On the Yukawa closure of the Ornstein–Zernike equation

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In this Research Note we describe a simplification of part of the solution of
the Ornstein–Zernike (OZ) equation for hard spheres with a Yukawa closure.
The simplification seems particularly useful when the system may undergo a
liquid–gas phase transition. The system of equations to be solved is, in the usual
notation

\[ h(|r|) = c(|r|) + \rho \int d^3 s \, c(|s|) h(|r - s|), \]
\[ h(r) = -1, \quad 0 < r < 1, \]
\[ c(r) = K \exp \left[ -\xi (r - 1) \right], \quad r > 1. \]

The solution proceeds by the method of Baxter [1] and introduces the function
\( q(r) \) which has the form [2]

\[ q(r) = \begin{cases} \frac{1}{2} a(r^2 - 1) + b(r - 1) + \beta d \{ 1 - \exp \left[ -\xi (r - 1) \right] \}, & 0 < r < 1 \\ \beta \exp \left[ -\xi (r - 1) \right], & r > 1. \end{cases} \]

The parameters \( a, b \) and \( d \) are given in terms of \( \beta \) and the reduced density
\( \eta = \pi \rho / 6 \) by

\[ a = a_{PY} + \frac{12 \beta \exp (\xi) \left\{ \left( 1 + 2 \eta - \frac{6 \eta}{\xi} \right) \left[ d - 1 - d \exp \left( -\xi \right)(1 + \xi) \right] + 3 \eta d \xi \exp \left( -\xi \right) \right\}}, \]
\[ b = b_{PY} - \frac{12 \beta \exp (\xi) \left\{ \left( \frac{3 \eta}{2} + \frac{1 - 4 \eta}{\xi} \right) \left[ d - 1 - d \exp \left( -\xi \right)(1 + \xi) \right] - \frac{1 - 4 \eta}{2} d \xi \exp \left( -\xi \right) \right\}}, \]

and

\[ d = [(-K + \beta D) \exp \left( -\xi \right) + E \beta^2] / F \beta^2, \]

where \( a_{PY} = (1 + 2 \eta)(1 - \eta)^2 \) and \( b_{PY} = -3 \eta / 2(1 - \eta)^2 \) are the corresponding
parameters for the hard sphere PY system and

\[ D = \xi - a_{PY} S - b_{PY} T, \]
\[ E = -6 \eta + \frac{12 \eta}{\xi(1 - \eta)^2} \left( 1 + 2 \eta - \frac{6 \eta}{\xi} \right) S - \frac{12 \eta}{\xi(1 - \eta)^2} \left( \frac{3 \eta + (1 - 4 \eta)}{\xi} \right) T, \]
\[ F = -6\eta[1 - \exp(-\xi)]^2 + \frac{12\eta}{\xi^2(1-\eta)^2} \left\{ \left[ \left( 1 + 2\eta - \frac{6\eta}{\xi} \right) [1 - \exp(-\xi)(1 + \xi)] \right. \\
+ 3\eta\xi \exp(-\xi) \right\} S - \left\{ \left( \frac{3\eta^2}{2} + \frac{1-4\eta}{\xi} \right) [1 - \exp(-\xi)(1 + \xi)] \right. \\
- \left. \frac{1-4\eta}{2} \xi \exp(-\xi) \right\} T, \]

(4c)

\[ S = \frac{12\eta}{\xi^2} \left[ 1 - \xi^2/2 - \exp(-\xi)(1 + \xi) \right], \]

(4d)

and

\[ T = \frac{12\eta}{\xi} [1 - \exp(-\xi)]. \]

(4e)

The equation for \( \beta \) (or which ever other parameter is kept 'fundamental') is known [2] to be a rather complicated quartic. Our particular formulation allows the reduction of this quartic to

\[ 36\eta^2 \beta^4 - X\beta^3 + 12\eta K\beta^2 - K^2 Y\beta + K^3 = 0, \]

(5)

with

\[ X = 6\eta \left\{ \xi \exp(-\xi) - \frac{6\eta}{\xi^2(1-\eta)} \left[ 2 - 2\xi - \exp(-\xi)(2 - \xi^2) \right] \\
- \frac{18\eta^2}{\xi^2(1-\eta)^2} [2 - \xi - \exp(-\xi)(2 - \xi)] \right\} \]

(6a)

and

\[ Y = \xi - \frac{6\eta}{\xi^2(1-\eta)} \left[ 2 - \xi^2 - 2 \exp(-\xi)(1 + \xi) \right] \\
- \frac{18\eta^2}{\xi^2(1-\eta)^2} [2 - \xi - \exp(-\xi)(2 + \xi)]. \]

(6b)

The quartic equation seems somewhat simpler than those published earlier. Only one root of equation (5) will give, in the limit \( \rho \to 0 \), ideal gas behaviour and the PY hard sphere solution in the limit \( K \to 0 \). With the correct root \( \beta \), the other parameters may be found and the properties of the system calculated by known methods [2–4]. We note, however, that obtaining the parameters explicitly in terms of \( \beta \) leads to explicit expressions for the virial and energy pressures which appear to be rather simpler to use than earlier work on this problem has been.

As \( \rho \to 0 \) the four roots of equation (5) have asymptotic expansions

\[ \beta_1 = \frac{K}{\xi} (1 + O(\eta)), \quad \beta_{2,3} = \pm \left[ -K \exp(\xi)/6\eta \right]^{1/2}(1 + O(\eta)), \]

\[ \beta_4 = \frac{\xi \exp(-\xi)}{6\eta} (1 + O(\eta)). \]

(7)

As \( K \to 0 \), \( \beta_4 \) does not reduce to zero and \( \beta_{2,3} \) diverge as \( \rho \to 0 \) so that root \( \beta_1 \) must be chosen. For \( K < 0 \) (corresponding in the mean spherical approximation to a repulsive potential) the curve \( \beta_1(K, \xi, \eta) \) is a smooth function of \( \eta \) and so may be identified without difficulty. For \( K > 0 \) (corresponding to an attractive potential)
only $\beta_4$ and $\beta_4$ are real as $\rho \to 0$. This behaviour of the roots persists for all $\eta$. In figure 1 we plot the two real roots as a function of $\eta$ for $\xi=2$ and $K=0.812, 1.0827, 1.218, 1.624$. The locus of points for which the discriminant of equation (5) is zero ($L_2$) and the locus of points for which the compressibility is infinite ($L_1$) (that is $a^2=0$) are also given. The graph of the roots is similar to that for the roots of the equation which arises in Baxter’s PY theory of adhesive hard spheres [5]. The behaviour of the roots (and of the consequent fluid structure) allows the phenomenon to be interpreted as a liquid–gas phase transition. At fixed $K$ and $\xi$, the range of values of $\eta$ between the intersections of the graph of roots with the curve $L_1$ is then the metastable limit of the two-phase region.

An interesting extension of this work is to consider the mean spherical model for a mixture of two fluids with equal density and equal diameter with the interaction potential

\[
\Phi_{ij} = \begin{cases} 
\infty, & r < 1, \\
-\frac{L}{r} \exp[-\xi(r-1)], & r > 1,
\end{cases} \\
\Phi_{12} = \begin{cases} 
\infty, & r < 1, \\
L \exp[-\xi(r-1)]/r, & r > 1,
\end{cases}
\tag{8}
\]
with \( L > 0 \); thus like particles attract and unlike particles repel. Introducing

\[
t^\pm(r) = \frac{1}{2}(t_{11}(r) \pm t_{12}(r)),
\]

(9)

for \( t = h \) or \( c \), the Ornstein–Zernike equation for the mixture decouples. The equation for \( h^+, c^+ \) is simply the hard sphere PY equation, while for \( h^- \) and \( c^- \) the equations are

\[
\begin{align*}
    & h^-(|r|) = c^-(|r|) + \rho \int d^3 s c^-(|s|) h^-(|r-s|), \\
    & h^-(r) = 0, \quad r < 1, \\
    & c^-(r) = \frac{K}{r} \exp[-\xi(r-1)], \quad r > 1,
\end{align*}
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\end{align*}
\]

with \( K = L/kT \). The results for this system are identical to those for the one-component system discussed earlier but with

\[
q^-(r) = \begin{cases} 
\beta d [1 - \exp(-\xi(r-1))], & 0 < r < 1, \\
\beta \exp(-\xi(r-1)), & r > 1,
\end{cases}
\]

(11)

\[
d = \frac{6\eta\beta^2 \exp(\xi) - \beta \xi + K}{6\eta\beta^2 \exp(\xi)[1 - \exp(-\xi)]^2}
\]

(12)

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\begin{align*}
    & h^-(|r|) = c^-(|r|) + \rho \int d^3 s c^-(|s|) h^-(|r-s|), \\
    & h^-(r) = 0, \quad r < 1, \\
    & c^-(r) = \frac{K}{r} \exp[-\xi(r-1)], \quad r > 1,
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\]

(12)

Figure 2. The behaviour of the parameter \( \beta \) as a function of density \( \eta \) for \( \xi = 3 \) along isotherms \( K = 0.1 \) ( ), \( K = 0.25 \) ( ), \( K = 0.5 \) ( ) and \( K = 0.8 \) ( ). The curves \( L_1 \) and \( L_2 \) are defined in the text.
and $\beta$ satisfying

$$36\eta^2 \beta^4 - 6\eta^2 \xi \exp(-\xi)\beta^3 + 12\eta K\beta^2 - K\xi\beta + K^3 = 0. \quad (13)$$

As before we select the root for which $\beta \sim K/\xi(1 + O(\eta))$ as $\eta \to 0$. In figure 2 we plot the two roots of equation (13) and the loci of points on which the two real roots are equal ($L_2$) and on which $1 - 2\pi \int_0^\infty g^-(r) \, dr = 0$ ($L_1$), for $\xi = 3$ with $K = 0.1, 0.25, 0.5$ and 0.8. Clearly $\beta_1$ is the smaller real root, always. The function $h_{11}(r)$ is fluid-like while $h_{12}(r)$ shows a much suppressed first peak, reflecting the nearest-neighbour exclusion. As $\eta$ increases, the first peak in $h_{12}(r)$ increases in height until the limit $L_1$ is reached and the system apparently undergoes a separation into a one-rich and a two-rich phase.

References