II. Analytic solution of the Percus–Yevick approximation for a model of homogeneous association

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The formalism and model introduced in a previous paper [1984, Molec. Phys., 51, 253] and used there to study the inhomogeneous association reaction \( A + B \leftrightarrow AB \) is used here to consider the homogeneous association reaction \( 2A \leftrightarrow A_2 \). Two approximations are introduced to obtain an analytic theory. The first is the Percus–Yevick approximation. The second is the neglect of rigid polygonal \( n \)-mers, \( n \geq 3 \). (These are sterically possible in our model, but can be expected in most cases to form only rarely because of their restricted geometry.) Representative quantitative results for association probabilities, association constants and radial distribution functions as functions of thermodynamic state are given and discussed. Our model has a dimensionless association parameter \( \tau \) that is a combined measure of association strength and temperature; for a given atomic number density \( \rho_A \) there is a value of \( \tau \) at which diatomic association is complete. Under the assumptions of our theory one then has a fluid of homonuclear diatomics, the hard dumbbell fluid. It is found that in this case our theory reduces to the zero pole approximation of Morriss and Cummings for this fluid.

1. INTRODUCTION

In a recent paper [1], Cummings and Stell initiated an analytic approach to the study of chemical reactions in non-ideal systems. These authors considered the simplest, inhomogeneous association reaction [1]

\[
A + B \leftrightarrow AB
\]  

by considering a model equimolar mixture of \( A \) and \( B \) atoms in which the three pair potentials \( \phi_{AA}(r), \phi_{AB}(r) \) and \( \phi_{BB}(r) \) are given by

\[
\begin{align*}
\phi_{AA}(r) &= \phi_{BB}(r) = \infty, & r < \sigma, \\
&= 0, & r > \sigma,
\end{align*}
\]  

\[
\phi_{AB}(r)/k_B = \varepsilon_1, & 0 < r < L - w/2, \\
= -\varepsilon_2, & L - w/2 < r < L + w/2, \\
= \varepsilon_1, & L + w/2 < r < \sigma, \\
= 0, & r > \sigma,
\]

where \( \varepsilon_1, \varepsilon_2 \) are the association and repulsive potentials, \( k_B \) the Boltzmann constant, \( L \) the physical distance, \( w \) the width of the hard core region, and \( \sigma \) the hard core diameter.

In this paper we extend these ideas to the homogeneous case \( 2A \leftrightarrow A_2 \) by introducing two approximations. The first is the Percus–Yevick approximation, which neglects the effects of correlations between \( A \) and \( B \) atoms. This approximation is well known to be quite accurate for most fluids, and it is expected to be even more accurate in our case because of the strong association potentials. The second approximation is the neglect of rigid polygonal \( n \)-mers, \( n \geq 3 \). These are sterically possible in our model, but can be expected to form only rarely because of their restricted geometry. Representative quantitative results for association probabilities, association constants and radial distribution functions as functions of thermodynamic state are given and discussed. Our model has a dimensionless association parameter \( \tau \) that is a combined measure of association strength and temperature; for a given atomic number density \( \rho_A \) there is a value of \( \tau \) at which diatomic association is complete. Under the assumptions of our theory one then has a fluid of homonuclear diatomics, the hard dumbbell fluid. It is found that in this case our theory reduces to the zero pole approximation of Morriss and Cummings for this fluid.
where \( k_B \) is Boltzmann's constant, \( \varepsilon_1 \) is the height of the potential mound which models the repulsion between the unlike species atoms and \( \varepsilon_2 \) is the depth of a deep attractive well of width \( w \) centred at interparticle separation \( L \). As argued in detail in [1] [referred to throughout this paper as I, with equation (i . j) from I being denoted by (I . i . j)], the pair potentials (1.2) define a mixture in which type \( A \) atoms can 'react' with type \( B \) atoms to form \( AB \) diatomics when a suitable definition for the existence of \( AB \) pairs is chosen. Two definitions were considered in I: a definition based on potential energy that considers two atoms as 'bound' into a diatomic if the potential energy of interaction is large and negative, and a 'structural' definition by which a diatomic molecule is presumed to exist when the separation between the centres of an \( A \) and a \( B \) atom is no more than \( L + w/2 \). The pair potentials (1.2) exhibit the property of steric saturation [2-4]: that is, given either of the above definition of binding, each \( A \) and \( B \) atom can belong to at most one diatomic molecule.

By considering the hamiltonian model (1.2) in the limit \( w \to 0 \), \( \varepsilon_2 \to \infty \) while holding the second virial coefficient fixed, Cummings and Stell were able to solve the Percus–Yevick (PY) [5] approximation analytically. They showed that when \( \varepsilon_1/T \) (where \( T \) is absolute temperature) is greater than \( \sim 3 \), the results for the mass action association constant \( k \) are qualitatively and quantitatively close to those for \( \varepsilon_1 \to \infty \), a limit in which the analysis becomes considerably simpler and the two definitions of associated pairs are synonymous and hence conceptually unambiguous. The mass action association constant \( k \) is given by

\[
k = \frac{\rho_{AB}/\rho_A \rho_B}{},
\]

where \( \rho_{AB} \) is the number density of \( AB \) dimers and \( \rho_i, i = A, B \), is the density of the respective monomers.

In this paper, we study the homogeneous association reaction

\[
2A \leftrightarrow A_2
\]

by considering a pure fluid composed of type \( A \) atoms which interact via a potential 'derived' from the prototype potential \( \phi_p(r) \) given by

\[
\phi_p(r)/k_B = \begin{cases} 
\varepsilon_1, & 0 < r < L - w/2, \\
-\varepsilon_2, & L - w/2 < r < L + w/2, \\
\varepsilon_1, & L + w/2 < r < \sigma, \\
0, & r > \sigma.
\end{cases}
\]

We consider this potential in the limit \( \varepsilon_1 \to \infty, \varepsilon_2 \to \infty, w \to 0 \) while holding the second virial coefficient fixed. This limit is discussed in detail in I; as in I, the limits \( \varepsilon_2 \to \infty \) and \( w \to 0 \) are taken to yield a mathematically tractable problem in the PY approximation; the limit \( \varepsilon_1 \to \infty \) is justified by the small difference between results in this limit and finite, reasonable values of \( \varepsilon_1 \). As in I, the latter limit makes the definition of the association constant unambiguous and further simplifies the algebraic structure of the solution. In this limit, the pair potential for the fluid is defined through the Mayer \( f \)-function \( f(r) = \exp \left( -\phi(r)/k_B T \right) - 1 \) as

\[
f(r) = \begin{cases} 
-1 + (L/12\pi) \delta(r-L), & 0 < r < \sigma, \\
0, & r > \sigma.
\end{cases}
\]

\[
(1.6)
\]
where \( \tau \) is a dimensionless measure of temperature. The mass action association constant \( k \) is defined by

\[
k = \rho_{A_2}/(\rho_A)^2.
\] (1.7)

Unlike the inhomogeneous association reaction (1.1), the pair potential defined by (1.6) does not totally preclude the formation of higher order \( n \)-mers, where \( n > 2 \). (That is, saturation at the diatomic level is not assured by geometric exclusion as in the case of the \( AB \) mixture.) However, in §2 the permitted class of \( n \)-mers, \( n > 2 \), is seen to be of quite special form. Neglecting these, the number density of \( A_2 \) diatomics is given by the same expression used in I (appropriately modified for the pure fluid case). Section 2 also contains the analytic solution of the Percus–Yevick approximation for the fluid with Mayer \( f \)-function (1.6).

The predictions of the Percus–Yevick approximation, including results for the fluid structure and association constant, are given in §3. We find that in the complete association limit \( (k \to \infty, \text{which at each density occurs at sufficiently low temperature}) \) the model fluid becomes within our approximation a completely associated homonuclear diatomic fluid. Interestingly, the PY approximation is precisely the zero pole approximation (ZPA) for the latter fluid derived by Morriss and Cummings [6] from a completely different viewpoint, thus providing insight into the conceptual basis of the ZPA. Concluding remarks are given in §4.

The ultimate aim of our research in the area of chemical reactions is to consider the general problem of combined phase and chemical equilibria. The principles for addressing such a problem are straightforward and long-established [7]: in addition to the usual conditions for phase equilibria (equality of temperature, pressure and chemical potential in each phase), the existence of one or more possible reactions between the species present implies that the chemical potentials are additionally constrained stoichiometrically. That is, if there are \( m \) distinct components present with \( R \) independent reactions possible between them, then the chemical potentials \( \mu_i^\alpha \) of component \( i \) in phase \( \alpha \) are subject to the \( R \) constraints

\[
\sum_{i=1}^{m} v_{ji} \mu_i^\alpha = 0, \quad j = 1, \ldots, R. \tag{1.8}
\]

Here, \( v_{ji} \) is the stoichiometric coefficient of species \( i \) in reaction \( j \) when the reaction \( j \) is written in the form

\[
\sum_{i=1}^{m} v_{ji} F_i = 0, \tag{1.9}
\]

where \( F_i \) is the molecular formula of species \( i \). The constraints (1.8) lead to a set of reaction equilibrium constants in terms of activity coefficients which rigorously depend only on temperature. In many chemical engineering applications [7, 8], it is necessary to consider combined chemical and phase equilibria. Stated in its most general form, the problem consists of finding the equilibrium concentration of each species in each phase given the state conditions (pressure and temperature) and the association constants for each independent reaction in terms of activities. In general, it is also necessary to specify the concentration of one or more components in one or more phases to yield a problem which is well posed mathematically; alternatively (or additionally), mass balance equations in terms of elemental abundances may be specified.
The usual modelling approach is to assume correlations for the activity (or, equivalently, fugacity or chemical potential) of each component in each phase (which in general, of course, is not related in any simple fashion to the concentrations), make some simplifying assumptions (e.g. ideality of the gas phase, restriction of the reaction to a single phase, etc) and proceed with the task of computing $x_i^\alpha$, the mole fraction of component $i$ in phase $\alpha$, for each phase and species.

Our approach is quite distinct from this, and yet aims to study at a fundamental level the same phenomena. We seek to model both the pair interactions between atoms which give rise to phase equilibria and the chemical interactions which give rise to chemical equilibria with simple pair potentials and allow the Boltzmann weighting to determine both physical and chemical equilibria. Thus, instead of inputting to the calculation the association constant in its activity form, we derive from a fundamental statistical mechanical approach the association constant in its mass action form. Through this approach, we hope ultimately to understand systems which exhibit combined physical and chemical equilibrium, including those in which a subtle (and, in some respects, controversial) interplay between phase and chemical equilibrium is observed [9–12].

The model described in this and the previous paper has trivial phase equilibria in that only one phase is present; it is non-trivial in that the density and temperature regime modelled goes well beyond the ideal gas state. In future publications, the role of a solvent will be examined; in the next paper in this series, in order to delineate steric effects, a hard sphere solvent will be considered. Subsequently, it is anticipated that solvents which exhibit liquid–gas criticality will be employed, enabling us to examine the chemical equilibrium and structure in the vicinity of the line of mixture critical points.

2. Analytic solution of the Percus–Yevick approximation

The PY approximation is stated in terms of the total correlation function $h(r) = g(r) - 1$ where $g(r)$ is the radial distribution function (proportional to the probability of finding an atom distance $L$ away from an atom located at the origin) and the direct correlation function $c(r)$ which is defined by the Ornstein–Zernike (OZ) [13] equation

$$h(r) = c(r) + \rho \int c(s)h(|r - s|) ds. \quad (2.1)$$

Here, $\rho$ is the total density of atoms and includes both monomers and atoms bound into $n$-mers, $n \geq 2$. The PY approximation is given by

$$c(r) = f(r)y(r) = f(r)[1 + h(r) - c(r)], \quad (2.2)$$

where $f(r)$ is the Mayer f-function defined earlier. This closure implies that $h(r)$ [and, as a consequence of (2.1), $c(r)$] contains a delta function at $r = L$, while $c(r)$ is zero outside the core. Thus, the PY approximation yields

$$h(r) = -1 + \frac{\lambda L}{12} \delta(r - L), \quad 0 < r < \sigma, \quad (2.3a)$$

$$c(r) = 0, \quad r > \sigma. \quad (2.3b)$$
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Given the probabilistic interpretation of \( g(r) \), the average number of atoms at separation \( L \) from an atom located at the origin, is given by (see the discussion in §1 of I)

\[
\langle N \rangle = 4\pi \rho \int_{-L}^{L} g(r) r^2 \, dr = 2\eta \lambda \left( \frac{L}{\sigma} \right)^3 ,
\]  

(2.4)

where \( \eta = (\pi/6)\rho \sigma^3 \) is the usual dimensionless density. For the binary mixture described in I, steric saturation in the pair potential means that any atom located at separation \( L \) is necessarily part of a dimer with the atom located at the origin; in other words, the two atoms involved cannot be part of a higher order \( n \)-mer, \( n > 3 \). For the hamiltonian model considered here, this is no longer true. Steric saturation does not operate to the extent that it operates in the binary mixture as reflection on the nature of the pair potential quickly reveals. For \( L \leq \sigma/2 \), a high degree of saturation does operate, however, since geometric considerations imply that the only possible trimer formed from three atoms interacting with the Mayer \( f \)-function (1.6) has the shape of an equilateral triangle; similarly, the only possible four-atom molecule possible has each atom at the corner of a regular tetrahedron. Each \( n \)-mer formed must have the distance between each and every pair of atoms equal to \( L \) and thus corresponds to a polyhedron with the centres of the atoms rigidly fixed relative to each other. This is to be contrasted with \( L > \sigma/2 \), where, for example, in the case of trimers, a flexible configuration representing a range of deviation from strict linearity is possible since two of the atoms are permitted to not overlap. Thus, a whole family of flexible linear trimers is possible for \( L > \sigma/2 \) that is not possible for \( L \leq \sigma/2 \); similarly, for each \( n > 3 \), a corresponding family of \( n \)-mers is possible for \( L > \sigma/2 \).

It is apparent, then, that for \( L \leq \sigma/2 \), the available configurational space for the polygonal \( n \)-mers, \( n > 2 \), is very small indeed compared to the space available for \( n \)-mers, \( n > 2 \), when \( L > \sigma/2 \), and we shall therefore neglect the formation of \( n \)-mers, \( n > 2 \) in our treatment here. We regard this as an approximation in the same sense that the PY equation is an approximation. Both approximations can be systematically corrected, but we shall defer an investigation of such corrections for future work since taken together the two approximations constitute a natural and appealing lowest order theory.

Assuming, then, that \( \langle N \rangle \) refers to the expected number of nearest neighbours at \( r = L \) that form a dimer with the atom located at the origin, it follows that the number density of dimers is given by

\[
\rho_{A_2} = \frac{1}{2} \rho \langle N \rangle = \rho \eta \lambda \left( \frac{L}{\sigma} \right)^3 ,
\]  

(2.5)

where the factor of \( \frac{1}{2} \) accounts for the fact that the molecule at the origin and the molecule at \( r = L \) are indistinguishable. (This is to be contrasted with the binary mixture considered in I, where the factor of \( \frac{1}{2} \) is not used since the atoms are of distinct species.) Under this same assumption

\[
\rho_A = \rho - 2\rho_{A_2} ,
\]  

(2.6)

where \( \rho_A \) is the density of monomers and the factor of 2 in front of \( \rho_{A_2} \) is required to take into account the fact that each dimer formed reduces the number of
monomers by two. Defining the dimensionless association constant $K$ to be $k/\sigma^3$, we have from equations (1.7) and (2.4)-(2.6)

$$K = \frac{\pi \lambda (L/\sigma)^3}{6[1 - 2\eta \lambda (L/\sigma)^3]^2}. \quad (2.7)$$

Since $c(r)$ is zero for $r > \sigma$, the original Baxter factorization of the OZ equation for a pure simple fluid [14] is directly applicable, yielding

$$rh(r) = -q'(r) + 2\pi \rho \int_0^\sigma dtq(t)(r - t)h(|r - t|), \quad (2.8a)$$

$$rc(r) = -q'(r) + 2\pi \rho \int_0^{\sigma - r} dtq(t)q'(r + t). \quad (2.8b)$$

Applying the closure (2.3a) inside the core to equation (2.8a), we obtain the following delay-differential equation for $g(r)$:

$$q'(r) + p[q(r + L) - q(r - L)] + \frac{\lambda L^2}{12} \delta(r - L) = ar + b, \quad (2.9)$$

where

$$p = \frac{\pi \rho L^2}{6}, \quad (2.10)$$

$$a = 1 - 2\pi \rho \int_0^\sigma q(t) \ dt, \quad (2.11a)$$

$$b = 2\pi \rho \int_0^\sigma t q(t) \ dt. \quad (2.11b)$$

We have solved this problem explicitly for $L = \sigma/2$ and $L = \sigma/3$ and now proceed to give the details of the solution for $L = \sigma/2$. The solution for $L = \sigma/3$ is given in brief outline in Appendix A.

The method of solving equation (2.9) for $L = \sigma/2$ is the same as that used in §3.1 of I, and so we simply quote the result here. For $L = \sigma/2$, the parameter $p$ and its dimensionless counterpart $\nu$ are given by

$$p = \frac{\pi \rho \lambda \sigma^2}{24}, \quad \nu = \frac{\eta \lambda}{4} \quad (2.12)$$

and $q(r)$ is found to be

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

$$= \frac{a}{p} r + \frac{a}{p^2} \left(1 - \frac{\nu}{2}\right) + \frac{b}{p} + A \sin \left[p(r - \sigma/2)\right]$$

$$- B \cos \left[p(r - \sigma/2)\right], \quad \sigma/2 < r < \sigma. \quad (2.13)$$

The boundary conditions on $q(r)$ are given by

$$q(\sigma) = 0,$$

$$q(\sigma^-/2) = q(\sigma^+/2) + \frac{\lambda \sigma^2}{48}. \quad (2.14)$$
Equations (2.11) and (2.14) yield four linear equations in the four unknowns $a, b, A, B$ which can be written in the form

$$\mathbf{M} = \begin{bmatrix} a \\ b/\sigma \\ A/\sigma^2 \\ B/\sigma^2 \end{bmatrix} = \begin{bmatrix} -\lambda/48 \\ 0 \\ 1 \\ 0 \end{bmatrix}.$$ \hspace{1cm} (2.15)

The elements of the matrix $\mathbf{M}$ are found by substituting $f = 1$ into equations (1.3.27). The solution to (2.15) is given by

$$a = \frac{1}{\Delta} \left( -\lambda \frac{T_{11} + T_{31}}{48} \right), \hspace{1cm} (2.16a)$$

$$b = \frac{1}{\Delta} \left( -\lambda \frac{T_{12} + T_{32}}{48} \right), \hspace{1cm} (2.16b)$$

$$A = \frac{1}{\Delta} \left( -\lambda \frac{T_{13} + T_{33}}{48} \right), \hspace{1cm} (2.16c)$$

$$B = \frac{1}{\Delta} \left( -\lambda \frac{T_{14} + T_{34}}{48} \right). \hspace{1cm} (2.16d)$$

In equations (2.16), $\Delta$ is the determinant of the matrix $\mathbf{M}$ and is given by equation (I.A 1) with $f = 1$. The $T_{ij}$ parameters are cofactors of the matrix $\mathbf{M}$ and are given by equations (I.A 2) through (I.A 9) with $f = 1$. The final step in the solution of the present problem is to determine $\lambda$ as a function of $\eta$ and $\tau$. This is done using the method described in detail in I; in the present case the PY approximation is found to imply that

$$\lambda \tau = y(L) = 1 + h(L) - c(L), \hspace{1cm} (2.17)$$

which, for $L = \sigma/2$, becomes

$$\lambda \tau = \frac{2a}{v} + 2vA'$$

$$- \frac{24\eta}{2v^2} \left[ \frac{a^2}{8v^2} - \frac{3a^2}{8v^2} - \frac{ab'}{v^2} - \frac{A'b'}{v} - \frac{B'b'}{v} - s - \frac{B' - b'}{v} (1 - c) \right]$$

$$+ \frac{A'a}{v^2} (1 - c + 2s - vs) + \frac{B'a}{v^2} \left( 2 - 2c - s + vc - \frac{v}{2} \right) + \frac{A'^2}{4} (v + \sin v)$$

$$+ \frac{A'B'}{2} (1 - \cos v) + \frac{B'^2}{4} (v - \sin v), \hspace{1cm} (2.18)$$

where $b', A'$ and $B'$ are the dimensionless quantities

$$b' = \frac{b}{\sigma}, \hspace{0.5cm} A' = \frac{A}{\sigma^2}, \hspace{0.5cm} B' = \frac{B}{\sigma^2}. \hspace{1cm} (2.19)$$

Equation (2.19) represents a single non-linear equation for the parameter $\lambda = \lambda(\eta, \tau)$. At low density, careful examination of the limit $\eta \rightarrow 0$ reveals that $\lambda \rightarrow 1/\tau$ in this limit; beginning at low density, we solve equation (2.19) numeri-
cally at fixed temperatures by increasing the density in small increments. The pair correlation function can be found using an algorithm similar to that used in I. This completes the analytic solution of the problem.

3. Results

Results will primarily be reported for $L = \sigma/2$, although some results for $L = \sigma/3$ will also be given. Figures 1 and 2 show the behaviour of the parameter $\lambda$ as a function of $\eta$ along selected isotherms for $L = \sigma/2$ and $\sigma/3$. (The order of magnitude used for $\tau$ is justified in Appendix B by comparing the model with the dissociation equilibrium of dinitrogen tetroxide with nitrogen dioxide.) Note that at each $\tau$ a density $\eta$ is reached at which $K \rightarrow \infty$ which (given the assumptions described in the previous section) corresponds to a completely associated fluid: that is, a homonuclear diatomic fluid in which each molecule is composed of two hard spheres fused together so that the separation between the hard sphere centres is $L$. This fluid is called the hard dumbell fluid (HDF) by Morriss and Cummings [6]. This information can be inverted and presented in a different form. For $\langle N \rangle = 1$, it is clear that

$$\lambda = \frac{1}{2\eta} \left( \frac{L}{\sigma} \right)^{-3}$$

so inserting this value of $\lambda$ into equation (2.18) and solving for $\tau$ the temperature at which $\langle N \rangle = 1$ can be obtained as a function of density $\eta$. This density-

![Figure 1](image_url)

Figure 1. The parameter $\lambda$ as a function of density $\eta$ along the isotherms $\tau = 0.02$, 0.025, 0.05, 0.1 and 0.2 which are labelled accordingly. The results shown are for the elongation $L = \sigma/2$. The dotted curve indicates the point of complete association ($\langle N \rangle = 1, K \rightarrow \infty$).
dependent $\tau$ is displayed in figure 3 for $L = \sigma/2$ and $L = \sigma/3$, and it is clear that $\tau$ is finite and positive even in the limit $\eta \to 0$. The parameter $\tau$ is a dimensionless measure of temperature; more precisely, it is a measure of ratio of the depth of the attractive well in the pair potential which gives rise to association to the temperature. Hence, decreasing $\tau$ corresponds has two interpretations: for a fixed potential, it corresponds to reducing the temperature; for a fixed temperature, it corresponds to increasing the depth of the attractive well, which in turn corresponds to a density-dependent pair potential. We prefer to interpret figure 3 in the latter fashion: by choosing a density-dependent pair potential, it is possible to cause the fluid to be completely associated for all physically sensible densities. This statement pertains only to the PY approximation combined with our assumption about negligible formation of $n$-mers, $n > 2$ [16]. The fascinating aspect of this analysis is that if one chooses the state-dependent pair potential described above and solves the PY approximation for it (corresponding to setting $\lambda$ in the analysis of the previous section to the value given in equation (3.1)), then one recovers the zero pole approximation (ZPA) for the HDF derived by Morriss and Cummings using a completely different line of reasoning. From the present viewpoint, then, the ZPA corresponds to the PY approximation for an atomic fluid interacting with a density-dependent pair potential which gives rise to chemical association. This observation provides some insight into the failure of the ZPA for dumbell elongations greater than $\sigma/2$: from the analysis of I and the remarks in the introduction of this paper, elongations greater than $\sigma/2$ correspond to elongations at which in the corresponding associating simple fluid there is no...
steric saturation operating to prevent the formation of flexible linear \( n \)-mers. [In Appendix C, a qualitative estimate of the number of trimers is derived and the error in our assumption of negligible higher-order polymerization is discussed.]

Figure 4 shows the association constant \( K \) for \( L = \sigma/2 \) as a function of density along selected isotherms. As the density is increased, the degree of association increases, steadily at first then diverging rapidly. This is qualitatively the same as the behaviour obtained in the inhomogeneous association model described in I and is in accord with our intuition on the effect of increasing density. The effect of temperature can be deduced by considering a fixed value of density and noting from figure 4 that as the temperature is decreased \( K \) (and hence the degree of association) increases until it diverges. Since the association reaction is exothermic, this behaviour is consistent with Le Chatelier's principle.

Thus, at any given density, \( \tau \) can be reduced from infinity (where the fluid is simply a hard sphere fluid) to a value at which complete association occurs. In figure 5, the radial distribution function is shown for \( \tau = 0.2 \ (K = 2.615) \) down to \( 0.03782 \), the value at which \( K = \infty \) and we recover the ZPA for the HDF. We see that as \( \tau \) is reduced the population of atoms at and near contact \( (r \approx \sigma) \) is dramatically reduced as the association increases. This is because atoms find it energetically preferable to be separated by distance \( L \) (and so chemically bonded) as the temperature is decreased. This reduces the possibility of atoms being located at \( r \approx \sigma \) since the available surface area of an atom is reduced considerably when it forms a dimer.
Figure 4. The association constant $K$ along the isotherms $\tau = 0.02, 0.025, 0.05, 0.1$ and $0.2$ labelled accordingly. The divergence to $\infty$ corresponds to the complete association limit. Qualitatively similar results are obtained for $L = \sigma/3$.

Figure 5. The radial distribution function $g(r)$ for $L = \sigma/2$ at density $\eta = 0.2$ for temperatures $\tau = 0.2$ (-----), $0.1$ (----), $0.05$ (-----) and $0.03782$ (-----). At the temperatures given, the respective values of $K$ are $2.615, 8.508, 107.9$ and $\infty$, the latter corresponding to complete association.
Figure 6 displays the radial distribution function along the isotherm $\tau = 0.2$ at various densities. As the density is increased, the radial distribution function exhibits two features: the development of oscillations characteristic of the dense fluid state and increasingly pronounced cusp behaviour at $r = \sigma + L$ as the complete association density is approached. The latter effect is particularly evident in the shape of the curve between $r = \sigma$ and $r = \sigma + L$ which at low density is monotonic but develops a distinct minimum as the density is increased.

4. Conclusion

In this paper, the PY approximation has been solved for a simple model of homogeneous association. The analysis represents an explicit construction of a diatomic fluid from the particle-particle viewpoint of Stell and co-workers [2–4] and yields the ZPA for the HDF as a limit.

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APPENDIX A

Outline of the solution for $L = \sigma/3$

For $L = \sigma/3$, the Baxter $q$-function is given by

$$q(r) = \frac{a}{2} r^2 + \left[ \frac{a}{2p} (-1 + \frac{2}{3} \nu) + b \right] r + A + B \cos \left(\sqrt{2p}r\right) + C \sin \left(\sqrt{2p}r\right),$$

$0 < r < \sigma/3,$

$$= - \frac{a}{2p} (-1 + \frac{2}{3} \nu) + B\sqrt{2} \sin \left[\sqrt{2p}(r - \sigma/3)\right] - C\sqrt{2} \cos \left[\sqrt{2p}(r - \sigma/3)\right],$$

$\sigma/3 < r < 2\sigma/3,$

$$= \frac{a}{2} r^2 + \left[ \frac{a}{2p} \left(1 - \frac{2}{3} \nu\right) + b \right] r + \frac{b}{p} \left(1 - \frac{2}{3} \nu\right) + A - B \cos \left[\sqrt{2p}(r - 2\sigma/3)\right] - C \sin \left[\sqrt{2p}(r - 2\sigma/3)\right],$$

$2\sigma/3 < r < \sigma,$ \hspace{1cm} (A1)

where the parameters $a, b, A, B$ and $C$ satisfy the equations

$$\mathbf{M} \begin{bmatrix} a \\ b' \\ A' \\ B' \\ C' \end{bmatrix} = \begin{bmatrix} \lambda/108 \\ 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}. \hspace{1cm} (A2)$$

Here, $b' = b/\sigma$, $A' = A/\sigma^2$, $B' = B/\sigma^2$ and $C' = C/\sigma^2$ and the matrix $\mathbf{M}$ is the same as that obtained in Appendix B of I with $f = 1$. The solution of this equation is by

$$a = \frac{1}{\Delta} \left(\frac{\lambda}{108} T_{11} + T_{41}\right), \hspace{1cm} (A3a)$$

$$b' = \frac{1}{\Delta} \left(\frac{\lambda}{108} T_{12} + T_{42}\right), \hspace{1cm} (A3b)$$

$$A' = \frac{1}{\Delta} \left(\frac{\lambda}{108} T_{13} + T_{43}\right), \hspace{1cm} (A3c)$$

$$B' = \frac{1}{\Delta} \left(\frac{\lambda}{108} T_{14} + T_{44}\right), \hspace{1cm} (A3d)$$

$$C' = \frac{1}{\Delta} \left(\frac{\lambda}{108} T_{15} + T_{45}\right), \hspace{1cm} (A3e)$$

where $\Delta$, the determinant of $\mathbf{M}$, and the $T_{ij}$ are given by equations (I.B.7)–(I.B.17) with $f = 1$. The nonlinear equation for $\lambda$ analogous to equation (2.18) is
given by

\[
\lambda \tau = 6 \nu B' - 36 \eta \left\{ \frac{a^2}{36 \nu^3} (3 + \nu - 2 \nu^2) + \frac{ab'}{18 \nu^5} (3 - 2 \nu) + \frac{aB'}{2 \nu^2} \left[ 3 - \frac{2 \nu}{3} - \frac{2 \nu c}{3} + \frac{\sqrt{2 \nu s}}{3} + \frac{2 \nu^2 s}{3} \right] \right. \\
+ \frac{aC'}{2 \nu^2} \left[ \frac{\sqrt{2 \nu c}}{3} - \frac{\sqrt{2 \nu^2 c}}{3} - 3s + \frac{s^2 \nu s}{3} \right] + b'B' \frac{\sqrt{2 s}}{3} \\
- b'C' \frac{\sqrt{2 c}}{3} + A'B' \frac{\sqrt{2 s}}{3} + A'C' \frac{\sqrt{2 (1 - c)}}{3} + (B'^2 + C'^2) \frac{2 \nu}{3},
\]

where

\[
c = \cos \left\{ \frac{\sqrt{2 \nu}}{3} \right\}, \quad s = \sin \left\{ \frac{\sqrt{2 \nu}}{3} \right\}, \quad \nu = \frac{\eta \lambda}{9}
\]

APPENDIX B

Estimation of realistic values for the dimensionless temperature \( \tau \)

Reasonable values for the parameter \( \tau \) can be estimated by considering typical gas-phase association reactions such as the association equilibrium between nitrogen dioxide and dinitrogen tetroxide

\[
2 \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4.
\]

Assuming that \( \text{NO}_2 \) and \( \text{N}_2\text{O}_4 \) can be regarded as ideal gases at 25°C and atmospheric pressure, the mole fraction association constant \( K_x \) is given by [7, Chapter 4; 15]

\[
K_x = \frac{x_{A_2}}{x_A^2} = \exp \left[ - \frac{\Delta G_i^0}{RT} \right] = 0.9998,
\]

where \( \Delta G_i^0 = G_i^0, \text{N}_2\text{O}_4 - 2G_i^0, \text{NO}_2 \) and \( G_i^0, \text{NO}_2 \) is the Gibbs free energy of formation of \( i \) at 25°C. In equation (B 2), \( x_i \) is the mole fraction of species \( i \). This ratio is readily expressed in terms of \( \eta \) and \( \lambda \) using equations (2.5) and (2.6)

\[
\frac{x_{A_2}}{x_A^2} = \frac{\mu (1 - \mu)}{(1 - 2 \mu)^2},
\]

where

\[
\mu = \eta \lambda \left( \frac{L}{\sigma} \right)^3.
\]

Equating the expressions for \( K_x \) in equations (B 2) and (B 3), we find that

\[
\mu = \frac{4K_x + 1 - \sqrt{(4K_x + 1)}}{2(K_x + 1)}.
\]

With the value of \( K_x \) given in equation (B 2), and assuming that \( \eta \) is in the range 0.02 to 0.05 (typical gas phase densities) and that \( \lambda \approx 1/\tau \) (since the density is low) equation (B 5) yields \( \tau \approx 0.01-0.025 \) for \( L \approx \sigma/2 \). For \( L \approx \sigma/3 \), \( \tau \) would be approximately one third of these values.
APPENDIX C

Estimation of the density of trimers

By analogy with the arguments leading to the expression (2.5) for the number density of dimers, for the number density of trimers, $\rho_{A_3}$, we obtain

$$\rho_{A_3} = \frac{1}{8} \rho \int \int g_3(r_{12}, r_{13}, r_{23}) \, dr_2 \, dr_3. \quad (C\,1)$$

Let us assume that $g_3$, the triplet distribution function, is given by the Kirkwood superposition approximation (KSA)

$$g_3(r_{12}, r_{13}, r_{23}) = g(r_{12})g(r_{13})g(r_{23}), \quad (C\,2)$$

which is exact to leading order in $\rho$. Using the functional form of $g(r)$ inside the core which follows from equation (2.3) and performing the integral in bipolar coordinates, equation (C 1) becomes

$$\rho_{A_3} \approx \frac{\rho \eta^3}{\pi} \frac{L^3}{72}. \quad (C\,3)$$

Combining equations (2.5) and (C 3), we find that

$$\frac{\rho_{A_3}}{\rho_{A_2}} \approx \frac{\eta}{144} \left( \frac{L}{\sigma} \right)^3 \frac{\lambda^2}{72}. \quad (C\,4)$$

Consider now figures 1 and 2. The dotted line in both figures corresponds to $\langle N \rangle = 1$. For low density and moderate to high temperature, both $\langle N \rangle$ and $\lambda/144$ are small, suggesting that the density of trimers is negligibly small based on this estimate. At low temperature (say $\tau = 0.02$ for which $\lambda \approx 90$ at $\langle N \rangle = 1$), the KSA estimate suggests that the assumption of a negligibly small density of trimers is not satisfactory.

This observation yields yet another insight into the failure of the ZPA for the hard dumbbell fluid at low density [6]. When viewed from the vantage point developed in Section 3 of this paper—that is, that the ZPA represents the PY approximation for a fluid with pair potential (1.6) and density-dependent dimensionless temperature $\tau$ such that $\langle N \rangle = 1$ and $\lambda$ is given by (3.1)—we see that as the density becomes small ($\eta \approx 0.1$, say) the proportion of trimers increases rapidly. This is because in the complete association limit equation (C 4) becomes

$$\frac{\rho_{A_3}}{\rho_{A_2}} \approx \left( \frac{L}{\sigma} \right)^3 \frac{1}{288 \eta}. \quad (C\,5)$$

At high densities, this estimate suggests that the proportion of trimers is very small indeed, while at low density (where the ZPA ultimately becomes unphysical as the density tends to zero) the proportion of trimers (and presumably higher order $n$-mers) is becoming unboundedly large. Since the KSA is exact in the low density limit, it can be expected to give quantitatively reliable results for the integral (C 1) in that limit.
REFERENCES