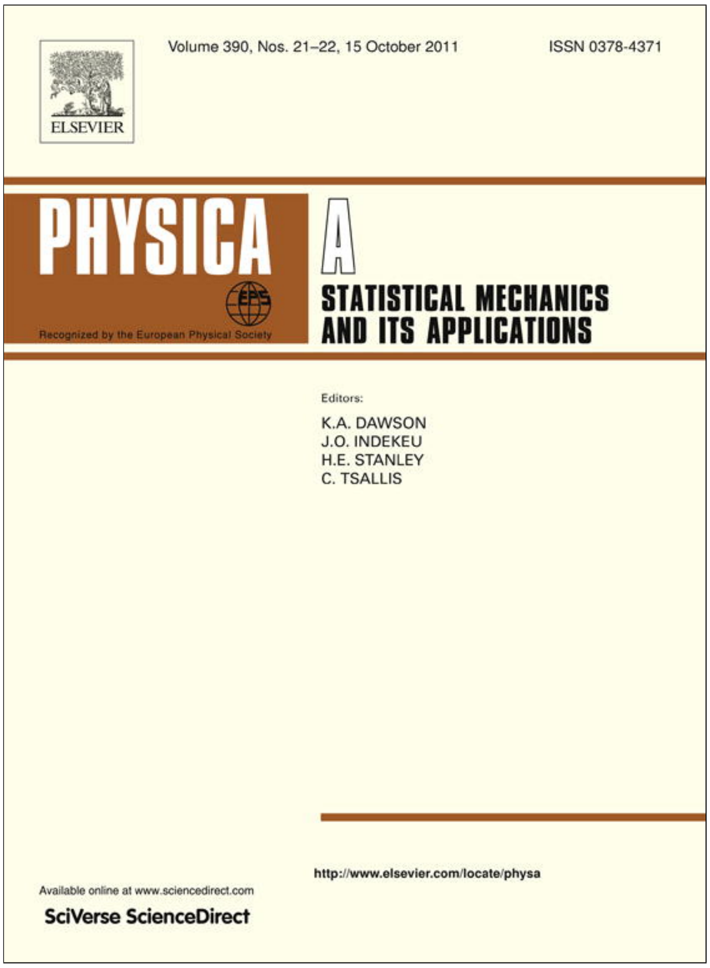

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A modified soft-core fluid model for the direct correlation function of the square-shoulder and square-well fluids

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ABSTRACT

We propose a simple analytical expression of the direct correlation function for the square-shoulder and square-well fluids. Our approximation is based on an ansatz for the direct correlation function of a modified soft-core fluid, whose parameters are adjusted by fitting the data obtained from Monte Carlo computer simulations. Moreover, it is complemented with a Wertheim-like parametrization to reproduce correctly the direct correlation inside the hard-core. We demonstrate that this approach is in quantitative agreement with the numerical solution of the Ornstein–Zernike equation within the Percus–Yevick approximation. We also show that our results are accurate in a large regime of densities for different interaction ranges and potential strengths. Therefore, this opens up the possibility of introducing the square-shoulder or the square-well potentials as new reference systems in advanced theoretical approximations.

1. Introduction

During the past few years, physicists have dealt with the nature of the (effective) interactions between particles in either simple or complex fluids [1–3]. Usually, the resulting interaction is not given in analytic form. However, a simplified version of such interaction potential can provide a realistic description of the system properties. For example, the so-called discrete potential fluids have provided a useful description to study the thermodynamic properties of a large variety of fluids. One can find in the literature that systems like water [4], methanol [5], polymers [6], electrolytes [7], among others, can be successfully modeled by using the well-known square-shoulder (SS) or square-well (SW) (or a combination of them) fluids. An advantage of both SS and SW fluids is that they can be used to discretize continuous potentials thus facilitating their incorporation in elaborated theoretical frameworks [8,9]; this discretization procedure allows to capture, in a simple way, the structural and thermodynamic properties of continuous potentials [10–12].

In fact, due to the potential application of the SS fluid in different approaches, a renewed interest on its structural and thermodynamic properties has been recently reported [13–15]. Particularly, we have introduced a simple soft-core fluid model to include a parametrization of the direct correlation function of the SS fluid. Moreover, Yuste et al. [14] have developed an analytic approximation based on the rational function approximation method to obtain a simple expression for its radial distribution function. Noteworthy, in our recent work [13] we only focused on the SS fluid while here both SS and SW fluids are explicitly considered.

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We should remark that most theoretical approximations, as thermodynamic perturbation-like theories [16] or the self-consistent Ornstein–Zernike approximation (SCOZA) [17], model the SS and SW fluids as a hard-sphere fluid (the so-called reference system) with a characteristic tail. In particular, this picture has been successfully applied to characterize the liquid–vapor phase diagram of the SW fluid [17] and a model fluid composed by a combination of a SS plus an attractive SW [18]; the latter exhibits a rather interesting and complex behavior with multiple fluid–fluid transitions [18].

Generally speaking, a successive combination of SW and SS cannot be simply modeled with a HS fluid as reference system. This limitation resides in the fact that some theoretical approximations, like the SCOZA, fail to numerically converge when a repulsive contribution, apart from the hard-core repulsion, is considered [19]. A detailed analysis of the numerical stability of SCOZA with discrete potential fluids can be found in Ref. [20].

Then, the aim of this work is to develop simple and useful analytical expressions for the direct correlation function (DCF) of both SS and SW fluids, which can be used directly as a new reference system, like in the extension of SCOZA for discrete potential fluids [20]. After the present introduction, in Section 2 we describe the functional form of the SS and SW potentials. We briefly discuss the Ornstein–Zernike (OZ) equation, the Percus–Yevick (PY) closure relation and the Wertheim parametrization for the DCF of the HS fluid. Also, our ansatz based on a modified soft-core fluid model is introduced. In Section 3 we compare our approximation with the full numerical solution of the *OZ* equation within the PY approximation [21]. The resulting DCFs are used to compute the radial distribution functions (RDFs) of both fluids and tested against Monte Carlo computer simulations. The paper ends with a section of concluding remarks.

2. Direct correlation function for the square-shoulder and square-well fluids

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

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

where r is the interparticle distance, ϵ is the (positive) height of the shoulder and λ is the reduced range of the potential barrier. Eq. (1) takes the conventional definition of the square-well potential, $\phi_{SW}(r)$, by replacing ϵ through $-\epsilon$.

The Ornstein–Zernike (*OZ*) equation for an isotropic and homogeneous monodisperse system is giving by the relation [22]

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

where ρ is the particle number density, $c(r)$ is the direct correlation function and $h(r)=g(r)-1$ is the total correlation function, $g(r)$ being the well-known radial distribution function. Eq. (2) needs an additional relation in order to fully link the previous structure functions with the interaction potential between particles. Such a relation takes the following general form [23],

$$c(r)=\exp[-\beta\phi(r)+\gamma(r)+B(r)]-\gamma(r)-1, \tag{3}$$

where $\beta=(k_BT)^{-1}$ is the inverse of the thermal energy with k_B being the Boltzmann constant, T the absolute temperature, $\gamma(r)=h(r)-c(r)$ and $B(r)$ is the so-called bridge function. In general, $B(r)$ is unknown, however, further approximations for the bridge function lead to a family of approximations usually called closure relations [23].

A useful closure relation for systems with short-range interactions is the well-known Percus–Yevick approximation [23],

$$c(r)=[\exp(-\beta\phi(r))-1]y(r)=f(r)y(r) \tag{4}$$

where $y(r)=\exp(\beta\phi(r))[h(r)+1]$ and $f(r)=\exp(-\beta\phi(r))-1$ is the Mayer function. Eq. (4) can directly be obtained from Eq. (3) either by assuming that $B(r)=0$ and expanding the exponential term $e^{\gamma(r)}$ up to linear terms in $\gamma(r)$ or by setting $B(r)=-\gamma(r)+\ln[\gamma(r)+1]$.

Although the functional form of the interaction potential described in (1) is quite simple, there is no analytical solution for the structure functions. Therefore, a numerical procedure is needed to compute the DCF for both SS and SW fluids within the PY approximation. In particular, we propose here an alternative analytical expression based on a modified soft-core fluid model, which is discussed further below.

2.1. Wertheim parametrization

In particular, Eq. (1) reduces to the well-known hard-sphere interaction potential when $\epsilon=0$ or $\beta=0$ (infinite temperature limit). Since the pioneering work of Wertheim [21], it has been shown that the DCF of the HS fluid within the PY approximation takes a simple analytic form,

$$c_{HS}(r)=-\frac{1}{(1-\eta)^4}\left[(1+2\eta)^2-6\eta\left(1+\frac{1}{2}\eta\right)^2\frac{r}{\sigma}+\frac{1}{2}\eta(1+2\eta)^2\left(\frac{r}{\sigma}\right)^3\right]\quad r<\sigma, \tag{5}$$

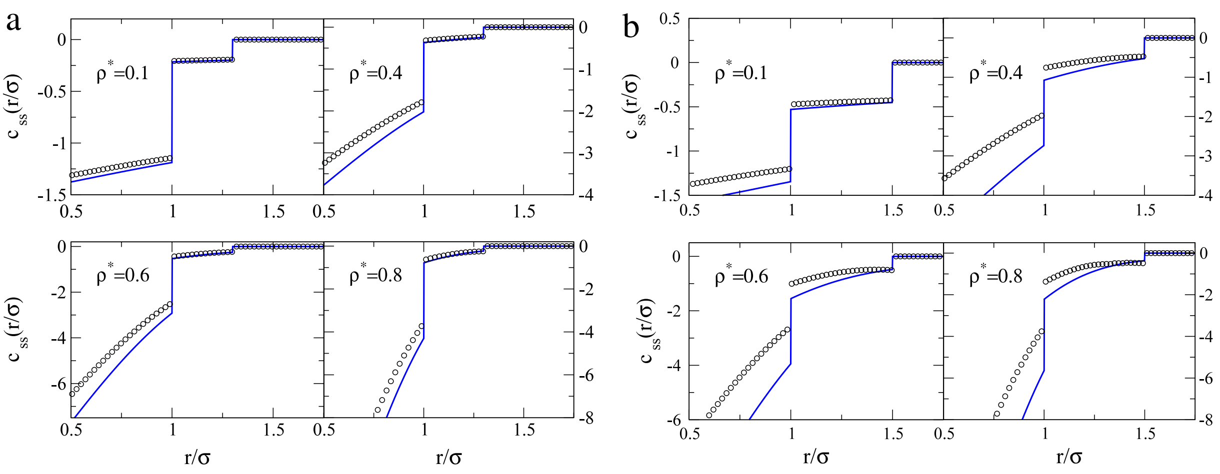

Fig. 1. Direct correlation functions obtained from Eq. (6) for the SS fluid with potential parameters (a) $\lambda = 1.3$, $\beta\epsilon = 0.2$ and (b) $\lambda = 1.5$, $\beta\epsilon = 0.5$ with $\alpha = \gamma = 1.0$. Solid lines are results from the PY approximation.

and $c_{HS}(r) = 0$ for $r > \sigma$, and $\eta = \frac{\pi}{6}\rho\sigma^3$ is the volume fraction. Eq. (5) is accurate at very low densities, but it fails when the density increases. Nevertheless, Henderson and Grundke found that the functional form of Eq. (5) is correct even at high densities if a density-dependent correction factor is introduced [24]. This correction allows fitting quantitatively the PY solution inside the hard-core. Henderson's correction parameter is given by the relation $\Gamma = 1 - 0.127\rho^{*2}$ [24], where $\rho^* \equiv \rho\sigma^3$ is the reduced density. Then, a simple parametrization for the DCF of the HS fluid, within the PY approximation, can be obtained by replacing $c_{HS}(r)$ with $\Gamma c_{HS}(r)$.

2.2. Ansatz: modified soft-core fluid model

Motivated by the simple choice proposed by Henderson and Grundke [24], soft-core model fluids have been developed by Waisman [25] and Cummings et al. [26] to obtain analytic expressions for the DCF of HS and soft-core fluids. Following similar ideas, we here propose a simple ansatz for the DCF of either SS or SW fluids. This ansatz is based on a modified soft-core fluid, which basically considers that the total correlation function, $h(r)$, takes the form: $h(r) = -1 + \exp(-\beta\epsilon)$, in the interval $0 \le r < \lambda\sigma$ (see, e.g., [26]). Therefore, our choice for the DCF is strongly based on the fact that, according to the *OZ* equation (see Eq. (2)), in the limit of vanishing particle density, i.e., $\rho \to 0$, both correlation functions are equal, i.e., $h(r) \approx c(r)$. Thus, we assume that $c(r)$ keeps a functional form similar to the one chosen for $h(r)$.

Then, we here consider that the $c(r)$ for either the SS or the SW can, in general, be written in the following form,

$$c(r) = \begin{cases} c_{HS}(r)\alpha\exp(-\beta\epsilon) & 0 \le r < \sigma, \\ c^E_{HS}(r)(1 - \gamma\exp(-\beta\epsilon)) & \sigma \le r \le \lambda\sigma, \\ 0 & r > \lambda\sigma, \end{cases} \tag{6}$$

where α and γ are unknown and dimensionless parameters which could be calculated, for example, by using arguments of thermodynamic self-consistency or by fitting the simulation data, ϵ is the height (depth) of the SS (SW), $c_{HS}(r)$ is the DCF of the HS fluid including Henderson's correction factor and $c^E_{HS}(r)$ is the extended analytical version of $c_{HS}(r)$ (see Eq. (5)) evaluated in the interval $\sigma \le r \le \lambda\sigma$. Eq. (6) takes the functional form of the DCF for the SW fluid by replacing ϵ with $-\epsilon$.

Our ansatz can be simply considered as a kind of weighted hard-sphere direct correlation function. The weight function is an explicit function of the interaction potential parameters, i.e., ϵ and λ, in the region of the tail and, of course, the number particle density. As we will see further below, a quadratic expansion in the density for the parameters α and γ will allow us to accurately describe the DCF of both fluids.

3. Structural properties

3.1. Square-shoulder fluid

Fig. 1(a) and (b) show the DCF, $c_{SS}(r)$, given by Eq. (6) 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 and setting $\alpha = \gamma = 1$. The potential parameters were taken from Ref. [18]. Clearly, one can observe that our simple ansatz gives a qualitative description of the behavior of the DCF when it is compared with the full numerical solution of the *OZ* equation within the PY approximation (solid lines). However, stronger deviations are evidently seen when the density and the potential parameters increase. Such deviations are larger inside the hard-core.

Despite the differences between the analytical expression for the $c_{SS}(r)$ and the corresponding numerical solution based on the PY closure relation, one can still compute the radial distribution function, $g_{SS}(r)$, of the SS fluid. Figs. 2 and 3 show

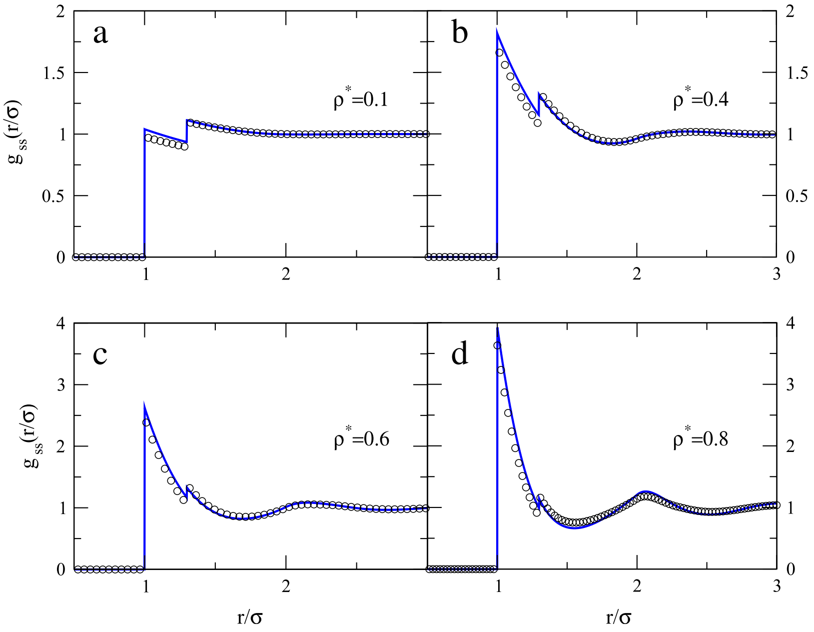

Fig. 2. Radial distribution functions of the SS fluid with potential parameters $\lambda = 1.3$ and $\beta\epsilon = 0.2$ for different reduced densities ρ^*. Symbols are obtained from MC computer simulations and lines from Eq. (6) with $\alpha = \gamma = 1$ together with the *OZ* equation [23].

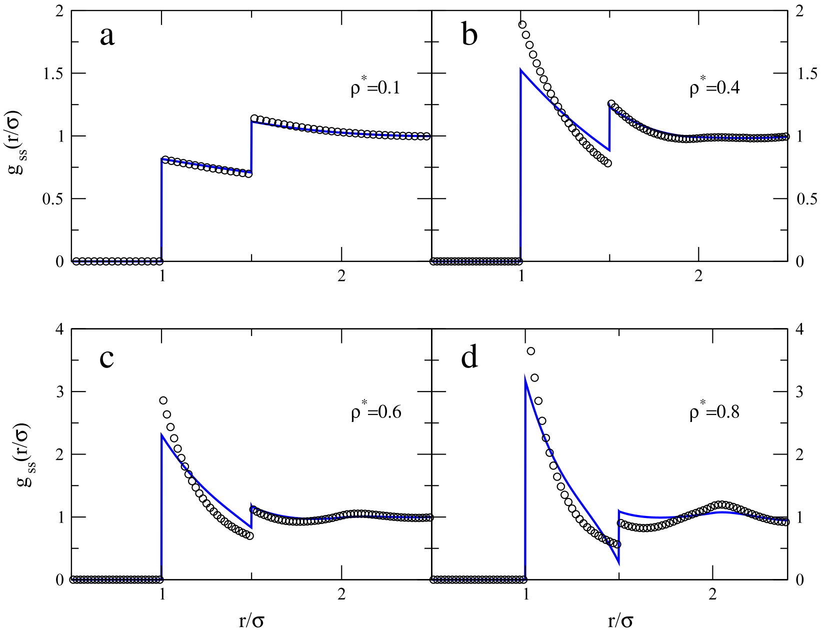

Fig. 3. Radial distribution functions of the SS fluid with potential parameters $\lambda = 1.5$ and $\beta\epsilon = 0.5$ for different reduced densities ρ^*. Symbols are obtained from MC computer simulations and lines from Eq. (6) with $\alpha = \gamma = 1$ together with the *OZ* equation [23].

the $g_{SS}(r)$'s (solid lines) obtained from Eq. (6) for the systems already discussed in Fig. 1. We also compare our results with Monte Carlo (MC) computer simulations in the *NVT* ensemble (open circles). MC computer simulations are performed using a cubic box of length $L^3 = N/\rho$ with N being the number of particles in the simulation box. We follow the standard Metropolis algorithm [27]. Simulations with $N = 1000$, 2197 and 4096 particles were carried out to analyze possible finite size effects. Randomly selected initial configurations were equilibrated during 10^7 MC steps. The equilibration process is also monitored following the evolution of the total potential energy and the averages were performed during 10^8 MC steps. The parameters space explored is out of any phase-separation region. Our findings indicate that the $g_{SS}(r)$ reproduces qualitatively the simulation data, in particular those cases displayed in Fig. 2, although larger deviations are found when either the density is increased or the potential range and strength are larger, see Fig. 3. However, there is still some freedom that can be exploited: for all the potential parameters and densities here considered, we assumed that α and γ are set to unity. However, both can be adjusted to reproduce the simulation data, i.e., $\alpha = \alpha[\lambda, \beta\epsilon; \rho]$ and $\gamma = \gamma[\lambda, \beta\epsilon; \rho]$. Then, it is convenient to find a way to express such parameters in terms of the density and potential parameters.

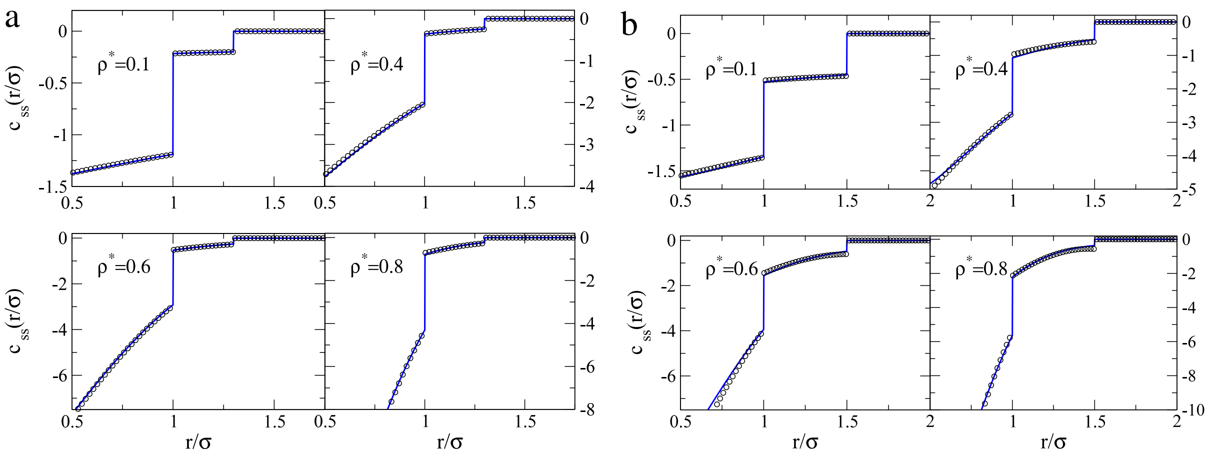

Fig. 4. Direct correlation function of the SS fluid with potential parameters (a) $\lambda = 1.3$, $\beta\epsilon = 0.2$ and (b) $\lambda = 1.5$, $\beta\epsilon = 0.5$, same as in Fig. 1. Symbols are obtained from Eq. (6) with α_{SS} and γ_{SS} described in Eq. (7) and solid lines from the PY approximation.

Therefore, through extensive computer simulations we have found that the $c(r)$ given by Eq. (6) keeps its functional form for any system investigated, although $c_{HS}(r)$ in the interval $\sigma < r < \lambda\sigma$ should be evaluated using the choice $r \to (1.06 - \frac{6}{5\pi}\eta)r$. Moreover, the parameters α and γ can simply be fitted through a quadratic polynomial of the density,

$$\alpha_{SS} = \kappa_0^{(1)} + \kappa_1^{(1)}\eta + \kappa_2^{(1)}\eta^2, \qquad \gamma_{SS} = \kappa_0 + \kappa_1\eta + \kappa_2\eta^2, \tag{7}$$

whose coefficients depend explicitly on the potential strength and range and, particularly, have the following form $\kappa_0^{(1)} = 1 + (0.1842\lambda + 0.7477)\beta\epsilon + (0.4117\lambda - 0.163)(\beta\epsilon)^2$, $\kappa_1^{(1)} = \frac{6}{\pi}((-3.547\lambda + 6.837)\beta\epsilon + (24.33\lambda - 25.29)(\beta\epsilon)^2)$, $\kappa_2^{(1)} = \frac{36}{\pi^2}((3.869\lambda - 7.491)\beta\epsilon + (-30.48\lambda + 35.52)(\beta\epsilon)^2)$, $\kappa_0 = 1 + (0.06343\lambda - 0.0863)\beta\epsilon + (-0.6497\lambda + 0.9567)(\beta\epsilon)^2$, $\kappa_1 = \frac{6}{\pi}((1.03\lambda - 1.276)\beta\epsilon - (2.034\lambda + 1.963)(\beta\epsilon)^2)$, and $\kappa_2 = \frac{36}{\pi^2}((-11.3\lambda + 2.234)\beta\epsilon + (22.77\lambda + 0.9833)(\beta\epsilon)^2)$.

We should point out that although the chosen form for the parameters is completely arbitrary, i.e., relation (7) and its coefficients are not unique, one has to take into account that both parameters have to reduce to the unity in either limit $\beta = 0$, i.e., very high temperatures, or $\epsilon = 0$ to reproduce correctly the hard-sphere limit. In the above case, such a limit is indeed included in the functional form of the parameters described in (7).

In Fig. 4(a) and (b) we show the $c_{SS}(r)$ with the same potential parameters as in Fig. 1(a) and (b), respectively. From the figures it becomes clear that the fit for the adjustable parameters, α and γ, works much better than to set their values to the unity, especially in the case of the highest density considered. Thus, we can conclude that in the case of the SS fluid, the DCF given by (6) reproduces the whole behavior inside and outside the core including systems with longer range and higher barrier strength.

Although it is clear the good agreement between our approach (Eq. (6)) and the PY approximation for the systems reported in Fig. 4, we should stress that commonly approximations for the direct correlation functions do not preserve the hard-core condition when they are used into the *OZ* equation to evaluate the $g(r)$. Such a limitation is also characteristic of our approach; the differences are extremely small and increase slightly with increasing density (data not shown). However, we explicitly enforce the hard-core (HC) condition ($h(r) = -1$ for $r < \sigma$) during the numerical solution of the *OZ* equation. This is technically done by imposing the condition $c(r) = -\gamma(r) - 1$ for $r < \sigma$ in the Ng algorithm [28], which is here used to numerically solve the *OZ* equation.

For the sake of the clarity, we have only shown the results imposing the HC condition in the solution of the *OZ* equation together with Eq. (6). Nevertheless, we have also computed the structure functions using the full expression given by Eq. (6) and obtained basically the same results with very small discrepancies inside the core (data not shown). This means that the results obtained considering Eq. (6) can be used to determine analytically and qualitatively both thermodynamic and structural properties of the square-shoulder or square-well fluids. This represents the main advantage and contribution of our formulation.

Then, we use now Eq. (6) together with the quadratic expansion for both parameters α and γ together with the *OZ* equation to compute the $g_{SS}(r)$ of the systems described in Fig. 4. The results are plotted in Figs. 5 and 6, where an excellent agreement between our ansatz, the PY approximation (shown only for the cases of Fig. 6) and MC simulations is found. Nonetheless, at intermediate ($\rho^* \approx 0.6$) and high ($\rho^* \approx 0.8$) densities the contact value is slightly underestimated. For high densities, the corresponding values at the edge of the shoulder are overestimated by our theoretical approach; such a difference is clearly small. However, it is noticeable that the precision of the present approach is higher than our recent parametrization [13]. Therefore, our analytical expression (6) is a good approximation for computing the RDFs of SS fluids. In particular, our approach is accurate up to a reduced density $\rho^* = 0.9$ and values of the potential parameters $1 < \lambda \leq 2$ and $0 < \beta\epsilon \leq 0.5$. This also means that our ansatz not only reproduces the structural properties of the SS fluid, it can be used to calculate its thermodynamic properties, at least, for those monodisperse systems within the fluid phase region.

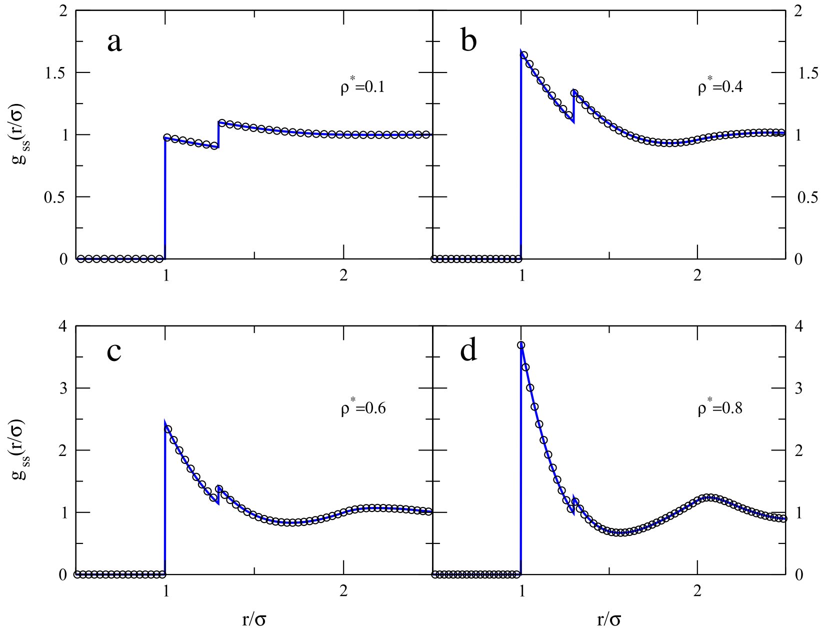

Fig. 5. Radial distribution functions of the SS fluid with potential parameters $\lambda = 1.3$ and $\beta\epsilon = 0.2$, same as Fig. 2, for different reduced densities ρ^*. Symbols are obtained from Monte Carlo computer simulations and lines from the *OZ* equation with $c(r)$ given by (6) and α_{SS} and γ_{SS} taken from (7).

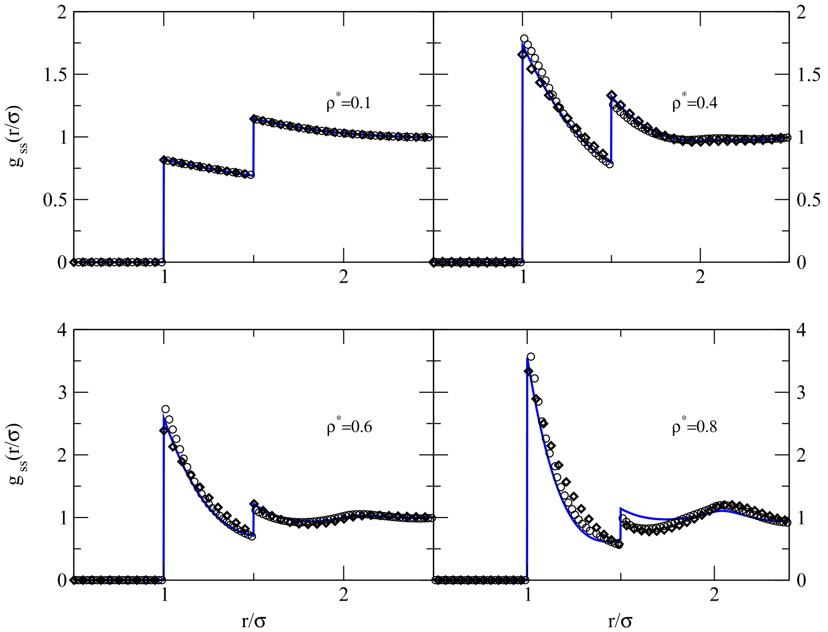

Fig. 6. Radial distribution functions of the SS fluid with potential parameters $\lambda = 1.5$ and $\beta\epsilon = 0.5$, same as Fig. 3, for different reduced densities ρ^*. Symbols are obtained from Monte Carlo computer simulations, lines from the *OZ* equation with $c(r)$ given by (6) and α_{SS} and γ_{SS} taken from (7), and rhombuses are obtained from the PY approximation.

3.2. Square-well fluid

As we remarked previously, the SS potential takes the conventional definition of the SW potential by replacing ϵ through $-\epsilon$. Therefore, Eq. (6) is used to determine the DCF of the SW fluid, $c_{SW}(r)$, with the parameters adjusted accordingly. After extensive MC computer simulations, we have found that, similarly to the previous case, the parameters α and γ for the SW fluid can also be described using a quadratic expansion in the density,

$$\alpha_{SW} = \kappa_1^{(2)} + \kappa_2^{(2)}\eta + \kappa_3^{(2)}\eta^2, \qquad \gamma_{SW} = 1 + \kappa_1^{(3)}\eta + \kappa_2^{(3)}\eta^2, \tag{8}$$

with $\kappa_1^{(2)} = 1-(0.6485\lambda+0.1183)\beta\epsilon+(0.955\lambda-0.781)(\beta\epsilon)^2$, $\kappa_2^{(2)} = \frac{6}{\pi}((0.3697\lambda-2.96)\beta\epsilon+(-5.023\lambda+9.388)(\beta\epsilon)^2)$, and $\kappa_3^{(2)} = \frac{36}{\pi^2}((0.5875\lambda-0.3543)\beta\epsilon+(4.725\lambda-7.457)(\beta\epsilon)^2)$, $\kappa_1^{(3)} = \frac{6}{\pi}((-0.873\lambda+1.305)\beta\epsilon+(1.082\lambda-2.812)(\beta\epsilon)^2)$,

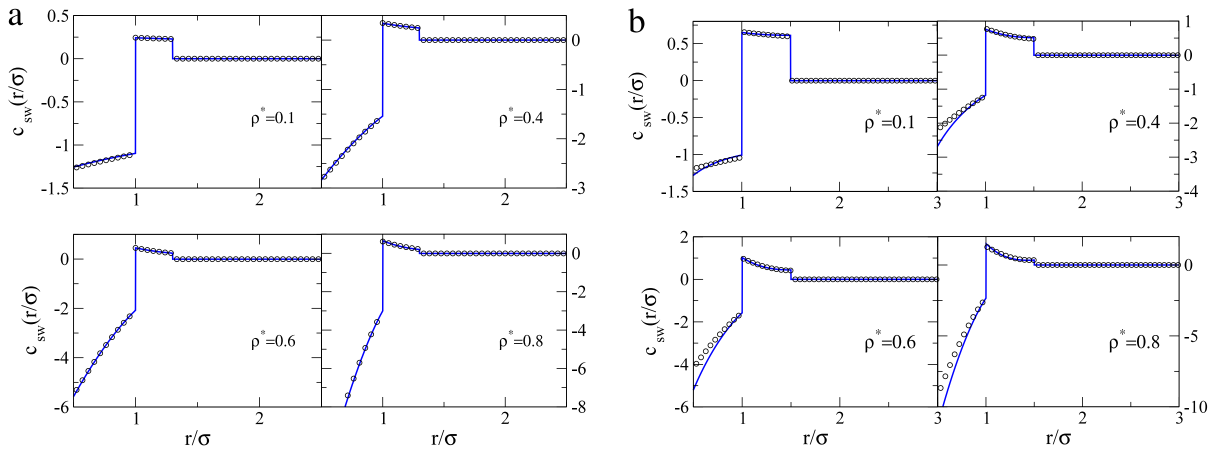

Fig. 7. Direct correlation function of the SW fluid with potential parameters (a) $\lambda = 1.3$, $\beta\epsilon = 0.2$ and (b) $\lambda = 1.5$, $\beta\epsilon = 0.5$. Symbols are obtained from Eq. (6) with α_{SW} and γ_{SW} described by Eq. (8), and solid lines from the PY approximation.

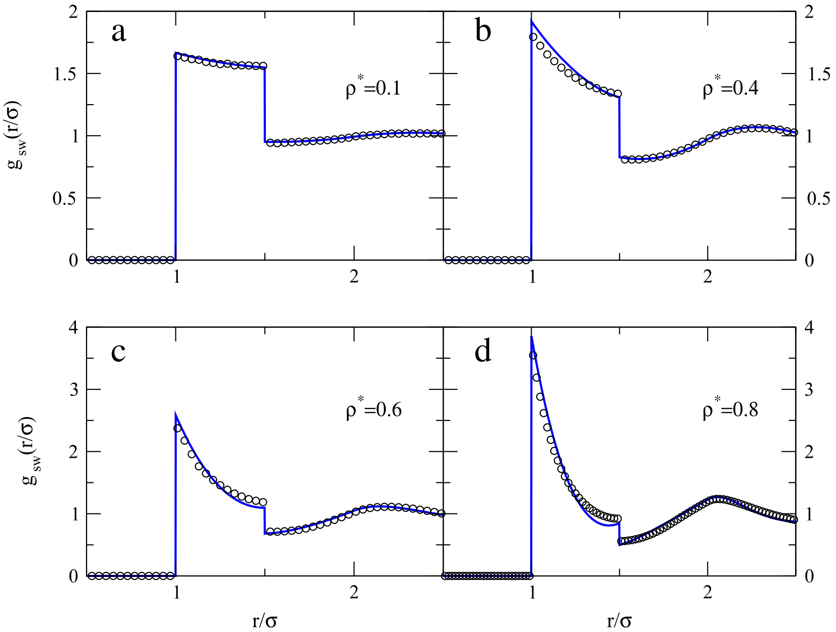

Fig. 8. Radial distribution functions of the SW fluid with potential parameters $\lambda = 1.5$ and $\beta\epsilon = 0.5$, same as Fig. 7(b), for different reduced densities ρ^*. Symbols are obtained from Monte Carlo computer simulations and lines from the *OZ* equation using (6) with α_{SW} and γ_{SW} described by Eq. (8).

and $\kappa_2^{(3)} = \frac{36}{\pi^2}((1.174\lambda - 2.395)\beta\epsilon + (-1.598\lambda + 3.66)(\beta\epsilon)^2)$. Both parameters also satisfy the hard-sphere limit when either $\beta = 0$ or $\epsilon = 0$.

In Fig. 7(a) and (b) we show the $c_{SW}(r)$ for the potential parameters $\lambda = 1.3, \epsilon = 0.2$ and $\lambda = 1.5, \epsilon = 0.5$, respectively. The results (open symbols) are compared with the numerical solution to the *OZ* with the PY closure relation (solid lines). Notably, our analytical expression gives a quantitative description of the $c_{SW}(r)$ in a large range of potential parameters and densities. In fact, its accuracy seems to be higher than in the case of the SS fluid.

Finally, Eq. (6) is used together with the *OZ* equation to obtain the radial distribution function, $g_{SW}(r)$, of the SW fluid. Fig. 8 shows the $g_{SW}(r)$ for the system described in figure Fig. 7(b). Our results are directly compared with MC simulation data and remarkable agreement between our approach and the simulation results is found. Then, we conclude that Eq. (6) could also be applicable to the square-well with good confidence up to a reduced density $\rho^* = 0.9$ and values of the potential parameters: $1 < \lambda \leq 2$ and $0 < \beta\epsilon \leq 0.5$. Additionally, is can be also employed to compute analytically the thermodynamic properties of the SW fluid.

So far we have applied the same approximation and methodology used in the SS fluid to obtain an analytical expression for the direct correlation function of the SW fluid. In fact, in the case of the SS fluid, this approach is as accurate as the parametrization we have recently developed exclusively for the SS [13]. However, the main advantage of the current work is that our simple ansatz based on a rescaled hard-sphere $c(r)$ also holds for the SW fluid.

4. Conclusions

In summary, we have introduced an analytic approximation, based on a modified soft-core fluid model, for the direct correlation function of both square-shoulder and square-well fluids. This approximation basically assumes that the $c(r)$ can be described in terms of a rescaling of the hard-sphere's direct correlation function in both the hard-core and the shoulder or the well region. We have shown that the accuracy of this theoretical model is comparable to the results obtained within the PY approximation for both fluids. Furthermore, the pair correlation functions are in good agreement with MC computer simulations. In the case of the square-shoulder fluid, it is as accurate as the previous parametrization reported in Ref. [13]. Thus, our approach is able to reproduce the thermodynamics of the systems under consideration provided they lie in the fluid phase of the phase diagram.

Additionally, we should point out that due to its simplicity and applicability, our analytical expression might be easily incorporated in more elaborated theories, like in perturbative approximations or in SCOZA, to compute either the structural properties or the phase diagram of DPF when the square-shoulder or the square-well fluids are considered as the new reference systems.

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