the absence of a solvent [3]. Chandler and Pratt [4, 5] developed a comprehensive formalism for the study of condensed phase chemical equilibria, and an approximate form of their theory (described in more detail in §2.5 below) yields a shift in $K$ which is of the order of magnitude of the experimentally observed values. They explain this result in terms of the steric effect of the solvent on the reacting solute. In essence, they find that association is dramatically increased in a liquid solvent because the solvent molecules drive pairs of NO$_2$ groups together in order to save space in the dense fluid medium.

The role of steric effects on reactions (1.1) and (1.2) will be examined in this paper by considering mixtures in which the reacting components (solute) are immersed in a hard sphere solvent. Thus, in the case of the association reaction (1.1) between unlike species $A$ and $B$ molecules, a three component mixture of $A$ and $B$ molecules with a hard sphere solvent $C$ will be considered, the pair interactions $\phi_{ij}(r)$ being given by

$$\phi_{ij}(r) = \begin{cases} \infty, & r < \sigma, \\ 0, & r > \sigma, \end{cases}$$

$$ij = AA, BB, AC, BC, CC,$$

$$f_{AB}(r) = \exp \left[ -\phi_{AB}(r)/k_BT \right] - 1$$

$$= -1 + \frac{12L}{\tau} \delta(r - L), \quad r < \sigma,$$

$$= 0, \quad r > \sigma.$$
the association reaction (1.2) between like species, a two component mixture is used (solute \( A \) and hard sphere solvent \( C \)), the pair interactions being given by

\[
\phi_{ij}(r) = \begin{cases} 
\infty, & r < \sigma, \\
0, & r > \sigma,
\end{cases}
\]

\( ij = AC, \quad CC, \)

\[
f_{AA}(r) = \exp \left[-\frac{\phi_{AA}(r)/k_BT}{\frac{12L}{\tau}}\right] - 1
\]

\[
= -1 + \frac{12L}{\tau} \delta(r - L), \quad r < \sigma,
\]

\[
= 0, \quad r > \sigma.
\]

(1.6)

In §2, the Percus–Yevick approximation [6] for the mixture with interactions (1.5) is solved analytically; results are presented in §3. The modifications of the analysis required to solve the PY approximation for the two-component mixture (1.6) are described in §4 and selected results are also presented. Section 5 contains our conclusions and discussions.

Since the solvent in the calculations presented in this paper is a hard sphere solvent, we are probing solvent-induced effects on the chemical equilibrium which are strictly steric in nature. In particular, there is no liquid–gas phase transition in the hard sphere fluid with the consequence that solvent effects related to, for example, solvent vapour–liquid critical points cannot be probed in this model. In the next paper in this series, a model applicable to such phenomena is developed by considering reaction (1.1) in a simple fluid solvent which in the integral equation approximation used undergoes a liquid–gas phase transition at low temperature. This permits the examination of solvent criticality and phase equilibria on the chemical reaction equilibrium of the solute.

2. ANALYTIC SOLUTION OF THE PY APPROXIMATION FOR THE REACTION

\[ A + B \rightleftharpoons AB \] IN SOLUTION

In this section, we consider the solution of the PY approximation for the three-component mixture with pair interactions given by equations (1.5). Species \( A, B \) and \( C \) molecules are denoted by the indices 1 to 3 respectively. The mixture Ornstein–Zernike (OZ) equation [7] for an \( m \)-component mixture is given by

\[
h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^{m} \rho_k \int c_{ik}(|\mathbf{s}|)h_{kj}(|\mathbf{r - s}|) \, d\mathbf{s}
\]

(2.1)

where \( h_{ij}(r) \) and \( c_{ij}(r) \) are the total and direct correlation functions between species \( i \) and \( j \) molecules, \( \rho_i \) is the number density of species \( i \) molecules, and the integral is performed over all space. The PY approximation is given by

\[
c_{ij}(r) = f_{ij}(r)[1 + h_{ij}(r) - c_{ij}(r)],
\]

(2.2)
which, for the interactions (\ref{eq:1.5}) yields

\[
\begin{align*}
  h_{ij}(r) &= -1, \\
  &\quad i,j = 11, 22, 13, 23, 33, \\
  h_{12}(r) &= -1 + \frac{\lambda L}{12} \delta(r - L) \quad r < \sigma, \\
  c_{ij}(r) &= 0, \\
  &\quad r > \sigma, \\
  &\quad 1 \leq i, j \leq 3.
\end{align*}
\]  

(2.3)

Since each $c_{ij}(r)$ is finite-ranged, the Baxter Wiener–Hopf factorization \cite{8, 9} for mixtures \cite{10} is immediately applicable, yielding the set of factorized equations

\[
\begin{align*}
  r h_{ij}(r) &= -q'_{ij}(r) + 2\pi \sum_{k=1}^{m} \rho_{k} \int_{0}^{r} q_{ik}(t)(r - t) h_{kj}(|r - t|) \, dt, \\
  r c_{ij}(r) &= -q_{ij}(r) + 2\pi \sum_{k=1}^{m} \rho_{k} \int_{0}^{r} q_{ki}(t) q_{jk}(r + t) \, dt.
\end{align*}
\]  

(2.4)

We choose $\rho_{1} = \rho_{2} = \rho_{V}$, the density of solute atoms, and $\rho_{3} = \rho_{V}$, the solvent density. From symmetry considerations, it follows that $h_{13}(r) = h_{23}(r)$ and $h_{11}(r) = h_{22}(r)$; analogous relations hold for the direct correlation functions. As a consequence of these identities, we find that $q_{11}(r) = q_{22}(r)$, $q_{12}(r) = q_{21}(r)$, $q_{13}(r) = q_{23}(r)$ and $q_{31}(r) = q_{32}(r)$. The second of these relations is in some sense the least trivial, since in general $q_{ij}(r)$ does not equal $q_{ji}(r)$ (unlike the corresponding, usual symmetry in the total and direct correlation functions); it follows in this case since species 1 and 2 atoms are at the same density and have equal diameters.

Taking the above symmetries into consideration, we find that equation (2.4a) yields five distinct equations,

\[
\begin{align*}
  r h_{11}(r) &= -q'_{11}(r) + 2\pi \rho_{V} [q_{11} \otimes h_{11}(r) + q_{12} \otimes h_{12}(r)] + 2\pi \rho_{V} q_{13} \otimes h_{13}(r), \\
  r h_{12}(r) &= -q'_{12}(r) + 2\pi \rho_{V} [q_{11} \otimes h_{12}(r) + q_{13} \otimes h_{11}(r)] + 2\pi \rho_{V} q_{13} \otimes h_{13}(r), \\
  r h_{13}(r) &= -q'_{13}(r) + 2\pi \rho_{V} [q_{11} \otimes h_{13}(r) + q_{12} \otimes h_{11}(r)] + 2\pi \rho_{V} q_{13} \otimes h_{13}(r), \\
  r h_{31}(r) &= -q'_{31}(r) + 2\pi \rho_{V} [q_{31} \otimes h_{11}(r) + q_{32} \otimes h_{12}(r)] + 2\pi \rho_{V} q_{33} \otimes h_{13}(r), \\
  r h_{33}(r) &= -q'_{33}(r) + 4\pi \rho_{V} q_{31} \otimes h_{13}(r) + 2\pi \rho_{V} q_{33} \otimes h_{13}(r),
\end{align*}
\]  

(2.5)

where $f \otimes g(r)$ symbolizes the convolution

\[
f \otimes g(r) = \int_{0}^{r} f(t) g(|r - t|) \, dt.
\]

As in the previous two papers in this series \cite{1, 2}, our task is to determine the functional form of the Baxter $q$-functions $q_{ij}(r)$, relate the parameter $\lambda$ to the temperature $\tau$ and the densities $\rho_{U}$ and $\rho_{V}$, derive an expression for the association constant and to provide an algorithm for computing the radial distribution functions $g_{ij}(r) = 1 + h_{ij}(r)$. The results in this section are given in explicit form for $L = \sigma/2$; the corresponding results for $L = \sigma/3$ are easily derived by applying the steps for $L = \sigma/2$ outlined in this section to the corresponding analysis for $L = \sigma/3$ given in I.
2.1. The Baxter q-functions

We begin by considering the functions $q_{ij}(r)$, $j = 1, 2, 3$. Substituting the closures (2.3 a) and (2.3 b) into equations (2.5 a)-(2.5 c), we obtain the following differential-difference equations:

$$q'_{12}(r) + p[q_{12}(r + L) - q_{12}(r - L)] = a_1 r + b_1,$$

$$q'_{13}(r) = a_1 r + b_1,$$

where

$$p = \frac{\pi \rho_U \lambda L^2}{6}, \quad v = p \sigma = \eta_U \lambda (L/\sigma)^2; \quad \eta_i = \frac{\pi}{6} \rho_i \sigma^3; \quad i = U, V,$$

$$a_1 = 1 - 2\pi \rho_U \int_0^\sigma \left[q_{11}(t) + q_{12}(t)\right] dt - 2\pi \rho_V \int_0^\sigma q_{13}(t) dt,$$

$$b_1 = 2\pi \rho_U \int_0^\sigma t[q_{11}(t) + q_{12}(t)] dt + 2\pi \rho_V \int_0^\sigma t q_{13}(t) dt.$$

The boundary and discontinuity conditions on the functions $q_{ij}(r)$ are

$$q_{11}(a) = q_{12}(a) = q_{13}(0) = 0, \quad q_{12}(0) = q_{12}(L^+) = q_{12}(L^-) + \frac{\lambda L^2}{12}.$$

From equations (2.8) and (2.11), the functional form of $q_{13}(r)$ is given by

$$q_{13}(r) = \begin{cases} a_1 (r - \sigma)^2 + b_1 (r - \sigma), & r < \sigma, \\ 0, & r \geq \sigma. \end{cases}$$

To determine $q_{11}(r)$ and $q_{12}(r)$, a method similar to that used in I must be employed. Thus, we define the functions

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

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

so that

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

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

The functions $q_+(r)$ and $q_-(r)$ then satisfy the equations

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

$$q'_-(r) - p[q_-(r + L) - q_-(r - L)] - \frac{\lambda L^2}{12} \delta(r - L) = 0,$$

with

$$a_+ = 2a_1 = 2 - 4\pi \rho_U \int_0^\sigma q_+(t) dt - 4\pi \rho_V \int_0^\sigma q_{13}(t) dt,$$

$$b_+ = 2b_1 = 4\pi \rho_U \int_0^\sigma t q_+(t) dt + 4\pi \rho_V \int_0^\sigma t q_{13}(t) dt.$$
The boundary and discontinuity conditions on \( q_+(r) \) and \( q_-(r) \) are given by

\[
q_+(\sigma) = 0, \quad q_+(L^-) = q_+(L^+) + \frac{\lambda L^2}{12}, \quad (2.17 \text{a})
\]

\[
q_-(\sigma) = 0, \quad q_-(L^-) = q_-(L^+) - \frac{\lambda L^2}{12}. \quad (2.17 \text{b})
\]

We now solve equations (2.15) specifically for \( L = \sigma/2 \); for the reasons noted earlier in this section, explicit results for \( L = \sigma/3 \) will not be given in this paper.

The solution of equation (2.15a) is obtained using the methods of I, and we simply quote the result here:

\[
q_+(r) = -\frac{a_+}{p} r + \frac{b_+}{p^2} \left(1 - \frac{v}{2}\right) - \frac{1}{2}\left[1 - \frac{v}{2}\right] + A_+ \cos (pr) + B_+ \sin (pr), \quad 0 < r < \frac{\sigma}{2}
\]

\[
= \frac{a_+}{p} r + \frac{b_+}{p^2} \left(1 - \frac{v}{2}\right) + A_+ \cos \left[p(r - \sigma/2)\right] - B_+ \sin \left[p(r - \sigma/2)\right], \quad \frac{\sigma}{2} < r < \sigma. \quad (2.18)
\]

Equation (2.18), when combined with equations (2.16) and (2.17a), yields the following linear equations for the parameters \( a_+, b_+, A_+ \) and \( B_+ \):

\[
\frac{1}{2} \left[ 1 + \frac{24\eta v(1 - v/4)}{v^2} - 4\eta v \right] - 6\eta v b'_+ + \frac{24\eta v}{v} \\
\times [(1 - c + s)A'_+ + (1 - c - s)B'_+] = 2, \quad (2.21)
\]

\[
a_+ \left[ \frac{24\eta v}{v^2} + \frac{3\eta v}{2} \right] + b'_+ \left[ 1 - \frac{6\eta v}{v} + 2\eta v \right] \\
- \frac{24\eta v}{v^2} \left[ -1 + \frac{v}{2} + (1 - v)c + \left(1 + \frac{v}{2}\right)s \right] A'_+ \\
- \frac{24\eta v}{v^2} \left[ 1 + \left(1 - \frac{v}{2}\right)c + (1 - v)s \right] B'_+ = 0, \quad (2.22)
\]

where

\[
b'_+ = \frac{b_+}{\sigma}, \quad A'_+ = \frac{A_+}{\sigma^2}, \quad B'_+ = \frac{B_+}{\sigma^2}, \quad (2.23)
\]

\[
s = \sin \left(\frac{v}{2}\right), \quad c = \cos \left(\frac{v}{2}\right). \quad (2.24)
\]
Equations (2.19)–(2.22) can be written in the form

\[
\begin{bmatrix}
  a_+ \\ b_+ \\ A'_+ \\ B'_+
\end{bmatrix} =
\begin{bmatrix}
  -\lambda/48 \\ 0 \\ 2 \\ 0
\end{bmatrix},
\] (2.25)

where the elements of the matrix \( \mathbf{M} \) are defined obviously. The solution of equation (2.25) is given by

\[
a_+ = \frac{1}{\Delta} \left( -\lambda \cdot T_{11} + 2T_{31} \right), \quad (2.26a)
\]
\[
b_+ = \frac{1}{\Delta} \left( -\lambda \cdot T_{12} + 2T_{32} \right), \quad (2.26b)
\]
\[
A'_+ = \frac{1}{\Delta} \left( -\lambda \cdot T_{13} + 2T_{33} \right), \quad (2.26c)
\]
\[
B'_+ = \frac{1}{\Delta} \left( -\lambda \cdot T_{14} + 2T_{34} \right). \quad (2.26d)
\]

Here, \( \Delta \) is the determinant and \( T_{ij} \) the \( ij \) cofactor of \( \mathbf{M} \) given by

\[
\Delta = \Delta^0 + \frac{12\eta_u \eta_v}{v^3} \left[ 8 - 4v + v^2 - 8c + (8 - 4v + v^2)s \right] + (\eta_v^2 - 2\eta_v)(1 + s),
\] (2.27)

\[
T_{11} = T_{11}^0 + \frac{24\eta_u \eta_v}{v^2} \left[ 4v - 6 + (6 - v)c + (-6 + 2v)s \right], \quad (2.28a)
\]
\[
T_{12} = T_{12}^0 + \frac{12\eta_u \eta_v}{v^2} \left[ 8 - 5v + (-8 + v)c + (8 - 3v)s \right], \quad (2.28b)
\]
\[
T_{13} = T_{13}^0 + \frac{12\eta_u \eta_v}{v^4} \left[ 12 - 6v + v^2 + (-12 + 2v - v^2)c 
\right.
\]
\[
\left. + (12 - 10v + v^2)s \right] + (\eta_v^2 - 2\eta_v)(1 + s) \quad (2.28c)
\]
\[
T_{14} = T_{14}^0 + \frac{12\eta_u \eta_v}{v^4} \left[ 12 - 4v + (-12 + 10v - v^2)c 
\right.
\]
\[
\left. + (12 + 2v - v^2)s \right] + (\eta_v^2 - 2\eta_v)(1 + s), \quad (2.28d)
\]
\[
T_{31} = T_{31}^0 + 2\eta_v(1 + s), \quad (2.29a)
\]
\[
T_{32} = T_{32}^0 + 2\eta_v(1 + s), \quad (2.29b)
\]
\[
T_{33} = T_{33}^0 + \frac{\eta_v}{2v^2} \left[ 4 - v - 2vc + (v - 4)s \right] \quad (2.29c)
\]
\[
T_{34} = T_{34}^0 + \frac{\eta_v}{2v^2} \left[ (4 - v)c - 2vs \right]. \quad (2.29d)
\]

The superscript ‘0’ in equations (2.27)–(2.29) is used to denote the value of the corresponding parameter in the limit \( \eta_v \to 0 \), and so \( \Delta^0 \) and the \( T_{ij}^0 \) are given by equations (I.A 1)–(I.A 9) with \( f = 2 \) and \( \eta = \eta_v \) (or, equivalently, \( \zeta = 2\eta_v \)).
This completes the solution of \( q_+ (r) \); we now consider \( q_- (r) \). The solution is straight-forward and we simply quote the result

\[
q_- (r) = A_- \cos (pr) + B_- \sin (pr), \quad 0 < r < \frac{\sigma}{2},
\]

\[
= A_- \cos \left[ p(r - \sigma/2) \right] - B_- \sin \left[ p(r - \sigma/2) \right], \quad \frac{\sigma}{2} < r < \sigma,
\]  \tag{2.30}

where

\[
A_- = \frac{A_-}{\sigma^2} = \frac{-\lambda c}{48(1 - s)}, \tag{2.31 a}
\]

\[
B_- = \frac{B_-}{\sigma^2} = \frac{-\lambda s}{48(1 - s)}. \tag{2.31 b}
\]

Combining equations (2.18) and (2.30) with (2.14), we obtain the final expressions for \( q_{1j} (r) \) and \( q_{2j} (r) \),

\[q_{11} (r) = -\frac{a_1}{p} r + \frac{a_1}{p^2} (1 - v/2) - \frac{b_1}{p} + A_S \cos (pr) + B_D \sin (pr), \quad 0 < r < \frac{\sigma}{2},\]

\[
= \frac{a_1}{p} r + \frac{a_1}{p^2} (1 - v/2) + \frac{b_1}{p} + A_D \cos \left[ p(r - \sigma/2) \right] - B_S \sin \left[ p(r - \sigma/2) \right], \quad \frac{\sigma}{2} < r < \sigma, \tag{2.32 a}
\]

\[q_{12} (r) = -\frac{a_1}{p} r + \frac{a_1}{p^2} (1 - v/2) - \frac{b_1}{p} + A_D \cos (pr) + B_S \sin (pr), \quad 0 < r < \frac{\sigma}{2},\]

\[
= \frac{a_1}{p} r + \frac{a_1}{p^2} (1 - v/2) + \frac{b_1}{p} + A_S \cos \left[ p(r - \sigma/2) \right] - B_D \sin \left[ p(r - \sigma/2) \right], \quad \frac{\sigma}{2} < r < \sigma. \tag{2.32 b}
\]

In equations (2.32),

\[
a_1 = a_+ /2, \quad b_1 = b_+ /2,
\]

\[
A_S = (A_+ + A_-)/2, \quad A_D = (A_+ - A_-)/2,
\]

\[
B_S = (B_+ + B_-)/2, \quad B_D = (B_+ - B_-)/2.
\]

The dimensionless primed quantities \( b'_1, A'_S, A'_D, B'_S \) and \( B'_D \) are defined in the usual way (cf. equations (2.23) and (2.31)). This completes the analysis for \( q_{1j} (r) \), \( j = 1, 2, 3 \). We now turn our attention to the functions \( q_{3j} (r) \), \( j = 1, 3 \). Substituting the closures (2.3) into equations (2.5 d) and (2.5 e), we find

\[
q'_{31} (r) + p[q_{31} (r + L) - q_{31} (r - L)] = a_3 r + b_3, \tag{2.33}
\]
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\[ q_{33}(r) = a_3 r + b_3, \]  
\[ a_3 = 1 - 4\pi \rho v \int_0^\sigma q_{31}(t) dt - 2\pi \rho v \int_0^\sigma q_{33}(t) dt, \tag{2.35 a} \]
\[ b_3 = 4\pi \rho v \int_0^\sigma t q_{31}(t) dt + 2\pi \rho v \int_0^\sigma t q_{33}(t) dt. \tag{2.35 b} \]

The boundary conditions on the functions \( q_{3j}(r) \) are
\[ q_{31}(0^-) = q_{33}(0^-) = 0 \tag{2.36} \]
and we observe that \( q_{31}(r) \) is continuous at \( r = L \). The solution of equation (2.34) is immediate and is given by
\[ q_{33}(r) = \frac{1}{2} a_3 (r - \sigma)^2 + b_3 (r - \sigma), \quad r < \sigma, \]
\[ = 0, \quad r \geq \sigma. \tag{2.37} \]

The solution of equation (2.33) is straightforward, yielding
\[ q_{31}(r) = -\frac{a_3}{p} r + \frac{a_3}{p^2} (1 - \nu/2) + \frac{b_3}{p} + A_3 \cos (pr) + B_3 \sin (pr), \]
\[ 0 < r < \frac{\sigma}{2}, \]
\[ = \frac{a_3}{p} r + \frac{a_3}{p^2} (1 - \nu/2) - \frac{b_3}{p} + A_3 \cos \left[p(r - \sigma/2)\right] - B_3 \sin \left[p(r - \sigma/2)\right], \quad \frac{\sigma}{2} < r < \sigma. \tag{2.38} \]

Equations (2.35) and (2.36) and continuity of \( q_{13}(r) \) at \( r = L \) result in four linear equations for the parameters \( a_3, b_3, A_3 \) and \( B_3 \) which can be written in the form
\[ \mathbf{M} \begin{bmatrix} a_3 \\ b'_3 \\ A'_3 \\ B'_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}, \tag{2.39} \]
where
\[ b'_3 = \frac{b_3}{\sigma}, \quad A'_3 = \frac{A_3}{\sigma^2}, \quad B'_3 = \frac{B_3}{\sigma^2} \tag{2.40} \]
and where \( \mathbf{M} \) is the same matrix as that appearing in equation (2.25). Consequently, the expressions for the determinant and cofactors given in equations (2.27) and (2.29) are applicable to the present equation as well. Thus, we find that
\[ a_3 = \frac{T_{31}}{\Delta}, \tag{2.41 a} \]
\[ b'_3 = \frac{T_{32}}{\Delta}, \tag{2.41 b} \]
\[ A'_3 = \frac{T_{33}}{\Delta}, \tag{2.41 c} \]
where $T_{3i}, i = 1, 2, 3, 4$, are given by equations (2.29). This completes the derivation of the functional forms for the Baxter $q$-functions for $L = \sigma/2$.

### 2.2. Determination of the parameter $\lambda$

The next step in the analytic solution is to relate $\lambda$ to the temperature $\tau$ and the densities $\eta_U$ and $\eta_V$ via the PY approximation. As in I, we can show that

$$y_{12}(r) = 1 + h_{12}(r) - c_{12}(r)$$

is continuous at $r = L$, so that the PY approximation, equation (2.2), yields

$$\lambda \tau = y_{12}(L). \tag{2.42}$$

After some tedious but straightforward algebra, for $L = \sigma/2$ this equation becomes

$$\lambda \tau = \frac{2a_1}{\nu} + 2\nu A_s - F_1 - F_3, \tag{2.43}$$

where $F_1$ and $F_3$ are given by

$$F_1 = 24\eta_U\left[\frac{a_2}{\nu^3} - \frac{3a_3}{4\nu^2} - \frac{a_1b'_1}{\nu^2} - \frac{b'_1}{\nu}(A'_s + A'_d)s - \frac{b'_1}{\nu}(B'_s + B'_d)(1 - c)\right]$$

$$+ \frac{a_1}{\nu^2}(A'_s + A'_d)(1 - c + 2s - vs)$$

$$+ \frac{a_1}{\nu^2}(B'_s + B'_d)(2 - 2c - s + vs - \nu/2)$$

$$+ \frac{A'^2_s + A'^2_d}{4}(v + \sin \nu) + \frac{A'^2_s B^2_s + A'^2_d B^2_d}{2}(1 - \cos \nu)$$

$$+ \frac{B'^2_s + B'^2_d}{4}(v - \sin \nu) \right], \tag{2.44a}$$

$$F_3 = 24\eta_V\left[\frac{a_2}{2\nu^3} - \frac{3a_3}{8\nu^2} - \frac{a_3b'_3}{2\nu^2} - \frac{b'_3}{\nu}A'_3s - \frac{b'_3}{\nu}B'_3(1 - c)\right]$$

$$+ \frac{a_3}{\nu^2}A'_3(1 - c + 2s - vs) + \frac{a_3}{\nu^2}B'_3(2 - 2c - s + vs - \nu/2)$$

$$+ \frac{A'^2_3}{4}(v + \sin \nu) + \frac{A'^2_3 B'^2_s}{2}(1 - \cos \nu) + \frac{B'^2_3}{4}(v - \sin \nu) \right]. \tag{2.44b}$$

Equation (2.43) combined with equations (2.44) constitutes a single non-linear equation for the parameter $\lambda$ which can easily be solved using standard techniques.
2.3. Expression for the association constant

The association constant for the reaction (1.1) is given by

\[ k = \frac{P_{AB}}{\rho_A \rho_B}. \]  

(2.45)

Formally, the expressions given in I for the dimensionless association constant \( K = k/\sigma^3 \) and for the expected number \( \langle N \rangle \) of \( B(A) \) atoms distant \( L \) from a given \( A(B) \) atom remain valid and are quoted without further comment.

\[ \langle N \rangle = 2\eta_v \lambda (L/\sigma)^3, \]  

(2.46)

\[ K = \frac{\pi \lambda (L/\sigma)^3}{3[1 - \langle N \rangle]^2}. \]  

(2.47)

2.4. Calculation of the radial distribution functions

The method used to compute the radial distribution functions \( q_{11}(r) \), \( g_{12}(r) \), \( g_{13}(r) \) and \( g_{33}(r) \) is an extension of Perram’s method [1, 2, 11] for hard sphere mixtures with suitable modification for the presence of the delta function in \( g_{13}(r) \) at \( r = L \). This modification for the \( AB \) binary mixture was described in detail in I and its generalization to the present ternary mixture is straightforward; consequently, the explicit form of the algorithm will not be given, and the reader is referred to I for further details.

2.5. The limit of vanishing solute density

We now consider the important limit of vanishing solute density \( \rho_v \to 0 \) where the reacting species (\( A \) and \( B \)) are present at infinite dilution in the hard sphere solvent. (Of course, the other limit of vanishing solvent density, \( \rho_v \to 0 \), corresponds to the model described in I.) In principle, one could simply take the limit \( \rho_v \to 0 \) in equations derived in §§ 2.1 through 2.3 above; however, the limit is very difficult to evaluate directly since the parameter \( v \to 0 \) as \( \rho_v \to 0 \). Rather, it is much easier to return to the starting equations (2.5), perform the limit at this point in the analysis and derive the Baxter \( q \)-functions from there. This is the approach we now take.

For \( \rho_v \to 0 \), equations (2.5) become

\[ rh_{11}(r) = -q'_{11}(r) + 2\pi \rho_v q_{13} \otimes h_{13}(r), \]  

(2.48a)

\[ rh_{12}(r) = -q'_{12}(r) + 2\pi \rho_v q_{13} \otimes h_{13}(r), \]  

(2.48b)

\[ rh_{13}(r) = -q'_{13}(r) + 2\pi \rho_v q_{13} \otimes h_{33}(r), \]  

(2.48c)

\[ rh_{31}(r) = -q'_{31}(r) + 2\pi \rho_v q_{33} \otimes h_{13}(r), \]  

(2.48d)

\[ rh_{33}(r) = -q'_{33}(r) + 2\pi \rho_v q_{33} \otimes q_{33}(r). \]  

(2.48e)
Substituting the closure (2.3) into equations (2.48), we obtain

\[ q'_{11}(r) = a_1 r + b_1 \]  
\[ q'_{12}(r) + \frac{\lambda L^2}{12} \delta(r - L) = a_1 r + b_1, \]  
\[ q'_{13}(r) = a_1 r + b_1, \]  
\[ q'_{31}(r) = a_3 r + b_3, \]  
\[ q'_{33}(r) = a_3 r + b_3, \]

where

\[ a_1 = 1 - 2\pi \rho_v \int_0^\sigma q_{13}(t) \, dt, \]  
\[ b_1 = 2\pi \rho_v \int_0^\sigma t q_{13}(t) \, dt, \]  
\[ a_3 = 1 - 2\pi \rho_v \int_0^\sigma q_{33}(t) \, dt, \]  
\[ b_1 = 2\pi \rho_v \int_0^\sigma t q_{33}(t) \, dt. \]

It is not difficult to see that the \( q \)-functions have the form

\[ q_{12}(r) = \frac{1}{2} a(r - \sigma)^2 + b(r - \sigma) - \frac{\lambda L^2}{12} \theta(r - L), \quad r < \sigma, \]  
\[ = 0, \quad r \geq \sigma, \]  
\[ q_{11}(r) = q_{13}(r) = q_{31}(r) = q_{33}(r), \]  
\[ = \frac{1}{2} a(r - \sigma)^2 + b(r - \sigma), \quad r < \sigma, \]  
\[ = 0, \quad r \geq \sigma, \]

where

\[ a = \frac{1 + 2\eta_v}{(1 - \eta_v)^2}, \quad b = \frac{-3\eta_v}{2(1 - \eta_v)^2} \]

and \( \theta(x) \) is the Heaviside step function given by

\[ \theta(x) = 0, \quad x < 0, \]  
\[ = 1, \quad x \geq 0. \]

The parameters \( a \) and \( b \) are simply the coefficients which appear in the Baxter \( q \)-function in the analytic solution of the PY approximation for the hard sphere fluid with density \( \eta_v \). This is not surprising, since in the limit of infinite dilution of the reacting species, the fluid is simply a hard sphere fluid with density \( \eta_v \). Consequently, all of the Baxter \( q \)-functions are equal to the hard sphere Baxter \( q \)-function except for \( q_{12}(r) \) whose derivative contains a delta function. This observation leads to the conclusion that the correlation functions \( h_{11}(r), h_{13}(r) \)
and $h_{33}(r)$ are simply hard sphere correlation functions at density $\eta_V$ (denoted $h_{HS}(\rho_V; r)$) while $h_{12}(r)$ is given by

$$rh_{12}(r) = rh_{HS}(\rho_V; r) + \frac{\lambda L^2}{12} \delta(r - L).$$  \hspace{1cm} (2.53\ a)

A similar result holds for $c_{12}(r)$

$$rc_{12}(r) = rc_{HS}(\rho_V; r) + \frac{\lambda L^2}{12} \delta(r - L).$$  \hspace{1cm} (2.53\ b)

In view of equations (2.53), we find that $y_{12}(r)$ is very simple in the infinite dilution limit, so that $\lambda$ is given in this limit by

$$\lambda \tau = y_{HS}(\rho_V; r = L).$$  \hspace{1cm} (2.54)

More explicitly,

$$\lambda = \frac{1}{\tau} y_{HS}(\rho_V; r = L).$$  \hspace{1cm} (2.55)

This equation is valuable numerically since for a given $\rho_V$, it yields and starting value for $\lambda$ so that $\lambda$ can be solved for numerically starting at $\rho_V = 0$ and incrementing $\rho_V$ in small steps to the desired value. It is also valuable in another context: it yields the expression for the association constant $K$ at infinite dilution in the hard sphere solvent. But first we evaluate $K$ in the double limit $\rho_U \to 0, \rho_V \to 0$ which would correspond to the dilute gas association constant for reaction (1.1) in the absence of a solvent. From equation (2.47) and the fact that in this double limit $\lambda \to \frac{1}{\tau}$, we obtain

$$K_0 = K(\rho_U = 0, \rho_V = 0) = \frac{\pi}{3\tau} (L/\sigma)^3.$$  \hspace{1cm} (2.56)

In the limit $\rho_U \to 0$ with $\rho_V$ non-zero, equation (2.55) combined with equation (2.47) yields

$$K^\infty(\rho_V) \equiv K(\rho_U = 0, \rho_V) = \frac{\pi}{3\tau} (L/\sigma)^3 y_{HS}(\rho_V; r = L).$$  \hspace{1cm} (2.57)

Equations (2.56) and (2.57) together give the result

$$\frac{K^\infty(\rho_V)}{K_0} = \frac{K(\rho_U = 0, \rho_V)}{K_0} = y_{HS}(\rho_V; r = L).$$  \hspace{1cm} (2.58)

This equation, which we have obtained in the context of the PY approximation, is in fact exact for our model. This follows from the use of a relation derived by one of us [12] some time ago that holds in the limit $\rho_V \to 0$ limit for all models in which the solute–solute and solute–solvent pair potentials are equal. In both the association reactions (1.1) and (1.2) considered in this paper, this condition is satisfied. In our notation, Stell’s relation, equation (2.2) of [12] is

$$g_{ij}(r) = \exp (-\phi_{ij}(r)/k_B T) y_{CC}(r), \quad ij = AA, AB, BB.$$  \hspace{1cm} (2.59)

Using this in our definition of $K$, given by (1.1.12), immediately yields equation (2.58). The same result was also derived by Chandler and Pratt [5] from their formal theory of chemical reaction equilibria on the basis of a series of approximations. Chandler and Pratt argued that since $y_{HS}(\rho_V; r = L)$ is of the order $10^2$
at liquid state densities, this explained the order of magnitude of the shift in the
association constant characterizing the dissociation equilibrium of nitrogen
dioxide and dinitrogen tetroxide described in the §1 above.

3. RESULTS FOR THE CHEMICAL EQUILIBRIUM $A + B \rightleftharpoons AB$
IN SOLUTION

In this section, we report results for the hard sphere solvent effects on the
chemical equilibrium $A + B \rightleftharpoons AB$ for the case $L = \sigma/2$. The results obtained for
$L = \sigma/3$ do not differ qualitatively from those reported here.

As shown in §2.2, to obtain results for the model defined by the set of inter-
actions (1.5) for given state parameters $\rho_u$, $\rho_v$ and $\tau$ it is necessary to solve the
single non-linear equation (2.43) for the single unknown parameter $\lambda$. In §2.5, it
was shown that $\lambda$ has a particularly simple form in the limit $\rho_v \to 0$ for arbitrary
$\rho_v$. Thus, numerically it is convenient to start at the point $(\rho_u, \rho_v) = (0, \rho_v)$ and
increment $\rho_u$ in small steps to the desired value by solving (2.43) at each point
using a standard numerical technique (such as false position or bisection).

One particularly revealing way of presenting results on the solvent effect is to
consider mixtures at constant temperature ($\tau$) and at constant dimensionless total
density $\rho^* = (\rho_A + \rho_B + \rho_C)\sigma^3$. The mole fraction of solute in the solution is then
given by

$$x_{\text{solute}} = \frac{\rho_A + \rho_B}{\rho_A + \rho_B + \rho_C}$$  \hspace{1cm} (3.1)

and the solvent mole fraction by

$$x_{\text{solvent}} = \frac{\rho_C}{\rho_A + \rho_B + \rho_C}. \hspace{1cm} (3.2)$$

(Note that $x_{\text{solute}}$ is the mole fraction of all $A$ and $B$ monomers and counts both $A$
and $B$ free monomers and the monomers bound together into $AB$ dimers.) For
$x_{\text{solvent}} \to 1$, we have a solution in which the reacting species are present at infinite
dilution, while in the opposite limit ($x_{\text{solvent}} \to 0$) we recover the model described
in I.

We begin by considering $\langle N \rangle$, the expected number of $B$ atoms bound to a
given $A$ atom and defined in equation (2.46). In figure 1, $\langle N \rangle$ is shown as a
function of solvent mole fraction at temperature $\tau$ of 0.01 and at five fixed total
densities $\eta$, where $\eta = (\pi/6)\rho^*$. At the lowest density ($\eta = 0.1$), which corresponds
to a fairly dense gas state (since in these reduced units $\eta \approx 0.15$ would represent a
typical critical density for systems exhibiting liquid–vapour coexistence), the
complete association line ($\langle N \rangle = 1$) is not reached either in the pure reacting
species case $x_{\text{solvent}} = 0$ or in solution. Clearly, at fixed temperature, $\langle N \rangle$ is a
monotonic decreasing function of $x_{\text{solvent}}$ since as reacting solute molecules are
replaced by solvent molecules the degree of binding into pairs which can take
place is increasingly limited.

In figure 2, we consider $K/K_0$, where $K_0$, discussed in §2.5 above, is the
value which $K$ would have in the ideal gas state in the absence of a solvent (i.e.
$K_0$ equals $K$ in the dual limit $\rho_u \to 0$, $\rho_v \to 0$). The temperature is again fixed at
$\tau = 0.01$ and there are five representative values of $\eta$ spanning the range from
moderately dense gas ($\eta = 0.1$) to very dense liquid ($\eta = 0.5$).
Figure 1. The expected number $\langle N \rangle$ of species $B$ atoms distant $L = \sigma/2$ away from a species $A$ atom for the reaction (1.1) in a hard sphere solvent at temperature $\tau = 0.01$ and at total reduced densities $\eta = 0.1, 0.2, \ldots, 0.5$. The expected number is shown as a function of the mole fraction of solvent in the mixture defined by equation (3.2).

The experimental results shown in the table in §1 would correspond, in this model, to the regime $x_{\text{solvent}} \approx 1$, i.e. the regime in which the reactants are present at near infinite dilution in the hard sphere solvent. Moreover, the solvents in this

Figure 2. The ratio of the equilibrium ratio $K$ to its ideal gas value $K_0$ for the reaction (1.1) in a hard sphere solvent at temperature $\tau = 0.01$ and at total reduced densities $\eta = 0.1, 0.2, \ldots, 0.5$ for atoms capable of binding at $L = \sigma/2$. The ratio $K/K_0$ is shown as a function of the mole fraction of solvent in the mixture defined by equation (3.2).
table are in the liquid state so that $\eta \simeq 0.4 - 0.5$. We see then that our model exhibits very strong solvent effects in this regime, with $K$ shifted dramatically from its ideal gas value and by an amount which is of the order of magnitude of the experimental results. We observe that figure 2 is consistent with our intuition, namely that for a given total density, $K$ is larger (and the extent of reaction greater) when there is more reactant present (or, in other words, $x_{\text{solvent}}$ is lower). For industrial processes in which the extents of reaction are dominated by steric effects (as in the model here) it is clear that to optimize yield from a chemical reaction concentrating the reactants is a more effective strategy than performing the reaction in solution. (This conclusion assumes, of course, that as in our model that the pure solvent and pure reacting solute are in the same condensed phase at the specified temperature and density. In practice, one is much more likely to be confronted with a specified temperature and pressure—such as ambient temperature and pressure—at which the reaction is to be performed and at which the reactants are gaseous and the solvent liquid. This is the case for the chosen example of dinitrogen tetroxide equilibrium. Clearly, in these circumstances, the constant $\tau$ and $\eta$ lines in figure 2 would represent pressure changes of many orders of magnitude so that the strategy of concentrating reactants described above becomes impractical.)

Perhaps the most interesting curve in figure 2 is the moderate density ($\eta = 0.1$) curve which suggests that the effect of solvent and presence of reactants are nearly compensating. That is, the value of $K$ obtained when only reactants are present ($x_{\text{solvent}} = 0$) is much the same as the value obtained at infinite dilution.

In figure 3, we show the ratio $K/K_0$ as a function of the solvent density for six values of solute density (varying from 0 to 0.5). At each solute density as the solvent density is increased the value of $K/K_0$ increases, the rapidity with which this occurs being dependent on the density of the reacting solute. For each solute density, except $\eta_v = 0$ corresponding to infinitely dilute reactants, there is a solvent density at which the complete association limit is reached. At any given solute density, the equilibrium ratio $K$ can be varied over several orders of magnitude with small changes of density. This suggests that one might be able to control reaction equilibria (and thus reaction rates) by varying solvent density just as one can control solubility over a wide range in a supercritical solvent through solvent density changes, the basis of supercritical extraction techniques [13]. It is therefore not surprising there have been recent suggestions that supercritical fluid solvents might be used to control reaction rates in industrially important organic synthesis reactions [14].

We now focus attention on the structure of the fluid mixture undergoing chemical reaction. We begin by looking at results for the low total density ($\eta = 0.1$) for three solvent mole fractions: $x_{\text{solvent}} = 0.0, 0.4$ and 0.8. (For $x_{\text{solvent}} = 1.0$, all the radial distribution functions are equal for $r > \sigma$ as is clear from §2.5.) In figure 4, we portray the radial distribution functions $g_{11}(r) = g_{AA}(r) = g_{BB}(r)$, $g_{12}(r) = g_{AB}(r)$, $g_{13}(r) = g_{AC}(r) = g_{BC}(r)$ and $g_{33}(r) = g_{CC}(r)$ for $\tau = 0.01$, $\eta = 0.1$ and $x_{\text{solvent}} = 0.0$. Thus, the $g_{11}(r)$ and $g_{12}(r)$ are the same as those which would be obtained in the absence of a solvent and are similar to those described in 1; i.e. there is a cusp at $r = \sigma + L = 3\sigma/2$ and $g_{12}(\sigma)$ is less than $g_{11}(\sigma)$ indicating a lower population of unlike species pairs at contact. (Note that only the intermolecular part of $g_{ij}(r)$ is shown; the delta functions in $g_{12}(r)$ and $g_{13}(r)$ at $r = L = \sigma/2$ have not been shown.) The solvent species, species 3, which is present in this mixture
at infinite dilution, exhibits considerable short range order. Compared to a one component hard sphere fluid at volume fraction \( \eta = 0.1 \) (equal to the total density of the reacting fluid mixture considered here), the solvent molecules are shifted preferentially to shorter separations, perhaps indicating a tendency for solvent molecules to want to aggregate into a 'solvent rich' phase. (Of course, no phase separation takes place but the point being made here is that the steric interactions considered in this model might conceivably contribute to phase separation in a system with more realistic interactions.) At \( x_{\text{solvent}} = 0.4 \), shown in figure 5, we see that \( g_{12}(r) \) has not increased perceptibly, but that \( g_{11}(r) = g_{22}(r) \) has increased (which is to be expected since the number of species 1 and 2 atoms has increased). The solvent is still more structured at short range than a hard sphere fluid but is less so than at \( x_{\text{solvent}} = 0.0 \). Figure 6 shows \( x_{\text{solvent}} = 0.8 \). The most prominent feature in this figure is the beginning of the approach of each of the correlation functions to the single hard sphere correlation function, a structural reflection of the fact that at infinite dilution \( (x_{\text{solvent}} = 1) \) no dimers are present and a solute molecule cannot distinguish between another solute molecule and a solvent molecule. This structural feature is seen clearly in figure 7 which shows a reasonably high total density state \( (\eta = 0.3, \tau = 0.01) \) with \( x_{\text{solvent}} = 0.993 \). In this figure it is clear that all the correlation functions are close to the pure hard sphere fluid at volume fraction 0.3.

In contrast, figure 8 shows the structure at the same density but at \( x_{\text{solvent}} = 0.699 \), very close to the solvent mole fraction at which total association \( \langle N \rangle = 1 \) takes place. As in the lower density case, the solvent structure exhibits stronger short range order than the corresponding hard sphere fluid.

At higher density near \( \langle N \rangle = 1 \), as in figure 9, we see some similarities between the correlation functions: the solvent–solvent correlation is close to the
Figure 4. The radial distribution functions $g_{12}(r)$ (---), $g_{11}(r) = g_{22}(r)$ (----), $g_{13}(r) = g_{23}(r)$ (· · · ·), $g_{33}(r)$ (—)— and $g_{RS}(r)$ (——) for the reaction (1.1) in a hard sphere solvent at temperature $\tau = 0.01$, total reduced density $\eta = 0.1$ and $x_{\text{solv}} = 0.0$ for atoms capable of binding at $L = \sigma/2$. The solid and dashed curves with the lower contact values are $g_{12}(r)$ and $g_{RS}(r)$ respectively. The hard sphere radial distribution function is calculated at reduced density $\eta$. Note that components 1, 2 and 3 correspond to species $A$, $B$ and $C$.

Figure 5. The radial distribution functions $g_{ij}(r)$ for the reaction (1.1) in a hard sphere solvent at temperature $\tau = 0.01$, total reduced density $\eta = 0.1$ and $x_{\text{solv}} = 0.4$ for atoms capable of binding at $L = \sigma/2$. The legend is the same as for figure 4.
Figure 6. The radial distribution functions $g_{ij}(r)$ for the reaction (1.1) in a hard sphere solvent at temperature $\tau = 0.01$, total reduced density $\eta = 0.1$ and $x_{\text{solv}} = 0.8$ for atoms capable of binding at $L = \sigma/2$. The legend is the same as for figure 4.

Figure 7. The radial distribution functions $g_{ij}(r)$ for the reaction (1.1) in a hard sphere solvent at temperature $\tau = 0.01$, total reduced density $\eta = 0.3$ and $x_{\text{solv}} = 0.993$ for atoms capable of binding at $L = \sigma/2$. The legend is the same as for figure 4.
Figure 8. The radial distribution functions $g_{ij}(r)$ for the reaction (1.1) in a hard sphere solvent at temperature $\tau = 0.01$, total reduced density $\eta = 0.3$ and $x_{\text{solvent}} = 0.699$ for atoms capable of binding at $L = \sigma/2$. The legend is the same as for figure 4.

Figure 9. The radial distribution functions $g_{ij}(r)$ for the reaction (1.1) in a hard sphere solvent at temperature $\tau = 0.01$, total reduced density $\eta = 0.4$ and $x_{\text{solvent}} = 0.901$ for atoms capable of binding at $L = \sigma/2$. The legend is the same as for figure 4.
corresponding hard sphere fluid and the solvent–solute correlation is similar to the 1–1 (≡ 2–2) solute–solute correlation. This is in contrast to the results at lower density. This suggests that at high density, where steric forces dominate the interactions, one can deduce that the solvent structure is largely unchanged by the presence of the reacting solutes, a deduction which is likely to be general rather than specific to the model considered here. The similarity between solvent–solute and 1–1 solute–solute correlations is not general and is attributable to the equality of the solvent–solute and 1–1 (≡ 2–2) interactions.

4. Analytic solution of the PY approximation for the reaction 2A → A2 in solution

In this section, we consider the solution of the PY approximation for the two-component mixture with pair interactions given by equations (1.6); species A and C molecules will be denoted by the indices 1 and 2 respectively. The PY approximation (2.2) for the binary mixture with pair interactions (1.6) yields

$$h_{ij}(r) = \begin{cases} -1, & r < \sigma, \\ \frac{\lambda L}{12} \delta(r - L), & r < \sigma, \\ 0, & r > \sigma, \end{cases}$$

$$(4.1)$$

To be consistent with §2, we shall refer to $P_1$ as $\rho_1$, the density of solute atoms, and $P_2$ as $\rho_2$, the solvent density. The Baxter factorization for mixtures is applicable to the mixture with closures (4.1), yielding the factorized equations (2.4). In the present case, equation (2.4) yields five distinct equations,

$$rh_{11}(r) = -q'_{11}(r) + 2\pi \rho_v q_{11} \otimes h_{11}(r) + 2\pi \rho_v q_{12} \otimes h_{12}(r),$$

$$rh_{12}(r) = -q'_{12}(r) + 2\pi \rho_v q_{11} \otimes h_{12}(r) + 2\pi \rho_v q_{12} \otimes h_{22}(r),$$

$$rh_{21}(r) = -q'_{21}(r) + 2\pi \rho_v q_{21} \otimes h_{11}(r) + 2\pi \rho_v q_{22} \otimes h_{12}(r),$$

$$rh_{22}(r) = -q'_{22}(r) + 2\pi \rho_v q_{21} \otimes h_{12}(r) + 2\pi \rho_v q_{22} \otimes h_{22}(r),$$

$$(4.2)$$

where $f \otimes g(r)$ is defined in §2. As usual, our task is to determine the functional form of the Baxter $q$-functions $q_{ij}(r)$ relate the parameter $\lambda$ to the temperature $\tau$ and the densities $\rho_v$ and $\rho_v$, derive an expression for the association constant and to provide an algorithm for computing the radial distribution functions $g_{ij}(r)$. (As in §2, the latter is based on a straightforward extension of Perram's method [1, 2, 11] and so will not be covered here.) The results in this section are given in explicit form for $L = \sigma/2$; as in §2, the corresponding results for $L = \sigma/3$ will not be given since they can be derived easily by combining the analysis of this section with the results for $L = \sigma/3$ contained in [2].

4.1. The Baxter $q$-functions

We begin by considering the functions $q_{11}(r)$, $j = 1, 2$. Substituting the closures (4.1) and (4.1) into equations (4.2), we obtain the following
differential–difference equations:

\[ q_{11}'(r) + p[q_{11}(r + L) - q_{11}(r - L)] + \frac{\lambda L^2}{12} \delta(r - L) = a_1 r + b_1, \]  

\[ q_{12}(r) = a_1 r + b_1, \]  

where \( p \) is given by equation (2.9) and

\[ a_1 = 1 - 2\pi\rho v \int_0^\sigma q_{11}(t) \, dt - 2\pi\rho v \int_0^\sigma q_{12}(t) \, dt, \]  

\[ b_1 = 2\pi\rho v \int_0^\sigma t q_{11}(t) \, dt + 2\pi\rho v \int_0^\sigma t q_{12}(t) \, dt. \]  

The boundary and discontinuity conditions on the functions \( q_{ij}(r) \) are:

\[ q_{11}(\sigma) = q_{12}(\sigma) = 0, \quad q_{11}(L^-) = q_{11}(L^+) + \frac{\lambda L^2}{12}. \]  

From equations (4.4) and (4.6), the functional form of \( q_{12}(r) \) is given by

\[ q_{12}(r) = \begin{cases} \frac{1}{2} a_1 (r - \sigma)^2 + b_1 (r - \sigma), & r < \sigma, \\ 0, & r \geq \sigma. \end{cases} \]  

We determine \( q_{11}(r) \) using the method of [2] and simply quote the result here for \( L = \sigma/2 \).

\[ q_{11}(r) = -\frac{a_1}{p} r + \frac{a_1}{p^2} \left(1 - \frac{v}{2}\right) - \frac{b_1}{p} + A_1 \cos(pr) + B_1 \sin(pr), \]  

\[ 0 < r < \frac{\sigma}{2}, \]  

\[ q_{11}(r) = \frac{a_1}{p} r + \frac{a_1}{p^2} \left(1 - \frac{v}{2}\right) - \frac{b_1}{p} + A_1 \cos[p(r - \sigma/2)] - B_1 \sin[p(r - \sigma/2)], \]  

\[ \frac{\sigma}{2} < r < \sigma. \]  

Equation (4.8), when combined with equations (4.5) and (4.6), yields the following linear equations for the parameters \( a_1, b_1, A_1 \) and \( B_1 \):

\[ \frac{1}{v} a_1 + \frac{2}{v} b_1' - A_1 c - B_1'(1 + s) = \frac{-\lambda}{48}, \]  

\[ \frac{1}{v^2} (1 + v/2)a_1 + \frac{1}{v} b_1' - A_1's - B_1'c = 0, \]  

\[ a_1 \left[1 + \frac{12\eta v(1 - v/4)}{v^2} - 4\eta v\right] - 6\eta v b_1' + \frac{12\eta v}{v^2} \times [(1 - c + s)A_1' + (1 - c - s)B_1'] = 1, \]  

\[ a_1 \left[\frac{12\eta v}{v^2} + \frac{3\eta v}{2}\right] + b_1' \left[1 - \frac{3\eta v}{v} + 2\eta v\right] \]  

\[- \frac{12\eta v}{v^2} \left[-1 + \frac{v}{2} + (1 - v)c + \left(1 + \frac{v}{2}\right)s\right] A_1' \]  

\[- \frac{12\eta v}{v^2} \left[1 + \left(1 - \frac{v}{2}\right)c + (1 - v)s\right] B_1' = 0, \]
where

\[ b'_1 = \frac{b_1}{\sigma}, \quad A'_1 = \frac{A_1}{\sigma^2}, \quad B'_1 = \frac{B_1}{\sigma^2} \] (4.13)

and \( s, c \) are given by equations (2.24). Equations (4.9)-(4.12) can be written in the form

\[
M \begin{bmatrix} a_1 \\ b'_1 \\ A'_1 \\ B'_1 \end{bmatrix} = \begin{bmatrix} -\lambda/48 \\ 0 \\ 1 \\ 0 \end{bmatrix},
\] (4.14)

where the elements of the matrix \( M \) are defined obviously. The solution of equation (4.14) is given by

\[ a_1 = \frac{1}{\Delta} \left( \frac{-\lambda}{48} T_{11} + T_{31} \right), \] (4.15a)

\[ b'_1 = \frac{1}{\Delta} \left( \frac{-\lambda}{48} T_{12} + T_{32} \right), \] (4.15b)

\[ A'_1 = \frac{1}{\Delta} \left( \frac{-\lambda}{48} T_{13} + T_{33} \right), \] (4.15c)

\[ B'_1 = \frac{1}{\Delta} \left( \frac{-\lambda}{48} T_{14} + T_{34} \right). \] (4.15d)

Here, \( \Delta \) is the determinant and \( T_{ij} \) the \( ij \) cofactor of \( M \) given by

\[ \Delta = \Delta^0 + \frac{6\eta_v \eta_v}{v^3} [8 - 4v + v^2 - 8c + (8 - 4v + v^2)] + (\eta_v^2 - 2\eta_v)(1 + s). \] (4.16)

\[ T_{11} = T^0_{11} + \frac{12\eta_v \eta_v}{v^2} [4v - 6 + (6 - v)c + (-6 + 2v)s], \] (4.17a)

\[ T_{12} = T^0_{12} + \frac{6\eta_v \eta_v}{v^2} [8 - 5v + (-8 + v)c + (8 - 3v)s], \] (4.17b)

\[ T_{13} = T^0_{13} + \frac{6\eta_v \eta_v}{v^4} [12 - 6v + v^2 + (-12 + 2v - v^2)c\]

\[ + (12 - 10v + v^2)s] + (\eta_v^2 - 2\eta_v)(1 + s), \] (4.17c)

\[ T_{14} = T^0_{14} + \frac{6\eta_v \eta_v}{v^4} [12 - 4v + (-12 + 10v - v^2)c\]

\[ + (12 + 2v - v^2)s] + (\eta_v^2 - 2\eta_v)(1 + s), \] (4.17d)

\[ T_{31} = T^0_{31} + 2\eta_v(1 + s), \] (4.18a)

\[ T_{32} = T^0_{32} + 2\eta_v(1 + s), \] (4.18b)

\[ T_{33} = T^0_{33} + \frac{\eta_v}{2v^2} [4 - v - 2vc + (v - 4)s], \] (4.18c)
The superscript '0' in equations (4.16)–(4.18) is used to denote the value of the corresponding parameter in the limit $\eta_v \to 0$, and so $A^0$ and the $T_{ij}^0$ are given by equations (1.A.1)–(1.A.9) with $j=1$ and $\eta_1 = \eta_v$ (or, equivalently, $\zeta = \eta_v$). This completes the analysis for $q_{1j}(r)$, $j = 1, 2$. We now turn our attention to the functions $q_{2j}(r)$, $j = 1, 2$. Substituting the closures (4.1) into equations (4.2c) and (4.2d), we find

$$
q_{21}'(r) + p[q_{21}(r + L) - q_{21}(r - L)] = a_2 r + b_2,
$$

$$
q_{22}'(r) = a_2 r + b_2,
$$

where

$$
a_2 = 1 - 2\pi \rho \int_0^\sigma q_{21}(t) \, dt - 2\pi \rho \int_0^\sigma q_{22}(t) \, dt,
$$

$$
b_3 = 2\pi \rho \int_0^\sigma t q_{21}(t) \, dt + 2\pi \rho \int_0^\sigma t q_{22}(t) \, dt.
$$

The boundary conditions on the functions $q_{1j}(r)$ are

$$
q_{21}(\sigma) = q_{22}(\sigma) = 0
$$

and we note that $q_{21}(r)$ is continuous at $r = L$. The solution of equation (4.20) is immediate and is given by

$$
q_{22}(r) = \frac{1}{2} a_2 (r - \sigma)^2 + b_2 (r - \sigma), \quad r < \sigma, \\
= 0, \quad r \geq \sigma.
$$

The solution of equation (4.19) with closure (4.22) and continuity at $r = L$ is very similar to the solution of equation (2.33) in §2, and so we simply quote the results for $L = \sigma/2$. The function $q_{22}(r)$ is given by

$$
q_{21}(r) = -\frac{a_2}{p} r + \frac{a_2}{p^2} (1 - \nu/2) - \frac{b_2}{p} + A_2 \cos (pr) + B_2 \sin (pr),
$$

$$
0 < r < \frac{\sigma}{2},
$$

$$
= \frac{a_2}{p} r + \frac{a_2}{p^2} (1 - \nu/2) + \frac{b_2}{p} + A_2 \cos [p(r - \sigma/2)] - B_2 \sin [p(r - \sigma/2)],
$$

$$
\frac{\sigma}{2} < r < \sigma.
$$

The parameters $a_2$, $b_2$, $A_2$ and $B_2$ satisfy four linear equations which can be written in the form

$$
M \begin{bmatrix} a_2 \\ b_2 \\ A_2 \\ B_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix},
$$

(4.25)
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where

\[ b'_2 = \frac{b_2}{\sigma}, \quad A'_2 = \frac{A_2}{\sigma^2}, \quad B'_2 = \frac{B_2}{\sigma^2}. \] (4.26)

Thus, the expressions for the determinant and cofactor given in equations (4.16) and (4.18) are still applicable and we find that

\[ a_2 = \frac{T_{31}}{\Delta}, \] (4.27a)
\[ b'_2 = \frac{T_{32}}{\Delta}, \] (4.27b)
\[ A'_2 = \frac{T_{33}}{\Delta}, \] (4.27c)
\[ B'_2 = \frac{T_{34}}{\Delta}, \] (4.27d)

where \( T_{3i}, \ i = 1, 2, 3, 4, \) are given by equations (4.18). This completes the derivation of the functional forms for the Baxter \( q \)-functions for \( L = \sigma/2 \).

4.2. Determination of the parameter \( \lambda \)

Application of the PY approximation (2.2) yields

\[ \lambda = \frac{2a_1}{V} + 2Va'_1 - F_1 - F_2, \] (4.28)

where \( F_i, \ i = 1, 2 \) are given by

\[ F_i = 24\eta_i \left[ \frac{a_i^2}{2V^3} - \frac{3a_i^2}{8V^2} - \frac{a_i b'_i}{2V^2} - \frac{b'_i}{V} A'_i s - \frac{b'_i}{V} B'_i (1 - c) \right. \]
\[ + \frac{a_i}{V^2} A'_i (1 - c + 2s - vs) + \frac{a_i}{V^2} B'_i (2 - 2c - s + vs - v/2) \]
\[ + \frac{A'_i^2}{4} (V + \sin V) + \frac{A'_i^2 B'_i^2}{2} (1 - \cos V) + \frac{B'_i^2}{4} (V - \sin V) \] (4.29)

and where it is understood that \( \eta_1 = \eta_V \) and \( \eta_2 = \eta_V \). Equation (4.28) constitutes a single non-linear equation for the parameter \( \lambda \) which can be solved numerically.

4.3. Expression for the association constant

The association constant for the reaction (1.2) is given by

\[ k = \frac{PA_2}{(\rho A)^2}. \] (4.30)

The expressions given in [2] for the dimensionless association constant \( K = k/\sigma^3 \) and for the expected number \( \langle N \rangle \) of \( A \) atoms distant \( L \) from a given \( A \) atom remain valid and are simply quoted here.
Note while the expression for $\langle N \rangle$ given in equation (4.31) is the same as that for association between unlike species, equation (2.46), the 3 in the denominator of equation (2.47) is replaced by a 6 in equation (4.31). This difference arises from distinguishability considerations and is discussed in more detail in [2].

4.4. The limit of vanishing solute density

The analysis for the limit of vanishing solute density $\rho_v \to 0$, where the reacting species $A$ is present at infinite dilution in the hard sphere solvent is much the same as that presented in § 2.5 above and will not be repeated. The final result for $\lambda(\eta_v = 0; \eta_v)$ is the same as that given by equation (2.5) while the corresponding result for $K$ is

$$K_0 = K(\rho_v = 0, \rho_v = 0) = \frac{\pi}{6\tau} (L/\sigma)^3.$$  (4.33)

The expression given in § 2.5 for the ratio between the association constant at infinite dilution and its value in the ideal gas state still holds for the present homogeneous association reaction as an exact result from the relation of Stell [12] given in that section.

5. RESULTS FOR THE CHEMICAL EQUILIBRIUM $2A \rightleftharpoons A_2$ IN SOLUTION

The results obtained for the chemical equilibrium association ratio $K$ for the model of the reaction (1.2) solved in § 4 do not differ qualitatively from those described in § 3 for the model of the reaction (1.1) and so we do not dwell on them at any great length. In figure 10, the ratio $K/K_0$ is shown for reaction (5.1) for $\tau = 0.05$ as a function of $x_{\text{solute}}$ at various total densities $\eta$. As was found in § 3 for reaction (5.2), for liquid-like systems ($\eta \geq 0.4$), the ratio $K/K_0$ is large ($\approx 20-30$) at infinite dilution of reacting solute ($x_{\text{solute}} = 1$) and increases rapidly as $x_{\text{solute}}$ is decreased (corresponding to the replacement of solvent molecules with solute molecules capable of reaction). Again, as in § 3, for $\eta = 0.1$, $K/K_0$ shows little variation with solvent mole fraction.

The correlation functions ($g_{11}(r) \equiv g_{AA}(r)$, $g_{12}(r) \equiv g_{AC}(r)$ and $g_{22}(r) \equiv g_{CC}(r)$) exhibit qualitatively the same features as the corresponding correlation functions for reaction (5.2) described in § 3. In particular, $g_{22}(r)$ exhibits more structure than the corresponding radial distribution function for a hard sphere fluid at density $\eta$, although in the case of reaction (5.1) this is evidenced only by the more prominent oscillations in $g_{22}(r)$, the contact value of $g_{22}(r)$ being slightly below the corresponding hard sphere quantity (compared to the results in § 3 where the corresponding solvent–solvent correlation function exhibited enhanced oscillations and a higher contact value). A typical example is given in figure 11.

Additional interest in our model (5.1) arises from the fact that at the complete association limit ($\langle N \rangle = 1$) the model becomes equivalent to the zero pole approximation (ZPA) for a mixture of hard dumbbells and hard spheres first
Figure 10. The ratio of the equilibrium ratio $K$ to its ideal gas value $K_0$ for the reaction (1.2) in a hard sphere solvent at temperature $\tau = 0.05$ and at total reduced densities $\eta = 0.1, 0.2, \ldots, 0.5$ for atoms capable of binding at $L = \sigma/2$. The ratio $K/K_0$ is shown as a function of the mole fraction of solvent in the mixture.

Figure 11. The radial distribution functions $g_{11}(r) = g_{AA}(r)$ (-----), $g_{12}(r) = g_{AC}(r)$ (---), $g_{22}(r) = g_{CC}(r)$ (-----) and $g_{HS}(r)$ (---) for the reaction (1.2) in a hard sphere solvent at temperature $\tau = 0.05$, total reduced density $\eta = 0.3$ and $X_{\text{solvent}} = 0.7$ for atoms capable of binding at $L = \sigma/2$. The dashed curve with the higher contact value is $g_{HS}(r)$. The hard sphere radial distribution function is calculated at reduced density $\eta = 0.3$. 
introduced for the pure dumbell fluid by Morriss and Cummings [15]. In fact, the radial distribution functions shown in figure 11 are at complete association, so that the results given can be regarded as the ZPA prediction for a hard dumbell/hard sphere mixture with $\rho_{\text{dumbell}} = \rho_d/2$. Unfortunately, Monte Carlo results are not available for comparison with the theoretical results shown in figure 11.

6. CONCLUSIONS

The study of chemically reactive species using the analytic solution of the Percus–Yevick approximation for models of inter- and intra-molecular interactions which lead to sterically hindered association between molecule pairs has been extended to focus on the effect of a hard sphere solvent on the reaction equilibrium. At liquid-like densities, the order of magnitude of the solvent effect is in accord with experimental results and the trend displayed is consistent with Le Chatelier's principle. Thus, to the extent which it is possible to be certain without computer simulations to verify the accuracy of the Percus–Yevick approximation, it appears that the present model yields a qualitatively correct picture of solvent effects on chemical reaction equilibria in systems dominated by steric forces.

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