Pathologies in the sticky limit of hard sphere Yukawa models for colloidal fluids: a possible correction

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A known ‘sticky hard sphere’ model, starting from a hard sphere Yukawa potential and taking the limit of infinite amplitude and vanishing range with their product remaining constant, is shown to be ill-defined. This is because its Hamiltonian (which we call SHS2) leads to an exact second virial coefficient which diverges, unlike that of Baxter’s original model (SHS1). This deficiency has never been observed so far, since the linearization implicit in the ‘mean spherical approximation’ (MSA), within which the model is analytically solvable, partly masks such a pathology. To overcome this drawback and retain some useful features of SHS2, we propose both a new model (SHS3) and a new closure (‘modified MSA’), whose combination yields an analytical solution formally identical with the SHS2–MSA solution. This mapping allows the recovery of many results derived from SHS2, after a re-interpretation within a correct framework. Possible developments are indicated.

1. Introduction

In a seminal series of papers [1–3] Baxter first introduced the concept of the so-called ‘sticky hard sphere’ (SHS) models, as the simplest—albeit crude—modellization for real fluids of spherical particles with a strong surface adhesion. In Baxter’s original formulation [1–4] and its extension to the multi-component case [5, 6] (both hereafter referred to as the SHS1 model) the pair potential contains—in addition to a hard sphere (HS) repulsion—an infinitely deep and narrow attractive square-well, obtained according to a particular limiting procedure (Baxter’s ‘sticky limit’) that keeps the second virial coefficient finite [1].

Although this model appears rather pathological at first sight, it includes a number of interesting features which justify its wide popularity. First, the Ornstein–Zernike (OZ) integral equation of the statistical-mechanical theory of fluids can be analytically solved for it within the Percus–Yevick (PY) approximation and the solution exhibits a gas–liquid transition [1–4]. Second, Baxter’s model has already proved to be appropriate for describing some properties of colloidal suspensions, micelles, microemulsions and protein solutions with short-range interactions as well as some aspects of adsorption, flocculation and percolation phenomena, solvent-mediated forces, ionic mixtures, solutions with a small degree of size polydispersity and fluids of chain-like molecules (for an illustrative, although not exhaustive, list of references, see [7–10]). All this means that, in spite of its highly idealized character and known shortcomings [7], the SHS1 model is able to capture some important physical features of structure, thermodynamics, and phase behaviour of many real systems.

However, the SHS1 model has its main drawback in its problematic application to mixtures with a large number $p$ of components—as occurs for colloidal suspensions with large polydispersity—since this case requires the solution for a set of $p(p + 1)/2$ coupled quadratic equations [5], a task which cannot be accomplished analytically. This important fact has originated a more recent attempt to find an alternative SHS model, which could be analytically tractable even in the general multi-component case [11–23]. For pure fluids, Brey et al. [11] proposed to start from a hard sphere Yukawa (HSY) potential

$$
\beta \phi_{\text{HSY}}(r) = \begin{cases} +\infty, & 0 < r < \sigma, \\ -K e^{-z(r-\sigma)}/r, & r \geq \sigma, \end{cases}
$$

with

$$
K = \kappa K_0, \quad K_0 = e_0^* \sigma^2, \quad e_0^* = \beta z_0 \equiv \frac{1}{12 T^*},
$$

where $r$ is the distance between particles, $\beta = (k_B T)^{-1}$ ($k_B$ being the Boltzmann’s constant and $T$ the temperature), $\sigma$ denotes the HS diameter, $z$ the Yukawa inverse range, $e_0^*$ an energy, and $T^*$ a reduced temperature (as in

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SHS1, the factor 12 simplifies subsequent analysis). The definition of this second Hamiltonian (SHS2 model in the following) is completed by the definition of a ‘sticky limit’, which in this case amounts to taking \( z \to +\infty \) [11]. It is worth remarking that, unlike its counterpart in the SHS1 model, the starting potential \( \phi_{\text{HSY}}(r) \) is itself independent of temperature.

For the SHS2 model (in cases of both pure fluids and mixtures), the OZ equation can be solved analytically within the mean spherical approximation (MSA) [12, 13]. It turns out that the SHS2–MSA solution \( q(r) \) (or \( g_q(r) \)) for the Baxter form of the OZ equation has exactly the same \( r \)-dependence as the SHS1–PY solution, that is both are expressed in terms of a second-degree polynomial in \( r \). However, the difference between the two solutions lies in the density and temperature dependence of their polynomial coefficients (see below), which makes the SHS2–MSA solution readily usable even in the multi-component case [14, 15, 17–19], unlike the SHS1–PY solution.

Unfortunately, the common belief that the SHS1 and SHS2 Hamiltonians are different but equivalent representations of a unique SH potential [8, 10, 14–17, 24, 25] as well as a failure in appreciating the subtle distinction between model and solution† has often generated a number of misunderstandings and erroneous beliefs in the literature on SHS fluids. In particular, both aforementioned PY and MSA solutions have sometimes been regarded as corresponding to the same SH model (Baxter’s model) [8, 14–17, 24]. On the contrary, in the present paper we stress that the SHS1–PY and SHS2–MSA solutions are different not only by stemming from different closures, but, more importantly, since they refer to different Hamiltonians. In fact, unlike SHS1, the SHS2 model itself is ill-defined from a thermodynamical point of view, and thus SHS1 and SHS2 cannot be equivalent. We will prove this point by considering the exact second virial coefficient of the HSY potential (1) and showing that it diverges in the sticky limit (a very short preliminary account of these results has been given in [21]). As we further elaborate below, this pathology is hidden in the SHS2–MSA compressibility equation of state (EOS) but is mirrored by a similar singular behaviour of the corresponding MSA virial and energy EOSs, never investigated in previous studies.

The second and main goal of the present paper is to propose a new model (SHS3) which combines the advantages of both SHS1 and SHS2. As SHS1, it has a finite second virial coefficient, and thus it is a well-defined model. As SHS2, however, it admits a simple analytical solution within a new closure, referred to as the modified mean spherical approximation (mMSA) in the following. The remarkable property of the SHS3–mMSA solution for \( q(r) \) is that it turns out to be formally identical with the SHS2–MSA solution, and so are all quantities which are immediately derivable from it (such as structural properties and the compressibility EOS). As a consequence of this mapping, all SHS2–MSA results obtained in the past for these quantities can be recovered after an appropriate re-interpretation. In addition, we will provide new results for other quantities, notably the virial and energy EOSs, for which the SHS2–MSA solution fails badly. This is not the case in the SHS3–mMSA solution, where the energy EOS turns out to be finite, albeit mean-field-like. Finally, although the virial EOS displays a singular behaviour within the SHS3–mMSA as well, we will argue that, unlike the SHS2 case, this divergence is a consequence of the deficiency of the mMSA closure, and not of the SHS3 model itself.

Our findings thus provide a sound theoretical basis for a critical analysis of the existing literature on SHS models, and allow us to clarify misunderstandings and discard incorrect results previously reported in the literature.

The plan of the remainder of the paper is the following. In section 2 we will briefly recall the main features of the SHS2–MSA solution and describe the drawbacks of SHS2 in detail. The new model and the new closure, which constitute the central part of this work, are both discussed in Section 3. Final remarks and future perspectives close the paper (Section 4).

2. SHS2 model and its pathologies

For a one-component fluid of \( N \) molecules in a volume \( V \), with spherically symmetric interactions, the Baxter form of the OZ integral equation [2] is given by

\[
\begin{aligned}
re(r) &= -q(r) + 2\pi \rho \int_{\infty}^{\infty} dt q(t-r)q'(t), \\
rh(r) &= -q(r) + 2\pi \rho \int_{0}^{\infty} dt q(t)(r-t)h(|r-t|),
\end{aligned}
\]

(3)

where \( \rho = N/V \) denotes the number density, \( \epsilon(r) \) the direct correlation function (DCF), and \( h(r) = g(r) - 1 \), with \( g(r) \) being the radial distribution function (RDF). Moreover, the prime denotes differentiation with respect to \( r \). Solving the Baxter equations is tantamount to determining the factor correlation function \( q(r) \), an

†In order to avoid any possible confusion, we have adopted the following terminological distinction. An SHS model is unequivocally defined by the specification of its Hamiltonian, which is characterized by two elements: the choice of the starting potential and the definition of a ‘sticky limit’ procedure. On the other hand, a particular solution is identified by three elements: the two ingredients of the model, along with a ‘closure’ for the OZ equation.
auxiliary quantity from which \( c(r) \) and \( h(r) \) can be easily derived.

An approximate integral equation can be obtained by adding to the OZ equation some approximate ‘closure’ relating \( c(r) \), \( h(r) \) and the potential \( \phi(r) \).

2.1. MSA solution

For potentials with a hard-core part, the MSA reads

\[
e_{\text{MA}}(r) = \begin{cases} 
-1 + y(r), & 0 < r < \sigma, \\
-\beta \phi_{\text{tail}}(r), & r \geq \sigma, 
\end{cases}
\]

where \( y(r) \equiv \rho \int \! dr' c(r') h(|r - r'|) \) and \( \phi_{\text{tail}}(r) \) is the potential outside the core. Since \( g(r) = 1 + y(r) + c(r) \), the MSA may also be written as

\[
e_{\text{MA}}(r) = e_{\text{HS}}(r)[1 + y(r) - \beta \phi_{\text{tail}}(r)],
\]

where \( e_{\text{HS}}(r) = \exp[-\beta \phi_{\text{HS}}(r)] = \theta(r - \sigma) \), with \( \phi_{\text{HS}}(r) \) being the HS potential and \( \theta(x) \) the Heaviside step function (\( \theta(x) = 0 \) for \( x < 0 \) and \( \theta(x) = 1 \) for \( x \geq 0 \)).

For the HSY potential the MSA closure becomes

\[
e_{\text{HSY-MSA}}(r) = K e^{-z(r-\sigma)} / r, \quad r \geq \sigma,
\]

where the parameters are the same as in equation (1). The analytical MSA solution \( q_{\text{HSY-MSA}}(r) \), for the HSY fluid [27] yields in the sticky limit \( (z \to +\infty) \) the SHS2–MSA solution

\[
q_{\text{SHS2-MSA}}(r) = \left[ \frac{1}{2} a(r^2 - \sigma^2) + b\sigma(r - \sigma) + q_0 \sigma^2 \right] \theta(r - \sigma), \\
\quad \text{for } r \geq 0,
\]

\[
a = \frac{1 + 2\eta}{(1 - \eta)^2} - \frac{12q_0\eta}{1 - \eta}, \quad b = -\frac{3\eta}{2(1 - \eta)^2} + \frac{6q_0\eta}{1 - \eta},
\]

\[
q_0 = K_0 / \sigma^2 = \varepsilon_0^2,
\]

where \( \eta = (\pi/6)\rho_c^3 \) is the packing fraction. As noted, the expression (7) is formally identical with the SHS1–PY solution with the crucial difference that \( q_{\text{SHS2-MSA}} \) depends only on temperature (being proportional to \( T^{\sigma-1} \)), whereas \( q_{\text{SHS1-PY}} \) depends on both temperature and density (in a more complex way) [2].

Once \( q(r) \) is known, all structural and thermodynamic properties can, in principle, be calculated. It is worth mentioning that, with a few exceptions [12, 16, 20, 22, 23, 25], the thermodynamic properties of SHS2 are still mostly unexplored. However, we stress once again that the main aim of our paper is not to present new results on the SHS2–MSA thermodynamics (although this task will be accomplished too), but to reveal a dramatic fault of the SHS2 potential itself (irrespective of any approximate closure), which, surprisingly enough, has never been observed in the previous literature, but will emerge from the following simple analysis.

2.2. Sticky limit of the exact second virial coefficient of the HSY fluid

The Hamiltonian of the SHS1 model was introduced by Baxter as a limiting case, through a clever definition of both a starting potential and a limit procedure in such a way that the contribution of the vanishing square-well tail to the second virial coefficient, \( B_2 \), remains finite and non-zero. It is instructive to consider the behaviour of \( B_2 \) for the SHS2 model, by considering the result of the \( z \to +\infty \) limit for the exact second virial coefficient \( B_2^{\text{HSY-exact}} \) of the HSY fluid. This can be calculated from the general definition,

\[
B_2 = -2\pi \int_0^\infty dr r^2 f(r),
\]

with \( f(r) = e(r) - 1 \), and \( e(r) = \exp[-\beta \phi(r)] \) being the Boltzmann factor. One finds

\[
B_2^{\text{HSY-exact}} = \frac{2\pi}{3} \sigma^3 + \Delta B_2^{\text{HSY-exact}}
\]

where

\[
\Delta B_2^{\text{HSY-exact}} = -2\pi \int_0^\infty dr r^2 \left\{ \exp[zK_0 e^{-z(r-\sigma)/r}] - 1 \right\}.
\]

It is now easy to show that \( \Delta B_2^{\text{HSY-exact}} \) diverges in the \( z \to +\infty \) limit. To this aim we note that, for \( x = zK_0 e^{-z(r-\sigma)/r} \geq 0 \), one has \( e^x - 1 \geq x + x^2/2 \) and hence we can use the bound

\[
\int_{0}^{\infty} dr r^2 (e^x - 1) \geq \int_{0}^{\infty} dr r^2 \left( x + \frac{x^2}{2} \right) = K_0 \left( \frac{1}{z} + \frac{K_0}{4z} \right)\varepsilon_0^2.
\]

As the right-hand side of equation (11) diverges as \( z \to +\infty \), we have thus shown that

\[
B_2^{\text{SHS2-exact}} \equiv \lim_{z \to +\infty} B_2^{\text{HSY-exact}} = -\infty.
\]

This result is exact and independent of any closure, and reflects an inconsistency of the HSY potential with the definition of sticky limit employed when setting up the SHS2 Hamiltonian [11, 12]. As a consequence, the SHS2 Hamiltonian is ill-defined from the outset and the corresponding model (which cannot be a different representation of Baxter’s model) must be discarded.

This is, however, a surprising result in some respects. One may rightly wonder why no trace of the pathological nature of the SHS2 model has ever been revealed...
by a number of structural studies [14, 15, 17–19] carried out on its multi-component version. As discussed in Section 4, all these structural results based upon the one-component and multi-component SHS2–MSA solutions are, in fact, fully correct after their re-interpretation in terms of SHS3. Before doing this, however, it is instructive to consider those SHS2–MSA thermodynamic properties of the one-component fluid which have not been investigated so far. This will display the pathological nature of the model as shown next.

2.3. Sticky limit of the MSA equations of state for the HSY fluid

Mier-y-Teran et al. [12] obtained, for $Z = \beta P/\rho$, the MSA compressibility (C) EOS

$$Z_{C}^{\text{SHS2-MSA}} = \frac{1 + \eta + \eta^2}{(1 - \eta)^2} + \left[\frac{4 - 7\eta}{(1 - \eta)^3} + \frac{4\ln(1 - \eta)}{\eta}\right] \frac{1}{T^*} + \left[\frac{2 - \eta}{1 - \eta} + \frac{2\ln(1 - \eta)}{\eta}\right] \frac{1}{T^*},$$

(13)

by integrating with respect to density the compressibility equation [27]†

$$\left(\frac{\partial\beta P}{\partial \rho}\right)_T = [1 - 2\pi \rho \hat{q}(0)]^2 = a^2,$$

(14)

where $\hat{q}(k)$ denotes the unidimensional Fourier transform of $q(r)$.

On the other hand, no expressions for the SHS2–MSA virial and energy EOSs were given either in [12] or in subsequent literature on this subject, to the best of our knowledge. We thus tackle this analysis here.

The most direct way we have followed is to consider the $z \to +\infty$ limit of the HSY–MSA virial and energy pressures. Convenient expressions for these quantities were given by Cummings and Smith (equations (18)–(20) of [27]). Unfortunately, their sticky limit requires a rather elaborate analysis, which we will not report here. However, the final result is rather simple: both the virial and the energy MSA pressures of the HSY fluid diverge in the sticky limit. For the MSA energy EOS, the same conclusion can be drawn by exploiting the alternative form reported by Herrera et al. [28]. It is worth stressing again that this important feature has never been pointed out before, to our knowledge.

To convince the reader that our statement is correct, we now provide a simpler demonstration, based upon the analysis of the sticky limit of the MSA second virial coefficients of the HSY fluid, as obtained from the density expansion of $(Z_{C}^{\text{MSA}})_{C}$, $(Z_{V}^{\text{MSA}})_{V}$ and $(Z_{E}^{\text{MSA}})_{E}$. It is well known that, in any approximate theory, compressibility, virial and energy EOSs may yield different virial coefficients, and the first one at which this difference begins to appear depends on the chosen closure. We now show that, in the SHS2–MSA case, a non-consistency already appears at the $B_2$ level, and partly veils the singular character of the HSY fluid. Nonetheless, as will be shown below, both $(B_{2}^{\text{HSY-MSA}})_{V}$ and $(B_{2}^{\text{HSY-MSA}})_{E}$ are divergent in the sticky limit, and this strongly supports the aforementioned statement about the singular character of the virial and energy EOSs for the SHS2–MSA solution.

The quantity $(B_{2}^{\text{HSY-MSA}})_{C}$ can be easily computed directly from the density expansion of $\partial\beta P/\partial \rho$, given by equation (14), upon using equations (8) and (9). To evaluate $(B_{2}^{\text{HSY-MSA}})_{V}$ and $(B_{2}^{\text{HSY-MSA}})_{E}$, it proves convenient to exploit the following expressions for the MSA virial and energy EOSs of an HSY fluid [29, 30]

$$Z_{V}^{\text{HSY}} = 1 + 4\eta[G_{\text{HSY}}(\sigma^{+}) - I],$$

(15)

$$Z_{E}^{\text{HSY}} = Z_{S}^{\text{HS}} = 4\eta\left\{\frac{1}{2}G_{\text{HSY}}(\sigma^{+}) - G_{\text{HS}}(\sigma^{+}) - I\right\},$$

(16)

$$I = K\sigma^{-3}\int_{\sigma}^{\infty} dr g_{\text{HSY}}(r)(1 + zr)e^{-r(\sigma - \sigma)}.$$

(17)

Using the low-density expansion of the MSA approximation to $g_{\text{HSY}}(r)$, equation (5), one gets

$$(B_{2}^{\text{HSY-MSA}})_{C} = 4\nu_{0}\left[1 - \left(1 + \frac{1}{z\sigma}\right)\frac{1}{4T^*}\right],$$

(18)

$$(B_{2}^{\text{HSY-MSA}})_{V} = 4\nu_{0}\left[1 - \left(1 + \frac{1}{z\sigma}\right)\frac{1}{4T^*} - (z\sigma + \frac{2}{3}z^2\sigma^2)\frac{1}{192T^*}\right],$$

(19)

$$(B_{2}^{\text{HSY-MSA}})_{E} = 4\nu_{0}\left[1 - \left(1 + \frac{1}{z\sigma}\right)\frac{1}{4T^*} - z\sigma\frac{1}{192T^*}\right],$$

(20)

where $\nu_{0} = (\pi/6)^{3}$ is the particle volume. The difference between the three results for $B_{2}^{\text{HSY-MSA}}$ is a clear manifestation of the known thermodynamic inconsistency of the MSA [27,31]. It is, however, quite surprising that discrepancies already appear at the $B_2$ level. Note that $(B_{2}^{\text{HSY-MSA}})_{C} > (B_{2}^{\text{HSY-MSA}})_{E} > (B_{2}^{\text{HSY-MSA}})_{V}$. The differences magnify with increasing $z$, and become

†In the case of mixtures, additional requirements are necessary to perform this operation (see [20]).
dramatic in the sticky limit which yields
\begin{equation}
(B^\text{SHS2–MSA}^*)_C = 4v_0 \left(1 - \frac{1}{4T^*}\right), \quad (21)
\end{equation}
\begin{equation}
(B^\text{SHS2–MSA}^*)_V = -\infty = (B^\text{SHS2–MSA}^*_E). \quad (22)
\end{equation}

Equation (22) thus confirms our previous statement about the divergence of the MSA virial and energy pressures of the HSY fluid in the sticky limit. On the other hand, equation (21) gives a finite value for 
\( (B^\text{SHS2–MSA}^*)_C \) in agreement with the corresponding compressibility EOS. However, we stress that this result is due to the fact that the MSA involves an approximation at the level of the Boltzmann factor [32], that is
\begin{equation}
\varepsilon_{\text{MSA}}(r) = \theta(r - \sigma)[1 - \beta \phi_{\text{tail}}(r)], \quad (23)
\end{equation}
equivalent to the linearization \( \exp[-\beta \phi_{\text{tail}}(r)] \approx 1 - \beta \phi_{\text{tail}}(r) \) (as can be inferred from a comparison between the zeroth-order terms in the density expansion of \( g^{\text{exact}}(r) \) and \( g^{\text{MSA}}(r) \), i.e. \( g^{(0)}_{\text{exact}}(r) = c(r) = e_{\text{HS}}(r)\exp[-\beta \phi_{\text{tail}}(r)] \) and \( g^{(0)}_{\text{MSA}}(r) = e_{\text{HS}}(r)[1 - \beta \phi_{\text{tail}}(r)] \), respectively). The replacement of the exact \( e_{\text{HS}}(r) \) in the expression for \( B^\text{SHS2–MSA}^*_V \) with its MSA counterpart (23) just leads to the \( (B^\text{SHS2–MSA}^*)_C \) result, in the sticky limit.

Summarizing, we can conclude that the existence of the MSA solution, \( \phi_{\text{SHS2–MSA}}(r) \), is a fortuitous consequence of the fact that the divergent character of the SHS2 model is masked by the MSA linearization (23).

### 2.4. MSA internal energy

As a final point of this first part, we wish to point out an interesting difference in behaviour between the internal energy in the SHS2–MSA and SHS1–PY solutions.

Let us now consider the energy (E) equation,
\begin{equation}
uex = Uex/N = 2\pi\rho \int_0^\infty dr r^2 g(r)\phi(r), \quad (24)
\end{equation}
where \( Uex \) is the excess internal energy. Within the MSA, one gets for our HSY fluid
\[-\beta\varepsilonex_{\text{HY–MSA}} = 2\pi\rho \int_0^\infty dr r^2[1 + \gamma_{\text{HY–MSA}}(r) - \beta \phi_{\text{HY}}(r)][-\beta \phi_{\text{HY}}(r)]
\]
\[= 2\pi\rho \left[K_0 \int_0^\infty dr [1 + \gamma_{\text{HY–MSA}}(r)]e^{-2\sigma}/2 + K_0^2/2\right].
\]

Since \( \gamma_{\text{HY–MSA}}(r) \) is finite and sufficiently regular everywhere, it is easy to show, integrating by parts or using the property \( \lim_{z \to \infty} ze^{-z(r-\sigma)}/\theta(r-\sigma) = \delta_+(r-\sigma) \), that the last integral remains finite as \( z \to +\infty \). In conclusion, \( uex_{\text{HY–MSA}} \) diverges linearly. This should be compared with the logarithmic divergence found in SHS1–PY energy [1]. We speculate that this difference in the internal energy behaviour parallels that in the corresponding EOS. It is then clear that, in the SHS1–PY case, such a weak divergence does not in itself constitute an impediment to the existence of finite EOSs in the sticky limit [1, 7, 33].

As a side comment, it is worth noting that our finding [34], where an MSA energy with a non-singular sticky contribution (equation (42) of [34]) is reported.

### 3. New model and new closure

Given the above premise, one could at this point suspect that all previous findings based upon the SHS2 model (and notably those referring to polydisperse colloidal fluids [18–20]) should be discarded. This is not so, and all those results are in fact correct. The second aim of our paper is to show that an analytic solution with the same functional form as \( \phi_{\text{SHS2–MSA}}(r) \) is obtained within a new and well-defined model (which we call SHS3), coupled with a simple new closure. As a consequence, most of the results derived from SHS2 can be recovered after an appropriate re-interpretation.

#### 3.1. SHS3 potential

We define a new SHS Hamiltonian, which represents the simplest correct alternative to SHS2, and is analytically solvable within a novel closure. The basic idea hinges on Baxter’s trick of a logarithmic tail, combined with the infinite-ranged Yukawa expression of SHS2. The starting potential (hereafter referred to as M3) is
\begin{equation}
\phi_{\text{M3}}(r) = \begin{cases} +\infty, & 0 < r < \sigma; \\
-\ln[1 + zK_0 e^{-2\sigma}/r], & r \geq \sigma.
\end{cases} \quad (25)
\end{equation}
where \( K_0 \) depends on \( T \) according to equation (2), and the sticky limit corresponds again to \( z \to +\infty \).

We note that at large \( r \) values, the quantity \( x \equiv -\beta \phi_{\text{M3}}(r) = zK_0 e^{-2\sigma}/r \), appearing in the argument of the logarithm, becomes so small that the approximation \( \ln(1 + x) \approx x \) can be used. In other words, M3 has the same large-r asymptotic behaviour as \( -\beta \phi_{\text{HY}}(r) \), but differs from the Yukawa tail near contact. This is

\[\delta_+(x) \] is the asymmetrical Dirac delta function defined by: \( \int_{-\infty}^{\infty} dx F(x)\delta_+(x-x_0) = F(x_0) \), if \( A < x_0 < B \), and = 0, if \( x_0 \leq A \) or \( x_0 \geq B \). The Yukawa tail, \( \phi_{\text{Y}}(r) = -z\sigma e^{-r^2/2\sigma^2}e^{-z(r-\sigma)}\theta(r - \sigma) \), gives rise to a singularity, since \( \lim_{z \to \infty} ze^{-z(r-\sigma)}/\theta(r - \sigma) = \delta_+(r - \sigma) [13] \).
Note that this difference between the two potentials increases as $z$ increases. However, for the M3 model, the Boltzman factor reads

$$e_{M3}(r) = \theta(r - \sigma)[1 + zK_0e^{-z(r-\sigma)/\sigma}]$$ \tag{26}

with the essential consequence that the corresponding exact second virial coefficient remains finite in the sticky limit, that is

$$B_{2\text{M3-exact}} = 4\nu_0\left[1 - 3\nu_0^2\left(1 + \frac{1}{z\sigma}\right)\right]$$ \tag{27}

$$B_{2\text{SHS3-exact}} = \lim_{z\to+\infty} B_{2\text{M3-exact}} = 4\nu_0\left(1 - \frac{1}{4T^*}\right).$$ \tag{28}

Note that this $B_2$ expression, exact for SHS3, is formally identical with $B_{2\text{SHS2-MSA}}$, which is only approximate for SHS2.

As a further check that we are on the right track, we have also computed the exact SHS3 third virial coefficient

$$B_{3\text{SHS3-exact}} = \lim_{z\to+\infty} B_{3\text{M3-exact}} = 9^2\nu_0^2\left(10 - \frac{5}{T^*} + \frac{1}{T^*2} - \frac{1}{18T^*3}\right).$$ \tag{29}

It is remarkable that $B_{3\text{SHS3-exact}}$ coincides with $B_{3\text{SHS1-exact}}$, once $T^*$ is replaced with its counterpart $r$ of Baxter’s model [1].

3.2. Modified MSA closure and solution

We define a modified mean spherical approximation (mMSA)

$$c_{mMSA}(r) = \begin{cases} -[1 + \gamma(r)], & 0 < r < \sigma, \\ f_{\text{tail}}(r) = \exp[-\beta\phi_{\text{tail}}(r)] - 1, & r > \sigma. \end{cases}$$ \tag{30}

In terms of the RDF, this closure reads

$$g_{mMSA}(r) = e_{HS}(r)[1 + \gamma(r) + f_{\text{tail}}(r)] = e(r) + e_{HS}(r)\gamma(r),$$ \tag{31}

since $e_{HS}(r) [1 + f_{\text{tail}}(r)] = e(r)$.

Although this closure is not completely new (see [35, 36]), it was never formulated in the present general form. Yet it is a very natural choice, since it yields the correct zeroth-order term in the density expansion of the DCF: $c_{\text{exact}}(r) \to f(r)$ when $r \to 0$.

The advantage of coupling the M3 potential with the mMSA is that one finds $c_{M3-mMSA}(r) = f(r) = zK_0e^{-z(r-\sigma)/\sigma}/r$ (which is identical with the usual Yukawa closure. This mapping allows the immediate identification between the solution $q_{M3-mMSA}(r)$ with $q_{\text{HSY-MSA}}(r)$, and thus in the limit $z \to +\infty$ we get

$$q_{\text{SHS3-mMSA}}(r) = q_{\text{SHS2-MSA}}(r).$$ \tag{32}

In short, the solution given by equations (7)–(9) is recovered, but within a new well-defined model, with a finite second virial coefficient.

3.3. Equations of state

3.3.1. Compressibility route

Since $Z_{C\text{SHS3-mMSA}}$ can be computed directly from $q_{\text{SHS3-mMSA}}(r)$ and equation (14) (in fact, the sticky limit and $\rho$-integration commutate), it results that

$$Z_{C\text{SHS3-mMSA}} = Z_{C\text{SHS2-MSA}}.$$ \tag{33}

Expanding this quantity in powers of $\rho$, one finds that $(B_{3\text{SHS3-mMSA}})_C = B_{3\text{SHS3-exact}}$, whereas $(B_{3\text{SHS3-mMSA}})_C = \nu_0^3\left[10 - \frac{5}{3}T^* + \frac{1}{3}T^*2 - \frac{1}{18}T^*3\right]$ differs from $B_{3\text{SHS3-exact}}$.

3.3.2. Virial route

Let us insert equation (31) into the virial ($V$) equation,

$$Z_V = 1 + \frac{2\pi}{3}\rho \int_0^\infty dr r^3g(r)[-\beta\phi(r)] \equiv 1 + \frac{2\pi}{3}\rho J_V.$$ \tag{34}
The integral can be written as $J_1 = J_1 + J_2$, with

\[
J_1 = \int_0^\infty dr r^3 e(r) [-\beta \phi'(r)] = \int_0^\infty dr r^3 e'(r) = \int_0^\infty dr r^3 f'(r),
\]

\[
J_2 = \int_0^\infty dr e_{HS}(r)r^3 \gamma(r)[-\beta \phi'(r)]
= \int_0^\infty dr e_{HS}(r)r^3 \gamma(r)[-\beta \phi_{HS}(r) - \beta \phi_{tail}(r)].
\]

Integrating $J_1$ by parts and observing that the boundary terms vanish, one finds that $(2\pi/3)J_1 = B_2$. On the other hand, if $J_2$ is written as $J_{2a} + J_{2b}$, with $J_{2a} = \int_0^\infty dr e_{HS}(r)r^3 \gamma(r)[-\beta \phi_{HS}(r)]$, and using $e_{HS}(r)[-\beta \phi_{HS}^r(r)] = e_{HS}(r) = \delta(r - \sigma)$, one gets

\[
Z^\text{mMSA}_\nu = 1 + B_2 r + \frac{2\pi}{3} \rho \left\{ \sigma^3 \gamma^\text{mMSA}(\sigma) + \int_\sigma^\infty dr r^3 \gamma^\text{mMSA}(r)[-\beta \phi_{tail}(r)] \right\}. \tag{35}
\]

In the particular case of the M3 potential, $-\beta \phi_{tail}(r)$ assumes increasingly large negative values as $z$ increases, whereas $\gamma_{M3-\text{mMSA}}(r; z) \leq \gamma_{M3-\text{mMSA}}(\sigma; z)$ remains bounded, in such a way that the integral $J_{2a}$ diverges in the sticky limit (for shortness, our detailed analysis of this point is not reported here).

Equation (35) and these results imply that the mMSA-virial EOS diverges. However, since the second virial coefficient is finite and exact, and $(B^\text{SHS3-\text{mMSA}})_\nu$ diverges whereas $B^\text{SHS3-exact}$ is finite, the singularity of $Z^\text{SHS3-\text{mMSA}}$ is not due to the Hamiltonian, but is surely caused by the mMSA closure.

3.3.3. Energy route

Finally let us explore the energy (or free energy) route for temperature-dependent potentials. It can be shown [3] that, for any potential,

\[
\frac{\partial}{\partial \xi} \left[ \frac{\beta(A - A_{id})}{N} \right] = 2\pi \rho \int_0^\infty dr r^2 g(r) \frac{\partial \phi(r)}{\partial \xi}, \tag{36}
\]

where $\xi$ denotes an arbitrary parameter upon which $\beta \phi(r)$ depends and $A_{id}$ indicates the ideal gas free energy. In particular, when $\xi = \beta$ and $g(r) = g^\text{mMSA}(r)$, one gets

\[
\frac{\partial}{\partial \beta} \left[ \frac{\beta(A - A_{id})}{N} \right]_{\text{mMSA}} = 2\pi \rho \left( -\int_0^\infty dr r^2 \frac{\partial e(r)}{\partial \beta} + \int_\sigma^\infty dr r^2 \gamma^\text{mMSA}(r) \frac{\partial \beta \phi_{tail}(r)}{\partial \beta} \right).
\]

For the M3 potential, this expression becomes

\[
\frac{\partial}{\partial \beta} \left[ \frac{\beta(A_{M3-\text{mMSA}} - A_{\text{id}})}{N} \right] = -12\eta \epsilon_0 \left[ 1 + \frac{1}{2\sigma} + \frac{\gamma_{M3-\text{mMSA}}(\sigma; \beta, z)}{1 + 2\sigma \beta \epsilon_0} + O(z^{-2}) \right]. \tag{37}
\]

With the boundary condition $T \to \infty (\beta \to 0)$, corresponding to the HS case, this equation can be integrated with respect to $\beta$, and in the $z \to +\infty$ limit one finds

\[
\beta(A_{\text{SHS3-\text{mMSA}}} - A_{\text{HS}})/N = -\frac{1}{T^*}\eta, \tag{38}
\]

since the sticky limit and $\beta$-integration commute. From $Z = \eta \delta(A/N)/\beta \eta$ we then get

\[
Z^\text{SHS3-\text{mMSA}}_\nu = Z_{\text{HS}} - \frac{1}{T^*}\eta. \tag{39}
\]

It is noteworthy that these results for the Helmholtz free energy and the energy EOS are van der Waals-like. The effect of the surface adhesion enters these expressions only at the level of the second virial coefficient (which is exact), while all higher-order virial coefficients predicted by equation (39) coincide with the pure HS ones. The reason for this may be traced back to the fact that the mMSA closure takes into account only the zeroth-order term in the density expansion of the DCF outside the core.

4. Conclusion

Three different models of ‘sticky hard spheres’ have been treated in this paper. The first two (SHS1 and SHS2) were already present in the literature, while the last one (SHS3) is new and constitutes the main contribution of the present work.

All these models describe a fluid of rigid spherical particles with infinitely strong surface adhesion, defined through an appropriate ‘sticky limit’ which constitutes an essential part of the model. The choice of the starting potential strongly influences that of the approximate closure to be used to solve the OZ equation analytically.

In SHS1 a suitably defined square-well allows the solution within the PY approximation, whereas in SHS2 the starting point is a hard sphere Yukawa potential which requires the mean spherical approximation. However, the most crucial point is that, while SHS1 is a perfectly well-defined model, SHS2 is not since its exact second virial coefficient is divergent, as we have
proven in this paper. This singularity is mirrored by a similar behaviour appearing in both the virial and energy SHS–MSA EOSs, but it should be emphasized that it is a weakness of the model itself and is not due to the MSA. This means that the SHS2 model itself is not properly defined and must be abandoned.

To replace it, a proposal has been put forward in the second part of the paper. Our recipe is based upon the introduction of a new potential (M3), coupled with a new closure (mMSA), in such a way that the Baxter–OZ equations turn out to be analytically solvable, with formally the same solution \( q(r) \) found in the SHS2–MSA case. This remarkable correspondence allows a recovery of all previous results for structure factors and compressibility EOSs based upon the SHS2–MSA solution [14, 18–20], after a re-interpretation in terms of SHS3–mMSA.

The SHS3 model is the simplest correct alternative to SHS2. It is well defined, since the sticky limit of the exact second virial coefficient, \( B_{3}^{\text{SHS3-exact}} \), remains finite. Furthermore, its starting potential, M3, is asymptotically equivalent to the HSY one at large \( r \) values, being different from it only in the contact region.

As regards the closure, the mMSA is correct in the zero-density limit, and consequently has a higher thermodynamic consistency than the MSA. As a matter of fact, compressibility, virial and energy routes all generate the same, exact \( B_{2} \). On the other hand, one cannot expect from the mMSA to go further in consistency, since this closure is still rather poor, taking into account only the zeroth-order term in the density expansion of the DCF outside the core. We have shown that discrepancies are already found at the level of the third virial coefficient: \( (B_{3}^{\text{SHS3-mMSA}})_{V} \) diverges, while \( (B_{3}^{\text{SHS3-mMSA}})_{E} \) is temperature-independent and equal to its HS counterpart. Clearly, these three results could coincide within a more refined (density-dependent) closure.

It would be very interesting to investigate whether the SHS3 model admits further analytic solutions, within more sophisticated approximations (such as, in particular, the PY approximation). We plan to do such analysis in future work, including also a more detailed comparison with Baxter’s original model.

Finally, it is worth noting that the extension of the SHS3 model to mixtures can be easily carried out. We hope that the corresponding solution can provide a simple useful tool for further studies on structural and thermodynamic properties of polydisperse colloidal fluids.

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References

[28] Herrera, J. H., Ruiz-Estrada, H., and Blum, L., 1996, J. chem. Phys., 104, 6327. Note that equation (16) of this paper is misprinted and should read: \( \bar{a}_{i} = \pi \Gamma_{\bar{a}} \beta(3/2 \eta_{X}) \).


