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On the compressibility equation of state for multi-component adhesive hard sphere fluids

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The compressibility equation of state (EOS) for a multi-component sticky hard sphere model alternative to Baxter's one is investigated within the mean spherical approximation (MSA). For this model and this closure, as well as for a more general class of models and closures leading to Baxter functions $q_0(r)$ with density-independent stickiness coefficients, no compressibility EOS can exist for mixtures, unlike the one-component case (in view of this, an EOS recently reported in the literature turns out to be incorrect). The reason is the failure of the Euler reciprocity relation for the mixed second-order partial derivatives of the pressure with respect to the partial densities. This is in turn related to the inadequacy of the approximate closure (in particular, the MSA). A way out to overcome this drawback is presented in a particular example, leading to a consistent compressibility pressure, and a possible generalization of this result is discussed.

1. Introduction

Baxter's 'sticky hard sphere' model [1, 2] (hereafter referred to as the SHS1 model) has often been employed in studies on colloidal suspensions of adhesive particles. Its potential adds to a hard sphere (HS) repulsion an infinitely strong surface adsorption, defined by an attractive square-well tail with vanishing width and infinitely increasing depth, giving a finite non-zero contribution to the second virial coefficient ('sticky limit') [1]. The SHS1 model admits analytical solution if the Ornstein–Zernike (OZ) integral equations of the liquid state theory are coupled with the Percus–Yevick (PY) approximation [1–3]. The resulting expression for a fluid with $p$ components requires the knowledge of a set of density-dependent parameters $\{\lambda_p\}$, whose values have to be determined by solving numerically $p(p+1)/2$ coupled quadratic equations [2]. The applicability of the SHS1–PY solution is, therefore, limited to systems with a small number of components [4].

On the other hand, colloidal suspensions are rather commonly polydisperse. Polydispersity means that mesoscopic suspended particles of a same chemical species are not necessarily identical, but some of their properties (size, charge, etc.) may exhibit a discrete or continuous distribution of values. Even when all macroparticles belong to a unique chemical species, a polydisperse fluid must therefore be treated as a multi-component mixture, with very large $p$ values—of order $10^1$ to $10^3$ or more (discrete polydispersity)—or with $p \to \infty$ (continuous polydispersity).

The above-mentioned shortcomings of the SHS1–PY solution offer a strong motivation for investigating an alternative sticky hard sphere model, proposed by Brey et al. [5] and Mier-y-Teran et al. [6], and hereafter referred to as the SHS2 model. The adhesive part of its potential is defined starting from an attractive Yukawa tail, which, in the sticky limit, has both amplitude and inverse range tending to infinity, with their ratio remaining constant. In this case, the OZ equations are analytically solvable within the mean spherical approximation (MSA) [6, 7]. Although the SHS2–MSA solution is simpler than the SHS1–PY one, it has received much less attention, especially in the multi-component case.

In two previous papers [8, 9] we investigated structural properties of polydisperse fluids using a version of the SHS2 model where the coupling (stickiness) parameters, which define the strength of the Yukawa attraction, are factorized. This choice is the simplest one [10, 11]. In fact, a slightly different version of the SHS2 potential (with non-factorized coefficients), proposed by Tutschka and Kahl [12–14] leads to more complicated analytical results, without any increase of the physical insight.

Once the structural properties of a model are known, the next natural step is to study the corresponding thermodynamics. Unfortunately, neither for SHS1 [3] nor for SHS2 (see below) is this a simple task.

In this paper we focus in particular on the compressibility equation of state (EOS) of the SHS2 multi-component model, since the compressibility route represents the simplest method for obtaining the pres-
sure, given an analytical expression for Baxter’s factor correlation function $q_{ij}(r)$. Under rather general conditions, we show that no compressibility EOS can exist for the SHS2 multi-component model, within the MSA. We argue how this inconsistency stems from the MSA closure, and show a possible way out to overcome this difficulty, by using a simple illustrative example.

After this work had been completed, we became aware of a recent analysis by Ginoza [15], where the author discusses a factorized model essentially identical to the one considered in our previous work [8], but fails to recognize the MSA inconsistency, and thus reports an incorrect expression for the compressibility EOS.

Our findings agree with those by Tutschka and Kahl [13, 14], who observed the same inconsistency within their particular version of the SHS2 model.

2. The SHS2 model

The starting point of the SHS2 model is a fluid with particles interacting via a HS repulsion plus a particular Yukawa (HSY) attraction, i.e.

$$w_{ij}^{HSY}(r) = \begin{cases} +\infty, & 0 < r < \sigma_{ij} = (\sigma_i + \sigma_j)/2, \\ -zA_{ij} \exp[-z(r-\sigma_{ij})]/r, & r \geq \sigma_{ij}. \end{cases}$$

(1)

Here, $\sigma_i$ denotes the HS diameter of species $i$ (whose number density is $\rho_i$), $z$ is the inverse range of the Yukawa tail, all $A_{ij} = A_{ji}$ stickiness parameters are $\geq 0$ and the well depth, $\epsilon_{ij} = zA_{ij}/\sigma_{ij}$, depends on $z$ linearly. The OZ equations for HSY mixtures have been solved analytically [16] for any finite $z$, within the MSA closure, i.e. $c_{ij}(r) = -zA_{ij}(r)/\sigma_{ij}$ for $r > \sigma_{ij}$ ($c_{ij}(r)$ is the direct correlation function and $\beta = (k_BT)^{-1}$, with $k_B$ being Boltzmann’s constant and $T$ being the absolute temperature). The MSA solution for SHS2 can thus be obtained by taking the sticky limit, $z \to \infty$, of the solution $q_{ij}^{HSY-MSA}(r)$ for the HSY fluid. The result is

$$q_{ij}(r) = \begin{cases} \frac{1}{\xi_0} \left( a_i(r^2 - \sigma_i^2) + b_i(r - \sigma_i) + K_{ij} \right), & L_q < r \leq \sigma_{ij}, \\ 0, & \text{elsewhere,} \end{cases}$$

(2)

$$a_i = \frac{1}{A} + \frac{3(\xi_0 - \xi_3)}{A^2} \frac{X_i}{A}, \quad b_i = -\frac{3(\xi_0 - \xi_3)}{2A^2} \frac{X_i}{A},$$

(3)

$$X_i = \frac{\rho_i}{6} \sum_m m \omega_{im} M_{im}, \quad M_{im} = 12K_{im},$$

(4)

where $L_q = (\sigma_i - \sigma_j)/2$, $\xi_0 = (\pi/6) \sum_i \rho_i \sigma_i^3$ and $A = 1 - \xi_3$. The coefficients $K_{ij} = q_{ij}(\sigma_{ij})$, given by

$$K_{ij} = \frac{A_{ij}}{k_B T},$$

(5)

are density-independent and have dimensions of $[\text{length}]^2$.

Tutschka and Kahl’s version of the SHS2 model [12–14] hinges upon non-factorized parameters, $K_{ij}^{SHS2-MSA} = \gamma_{ij} \sigma_{ij}^3$, with $\gamma_{ij}$ obeying a Berthelot-type rule, i.e. $\gamma_{ij} = (\gamma_1 \gamma_2)^{1/2}$. Our version with factorized coefficients assumes that $A_{ij} = \epsilon_0 G_{ij} G_j$, where $\epsilon_0$ is an energy and $G_m$ has dimensions of length. Thus

$$K_{ij} = Y_i Y_j,$$

(6)

where

$$Y_m = \gamma_0 G_m, \quad \gamma_0^2 = \frac{\epsilon_0}{k_B T} = \frac{1}{12T^*},$$

(7)

with $T^*$ being a reduced temperature (as in Baxter’s model, the factor 1/12 is introduced for later convenience. In our previous papers [8, 9] it was absent and the correspondence between the two reduced temperatures is $T^* = T^{red}/12$).

Irrespective of the choice for the coefficients $A_{ij}$, the SHS1 and SHS2 potentials are different and should not be confused even in the sticky limit. An intuitive way of understanding this point is to notice that, as the well width goes to zero, the area of the square well in Baxter’s SHS1 model vanishes, whereas the area under the Yukawa tail in SHS2 remains finite [5]. This difference becomes important when evaluating thermodynamics. In fact, it can be shown that the virial pressure depends not only on the $q_{ij}(r)$ resulting after the sticky limit, but also on the functional form of the tail as well as on the way the sticky limit is taken [17].

At the level of approximate solution for $q_{ij}(r)$, the difference between the SHS2–MSA and SHS1–PY expressions lies only in the coefficients $K_{ij}$, which in the latter case read

$$K_{ij}^{SHS1-PY} = \frac{1}{12\tau_q} y_{ij}^{PY}(\sigma_{ij}) \sigma_{ij}^2 \equiv \frac{1}{12} \lambda_{ij} \sigma_{ij}^2,$$

(8)

where the dimensionless positive parameter $\tau_q$, which appears in the SHS1 potential, is related to both the temperature and the stickiness between particles of species $i$ and $j$, while $y_{ij}(\sigma_{ij})$ is the contact value of the cavity function. Note that $K_{ij}^{SHS1-PY}$ is non-factorized and density-dependent, since $y_{ij}(\sigma_{ij})$ depends on the densities of all components in the mixture. This difference, albeit seemingly harmless, has far reaching consequences, as will be shown in the following.

3. Compressibility equation of state

Once $q_{ij}(r)$ is known, one can calculate derivatives of the compressibility ($c$) pressure by means of two general relations, obtained from fluctuation theory in the grandcanonical ensemble and from Baxter’s factorization of the three-dimensional Fourier transform of $c_{ij}(r)$, i.e.
\[ \frac{\partial P}{\partial \rho} \bigg|_{T,\rho} = a_i - 2\pi \sum_m \rho_m \bar{a}_m(0), \]  
where \( \bar{q}_m(k) \) is the one-dimensional Fourier transform of \( q_m(r) \), \( \rho = \sum_i \rho_i \) is the total number density and \( x_i = \rho_i/\rho \) is the molar fraction of species \( i \). Moreover, \( \chi_T = \rho k_B T \chi_T \) denotes the isothermal susceptibility (\( K_T \) being the isothermal compressibility) and \( a_i = 1 - 2\pi \sum_i \rho_i \bar{a}_i(0) \). Note that the pressure is a function of \((T, \rho_1, \ldots, \rho_p)\) in equation (9), and of \((T, \rho, x)\) in equation (10), where \( x = (x_1, \ldots, x_{p-1}) \) represents the molar composition.

We can apply the previous relations to SHS models for colloidal fluids, after observing that equation (2) yields \( \bar{q}_m(0) = 12^{-1} a_m \sigma_m^3 + 3A^{-1} \sigma_m^2 - M_m \sigma_m^4 \). Inserting this term and the \( a_i \) given by equation (3) into equations (9) and (10), one gets an expression for \( \frac{\partial P}{\partial \rho_i} \bigg|_{T,\rho} \) along with

\[ \frac{\partial P}{\partial \rho} \bigg|_{T,\rho} = \chi_T^{-1} \left( \frac{\partial P}{\partial \rho} \bigg|_{T,\rho} \right) + \frac{2\langle X \rangle}{\Delta^2} - \frac{6\sigma^2 \langle \sigma X \rangle}{\Delta^3} + \frac{\langle X^2 \rangle}{\Delta^2}, \]  
where we have introduced compositional averages, such as \( \langle f \rangle \equiv \sum_m f_m \bar{f}_m \) and \( \langle f g \rangle \equiv \sum_m f_m g_m \bar{g}_m \). The derivative with superscript HS–PYc refers to the compressibility pressure of the corresponding HS mixture, evaluated within the PY approximation. Note that the two results hold for both the SHS2–MSA and SHS1–PY solutions, if the corresponding \( K_y \)'s are used.

In order to obtain the compressibility pressure, it might now be spontaneous to perform immediately the integration of equation (11) with respect to \( \rho \), at fixed composition \( x \), i.e. \( \int_0^\rho \chi_T^{-1} \text{d}\rho \). When applied to the first term on the right-hand side of equation (11), \( \frac{\partial P}{\partial \rho} \bigg|_{T,\rho} \), this procedure does indeed lead to the known PYc–EOS for HS mixtures. For the SHS models, the integration requires the knowledge of the dependence (if any) of the coefficients \( K_y \) on density.

In the SHS1–PY case, the aforesaid calculation is nevertheless practically impossible, due to the lack of an explicit expression for \( \chi_T(\rho) \). This difficulty has been by-passed by exploiting a further result by Baxter, which directly provides the PY compressibility pressure itself rather than the inverse susceptibility [2, 3]. On the other hand, in the SHS2–MSA case the density independence of \( K_y^{\text{HS2–MSA}} \) might suggest that the integration of \( \chi_T^{-1} \) is a straightforward operation. Unfortunately, this is not so.

In fact, to ensure that the whole procedure is correct, one must first test whether the differential \( \sum_i \chi_T(\rho_i) \text{d}\rho_i \) constructed with the partial derivatives given by equation (9), is exact, since \( P \) must be a state function. For this to occur, it is necessary that

\[ \frac{\partial}{\partial \rho_i} \left( \frac{\partial P}{\partial \rho_i} \right) = \frac{\partial}{\partial \rho_j} \left( \frac{\partial P}{\partial \rho_j} \right), \]  
for any pair \( i \) and \( j \). This symmetry condition (Euler reciprocity relation), obeyed by any exact theory, may not be met when using an approximate closure. In this case, no compressibility EOS can exist within the considered approximate theory. Now, we show that the equality (12) of the mixed second-order partial derivatives is not necessarily satisfied for SHS mixtures.

Let us assume, rather generically, that a certain SHS model with an approximate closure has a solution \( q_0(\tau) \) given by equations (2)–(4) with density-independent, symmetric, coefficients \( M_y = 12K_y = M_y \). Inserting this solution into equation (9) and taking the derivative of \( \partial P/\partial \rho_i \) with respect to \( \rho_j \) yields a rather lengthy expression for \( \partial^2 P/\partial \rho_i \partial \rho_j \). Upon discarding all terms which are apparently symmetric with respect to an exchange of indices \( i \) and \( j \), we are left with the following sum

\[ S_{ij}(\tau) = - \frac{1}{A} \sigma_i M_{ij} X_j + \frac{6\sigma^2}{A^3} \sigma_j^3 \sigma^3 \sigma_j X_j \]
\[ + \frac{1}{A^2} \left[ \sigma_i^2 (X_i - X_j^2) + 3\sigma_j^2 \sigma_j X_j + \sigma_i^3 \sigma_j \right] \times \left[ X_j^{(0)} - \frac{\pi}{6} \sum_i \rho_i X_i M_{ij} \right], \]

where \( X_i^{(0)} = (\pi/6) \sum \rho_i M_{ij} \). A compressibility EOS can exist, within an approximate theory of the considered kind, only if the relevant coefficients \( M_y \) are such that \( S_{ij}(\tau) = S_{ji}(\tau) \).

The choice \( M_{ij}^{\text{SHS2–MSA}} = 12\gamma_{ij} \sigma_j^2 \), with \( \gamma_{ij} = (\gamma_{ij} \gamma_{ij})^{1/2} \) [12–14], does not meet this requirement. On the other hand, it is easy to verify that even any choice with factorized coefficients, \( M_{ij} = M_{ij} G_i G_j \), fails to satisfy the necessary condition (\( M_0 \) is a density-independent factor, which in our model defined by equations (6) and (7) coincides with \( 1/T^* \)). \( S_{ij}(\tau) \) cannot be symmetric for a generic choice of \( G_i \)'s, but the same is true if we assume the power-law relationship between stickiness and size employed in [8, 9], i.e. \( G_i = \sigma_i \alpha / \langle \sigma \rangle \alpha - 1 \), where \( \langle \sigma \rangle \) denotes the average diameter and \( \alpha > 0 \). In this case, the value \( \alpha = 1 \) is however indicated as preferable, since it represents the only way of making the first term, \( -A^{-1} \sigma_i M_{ij} X_j \), symmetric.
Thus no compressibility EOS can exist within the SHS2–MSA theory with coefficients given either by any factorization rule $M_y = M_y G_i G_j$, or by the unfactorized choice of [12–14]. We note that in Ginoza’s recent analysis [15] this crucial point has not been realized, and the corresponding expression for the compressibility EOS is therefore incorrect.

It is clear that the violation of relation (12) can be traced back to the inadequacy of the MSA closure, which is responsible for the density-independence of the coefficients $M_y$ (or $K_y$). More generally, one might suspect that no compressibility EOS can exist for any solution $q_y(r)$ given by equations (2)–(4) as long as the $M_y$’s are density-independent.

Let us now assume that the $M_y$’s depend on the densities ($\rho_1, \ldots, \rho_y$). In this case, $\nabla^2 \beta P / \partial \rho \partial \rho_j$ contains further contributions stemming from derivatives. Again discarding those that are clearly symmetric, one gets the following terms

$$S_2(ij) = \frac{1}{\Delta} \sum_l \rho_l \left( \sigma_j + \frac{3\sigma_2}{\Delta} \sigma_j \sigma_i + \sigma_l \right) \frac{\partial M_{li}}{\partial \rho_j}$$

$$+ \frac{1}{\Delta^2} \frac{\pi}{6} \sum_{l,m} \rho_l \rho_m \left( 2 \sigma_i \frac{\partial \sigma_m}{\partial \rho_j} + \frac{6\sigma_2}{\Delta} \right)$$

$$\times \frac{\partial M_{ml}}{\partial \rho_j}$$

$$- \frac{1}{\Delta} \sigma_j \frac{\pi}{6} \sum_{l,m} \rho_l \rho_m \frac{\partial (M_{ml} M_{ml})}{\partial \rho_j}$$

$$- \frac{1}{\Delta^2} \frac{\pi}{6} \sum_{l,m,n} \rho_l \rho_m \rho_n \frac{\partial (M_{ml} M_{ml})}{\partial \rho_j},$$

which must be added to $S_1(ij)$, to form a new symmetry condition for $S(ij) \equiv S_1(ij) + S_2(ij)$.

We emphasize the fact that the density-dependent coefficients of the SHS1–PY solution, as given by equation (8), should satisfy the requirement $S(ij) = S(ij)$, but a direct test of this feature proves to be a highly non-trivial task. However, this observation suggests that a simple density-dependent modification of the best SHS2–MSA choice, $M_y = M_0 \sigma_j$, along the lines of the SHS1–PY solution, might lead to a fulfilment of the symmetry condition. Indeed, we find that the choice

$$M_y = M_0 \frac{1}{\Delta} \sigma_j,$$

with $M_0 = \phi \left( \frac{1}{T^*} \right)$, (15)

(where $\phi$ is an arbitrary function vanishing as $T^* \to \infty$) leads to a compressibility pressure $P$ satisfying condition (12).

Next, we discuss a possible physical origin of the factor $1/\Delta$ appearing in the above solution. First, we note that in $K_{SHS1-PY}^{SHS1-PY}$ of equation (8) one could relate $\sigma_j^2$ to a measure of adhesive interaction surface (since the centre of a particle $i$ moving around—but remaining in contact with—a particle $j$, must lie on a spherical surface with radius $\sigma_j$), while the density-dependent factor $y_j(\sigma_j)$ represents the probability of finding a particle of index $i$ touching any given particle of species $j$. On the other hand, in the corresponding modified expression (15), one could imagine $\sigma_i \sigma_j$ as representing the area of an interaction spherical surface with radius $(\sigma_i \sigma_j)^{1/2}$, while $1/\Delta$ may be reckoned as a crude approximation to $y_j(\sigma_j)$ (1/\Delta is indeed the simplest term, independent of the species indices $i$ and $j$, appearing in the expression of the cavity functions at contact).

There are (at least) two ways to relate the result (15) to some possible closure, which should represent an improvement over the MSA one. First, one might consider a generalized mean spherical approximation (GMSA) [18] instead of the MSA. This amounts to replacing the MSA,

$$c_y(r) = -\partial_y \ln \frac{\gamma_{MSA}(r)}{r}$$

for $r > \sigma_j$,

with the Yukawa closure $c_y(r) = z K_y \exp \left[ -\frac{z(r - \sigma_j)}{r} \right]$ for $r > \sigma_j$, with parameters $K_y$ not given by equation (5), but density-dependent and initially undetermined. The GMSA has often been used in the past, and its unknown coefficients $K_y$ have usually been determined by employing some thermodynamic consistency condition [18]. In the present case, one could regard the symmetry condition (12) as an alternative condition for the GMSA closure. Within this conceptual framework, equation (15) is the simplest solution.

Alternatively, we recall that the PY approximation may be written in the form $c_y(r) = f_y(r) y_j(r)$, while the MSA may be derived from it under the approximation $f_y(r) \approx -\partial_y$, with $y_j(r) \approx 1$, for $r > \sigma_j$. Hence one could define a new density-dependent closure for SHS potentials, assuming $c_y(r) = -y_j(\sigma_j) \exp \left[ -\frac{z(r - \sigma_j)}{r} \right]$ for $r > \sigma_j$. The use of $\partial_y \ln \gamma_{SHS1-PY}(r)$ with factorized coefficients, along with the rough approximation $y_j(\sigma_j) \approx 1/\Delta$, would then lead to the $M_y$ coefficients expressed by equation (15) with $\phi(1/T^*) = 1/T^*$.

Finally, it is worth reporting that the solution corresponding to equation (15) yields the following compressibility EOS for SHS2 mixtures

$$\beta P \gamma = \frac{\eta}{1 - \eta} + (3 - M_0) \frac{\eta^2}{1 - \eta}$$

$$+ \frac{1}{3} (3 - M_0) \frac{2\eta}{1 - \eta},$$

where $\gamma = (\pi/6) \sigma^3$ denotes the average volume of a particle, $\eta = \xi_3 = \rho \gamma$ is the packing fraction, while the
dimensionless parameters
\[ e_1 \equiv \langle \sigma \rangle^2 / \langle \sigma^2 \rangle, \quad e_2 \equiv \langle \sigma^2 \rangle / \langle \sigma^3 \rangle^2 \]
depend on the molar composition \( x \) and reduce to \( e_1 = e_2 = 1 \) for one-component fluids. Note that
\( M_0 = \phi(1/T^*) \) may or may not coincide with \( 1/T^* \), but must vanish as \( T^* \to \infty \), so that the PYc-EOS for HS mixtures is recovered.

The simplicity of equation (16) is due to the fact that now we get
\[
\alpha_i = \frac{1}{A} + (3 - M_0) \frac{v_0^i}{A^2}, \\
\phi_i = -(3 - M_0) \frac{v_0^i}{2A^2},
\]
\[
\tilde{q}_{ni}(0) = 12^{-1} \left\{ \left[ \frac{1}{A} + (3 - M_0) \frac{v_0^i}{A^2} \right] \sigma_i^2 \\
+ (3 - M_0) \frac{1}{A} \sigma_i^2 \right\},
\]

since \( X_i = M_0 \sigma_i / A \). These quantities are very similar to their HS counterparts, from which they differ only in having the HS factor 3 replaced with the temperature-dependent coefficient \( 3 - M_0 \).

Note that the one-component version of equation (16) differs from the SHS2-MSA result of Mier-y-Teran et al. [6], which may be written, after some rearrangement, as
\[
\beta_{P_{\text{SHS2-MSA}}} v_0 = \frac{1}{(1 - \eta)^3} + \frac{1}{T^* x} \eta + \left( \frac{4}{T^* x} + \frac{2}{T^* x^2} \right) \ln (1 - \eta) \\
+ \left( \frac{4}{T^* x} + \frac{1}{T^* x^2} \right) \frac{\eta}{3 - \eta} \left( \frac{\eta}{1 - \eta} \right)^2,
\]
where \( v_0 = (\pi/6) \sigma^3 \) and \( (T^*)^{-1} \) equals the parameter \( 12 \theta \) of [6]. The second and third virial coefficients corresponding to this MSA expression are
\[
B_2/v_0 = 4 - (T^*)^{-1} \quad \text{and} \quad B_3/v_0 = 10 - (10/3)(T^*)^{-1} + (1/3) \times (T^*)^{-2},
\]
respectively. On the other hand, for pure fluids our non-MSA EOS (16) gives
\[
B_2/v_0 = 4 - M_0 \quad \text{and} \quad B_3/v_0 = 10 - 4M_0 + (1/3)M_0^2,
\]
which can be easily compared with the MSA result, after assuming \( M_0 = (T^*)^{-1} \).

Finally, if one identifies \( M_0 \) with \( \tau^{-1} \) (\( \tau \) being Baxter's stickiness-temperature parameter for one-component fluids), then our SHS2 \( B_2 \) also coincides with the exact one of the SHS1 model, while \( B_1 \) markedly differs from its counterpart \( B_1^{\text{SHS1-PYC}} / v_0 = B_1^{\text{SHS1-exact}} / v_0 = 4 - \tau^{-1} \) and \( B_3^{\text{SHS1-PYC}} / v_0 = B_3^{\text{SHS1-exact}} / v_0 = 10 - 5\tau^{-1} + \tau^{-2} - (1/18)\tau^{-3} \) [3].

4. Conclusion

The PY compressibility EOS of Baxter's SHS1 model is in practice inapplicable to fluids with a large number of components. This difficulty urges one to search for either alternative closures or different models.

In this paper we have investigated the SHS2 model, which is analytically solvable within the MSA, and whose thermodynamics is still rather unexplored, especially in the multi-component case. In particular we have focused on the compressibility EOS, since it is the simplest route to obtain the pressure from \( q_\eta (r) \).

Mixtures require a more careful analysis than pure fluids, and it is always possible that an approximate multi-component theory suffers from some thermodynamic inconsistency not present in its one-component version. In particular, in order to ensure the existence of the compressibility EOS for mixtures, we have pointed out the necessity of an explicit check of the Euler reciprocity relation \( \partial^2 \beta P / \partial \rho_i \partial \rho_j = \partial^2 \beta P / \partial \rho_j \partial \rho_i \), which can be expressed in terms of \( q_\eta (r) \). This crucial condition is usually overlooked in the literature, perhaps because it would be automatically fulfilled by an exact theory. On the other hand, in any approximate theory such a symmetry condition may break down.

There are two main results of the present work. First, we have found that, although an MSA compressibility EOS is known for pure SHS2 fluids [6], its extension to mixtures is not possible, since the SHS2-MSA solution violates the aforesaid condition. As a direct consequence, the compressibility EOS recently reported by Ginoza [15] is faulty. We also have discussed how such an inconsistency occurs for any choice of factorized stickiness coefficients, as well as for Tutschka and Kahl's unfactorized one [12-14], and argued that it stems from a deficiency of the MSA closure. The reason appears to be the density-independence of the MSA coefficients \( K_{ij} = q_\eta (\sigma_{ij}) \). Second, we have presented an illustrative example, where the inclusion of a simple and plausible density-dependence in \( K_{ij} \) produces a fulfillment of the Euler condition, and generates a possible compressibility EOS.

These results seem to suggest that no multi-component compressibility EOS can exist for any closure leading to a solution \( q_\eta (r) \) of the form given by equations (2)-(4) with density-independent \( K_{ij} \) coefficients. This deficiency can be overcome only by abandoning the MSA and resorting to density-dependent closures. We have attempted to do this, by interpreting our results as originating from a different, more sophisticated, approximate theory.

Although it is clear that our expression (16) cannot be considered as the correct final solution to our problem, nevertheless it is not a simple academic exercise, but represents a useful step towards a satisfactory EOS for SHS mixtures.

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On the compressibility EOS for multicomponent adhesive hard sphere fluids

References