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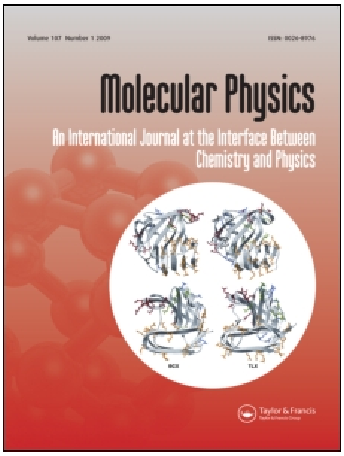

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RESEARCH ARTICLE

A parametrisation of the direct correlation function for the square-shoulder fluid

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We introduce a parametrisation of the direct correlation function for the square-shoulder fluid and demonstrate that this parametrisation is in quantitative agreement with the numerical solution of the Ornstein–Zernike equation within the Percus–Yevick approximation. Moreover, the radial distribution function obtained from the parametrisation reproduces quantitatively Monte Carlo simulation data. Our results show that the parametrisation is accurate over a large regime of densities for different interaction ranges and potential strengths.

Keywords: square-shoulder fluid; simple fluids; direct correlation functions; Ornstein–Zernike

1. Introduction

During the last few decades, so-called discrete potential fluids (DPFs) have been used as simple models to investigate a large variety of both simple and complex fluids, like water [1], methanol [2], polymers [3], electrolytes [4], among others. Moreover, discrete potentials have been incorporated in thermodynamic perturbation-like theories [5,6] and are able to capture, in a simple way, the main properties of continuous potentials [7].

The simplest and mostly investigated DPF is the well-known square-well (SW) fluid. By varying the interaction range this model system is able to mimic the behaviour of a large variety of real fluids (see e.g. [8] and references therein). The liquid–vapour (LV) phase diagram of the SW fluid has been studied by means of computer simulations, perturbation theories, as well as integral equation theories [9–20]. Recently, within the framework of the self-consistent Ornstein–Zernike approximation (SCOZA), its LV-coexistence has been reinvestigated and described with high accuracy [21].

A formidable advantage of the DPFs is the fact that analytical representations of the corresponding equations of state become more tractable than for continuous potentials [22]. Interestingly, the phase diagram of a DPF formed by a square shoulder plus an attractive square well exhibits a rather complex behaviour with multiple fluid–fluid transitions [23]. Recently, both the structural and thermodynamic properties of three DPFs, the square well, the square-well barrier and the square well–barrier well, have been studied in detail [7]. While the phase diagram of such systems has been explored by means of the Gibbs ensemble simulation technique [24], sophisticated theoretical approximations like SCOZA usually become unstable for DPFs that include repulsive parts in the interaction tail. In SCOZA the problem resides in the diffusion-like coefficient of the SCOZA partial differential equation (PDE) [21] which becomes negative when a repulsive part in the interaction (apart from the hard-core repulsion) is considered making a numerical solution of the PDE rather impossible.

Commonly, the hard-sphere system is used as the standard reference system in perturbation-like theories or in the numerical solution of SCOZA [21]. In particular, the Waisman parametrisation gives a good analytical representation of the direct correlation function of the hard-sphere system in a large regime of densities [25]. However, due to the limitations discussed above, SCOZA cannot be solved numerically via the standard route for DPFs composed of successive combinations of barriers and wells. One way to overcome this limitation is to redefine the reference system. The interaction potential of this new reference system must include the repulsive part of the

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interaction potential which destabilises the numerical solution. In the particular case of SCOZA, the direct correlation function is split into two terms: the correlation function of the reference system, which includes all the repulsive contributions, and the correlation function of the attractive contribution which is determined by solving the SCOZA PDE. This procedure has been applied to study the phase-diagram of DPFs [26] similar to those already investigated in [23].

The aim of this work is therefore to develop a simple and useful analytical expression for the direct correlation function of a particular case of DPF, which can be used as a new reference system in different theoretical approximations. In particular, in this work we are interested in the square-shoulder (SS) fluid. Our parametrisation scheme is based on a soft-core fluid model [27].

The paper is organised as follows: in Section 2 we describe the functional form of the interaction potential which characterises the SS fluid. The method of solution used in this work is based on Baxter's factorisation technique. So, we briefly recall Baxter's factorisation method for the analytical expressions of the direct correlation function (DCF) of the hard-sphere (HS) fluid. Section 3 describes the procedure to obtain the parametrisation of the DCF for the SS fluid. We compare our analytical solutions with the full numerical solution of the Ornstein–Zernike (OZ) equation within the Percus–Yevick (PY) approximation. In addition, the DCF obtained from the parametrisation is used to compute the radial distribution functions (RDFs). The RDFs are also tested against Monte Carlo computer simulations. Finally, the paper is closed with concluding remarks.

2. Model system and Baxter's factorisation method

We consider a system of spherical particles of diameter σ which are interacting via a square-shoulder potential, $\phi_{\mathrm{SS}}(r)$, given by

$$\phi_{\mathrm{SS}}(r) = \begin{cases} \infty, & r < \sigma, \\ \epsilon, & \sigma \le r \le \lambda\sigma, \\ 0, & r > \lambda\sigma, \end{cases} \tag{1}$$

where r is the interparticle distance, ϵ is the (positive) height of the shoulder and λ is the reduced range of the potential barrier.

2.1. *Baxter's factorisation*

For a one-component fluid with spherically symmetric interactions, the Ornstein–Zernike (OZ) equation is given by [28]

$$h(r) = c(r) + \rho \int c(\mathbf{r}')h(|\mathbf{r} - \mathbf{r}'|)\,\mathrm{d}r', \tag{2}$$

where ρ is the particle number density. The OZ equation defines the direct correlation function $c(r)$ in terms of the total correlation function, $h(r) = g(r) - 1$, $g(r)$ being the well-known radial distribution function. According to the Baxter factorisation technique [29], the OZ equation can be cast into the form

$$rc(r) = -q'(r) + 2\pi\rho \int_0^\infty \mathrm{d}u\, q(u)q'(r+u), \tag{3}$$

$$rh(r) = -q'(r) + 2\pi\rho \int_0^\infty \mathrm{d}u\, q(u)(r-u)h(|r-u|), \tag{4}$$

where the factor function $q(r)$ is an auxiliary function, and the prime denotes differentiation with respect to r. In order to solve Equation (2) or, alternatively, Equations (3) and (4), additional relations that link the structure functions to the interaction potential between the particles are needed. These approximative relations between $h(r)$ and $c(r)$ are usually called closure relations [29]. A useful closure relation for systems with repulsive short-range interactions is the well-known Percus–Yevick approximation [29] given by

$$c(r) = [\exp(-\beta\phi(r)) - 1]\,y(r) = f(r)\,y(r), \tag{5}$$

where $y(r) = \exp(\beta\phi(r))[h(r) + 1]$, $f(r) = \exp(-\beta\phi(r)) - 1$ is the Mayer function, $\beta \equiv (k_{\mathrm{B}}T)^{-1}$ is the inverse of the thermal energy with k_{B} being the Boltzmann constant, T the absolute temperature and $\phi(r)$ is the interaction potential.

Unfortunately, in the present form only a numerical procedure allows one to compute the DCF for the SS fluid within the PY approximation. Then, further approximations are needed to calculate an approximate analytical solution, as we will see below. To illustrate the method to find an analytic expression by means of Baxter's factorisation method, we briefly recall the solution procedure for the hard-sphere system [30].

2.2. *Hard-sphere fluid*

The hard-sphere interaction potential is given by the relation [29]

$$\phi_{\mathrm{HS}}(r) = \begin{cases} \infty, & r < \sigma, \\ 0, & r \ge \sigma. \end{cases} \tag{6}$$

Within the PY approximation for the hard-sphere interaction, the structure functions take the following values: $h(r) = -1$ for $0 \leq r < \sigma$ (hard-core condition) and $c(r) = 0$ for $r \geq \sigma$. The latter condition implies that $q(r) = 0$ for $r \geq \sigma$ [31]. Therefore, using both conditions together with Equation (4) we obtain the relation

$$-r = -q'(r) - 2\pi\rho \int_0^\sigma \mathrm{d}u\,(r-u)q(u) \quad \text{for } 0 \leq r \leq \sigma. \tag{7}$$

To satisfy Equation (7) $q'(r)$ for the HS system must be of the form

$$q'_{\mathrm{HS}}(r) = a_{\mathrm{HS}}r + b_{\mathrm{HS}}. \tag{8}$$

Now, by inserting Equation (8) into the r.h.s. of Equation (7) and comparing both l.h.s. and r.h.s. of the resulting equation, we find that the coefficients a_{HS} and b_{HS} are given by

$$a_{\mathrm{HS}} = 1 - 2\pi\rho \int_0^\sigma \mathrm{d}u\, q_{\mathrm{HS}}(u), \quad b_{\mathrm{HS}} = 2\pi\rho \int_0^\sigma \mathrm{d}u\, u q_{\mathrm{HS}}(u). \tag{9}$$

Then, by integrating $q'_{\mathrm{HS}}(r)$ and using the fact that $q_{\mathrm{HS}}(r) = 0$ for $r > \sigma$ [31], the factor function can be written as

$$q_{\mathrm{HS}}(r) = \frac{1}{2}a_{\mathrm{HS}}(r^2 - \sigma^2) + b_{\mathrm{HS}}(r - \sigma). \tag{10}$$

Inserting Equation (10) into Equation (9) yields

$$a_{\mathrm{HS}} = \frac{1+2\eta}{(1-\eta)^2}, \quad b_{\mathrm{HS}} = -\frac{3}{2}\frac{\eta}{(1-\eta)^2}\sigma, \tag{11}$$

where $\eta = (\pi/6)\rho\sigma^3$ is the packing fraction. Finally, by inserting Equations (10) and (11) in Equation (3), one obtains the analytic expression for the DCF of the hard-sphere fluid within the PY approximation,

$$c_{\mathrm{HS}}(r) = -\frac{1}{(1-\eta)^4}\left[(1+2\eta)^2 - 6\eta\left(1+\frac{1}{2}\eta\right)^2\frac{r}{\sigma} + \frac{1}{2}\eta(1+2\eta)^2\left(\frac{r}{\sigma}\right)^3\right]. \tag{12}$$

3. Square-shoulder fluid

3.1. *Soft-core fluid approach*

As we already discussed in the last section, in the procedure to obtain an analytical solution for $c(r)$ through Baxter's formalism, it is necessary to know the functional form (or, at least, a first approximation) of $h(r)$ of the system. In particular, the hard-core condition leads to $h(r) = -1$ in the interval $0 \leq r < \sigma$. However, the functional form of the total correlation function outside the hard core is, in general, unknown. On the other hand, for discrete-like potentials, $h(r)$ shows a non-zero contact value which makes the function discontinuous at $r = \sigma$. We here propose a simple approach for the factor function in terms of a soft-core fluid model which allows us to simplify the complete problem.

Let us assume that the factor function can be split into two terms:

$$q(r) = q_0(r) + q_{\mathrm{SC}}(r), \tag{13}$$

where $q_0(r)$, known as the reference factor function, takes the values $q_0(r) = 0$ for $r \geq \sigma$, and $q_{\mathrm{SC}}(r)$, defined as the soft-core factor function, becomes $q_{\mathrm{SC}}(r) = 0$ for $r > \lambda\sigma$. Similarly, we split the total correlation function into two contributions

$$h(r) = h_0(r) + h_{\mathrm{SC}}(r), \tag{14}$$

where each subindex has the same meaning as the one defined for the factor function (13).

Inserting Equations (13) and (14) into Equation (4), we obtain the following relation,

$$\begin{aligned} r(h_0(r) + h_{\mathrm{SC}}(r)) &= -(q'_0(r) + q'_{\mathrm{SC}}(r)) + 2\pi\rho\int_0^\infty \mathrm{d}u\,[q_0(u) + q_{\mathrm{SC}}(u)] \\ &\quad \times (r-u)[h_0(|r-u|) + h_{\mathrm{SC}}(|r-u|)] \\ &= -q'_0(r) - q'_{\mathrm{SC}}(r) + 2\pi\rho\left[\int_0^\sigma \mathrm{d}u\, q_0(u)(r-u)h_0(|r-u|)\right. \\ &\quad + \int_0^{\lambda\sigma} \mathrm{d}u\, q_{\mathrm{SC}}(u)(r-u)h_0(|r-u|) \\ &\quad + \int_0^{\sigma} \mathrm{d}u\, q_0(u)(r-u)h_{\mathrm{SC}}(|r-u|) \\ &\quad \left. + \int_0^{\lambda\sigma} \mathrm{d}u\, q_{\mathrm{SC}}(u)(r-u)h_{\mathrm{SC}}(|r-u|)\right]. \end{aligned} \tag{15}$$

We now proceed to analyse each integral in Equation (15). One can notice that the first and last integral depend only on the reference system and the soft-core fluid contribution, respectively, whereas the other ones are functions of the crossed terms. We here assume that the latter ones can be neglected because they are evaluated in regions where one expects that their contribution becomes negligible. In other words, the product $q_{\mathrm{SC}}h_0$, which appears in the second integral, is evaluated in $0 < r < \lambda\sigma$ where it is expected to have a small contribution inside the range of the potential. Therefore, $q_{\mathrm{SC}}h_0 \approx 0$ in the whole interval. In analogy, the third integral is approximated to zero, within our assumption, since the product q_0h_{SC} is expected to be irrelevant in the hard core. Then, the crossed terms will play no role in Equation (15).[1] This allows us to simplify Equation (15),

$$
\begin{aligned}
r(h_0(r)+h_{\mathrm{SC}}(r)) \approx {} & -q_0'(r)-q_{\mathrm{SC}}'(r) \\
& +2\pi\rho\int_0^{\sigma} \mathrm{d}u\, q_0(u)(r-u)h_0(|r-u|) \\
& +2\pi\rho\int_0^{\lambda\sigma} \mathrm{d}u\, q_{\mathrm{SC}}(u)(r-u)h_{\mathrm{SC}}(|r-u|).
\end{aligned}
\tag{16}
$$

Equation (16) is fulfilled if we find solutions of the following two Baxter equations for the reference system and the soft-core fluid separately,

$$
rh_0(r) = -q_0'(r) + 2\pi\rho\int_0^{\sigma} \mathrm{d}u\, q_0(u)(r-u)h_0(|r-u|),
\tag{17}
$$

and

$$
rh_{\mathrm{SC}}(r) = -q_{\mathrm{SC}}'(r) + 2\pi\rho\int_0^{\lambda\sigma} \mathrm{d}u\, q_{\mathrm{SC}}(u)(r-u)h_{\mathrm{SC}}(|r-u|).
\tag{18}
$$

We now consider the hard-sphere fluid, discussed in the previous section, as the reference system and, following the ideas for the soft-core fluid proposed originally by Cummings *et al.* [27], we here propose an ansatz for the total correlation function of the soft square-shoulder fluid, $h_{\mathrm{SS}}(r)$,

$$
h_{\mathrm{SS}}(r) = -1 + \alpha\, \exp(-\beta\epsilon), \quad r \le \lambda\sigma,
\tag{19}
$$

where α is an unknown and dimensionless parameter, which can be adjusted, for example, by enforcing thermodynamic self-consistency, and $\beta\epsilon$ is the height of the SS in units of $k_{\mathrm{B}}T$.

Inserting Equation (13) into Equation (3) we obtain,

$$
\begin{aligned}
rc(r) = {} & -[q_0'(r)+q_{\mathrm{SS}}'(r)] + 2\pi\rho\int_0^{\sigma} \mathrm{d}u\, q_0(u)q_0'(r+u) \\
& + 2\pi\rho\int_0^{\lambda\sigma} \mathrm{d}u\, q_{\mathrm{SS}}(u)q_{\mathrm{SS}}'(r+u) \\
& + 2\pi\rho\int_0^{\sigma} \mathrm{d}u\, q_{\mathrm{SS}}(u)q_0'(r+u) \\
& + 2\pi\rho\int_0^{\sigma} \mathrm{d}u\, q_0(u)q_{\mathrm{SS}}'(r+u).
\end{aligned}
\tag{20}
$$

Equation (20) is basically composed of three contributions, namely,

$$
rc(r) = rc_0(r) + rc_{\mathrm{SS}}(r) + rc_{\mathrm{RES}}(r),
\tag{21}
$$

where $c_0(r)$ is the direct correlation function of the hard-sphere fluid, given by Equation (12), $c_{\mathrm{SS}}(r)$ is the direct correlation function of the soft square-shoulder,

$$
rc_{\mathrm{SS}}(r) = -q_{\mathrm{SS}}'(r) + 2\pi\rho\int_0^{\lambda\sigma} \mathrm{d}u\, q_{\mathrm{SS}}(u)q_{\mathrm{SS}}'(r+u)
\tag{22}
$$

and $c_{\mathrm{RES}}(r)$ the residual direct correlation function,

$$
\begin{aligned}
rc_{\mathrm{RES}}(r) = {} & 2\pi\rho\int_0^{\sigma} \mathrm{d}u\, q_{\mathrm{SS}}(u)q_0'(r+u) \\
& + 2\pi\rho\int_0^{\sigma} \mathrm{d}u\, q_0(u)q_{\mathrm{SS}}'(r+u).
\end{aligned}
\tag{23}
$$

From Equation (23), one can notice that the residual term, defined inside the hard core, is given by the product of crossed terms, similar to the ones discussed in Equation (15), and then one could neglect them. However, the evaluation of $c_{\mathrm{RES}}(r)$ is straightforward once Equation (22) is solved. We have explicitly checked that such contribution becomes unimportant. Then, the direct correlation function of the system is simply given by the reference contribution plus the soft square-shoulder contribution.

Therefore, by inserting Equation (19) into Equation (18) we obtain the factor function of the SS,

$$
q_{\mathrm{SS}}'(r) = a_{\mathrm{SS}}\, r + b_{\mathrm{SS}},
\tag{24}
$$

then

$$
q_{\mathrm{SS}}(r) = \frac{1}{2}a_{\mathrm{SS}}\left(r^2-(\lambda\sigma)^2\right) + b_{\mathrm{SS}}\,(r-\lambda\sigma),
\tag{25}
$$

where

$$
\begin{aligned}
a_{\mathrm{SS}} &= E_\lambda\left[1-2\pi\rho\int_0^{\lambda\sigma} \mathrm{d}u\, q_{\mathrm{SS}}(u)\right], \\
b_{\mathrm{SS}} &= E_\lambda\left[2\pi\rho\int_0^{\lambda\sigma} \mathrm{d}u\, q_{\mathrm{SS}}(u)u\right],
\end{aligned}
\tag{26}
$$

with $E_\lambda = 1-\alpha\exp(-\beta\epsilon)$. Then, a straightforward integration leads to

$$
a_{\mathrm{SS}} = \frac{1+2\eta_2E_\lambda^2}{(1-E_\lambda^2\eta_2)^2}E_\lambda, \quad b_{\mathrm{SS}} = -\frac{3\eta_2\lambda\sigma E_\lambda^3}{2(1-E_\lambda^2\eta_2)^2},
\tag{27}
$$

where $\eta_2 = (\pi\rho/6)(\sigma\lambda)^3$. Then, by inserting Equation (25) into (22) the DCF of the soft SS fluid reads

$$
\begin{aligned}
c_{\mathrm{SS}}(r) = {} & -\frac{1}{2}a_{\mathrm{SS}}^2\eta r^3 + 6\eta\lambda^2(a_{\mathrm{SS}}+b_{\mathrm{SS}})^2 r \\
& - \eta\lambda^3 a_{\mathrm{SS}}(6b_{\mathrm{SS}}+4a_{\mathrm{SS}}) - a_{\mathrm{SS}}.
\end{aligned}
\tag{28}
$$

3.2. *Direct correlation function: comparison with PY closure*

In the following, we are going to test the predictions given by this approximation by firstly fixing the

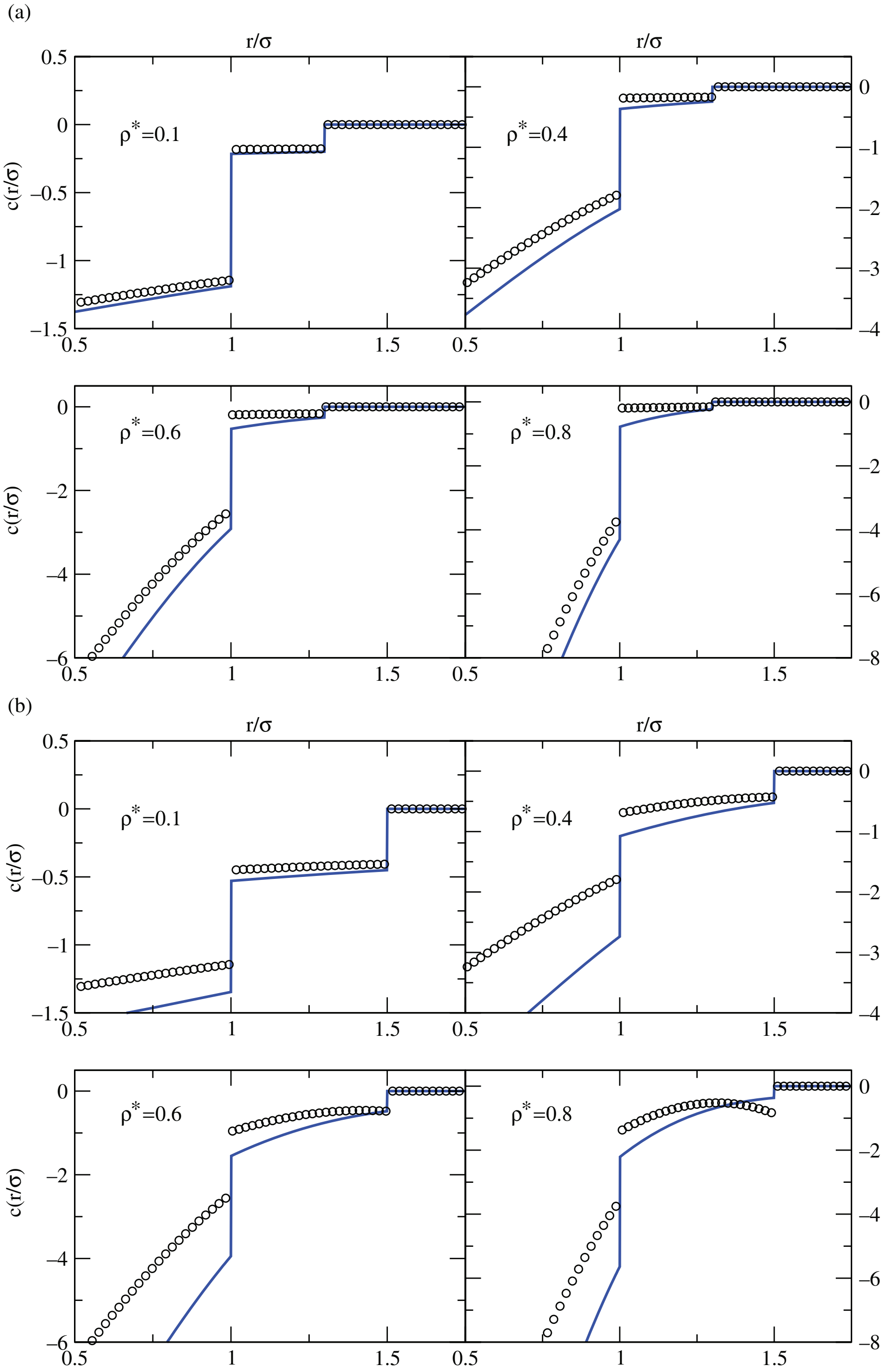

Figure 1. Direct correlation functions of the SS fluid with potential parameters (a) $\lambda = 1.3$, $\beta\epsilon = 0.2$ and (b) $\lambda = 1.5$, $\beta\epsilon = 0.5$. Symbols are obtained from our parametrisation with $\alpha = 1.0$ and lines from the PY closure relation.

unknown parameter α to 1 and afterwards defining α as a function of the thermodynamic state and the potential parameters that is able to reproduce the results obtained by the PY closure relation, which represents a good approximation for short-range repulsive interactions.

Figure 1(a) and (b) show the DCF given by Equation (28) for a SS system with potential parameters $\lambda = 1.3$, $\beta\epsilon = 0.2$ and $\lambda = 1.5$, $\beta\epsilon = 0.5$, respectively, for different reduced densities, $\rho^* \equiv \rho\sigma^3$. The potential parameters were taken from [23]. Clearly, one can observe that the parametrisation gives a qualitative description of the behaviour of the DCF when it is compared with the full numerical solution of the OZ equation within the PY approximation.

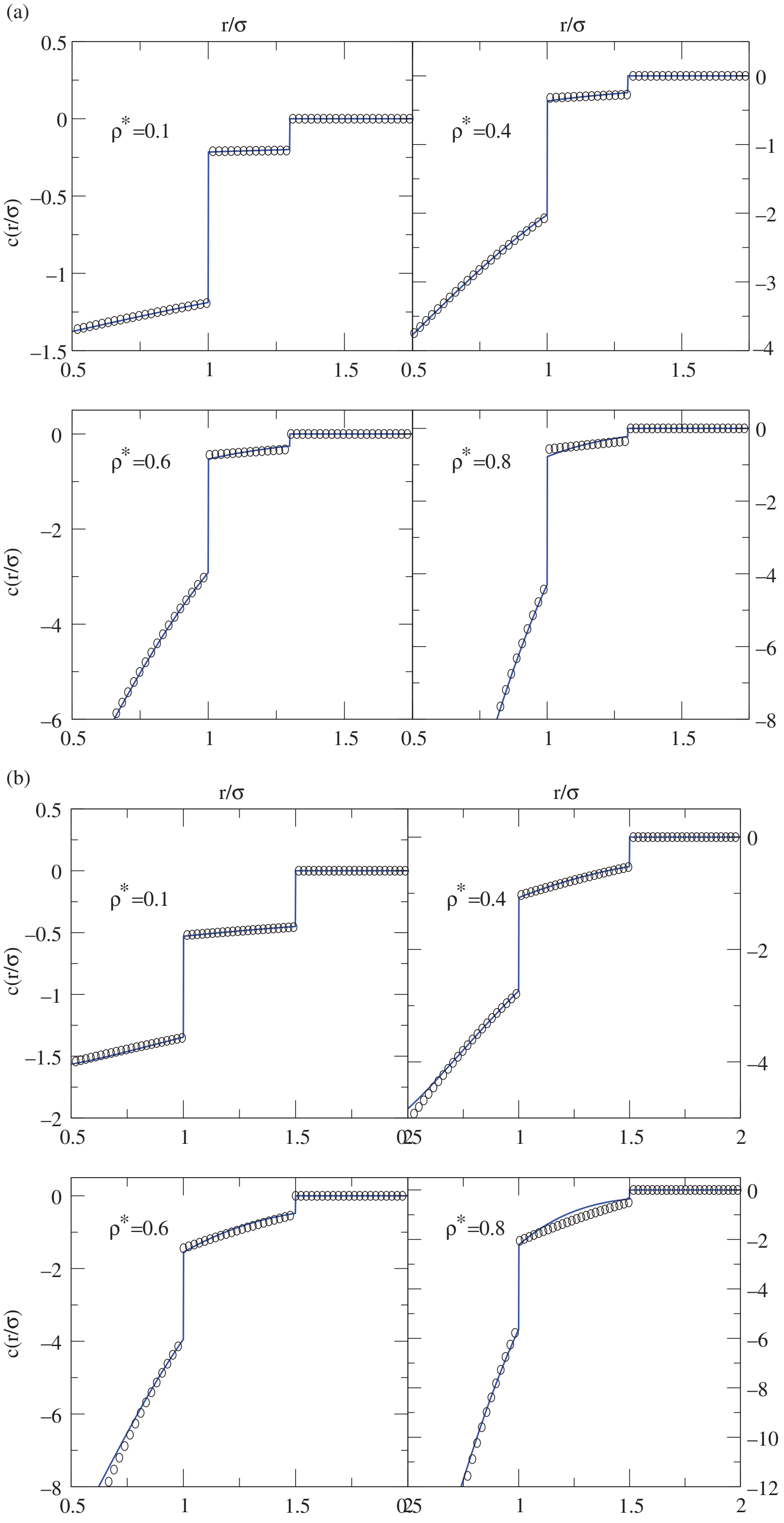

Figure 2. Direct correlation function of the SS fluid with the same potential parameters as in Figure 1(a) $\lambda = 1.3$, $\beta\epsilon = 0.2$ and (b) $\lambda = 1.5$, $\beta\epsilon = 0.5$. Lines are obtained from the PY approximation and symbols from our parametrisation Equation (29): in (a) parameter α takes the values: $\alpha(\rho^* = 0.1) = 0.96$, $\alpha(\rho^* = 0.4) = 0.857$, $\alpha(\rho^* = 0.806) = 4.8$, $\alpha(\rho^* = 0.8) = 0.77$; in (b) $\alpha(\rho^* = 0.1) = 0.911$, $\alpha(\rho^* = 0.4) = 0.086$, $\alpha(\rho^* = 0.6) = -0.92$, $\alpha(\rho^* = 0.8) = -2.31$.

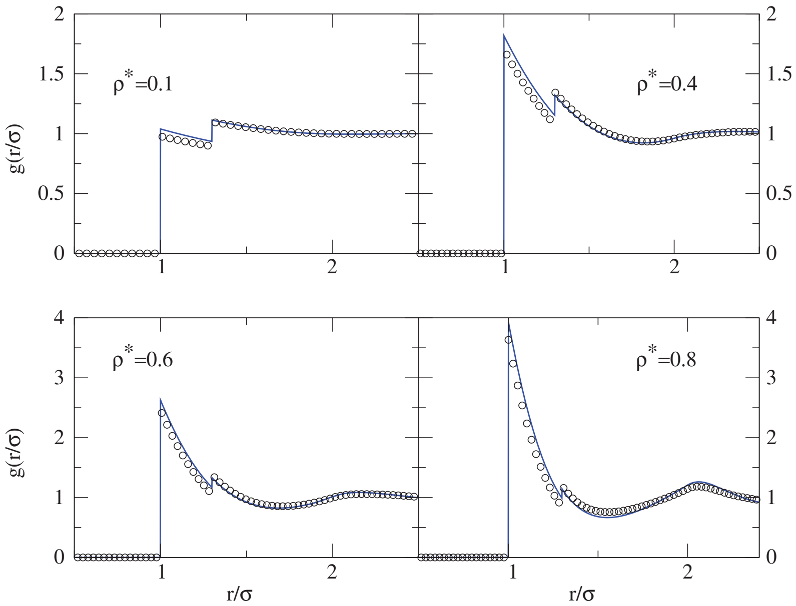

Figure 3. Radial distribution functions of the SS fluid with potential parameters $\lambda = 1.3$ and $\beta\epsilon = 0.2$ for different reduced densities ρ^*. Symbols are obtained from Monte Carlo computer simulations and lines from our parametrisation with $\alpha = 1.0$.

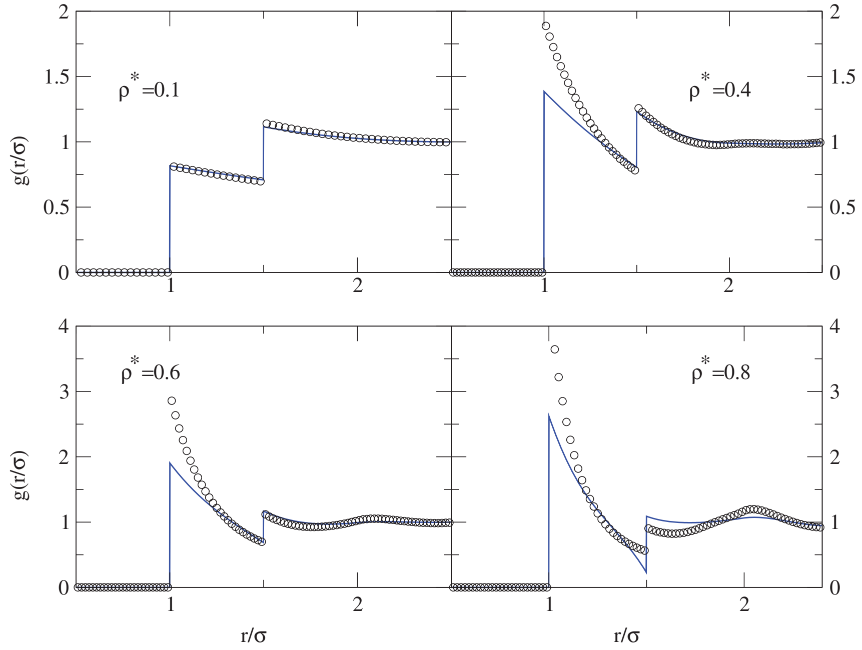

Figure 4. Radial distribution functions of the SS fluid with potential parameters $\lambda = 1.5$ and $\beta\epsilon = 0.5$ for different reduced densities ρ^*. Symbols are obtained from Monte Carlo computer simulations and lines from our parametrisation with $\alpha = 1.0$.

However, strong deviations are seen when the density, the potential range increase or the temperature decreases; such deviations are larger inside the hard core. However, there is still some freedom that can be exploited: for all the potential parameters and densities here considered, we assumed that α is set to one. However, α can be adjusted to reproduce either the theoretical or the simulation data. This means that such a parameter depends explicitly on the properties of the system; $\alpha = \alpha[\lambda, \beta\epsilon; \rho]$. Then, it is convenient to look for a way to express α in terms of the density and the potential parameters.

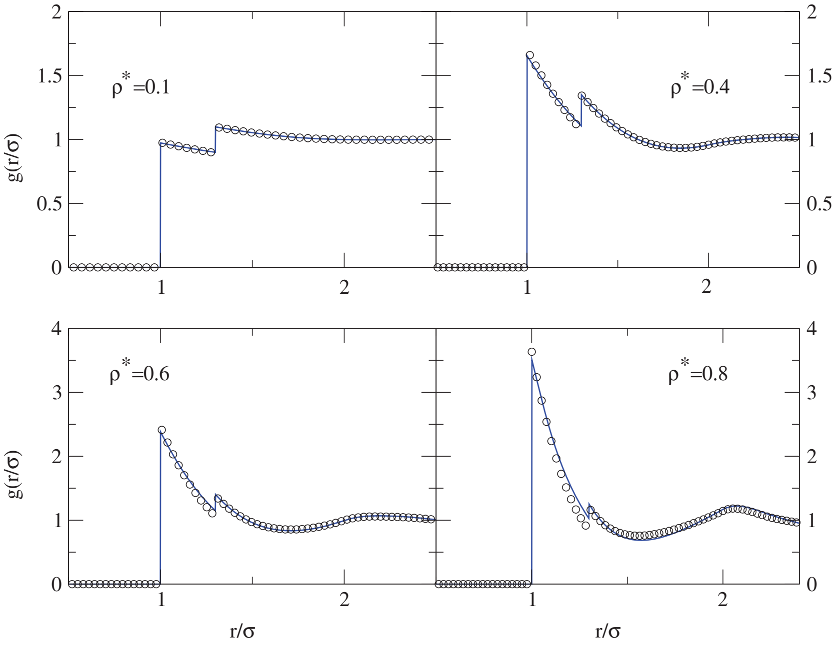

Figure 5. Radial distribution functions of the SS fluid with potential parameters $\lambda = 1.3$ and $\beta\epsilon = 0.2$, same as Figure 3(a), for different reduced densities ρ^*. Symbols are obtained from Monte Carlo computer simulations and lines from our parametrisation and α given by Equation (29).

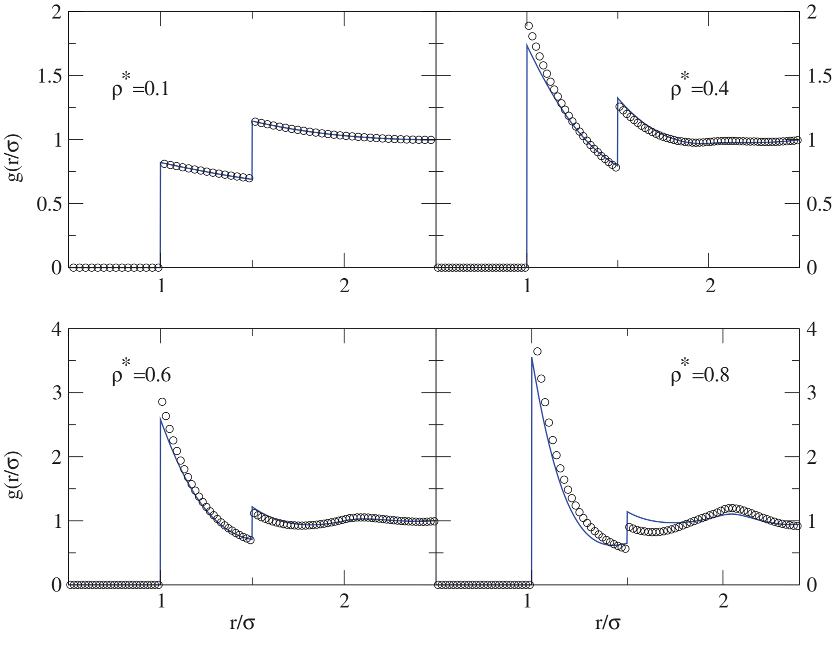

Figure 6. Radial distribution functions of the SS fluid with potential parameters $\lambda = 1.5$ and $\beta\epsilon = 0.5$, same as Figure 3(b), for different reduced densities ρ^*. Symbols are obtained from Monte Carlo computer simulations and lines from our parametrisation and α given by Equation (29).

A simple quadratic expansion in density leads to a good fit. Thus α is given by

$$\alpha = 1 + \kappa_1\eta + \kappa_2\eta^2, \tag{29}$$

whose coefficients depend, after extensive computer simulations, linearly on the potential strength and potential range, having the following functional form: $\kappa_1 = [-0.17 - (28.2/\pi)\beta\epsilon] + [-(5/21) + (17.64/\pi)\beta\epsilon]\lambda$, $\kappa_2 = [-4.6 + 17.6\beta\epsilon] + [(36.5/\pi) - 51.488\beta\epsilon]\lambda$.

In Figure 2(a) and (b) we show the $c_{SS}(r)$ with the same potential parameters as in Figure 1(a) and (b), respectively. From the figures it becomes clear that the parametrisation together with Equation (29) works better than the simple assumption that $\alpha = 1$, especially in the case of the highest density considered. In general, one can observe that the DCF reproduces successfully the whole behaviour inside and outside the core including systems with longer interaction range and lower temperature.

3.3. *Pair correlation function: comparison with MC*

To illustrate the applicability of our parametrisation, we now compare the pair correlation functions, $g(r)$'s, obtained by means of MC computer simulations with those calculated using Equation (28) and the Ornstein–Zernike equation. Before discussing our results, we should remark that usually approximations for the direct correlation functions do not preserve the hard-core condition on the $g(r)$. Such a limitation is also characteristic of our approach; deviations increase slightly with increasing density. However, in Figures 3–6 we explicitly enforce the hard-core (HC) condition ($h(r) = -1$ for $r < \sigma$). This is done as follows: outside the core the DCF $c(r)$ is given by the parametrisation while inside the core we set $c(r) = -\gamma(r) - 1$ which incorporates the HC condition. Together with the OZ relation we finally arrive at a $c(r)$ and $\gamma(r)$ that fullfill the HC condition. Additionally, we point out that, although our approach does not preserve entirely the HC condition in the $g(r)$, we have checked numerically that it preserves the positivity of the resulting structure factor over all the range of parameters we have explicitly considered (data not shown).

Figures 3 and 4 show the $g_{SS}(r)$'s (solid lines) obtained from the procedure described above for the systems already discussed in Figure 1 and $\alpha = 1$. We compare our results with MC computer simulations (open circles). The $g_{SS}(r)$ reproduces qualitatively the simulation data, although again larger deviations are found when either the density is increased or the potential range and strength are larger.

Now, our parametrisation and the relation for α (29) are employed together with the OZ equation to compute the $g_{SS}(r)$ of the systems described in Figure 2. The results are plotted in Figures 5 and 6, where an excellent agreement between theory and simulation is found although at very high densities ($\rho^* > 0.8$) the contact value is slightly underestimated by our theoretical approach.

We can conclude that our analytical expression is a good approximation for the $c(r)$ of SS fluids. According to our previous analysis, such an expression is accurate up to a reduced density $\rho^* = 0.9$ and values of the potential parameters $1 < \lambda \le 2$ and $0 < \beta\epsilon \le 0.5$.

4. Concluding remarks

We have developed a parametrisation of the direct correlation function for the hard-core square-shoulder fluid based on a simple soft-core potential model. The accuracy of our parametrisation is comparable to the results obtained within the PY approximation and works nicely for the systems under investigation. Additionally, the pair correlation functions obtained through MC simulations were well reproduced by our parametrisation.

Due to its simplicity and applicability, our parametrisation can be easily incorporated into elaborate theories, like thermodynamic perturbation theories, or even in more elaborate theoretical approaches, like SCOZA, to compute the structural properties or the phase diagram of DPF which consider the square-shoulder fluid as the new reference system. Work along these lines is in progress.

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Note

1. This assumption was already corroborated by using the resulting solution of Equation (15) into the numerical evaluation of the crossed terms (data not shown).

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