Direct correlation function of square well fluid with wide well:

First order mean spherical approximation

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(Dated:)

Abstract

An analytical expression for square-well fluid direct correlation function (DCF) obtained recently by Tang (Y. Tang, J. Chem. Phys. 127, 164504 (2007)) in the first-order mean spherical approximation is extended for wider well widths (2 < \lambda < 3). Theoretically obtained direct correlation functions and radial distribution functions for square-well fluid with \lambda = 2.1 and \lambda = 2.5 are compared with corresponding results of Monte-Carlo simulation.
I. INTRODUCTION

Recently, the systems of particles interacting with discrete potentials gained much attention from the scientific community. Such an increased interest to this class of model systems is associated primarily with their ability to mimic the bulk properties of variety of complex fluid systems, like associating fluids, colloids, cluster particles etc. The discrete hard-core potentials composed of an attractive square well and a repulsive square barrier were shown to induce the liquid-liquid phase transition in a single-component model fluid$^{1,2,4,5}$. Similar phase transitions take place in the real substances like water, carbon and phosphorus. Moreover, the effective potentials with square-well plus square-barrier components may be used to mimic colloidal particles interactions, which according to the DLVO theory are characterized by a long-range repulsive barrier and one or possibly two attractive wells. Finally, inhomogeneous fluids with discrete repulsive and attractive interaction potentials represent another intriguing area of research because they often serve as a benchmark to study a variety of interesting problems such as interfacial phenomena, surface adsorption, wetting, capillary condensation, etc.

The most suitable method to handle these systems seems to be the classical density-functional theory (DFT). There are several versions of the DFT derived usually from either weighted density approximation or perturbation expansions. Recently, Tang and Wu$^{6,7,8}$ have proposed a new DFT in which fundamental measure theory is combined with the so-called first-order mean-spherical approximation (FMSA). Its implementation requires knowledge of the thermodynamics and the direct correlation function of the model bulk fluid. In comparison with alternative approaches, DFT/FMSA possesses a number of advantages due to the both accuracy and simplicity of the FMSA solution. In combination with the DFT, the FMSA was already applied to study Lennard-Jones$^6$, Yukawa$^7$, Sutherland$^9$ fluid systems. Regarding the systems with discrete potentials, quite recently$^{10}$ the DFT/FMSA approach has been applied to study the structural properties of the square-well (SW) fluid model defined by the pair interaction potential,

$$u (r) = \begin{cases} \infty, & r < 1, \\ -\varepsilon, & 1 \leq r < \lambda, \\ 0, & r \geq \lambda. \end{cases} \quad (1)$$
with a unit hard-core diameter, the attractive strength $\varepsilon$ and the well width parameter $1 < \lambda < 2$; the FMSA solution for the direct correlation function (DCF) of this model system has been obtained in a separate study\textsuperscript{18}. It has been shown that DFT/FMSA gives good performance for entire considered range of attraction parameter $1 < \lambda < 2$.

The fact that FMSA is linear with respect to the interaction potential allows one to use linear combinations of the different potential functions for which FMSA solution is known. Regarding the case of the SW model this means that one can employ the linear combinations of the square wells ($\varepsilon > 0$) and/or square barriers ($\varepsilon < 0$) in order to form all variety of the discrete potential models. Unfortunately, majority of potential applications of the discrete SW-based potential models (e.g., see Refs.\textsuperscript{1,2,4,5} have the range of interaction that exceeds one particle diameter, that requires to consider $\lambda > 2$ in Eq.(1). This means that existing FMSA solution obtained by Tang\textsuperscript{18} is not sufficient to have FMSA be applied in the studies of the complex discrete potential models. The aim of present work is to extend the recent FMSA solution\textsuperscript{18} for the SW model fluid with $1 < \lambda < 2$ to the case of the SW fluids with $2 < \lambda < 3$. Obtaining of a such FMSA solution for the attractive SW model is crucial for the future application of both the FMSA as well as the DFT/FMSA to the systems with a combined (attractive SW plus repulsive SB) discrete potential. This will be shown in a forthcoming paper \textsuperscript{[10]}. The actual paper is organized as follows. In the next Section II we outline the necessary details of the FMSA solution for SW potential with $1 < \lambda < 3$. The FMSA results for the direct and pair correlation function will be presented and compared against computer simulation data in Section III. We conclude the paper in Section IV.

II. FMSA FOR SQUARE-WELL MODEL FLUIDS

The general FMSA formalism, developed by Tang and Lu, is presented in their paper\textsuperscript{16}. These authors solved the Ornstein-Zernike (OZ) equation,

$$\tilde{h}(k) = \tilde{c}(k) + \rho \tilde{h}(k) \tilde{c}(k)$$

for a one-component system of particles/molecules of a number density $\rho$ by employing the perturbative expansion for the total and direct correlation functions, $h$ and $c$, respectively,
over the pair interaction energy parameter $\varepsilon$,

\begin{align}
\tilde{h}(k) &= \tilde{h}_0(k) + \varepsilon \tilde{h}_1(k) + \ldots \\
\tilde{c}(k) &= \tilde{c}_0(k) + \varepsilon \tilde{c}_1(k) + \ldots,
\end{align}

where the subscript 0 denotes the contribution of a hard-sphere (HS) reference system while the subscript 1 stands for the first-order perturbation term. Here and in what follows, in accordance with the previous notation\textsuperscript{16} all symbols with the tilde denote the three-dimensional Fourier transforms,

\begin{align}
\tilde{h}(k) &= \frac{4\pi}{k} \int_{0}^{\infty} \sin(kr) rh(r) \, dr, \\
\tilde{c}(k) &= \frac{4\pi}{k} \int_{0}^{\infty} \sin(kr) rc(r) \, dr,
\end{align}

while all symbols with the hats denote the one-dimensional Fourier transforms or the Laplace transforms.

By employing the Hilbert transform, the general solution of the first order OZ equation can be obtained. The Fourier transform of the first order contribution to the total correlation function $h$ reads,

\begin{align}
\hat{h}_1(k) &= \frac{P(ik)}{\hat{Q}_0^2(ik)},
\end{align}

where

\begin{align}
P(ik) &= \frac{U_1(k)}{2\hat{Q}_0^2(-ik)} - \frac{e^{-ik}}{2i\pi} \int_{-\infty}^{\infty} \frac{U_1(y) e^{iy}}{(y-k) \hat{Q}_0^2(-iy)} \, dy,
\end{align}

and $\hat{Q}_0(ik)$ is the Baxter hard-sphere factorization function with a Laplace transform given by

\begin{align}
\hat{Q}_0(s) &= \frac{S(s) + 12\eta L(s) e^{-s}}{(1-\eta)^2 s^3},
\end{align}

with $\eta = \frac{1}{6\pi \rho}$, and

\begin{align}
S(t) &= (1-\eta)^2 t^2 + 6\eta (1-\eta) t^2 + 18\eta^2 t - 12\eta (1 + 2\eta), \\
L(t) &= \left(1 + \frac{\eta}{2}\right) t + 1 + 2\eta.
\end{align}

The function $U_1(k)$ in Eq. (17) is defined as

\begin{align}
U_1(k) &= \int_{1}^{\infty} rc_1(r) e^{-ikr} \, dr,
\end{align}
where, according to the FMSA closure,

\[ c_1(r) = -\beta u(r), \text{ for } r > 1, \]

with \( \beta = 1/k_B T \) and \( u(r) \) being the pair potential.

For smooth pair potentials \( u(r) \), for which \( U_1(k) \sim e^{-ik} \) (e.g., for the Yukawa potential), the integration contour in the right-hand side of Eq. \( 11 \) can be closed in the upper complex half-plane and evaluation of the integral does not require to calculate the residues at zeroes of the function \( \hat{Q}_0(-ik) \). This important simplification does not hold for the pair potentials that vanish for \( r > \lambda \) (\( \lambda > 1 \)), e.g. for the SW potential. For such a potential Tang and Lu expanded \( 1/\hat{Q}_0(-ik)^2 \) in a following way,

\[ \frac{1}{\hat{Q}_0(-ik)^2} = \left( 1 - \frac{(1 - \eta)^4}{e^{-ik}} \right)^6 \left[ 1 - 2\left( \frac{L(-ik)}{S(-ik)} e^{ik} \right) + 3 \left( \frac{L(-ik)}{S(-ik)} e^{ik} \right)^2 - \cdots \right], \]

and performed calculations according to the scheme described in the Appendix of their work. Since only the first term of the expansion \( 13 \) survives for \( \lambda \leq 2 \), therefore

\[ \hat{h}_1(k) = -\frac{(1 - \eta)^4}{\hat{Q}_0(i k)} e^{-ik} \text{Res} \left\{ \frac{W_\lambda(y)(-iy)^6 e^{iy}}{(y - k) S^2(-iy)} \right\}, \quad \lambda \leq 2, \]

where

\[ W_\lambda(k) = \int_\lambda^\infty r c_1(r) e^{-ikr} dr \]

should be calculated for \( c_1(r) \) smoothly extended from \( r \in [1, \lambda] \) to \( r \in [\lambda, \infty) \). For the SW potential we get

\[ W_\lambda(k) = \beta \varepsilon \frac{1 + ik \lambda}{(ik)^2} e^{-ik\lambda}. \]

Expression \( 14 \) is valid only for the pair potentials \( u(r) \) with the attractive well width that does not exceed one particle diameter, i.e., for \( \lambda \leq 2 \). In order to extend the actual FMSA scheme for larger values of parameter \( \lambda \), the contribution due to the second term in the expansion \( 13 \) should be taken into account. After doing that we obtain the following result,

\[ \hat{h}_1(k) = -\frac{(1 - \eta)^4}{\hat{Q}_0(i k)} e^{-ik} \text{Res} \left\{ \frac{W_\lambda(y)(-iy)^6 e^{iy}}{(y - k) S^2(-iy)} \left[ 1 - 2\left( \frac{L(-iy)}{S(-iy)} e^{iy} \right)^2 - \cdots \right] \right\}, \quad 2 < \lambda \leq 3, \]

which may be viewed as Eq. \( 14 \) supplemented with an additional term, that contributes to \( r > 2 \) region in the \( r \)-space.
The thermodynamic and structural properties of the square-well fluid for \( \lambda < 2 \) within the FMSA approximation have been reported in Refs.\textsuperscript{17,18,19}. Here, we would like to pay attention to the case with \( \lambda > 2 \), i.e., to the development of an additional term that already appears in Eq. (17). Let us denote it as

\[
\hat{h}_1^{(2)} (k) = \frac{24\eta (1 - \eta)^4 e^{-ik}}{Q_0^2 (ik)} \text{Res} \left\{ \frac{W_\lambda (y) (-iy)^6 L (-iy) e^{2iy}}{(y - k) S^3 (-iy)} \right\} ,
\]

After calculating the sum of residues in above expression, we obtain the following Laplace transform

\[
\hat{h}_1^{(2)} (s) = \frac{24\eta (1 - \eta)^4 e^{-s}}{Q_0^2 (s)} \left\{ \frac{C (-s) L (-s) e^{-s(\lambda-2)}}{S^3 (-s)} \right\} + \frac{1}{2} \sum_{i=0}^{2} \left( \frac{G_2 (t_i)}{s + t_i} + \frac{G_1 (t_i)}{(s + t_i)^2} + \frac{G_0 (t_i)}{(s + t_i)^3} \right) ,
\]

where \( C (s) = \lambda s^5 - s^4 \), while \( t_i \) correspond to the roots of \( S (t) = 0 \), and functions \( G_i (s) \) are,

\[
G_0 (s) = -2 \frac{C (s) L (s) e^{s(\lambda-2)}}{S_3^3 (s)} ,
\]

\[
G_1 (s) = 2 \frac{\left\{ \frac{d[C(s)L(s)]}{ds} + (\lambda - 2) C (s) L (s) \right\} e^{s(\lambda-2)}}{S_3^3 (s)} - 3 \frac{C (s) L (s) S_2 (s) e^{s(\lambda-2)}}{S_4^4 (s)} ,
\]

\[
G_2 (s) = - \frac{3 \left\{ \frac{d[C(s)L(s)]}{ds} + (\lambda - 2) C (s) L (s) \right\}}{S_3^3 (s)} + \frac{3 \left\{ \frac{d[C(s)L(s)]}{ds} + (\lambda - 2) C (s) L (s) \right\} e^{s(\lambda-2)}}{S_4^4 (s)}
\]

\[
+ \frac{3 \left\{ \frac{d[C(s)L(s)]}{ds} + (\lambda - 2) C (s) L (s) \right\} S_2 (s) e^{s(\lambda-2)}}{S_4^4 (s)} + \frac{C (s) L (s) S_3 (s) e^{s(\lambda-2)}}{S_4^4 (s)} ,
\]

with \( S_n (s) = d^n S (s) / ds^n \).

Then the Laplace transform of the first order contribution to the total correlation function \( h \) in the case of \( 2 < \lambda \leq 3 \) can be written as,

\[
\hat{h}_1 (s) = \frac{\beta \xi (1 - \eta)^2}{Q_0^2 (s)} \left[ \hat{p}^{(1)} (s) + 24\eta \hat{p}^{(2)} (s) \right] .
\]

In the above we introduced two functions

\[
\hat{p}^{(1)} (s) = e^{-s} \text{Res} \left\{ \frac{C (t) e^{(\lambda-1)t}}{(s + t) S^2 (t)} \right\} ,
\]

\[
\hat{p}^{(2)} (s) = e^{-s} \text{Res} \left\{ \frac{C (t) e^{(\lambda-2)t}}{(s + t) S^3 (t)} \right\} .
\]
and
\[ \hat{p}^{(2)}(s) = e^{-s} \text{Res} \left[ \frac{C(t) L(s) e^{(\lambda-2)t}}{(s+t) S^3(t)} \right]. \] (24)

The first one was examined in more details in Ref.\textsuperscript{18}, whereas the second function, in agreement with Eq. \textsuperscript{(19)}, reads

\[ \hat{p}^{(2)}(s) = e^{-s} \left\{ \frac{C(-s) L(-s) e^{-s(\lambda-2)}}{S^3(-s)} \right. \]
\[ + \frac{1}{2} \sum_{i=0}^{2} \left[ \frac{G_2(t_i)}{s+t_i} + \frac{G_1(t_i)}{(s+t_i)^2} + \frac{G_0(t_i)}{(s+t_i)^3} \right] \right\}. \] (25)

Following by Tang and Lu\textsuperscript{18}, the Laplace transform of the DCF can be obtained from

\[ \dot{c}(s) = \beta \varepsilon (1-\eta)^4 \left\{ \left[ \hat{Q}_p(s) \right]^{[0,\infty]} - \left[ \hat{Q}_p(-s) \right]^{[0,\infty]} \right\}, \] (26)

where superscript \([0, \infty]\) denotes the part that is nonzero only in \([0, \infty]\) region of the \(r\) space, and

\[ \hat{Q}_p(s) = \hat{Q}_0^2(-s) \left[ \hat{p}^{(1)}(s) + 24\eta \hat{p}^{(2)}(s) \right]. \] (27)

In order to invert \(\dot{c}(s)\) to the \(r\)–space, we should ignore all \([0, \infty]\) superscripts in relation \textsuperscript{(26)} and invert it to \(r\)–space. Since we are interested only in \(r > 0\) region, we assume that \(c(r) = 0\) for \(r < 0\). Note, that the contribution from the first term \(\hat{p}^{(1)}(s)\) in Eq. \textsuperscript{(27)} was already considered in Ref.\textsuperscript{18}. Let us examine now the second term of Eq. \textsuperscript{(27)},

\[ \hat{Q}_p^{(2)}(s) = 24\eta \hat{Q}_0^2(-s) \hat{p}^{(2)}(s). \] (28)

Taking into account that \(\hat{Q}_0(s)\) is analytical function in the whole complex plane, we may simplify the expression for \(\hat{p}^{(2)}(s)\) by subtracting some analytical function. Indeed, the subtracted analytical function being multiplied by \(\hat{Q}_0^2(-s)\) will result in a new analytical function, that has no impact on the resulting expressions for \(c_1(r)\) in the \(r\)–space. In such a way we replace the first term \(-C(-s) L(-s) e^{-s(\lambda-2)}/S^3(-s)\) in Eq. \textsuperscript{(25)} by expression

\[ \sum_{i=0}^{2} \left[ \frac{C_3(t_i)}{s+t_i} + \frac{C_2(t_i)}{(s+t_i)^2} + \frac{C_1(t_i)}{(s+t_i)^3} \right] e^{-s(\lambda-2)}, \]

where the coefficients \(C_1(t_i)\), \(C_2(t_i)\) and \(C_3(t_i)\) are found from the equality of residues at all poles \(t_i\) of the expression

\[ \text{Res}_{\{t_i\}} \left[ \left( \frac{C_3(t_i)}{s+t_i} + \frac{C_2(t_i)}{(s+t_i)^2} + \frac{C_1(t_i)}{(s+t_i)^3} \right) e^{-s(\lambda-2)} \right] = \text{Res}_{\{t_i\}} \left[ -\frac{C(-s) L(-s) e^{-s(\lambda-2)}}{S^3(-s)} \right]. \] (29)
The new simplified function $\hat{p}^{(2)}(s)$ reads

$$\hat{p}^{(2)}(s) = \sum_{i=0}^{2} \left( \frac{C_3(t_i)}{s + t_i} + \frac{C_2(t_i)}{(s + t_i)^2} + \frac{C_1(t_i)}{(s + t_i)^3} \right) e^{-s(\lambda-1)}$$

$$+ \frac{1}{2} \sum_{i=0}^{2} \left( \frac{G_2(t_i)}{s + t_i} + \frac{G_1(t_i)}{(s + t_i)^2} + \frac{G_0(t_i)}{(s + t_i)^3} \right) e^{-s}, \quad (30)$$

where

$$C_1(t_i) = \frac{C(t_i) L(t_i)}{S_1^3(t_i)},$$

$$C_2(t_i) = -\frac{\frac{d}{ds} [C(s) L(s)]_{s=t_i}}{S_1^3(t_i)} + \frac{3}{2} \frac{C(t_i) L(t_i) S_2(t_i)}{S_1^4(t_i)},$$

$$C_3(t_i) = \frac{\frac{d^2}{ds^2} [C(s) L(s)]_{s=t_i}}{2S_1^3(t_i)} - \frac{3}{2} \frac{\frac{d}{ds} [C(s) L(s)]_{s=t_i} S_2(t_i)}{S_1^4(t_i)} - \frac{C(t_i) L(t_i) S_3(t_i)}{2S_1^4(t_i)} + \frac{3}{2} \frac{C(t_i) L(t_i) S_2^2(t_i)}{S_1^5(t_i)}.$$

It is easy to find that the functions $G_i(s)$ from Eqs. (21)-(23) can be expressed in terms of $C_i(s)$ in the following way

$$G_0(s) = -2C_1(s) e^{(\lambda-2)s},$$

$$G_1(s) = -2 \left[ C_2(s) - (\lambda - 2) C_1(s) \right] e^{(\lambda-2)s},$$

$$G_2(s) = -2 \left[ C_3(s) - (\lambda - 2) C_2(s) + \frac{(\lambda - 2)^2}{2} C_1(s) \right] e^{(\lambda-2)s}.$$

Then the inverse Laplace transform of Eq. (30) reads

$$p^{(2)}(r) = \frac{1}{2} \sum_{i=0}^{2} \left( G_2(t_i) + (r - 1) G_1(t_i) \right)$$

$$+ \frac{(r-1)^2}{2} G_0(t_i) e^{-t_i(r-1) [H(r-1) - H(r - \lambda + 1)]}, \quad (31)$$

which is nonzero inside $[1, \lambda - 1]$, and $H(r)$ is the Heaviside step function. Substituting (30) and (31) into (28), we obtain

$$\frac{Q_p^{(2)}(s)}{24\eta} = \hat{p}^{(2)}(s) + \sum_{i=1}^{6} \frac{e_{0,i}}{(-s)^i} + \sum_{i=2}^{6} \frac{e_{1,i}}{(-s)^i} e^s + \sum_{i=4}^{6} \frac{e_{2,i}}{(-s)^i} e^{2s}$$

$$+ \sum_{i=0}^{6} \frac{e_{2,i}}{(-s)^i} e^{2s} \sum_{i=0}^{2} \left( \frac{G_2(t_i)}{s + t_i} + \frac{G_1(t_i)}{(s + t_i)^2} + \frac{G_0(t_i)}{(s + t_i)^3} \right) e^{-s}, \quad (32)$$
and

\[
\dot{Q}_p^{(2)} (-s) = \frac{p^{(2)} (-s)}{24 \eta} - \left[ \sum_{i=1}^{6} \frac{e_{0,i}}{s^i} + \sum_{i=2}^{6} \frac{e_{1,i}}{s^i} e^{-s} + \sum_{i=4}^{6} \frac{e_{2,i}}{s^i} e^{-2s} \right] \sum_{i=0}^{2} \left\{ C_3 (t_i) \left( \frac{1}{s-t_i} \right) - C_2 (t_i) + C_1 (t_i) \right\} e^{(\lambda-1)s} - \frac{1}{2} \left[ \sum_{i=1}^{6} \frac{e_{0,i}}{s^i} + \sum_{i=2}^{6} \frac{e_{1,i}}{s^i} e^{-s} \right] + \frac{6}{s^2} e^{-2s} \sum_{i=0}^{2} \left\{ C_2 (t_i) \left( \frac{1}{s-t_i} \right) - C_1 (t_i) \right\} e^{s},
\]

where the coefficients \( e_{n,i} \) of the expansion of the Baxter function \( \hat{Q}_0^{(2)} (s) \) are given in the Appendix.

In order to obtain the DCF in \( r \)–space we will use the method that is similar to that outlined in Ref.\(^\text{18}\). Namely, from Eqs. (32) and (33) it is evident, that the key expressions to be inverted are the functions of following form

\[
\hat{w} (s, z, n, m) = \frac{1}{s^n (s+z)^m} \left\{ \sum_{k=1}^{n} a_{k}^{nm} \frac{1}{s^k} + \sum_{k=1}^{m} b_{k}^{nm} \frac{1}{(s+z)^k}, \ z \neq 0, \right\}
\]

with coefficients

\[
a_{k}^{nm} = (-1)^{n-m} \frac{(m+n-k-1)!}{(n-k)! (m-1)! z^{m+n-k}},
\]

\[
b_{k}^{nm} = (-1)^{n} \frac{(m+n-k-1)!}{(m-k)! (n-1)! z^{m+n-k}}.
\]

The inverse Laplace transform of these functions reads

\[
\hat{w} (r, z, n, m) = \left\{ \sum_{k=1}^{n} a_{k}^{nm} \frac{1}{r^{k-1}} + \sum_{k=1}^{m} b_{k}^{nm} \frac{1}{(m+n-k)!} e^{-zr} \right\} H (r), \ z \neq 0,
\]

\[
\hat{w} (r, z, n, m) = \left\{ \sum_{k=1}^{n} a_{k}^{nm} \frac{1}{r^{k-1}} + \sum_{k=1}^{m} b_{k}^{nm} \frac{1}{(m+n-k)!} e^{-zr} \right\} H (r), \ z = 0,
\]

where \( H (r) \) is the Heaviside step function. With this in hands, we may now write down in terms of \( \hat{w} (r, z, n, m) \) the expressions for the inverse Laplace transforms of Eqs. (32) and
for \( r \geq 0 \),

\[
\frac{Q_p^{(2)}(r)}{24 \eta} = p^{(2)}(r) + \sum_{i=1}^{6} \sum_{j=0}^{2} \frac{e_{0,i}}{(-1)^i} \left[ C_3(t_j) w(r - \lambda + 1, t_j, i, 1) + C_2(t_j) w(r - \lambda + 1, t_j, i, 2) + C_1(t_j) w(r - \lambda + 1, t_j, i, 3) \right] H(r - \lambda + 1)
\]

\[
+ \sum_{i=2}^{6} \sum_{j=0}^{2} \frac{e_{1,i}}{(-1)^i} \left[ C_3(t_j) w(r - \lambda + 2, t_j, i, 1) + C_2(t_j) w(r - \lambda + 2, t_j, i, 2) + C_1(t_j) w(r - \lambda + 2, t_j, i, 3) \right] H(r - \lambda + 2)
\]

\[
+ \sum_{i=4}^{6} \sum_{j=0}^{2} \frac{e_{2,i}}{(-1)^i} \left[ C_3(t_j) w(r - \lambda + 3, t_j, i, 1) + C_2(t_j) w(r - \lambda + 3, t_j, i, 2) + C_1(t_j) w(r - \lambda + 3, t_j, i, 3) \right] H(r - \lambda + 3)
\]

\[
+ \frac{1}{2} \sum_{i=1}^{6} \sum_{j=0}^{2} \frac{e_{0,i}}{(-1)^i} \left[ G_2(t_j) w(r - 1, t_j, i, 1) + G_1(t_j) w(r - 1, t_j, i, 2) + G_0(t_j) w(r - 1, t_j, i, 3) \right] H(r - 1)
\]

\[
+ \frac{1}{2} \sum_{i=2}^{6} \sum_{j=0}^{2} \frac{e_{1,i}}{(-1)^i} \left[ G_2(t_j) w(r, t_j, i, 1) + G_1(t_j) w(r, t_j, i, 2) + G_0(t_j) w(r, t_j, i, 3) \right] H(r)
\]

\[
+ \frac{1}{2} \sum_{i=4}^{6} \sum_{j=0}^{2} \frac{e_{2,i}}{(-1)^i} \left[ G_2(t_j) w(r + 1, t_j, i, 1) + G_1(t_j) w(r + 1, t_j, i, 2) + G_0(t_j) w(r + 1, t_j, i, 3) \right] H(r + 1),
\]
\[
\frac{Q_p^{(2)}(-r)}{24\eta} = p^{(2)}(-r) - \sum_{i=1}^{6} \sum_{j=0}^{2} e_{0,i} \left[ C_3(t_j) w(r + \lambda - 1, -t_j, i, 1) - C_2(t_j) w(r + \lambda - 1, -t_j, i, 2) + C_1(t_j) w(r + \lambda - 1, -t_j, i, 3) \right] H(r + \lambda - 1)
\]
\[
- \sum_{i=2}^{6} \sum_{j=0}^{2} e_{1,i} \left[ C_3(t_j) w(r - \lambda - 1, -t_j, i, 1) - C_2(t_j) w(r - \lambda - 2, -t_j, i, 2) + C_1(t_j) w(r - \lambda - 2, -t_j, i, 3) \right] H(r + \lambda - 2)
\]
\[
- \sum_{i=4}^{6} \sum_{j=0}^{2} e_{2,i} \left[ C_3(t_j) w(r - \lambda - 3, -t_j, i, 1) - C_2(t_j) w(r - \lambda - 3, -t_j, i, 2) + C_1(t_j) w(r - \lambda - 3, -t_j, i, 3) \right] H(r + \lambda - 3)
\]
\[
- \frac{1}{2} \sum_{i=1}^{6} \sum_{j=0}^{2} e_{0,i} \left[ G_2(t_j) w(r + 1, -t_j, i, 1) - G_1(t_j) w(r + 1, -t_j, i, 2) + G_0(t_j) w(r + 1, -t_j, i, 3) \right] H(r + 1)
\]
\[
- \frac{1}{2} \sum_{i=2}^{6} \sum_{j=0}^{2} e_{1,i} \left[ G_2(t_j) w(r, -t_j, i, 1) - G_1(t_j) w(r, -t_j, i, 2) + G_0(t_j) w(r, -t_j, i, 3) \right] H(r)
\]
\[
- \frac{1}{2} \sum_{i=4}^{6} \sum_{j=0}^{2} e_{2,i} \left[ G_2(t_j) w(r - 1, -t_j, i, 1) - G_1(t_j) w(r - 1, -t_j, i, 2) + G_0(t_j) w(r - 1, -t_j, i, 3) \right] H(r - 1) .
\]

The above expressions are then substituted into inverse of Eq. (27),

\[
Q_p(r) = Q_p^{(1)}(r) + Q_p^{(2)}(r),
\]

where \(Q_p^{(1)}(r)\) is the inverse Laplace transform of the function \(\hat{Q}_p^{(1)}(s) = 24\eta\hat{Q}_0^{(2)}(-s)\hat{p}^{(1)}(s)\) and describes the contribution of the first term of the expansion (17); the expression for this contribution was given in Ref.\(^{18}\). Then the first-order perturbation contribution to the DCF of the SW model fluid with the radius of interaction that exceeds two particle diameters reads,

\[
rc_1(r) = \beta \varepsilon (1 - \eta)^4 [Q_p(r) - Q_p(-r)].
\]

The equations (38) and (39) have been presented here in a similar manner as it has been done in the work of Tang and Lu\(^{18}\) for the case of the SW model fluid with the range of interaction that does not exceed two particle diameters, i.e. for \(\lambda \leq 2\). The resulting expression for
$c_1 (r)$ in the case of $\lambda > 2$ is consequently rather long, but also quite straightforward. It may be summarized as follows,

$$rc_1 (r) = \begin{cases} 
0, & r > \lambda, \\
\beta \varepsilon r, & 1 < r \leq \lambda, \\
\beta \varepsilon (1 - \eta)^4 [Q_p (r) - Q_p (-r)], & r \leq 1,
\end{cases} \quad (41)$$

where $Q_p (r)$ is given by Eq. (40). The direct correlation function is discontinuous at $r = 1$ and $r = \lambda$. The continuity of the DCF inside the core, $r \in [0, 1]$, is evident from Eqs. (32) and (33), where the terms, that might contribute to the discontinuities at $r = \lambda - 2$ and $r = 3 - \lambda$, are at least of the second order in $1/s$.

III. RESULTS AND DISCUSSIONS

To examine the evolution experienced by the DCF of the SW fluid upon increase of the attractive well width, in Fig. 1 we show the first-order DCF $c_1 (r)$ evaluated for nine different values of width parameter $\lambda$ in the range from $\lambda = 1.5$ to $\lambda = 3.0$. All calculations are performed for fixed density $\rho = 0.75$ and temperature $\beta \varepsilon = 0.5$. Note, that the dependence of $c_1 (r)$ on the attractive well width $\lambda$ in the core region $r < 1$ is not trivial.

It is very well illustrated by the behavior of the value of $c_1 (r = 0)$. One can see that value of $c_1 (r = 0)$ is first decreasing upon $\lambda$ increases from $\lambda = 1.5$ to $\lambda \approx 1.7$ and after this starts to grow with $\lambda$ increases. However, after reaching the value of $\lambda \approx 2.2$, $c_1 (r = 0)$ starts to drop till the value of $\lambda \approx 2.6$ after which it begins to grow again.

In Figures 2 and 3 we show the total DCF $c (r)$ and total radial distribution function (RDF) $g (r) = h_1 (r) + 1$ of the SW fluid with attractive well width $\lambda = 2.1$ and 2.5 at the density $\rho = 0.75$. Both functions are obtained within the FMSA and from Monte-Carlo simulations. The FMSA results for the first-order correction term $h_1 (r)$ to the RDF were obtained numerically. The correspondin DCF and RDF of the hard-sphere reference system, $c_0 (r)$ and $g_0 (r)$, respectively, were obtained from the first-order GMSA theory of Tang and Lu. The results for the intermediate and low densities are not shown, since at such conditions the considered SW fluid seems to be unstable. Good agreement between Monte Carlo simulation data and FMSA theory results could be observed for the SW fluid with $\lambda = 2.5$ (see Fig. 2). The same doesn’t hold for the SW fluid with $\lambda = 2.1$. The
discrepancies between FMSA and simulation predictions are clearly visible for both DCF and RDF at the particle contact $r = 1$ and at the point of discontinuity at $r = \lambda = 2.1$. These shortcomings in the case of RDF can be corrected by employing exponential (EXP)\(^{23}\)

$$g^{EXP}(r) = g_0(r) e^{h_1(r)}$$

or linearized exponential (LEXP)\(^{24}\)

$$g^{LEXP}(r) = g_0(r) (1 + h_1(r))$$

approximations. Indeed, the LEXP approximation significantly improves the RDF of the SW fluid, giving better contact value at $r = 1$ and improving RDF values on both sides of the discontinuity at $r = \lambda = 2.1$ (see Fig. 3, right panel).

In Fig. 4 we present the inverse reduced isothermal compressibilities of the SW fluids that was obtained from

$$\frac{1}{\chi_T} = \beta \left( \frac{\partial P}{\partial \rho} \right)_T = 1 - 4 \pi \rho \int c(r) r^2 dr,$$ \hspace{1cm} (44)

The DCFs of the reference system of hard spheres were obtained from the first-order GMSA theory of Tang and Lu\(^{20}\). From Fig. 4 we note that at the high densities ($\eta \approx 0.5$) the compressibility of the SW fluid with $\lambda = 2.5$ increases rapidly and almost reaches the level of the fluid $\lambda = 2.0$. Mathematically, this can be explained by positive contribution into compressibility of the first-order DCF in the $r < 1$ region, which compensates the negative contribution due to the potential well.

On Fig. 5 we present spinodal curves and critical points for few long-range SW fluids obtained from condition $\left( \frac{\partial P}{\partial \rho} \right)_T = 0$ and (44).

IV. CONCLUSIONS

We extended the FMSA theory to deal with the square-well fluids of large wells width ($1 < \lambda < 3$) than those studied previously and obtained analytical expressions for the DCF. We obtained reasonable agreement of the DCF and RDFs with MC simulation data and proposed exponential (EXP) and linearized exponential (LEXP) approximations to correct RDF values close to the contact.
Acknowledgments

AT thanks MCSU for the hospitality while visiting the Department for the Modelling of Physico-Chemical Processes when this project has been initiated.

APPENDIX A: EXPANSIONS OF THE LAPLACE TRANSFORM OF THE BAXTER FACTORIZATION FUNCTION

Laplace transforms of the Baxter hard-sphere factorization function and square of the transform are

\[ \hat{Q}_0(s) = 1 + \sum_{i=1}^{3} \frac{a_i}{s_i} + \sum_{i=2}^{3} \frac{b_i}{s_i} e^{-s}, \quad (A1) \]

and

\[ \hat{Q}_0^2(s) = 1 + \sum_{i=1}^{6} \frac{e_{0,i}}{s^i} + \sum_{i=2}^{6} \frac{e_{1,i}}{s^i} e^{-s} + \sum_{i=4}^{6} \frac{e_{2,i}}{s^i} e^{-2s}, \quad (A2) \]

where

\[ b_2 = \frac{12\eta \left(1 + \frac{\eta}{2}\right)}{(1 - \eta)^2}, \quad b_3 = \frac{12\eta (1 + 2\eta)}{(1 - \eta)^2}, \]

\[ a_1 = b_2 - \frac{b_3}{2}, \quad a_2 = b_3 - b_2, \quad a_3 = -b_3, \quad (A3) \]

and

\[ e_{0,1} = 2a_1, \quad e_{0,2} = a_1^2 + 2a_2, \quad e_{0,3} = 2a_3 + 2a_1a_2, \]

\[ e_{0,4} = 2a_1a_3 + a_2^2, \quad e_{0,5} = 2a_2a_3, \quad e_{0,6} = a_3^2, \]

\[ e_{1,2} = 2b_2, \quad e_{1,3} = 2b_3 + 2a_1b_2, \quad e_{1,4} = 2a_1b_3 + 2a_2b_2, \]

\[ e_{1,5} = 2a_2b_3 + 2a_3b_2, \quad e_{1,6} = 2a_3b_3, \]

\[ e_{2,4} = b_2^2, \quad e_{2,5} = 2b_2b_3, \quad e_{2,6} = b_3^2. \]

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FIGURE CAPTIONS

Fig. 1 First-order DCF for several $\lambda$ values with $\varepsilon \beta = 0.5$ and $\rho = 0.75$.

Fig. 2 Full DCF (left panel) and full RDF (right panel) for SW fluid with $\lambda = 2.5$, $\varepsilon \beta = 0.5$ and $\rho = 0.75$. Lines denote FMSA results, symbols denote simulation results.

Fig. 3 Full DCF (left panel) and full RDF (right panel) for SW fluid with $\lambda = 2.1$, $\varepsilon \beta = 0.5$ and $\rho = 0.75$. Lines denote FMSA results, symbols denote simulation results. Dotted line denotes linearized exponential approximation (LEXP).

Fig. 4 Inverse reduced isothermal compressibility $\chi_T^{-1} = \beta \left( \frac{\partial P}{\partial \rho} \right)_T$ of the SW fluids at $\varepsilon \beta = 0.5$ and $\varepsilon \beta = 0.25$.

Fig. 5 Spinodal curves for SW fluids with $\lambda = 2.0, 2.2, 2.4, 2.5, 2.6, 2.8, 3.0$. 
$$\lambda = 3.0$$

$$\lambda = 2.8$$

$$\lambda = 2.6$$

$$\lambda = 2.4$$

$$\lambda = 2.2$$

$$\lambda = 2.0$$

$$\lambda = 1.7$$

$$\lambda = 1.5$$

FIG. 1:

FIG. 2:
FIG. 3:
FIG. 4:

\[ \beta \left( \frac{\partial P}{\partial \rho} \right)_T \]

\( \beta \epsilon = 0.25 \)

\( \lambda = 2.0 \quad \lambda = 2.1 \quad \lambda = 2.2 \quad \lambda = 2.3 \quad \lambda = 2.4 \quad \lambda = 2.5 \)

\[ \rho^* \]

\( \beta \epsilon = 0.5 \)

\( \lambda = 2.0 \quad \lambda = 2.1 \quad \lambda = 2.2 \quad \lambda = 2.3 \quad \lambda = 2.4 \quad \lambda = 2.5 \)
FIG. 5: