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PHYSICS

Improved first order mean-spherical approximation for simple fluids

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A perturbation approach based on the first-order mean-spherical approximation (FMSA) is proposed. It consists in adopting a hard-sphere plus short-range attractive Yukawa fluid as the novel reference system, over which the perturbative solution of the Ornstein-Zernike equation is performed. A choice of the optimal range of the reference attraction is discussed. The results are compared against conventional FMSA/HS theory and Monte-Carlo simulation data for compressibility factor and vapor-liquid phase diagrams of the medium-ranged Yukawa fluid. The proposed theory keeps the same level of simplicity and transparency as the conventional FMSA/HS approach does, but turns out to be more accurate.

Key words: *hard-core Yukawa fluid, mean-spherical approximation, perturbation theory, Monte Carlo simulations*

PACS: *01.65.Q*

1. Introduction

The most common and universal method in theories of fluids is the perturbation approach. Nonetheless, without analytic results of the integral equation theory for simple systems the perturbation expansion could not be accomplished. To be specific, the analytic results of the mean-spherical approximation (MSA) for the fluid of hard spheres (for which the MSA is identical to the Percus-Yevick theory) [1, 2] and the Yukawa fluid [3, 4] are used to describe the properties of the reference system. In addition to these conventional MSA results there is also a perturbed version of the MSA called the first-order mean-spherical approximation (FMSA) [5].

When compared to computer simulation data for the Yukawa fluid model, the FMSA theory has been shown to be reasonably good but still less accurate than the common MSA [6]. However, an advantage of the FMSA theory, hereinafter referred to as FMSA/HS since it employs the hard sphere (HS) fluid for the reference, is its simplicity and transparency. These are the factors causing its increasing attractiveness and potential applicability in the liquid state theory and also, in general, in the soft condensed matter theory. The most important ideas of the FMSA/HS theory are outlined in the following section.

The goal of this paper is to present a modification of the FMSA/HS theory. The modification pursues the idea that there is an alternative to the HS reference, namely a mean field theory based on a Yukawa fluid reference [7]. In section 3 the possible choices in this direction are considered. The results and discussions are the subject of section 4. The study is summarized in section 5.

2. Conventional FMSA/HS theory

The FMSA/HS is a theory based on the solution of the Ornstein-Zernike (OZ) equation,

$$\tilde{h}(k) = \tilde{c}(k) + \rho \tilde{h}(k) \tilde{c}(k) \tag{1}$$

by employing the perturbation expansions limited to the first order correction term,

$$
\begin{aligned}
\tilde{h}(k) &= \tilde{h}_{\mathrm{o}}(k) + \Delta\tilde{h}(k), \\
\tilde{c}(k) &= \tilde{c}_{\mathrm{o}}(k) + \Delta\tilde{c}(k), \\
\hat{Q}(k) &= \hat{Q}_{\mathrm{o}}(k) + \Delta\hat{Q}(k),
\end{aligned}
\tag{2}
$$

for the total, h, and direct, c, correlation functions combined with Baxter factorization function, Q, respectively. Here and in what follows all symbols with the tilde will denote the three-dimensional Fourier transforms, while all symbols with the hats will denote the one-dimensional Fourier transforms or the Laplace transforms. The terms with subscript "o" denote the contribution of a reference system, and Δh, Δc, ΔQ are the respective corrections.

The FMSA/HS theory has been developed by Tang and Lu [5, 8, 9] for the hard-core based fluid models

$$
u(r) = \begin{cases} \infty, & r < \sigma, \\ \phi(r), & r \geqslant \sigma, \end{cases}
\tag{3}
$$

with σ being the diameter of a hard core and $\phi(r)$ being the potential function for out-of-core pair interaction between molecules. In their studies Tang and Lu were considering the fluid of hard spheres (HS) as the reference (or unperturbed) system for which all three functions that enter expansions (2) are well known. In particular, for the total correlation function of the HS reference system, $h_{\mathrm{o}} \equiv h_{\mathrm{HS}}$, Tang and Lu used the expression

$$
\hat{g}_{\mathrm{o}}(s) \equiv \hat{g}_{\mathrm{HS}}(s) = \frac{L(s\sigma)\,\mathrm{e}^{-s\sigma}}{(1-\eta)^2\,\hat{Q}_{\mathrm{HS}}(s\sigma)\,s^2},
\tag{4}
$$

that is the Laplace transform of the radial distribution function $g_{\mathrm{HS}}(r) = h_{\mathrm{HS}}(r) + 1$ resulting from the solution of the OZ equation for HS fluid in the Percus-Yevick approximation [1]. The function $\hat{Q}_{\mathrm{HS}}(t)$ refers to the Laplace transform of the Baxter factorization function of the HS fluid,

$$
\hat{Q}_{\mathrm{o}}(t) \equiv \hat{Q}_{\mathrm{HS}}(t) = \frac{S(t) + 12\eta L(t)\,\mathrm{e}^{-t}}{(1-\eta)^2\,t^3},
\tag{5}
$$

where

$$
\begin{aligned}
S(t) &= (1-\eta)^2\,t^3 + 6\eta(1-\eta)\,t^2 + 18\eta^2 t - 12\eta(1+2\eta), \tag{6} \\
L(t) &= \left(1 + \frac{\eta}{2}\right)t + 1 + 2\eta \tag{7}
\end{aligned}
$$

and $\eta = \pi\rho\sigma^3/6$ is the packing fraction.

The main result obtained by Tang and Lu concerns an expression for correction Δh to the total correlation function (or radial distribution function) resulting from the out-of-core attraction $\phi(r)$. It reads [5]

$$
\Delta\hat{h}(k) = \frac{P(\mathrm{i}k\sigma)}{\hat{Q}_{\mathrm{HS}}^2(\mathrm{i}k\sigma)},
\tag{8}
$$

where

$$
P(\mathrm{i}k\sigma) = \frac{\Delta U(k)}{2\hat{Q}_{\mathrm{HS}}^2(-\mathrm{i}k\sigma)} - \frac{\mathrm{e}^{-\mathrm{i}k\sigma}}{2\mathrm{i}\pi} \int_{-\infty}^{\infty} \frac{\Delta U(y)\,\mathrm{e}^{\mathrm{i}y\sigma}}{(y-k)\,\hat{Q}_{\mathrm{HS}}^2(-\mathrm{i}y\sigma)}\mathrm{d}y,
\tag{9}
$$

with function $\Delta U(k)$ defined as

$$
\Delta U(k) = \int_{\sigma}^{\infty} r\Delta c(r)\,\mathrm{e}^{-\mathrm{i}kr}\mathrm{d}r.
\tag{10}
$$

In accordance with this approach the necessary closure to be used in equation (10) reads as

$$
\Delta c^{\mathrm{FMSA/HS}}(r) = -\beta\phi(r), \qquad \text{for} \qquad r \geqslant \sigma,
\tag{11}
$$

with $\beta = 1/k_{\mathrm{B}}T$ and T being the temperature.

In general, without any relation to the above version of the FMSA theory, a key point of its application to particular fluid model [determined by the out-of-core interaction potential $\phi(r)$] concerns an evaluation of the integral in equation (9). So far, within the framework of the FMSA/HS theory this has been done for the Yukawa, Lennard-Jones, Kihara and sticky fluids by Tang and Lu [8] and for the square-well fluids by Tang and Lu [9] and by Hlushak et al. [10]. In the particular case of the Yukawa (Y) fluid model,

$$\phi_{\mathrm{Y}}\left(r\right) = -\epsilon\sigma\frac{\mathrm{e}^{-z(r-\sigma)}}{r}\,, \tag{12}$$

for which the function $\Delta U\left(k\right) \sim \mathrm{e}^{-\mathrm{i}k\sigma}$, an integration contour in the right-hand side of equation (9) can be closed in the upper complex half-plane and evaluation of the integral is rather simple and does not require the calculation of the residues at zeroes of the function $\hat{Q}_{\mathrm{HS}}\left(-\mathrm{i}k\sigma\right)$. Then, the Laplace transform of the correction term (8) for the total correlation function of the Yukawa fluid within the FMSA/HS theory reads

$$\Delta\hat{h}^{\mathrm{FMSA/HS}}\left(s\right) = \frac{\beta\epsilon\sigma\mathrm{e}^{-s\sigma}}{\left(s+z\right)\hat{Q}_{\mathrm{HS}}^{2}\left(s\sigma\right)\hat{Q}_{\mathrm{HS}}^{2}\left(z\sigma\right)}\,. \tag{13}$$

Once the radial distribution function $\hat{g} = \hat{g}_{\mathrm{o}} + \Delta\hat{h}$ is known, the thermodynamics of the system can be calculated.

3. FMSA theory based on Yukawa reference system

The first order mean-spherical approximation theory that we are dealing with is a kind of perturbation theory approach. Usually, within the perturbation theory, in order to improve the performance of the first order approximation one should calculate the second order correction term. As an alternative to this common way here we propose to qualitatively modify the reference system over which the perturbation is calculated, and as a result to continue working within the same first order approximation. This is of particular importance since our aim is to keep the simplicity and transparency of the improved FMSA theory at the level established by the conventional FMSA/HS approach.

3.1. Division of the potential

Similar to the classical perturbation theory approach we proceed by dividing the initial interaction potential $u(r)$ into two parts

$$u\left(r\right) = u_{\mathrm{o}}\left(r\right) + \Delta u\left(r\right), \tag{14}$$

that are the reference and residual contributions, respectively. However, for the reference system potential $u_{\mathrm{o}}\left(r\right)$ we will require that besides the hard-core repulsion it should (i) include a piece of the attractive tail of the same strength ϵ as the total potential, and (ii) extend over the range that is somewhat shorter than the range of the total interaction. The function that allows us to satisfy and control these requirements in an easy and a natural way is the Yukawa (Y0) potential. Thus, we may define the desired reference fluid as follows:

$$u_{\mathrm{o}}\left(r\right) \equiv u_{\mathrm{Y0}}(r) = \left\{ \begin{array}{ll} \infty, & r < \sigma, \\ -\varepsilon\sigma\mathrm{e}^{-z_{\mathrm{o}}(r-\sigma)}/r, & r \geqslant \sigma. \end{array} \right. \tag{15}$$

The improved FMSA closure, referred to as FMSA/Y0, reads as follows:

$$\Delta c^{\mathrm{FMSA/Y0}}\left(r\right) = -\beta\phi\left(r\right) - \beta\epsilon\sigma\mathrm{e}^{-z_{\mathrm{o}}(r-\sigma)}/r, \qquad \text{for} \qquad r \geqslant \sigma\,, \tag{16}$$

where z_{o} is the so far undefined parameter.

3.2. Yukawa reference system

We note here that some authors have already suggested to utilize the non-HS reference system in liquid state theory (e.g., see [11, 12]). Moreover, the short-range attractive Yukawa fluid has been already considered as an alternative to the HS reference system by Melnyk et al. [7, 13–16] in their studies within the framework of an augmented van der Waals theory for simple fluids.

It is very important that, like in the case of the HS reference potential, all properties for the Yukawa reference potential (15), including the Baxter function $Q_\mathrm{o} \equiv Q_\mathrm{Y0}$, are available in the literature. They can be obtained either within the MSA theory for Yukawa fluid [e.g., see Blum and Hoye [4], Kalyuzhnyi et al. [17, 18]] or within the conventional FMSA/HS theory due to Tang and Lu as it is described in previous section 2. The MSA theory is more accurate than FMSA/HS theory, but the latter is simpler. For the purpose of the present study we decided to sacrifice the accuracy in order to maintain simplicity and transparency. Thus, in what follows the FMSA/HS theory will be employed to describe properties of the Y0 reference system. And, as we will see hereinafter, despite a less accurate description of the reference system, the FMSA/Y0 theory still shows a notable improvement against the FMSA/HS theory.

Following the conventional FMSA/HS approach, the Laplace transform of the radial distribution function of the Y0 reference system reads

$$\hat{g}_\mathrm{o}\left(s\right) \equiv \hat{g}_\mathrm{Y0}\left(s; z_\mathrm{o}\right) = \hat{g}_\mathrm{HS}\left(s\right) + \frac{\beta\epsilon\sigma\mathrm{e}^{-s\sigma}}{\left(s + z_\mathrm{o}\right)\hat{Q}_\mathrm{HS}^2\left(s\sigma\right)\hat{Q}_\mathrm{HS}^2\left(z_\mathrm{o}\sigma\right)}, \tag{17}$$

where the first term corresponds to the contribution of a hard-sphere repulsion, while the second one is the contribution due to the short-range attraction attributed to the Y0 reference system in accordance with equation (15). Similarly, the FMSA/HS result for the Baxter factorization function of the Y0 reference is

$$\hat{Q}_\mathrm{o}\left(t\right) \equiv \hat{Q}_\mathrm{Y0}\left(t; z_\mathrm{o}\sigma\right) = \hat{Q}_\mathrm{HS}\left(t\right) + 12\beta\varepsilon\eta\frac{z_\mathrm{o}\sigma\hat{Q}_\mathrm{HS}\left(-t\right)\mathrm{e}^{-t} - \left(t + z_\mathrm{o}\sigma\right)\hat{Q}_\mathrm{HS}\left(t\right)}{tz_\mathrm{o}\sigma\left(t + z_\mathrm{o}\sigma\right)\hat{Q}_\mathrm{HS}^2\left(z_\mathrm{o}\sigma\right)}. \tag{18}$$

3.3. Full system within the FMSA/Y0 theory

After all properties of interest for the Y0 reference fluid are specified, we turn to the entire system determined by the interaction potential $u(r)$ or more precisely by the out-of-core potential function $\phi(r)$. Although this function can be substituted by any potential function used in literature to represent the simple fluids [e.g., Lennard-Jones, Sutherland, Yukawa or Kihara potentials, etc.] for the purpose of present study we proceed with the Yukawa (Y) fluid model already defined according to equation (12).

By introducing Yukawa potential $\phi_\mathrm{Y}(r)$ into the FMSA/Y0 closure (16) we note that for both functions that enter $\Delta c^\mathrm{FMSA/Y0}(r)$, the function $\Delta U\left(k\right)$ is proportional to $\mathrm{e}^{-\mathrm{i}k\sigma}$ and the integral in equation (9) can be easily evaluated in the way it was already discussed in Introduction section. Then, the correction term $\Delta\hat{h}^\mathrm{FMSA/Y0}$ that is necessary to evaluate the radial distribution function of the full system,

$$\hat{g}\left(s; z_\mathrm{o}, z\right) = \hat{g}_\mathrm{o}\left(s; z_\mathrm{o}\right) + \Delta\hat{h}\left(s; z_\mathrm{o}, z\right), \tag{19}$$

is given by

$$\begin{aligned}
\Delta\hat{h}^\mathrm{FMSA/Y0}\left(s; z_\mathrm{o}, z\right) &= -\frac{\beta\epsilon\sigma\mathrm{e}^{-s\sigma}}{\left(s + z_\mathrm{o}\right)\hat{Q}_\mathrm{Y0}^2\left(s\sigma; z_\mathrm{o}\sigma\right)\hat{Q}_\mathrm{Y0}^2\left(z_\mathrm{o}\sigma; z_\mathrm{o}\sigma\right)} \\
&\quad + \frac{\beta\epsilon\sigma\mathrm{e}^{-s\sigma}}{\left(s + z\right)\hat{Q}_\mathrm{Y0}^2\left(s\sigma; z_\mathrm{o}\sigma\right)\hat{Q}_\mathrm{Y0}^2\left(z\sigma; z_\mathrm{o}\sigma\right)}.
\end{aligned} \tag{20}$$

The calculations of thermodynamics within the FMSA/Y0 approach can be made through the energy route, i.e., in the way that is quite similar to how it was done by Tang et al. within the

conventional FMSA/HS theory [6]. It consists in evaluating the internal energy using its definition through the radial distribution function,

$$\frac{U}{NkT} = 2\pi\rho\beta \int\limits_0^\infty \mathrm{d}r r^2 g\left(r; z_{\mathrm{o}}, z\right) u\left(r\right) = 12\eta\beta\varepsilon\sigma\mathrm{e}^{z\sigma}\hat{g}\left(z; z_{\mathrm{o}}, z\right). \tag{21}$$

This result is used to derive the Helmholtz free energy in the form

$$\frac{A - A_{\mathrm{id}}}{NkT} = a_0 + a_1 + a_2\,, \tag{22}$$

where

$$a_0 = \frac{4\eta - 3\eta^2}{\left(1 - \eta\right)^2}\,, \tag{23}$$

$$a_1 = -12\eta\frac{\beta\varepsilon L\left(z\sigma\right)}{\left(1 - \eta\right)^2 \hat{Q}_{\mathrm{HS}}\left(z\sigma\right)\left(z\sigma\right)^2}\,, \tag{24}$$

$$a_2 = -6\eta\beta^2\varepsilon^2 \left[\frac{1}{\left(z\sigma + z_{\mathrm{o}}\sigma\right)\hat{Q}_{\mathrm{HS}}^2\left(z\sigma\right)\hat{Q}_{\mathrm{HS}}^2\left(z_{\mathrm{o}}\sigma\right)}\right.$$
$$\left. - \frac{1}{\left(z\sigma + z_{\mathrm{o}}\sigma\right)\hat{Q}_{\mathrm{Y0}}^2\left(z\sigma; z_{\mathrm{o}}\sigma\right)\hat{Q}_{\mathrm{Y0}}^2\left(z_{\mathrm{o}}\sigma; z_{\mathrm{o}}\sigma\right)} + \frac{1}{2z\sigma\hat{Q}_{\mathrm{Y0}}^2\left(z\sigma; z_{\mathrm{o}}\sigma\right)\hat{Q}_{\mathrm{Y0}}^2\left(z\sigma; z_{\mathrm{o}}\sigma\right)}\right]. \tag{25}$$

In the limit $z_{\mathrm{o}} = z$ the above formulas reduce to the conventional FMSA/HS theory by Tang and Lu [6]. The chemical potential and pressure are obtained employing standard thermodynamic relations.

4. Results and discussions

4.1. How much of the attraction should be treated as the reference?

The above outlined FMSA/Y0 theory contains the parameter z_{o} that determines the range of reference attraction and needs to be specified. The most straightforward approach to proceed deals with the minimization of the free energy (22) of the Yukawa system over the range of possible values of z_{o}. Noting that z_{o} enters only a_2 contribution, we deduce that the outcome of the minimization, i.e., $z_{\mathrm{o,min}}$, depends only on the density of the fluid but not on the temperature. The corresponding density dependence of $z_{\mathrm{o,min}}$ for several Yukawa fluids is presented in figure 1. It is evident that in the limit of a vanishing density and for all systems considered, the parameter $z_{\mathrm{o,min}}$ tends to the value of $2z$.

This rather remarkable result for choosing the Y0 reference system in such a strict form is quite probably limited to the FMSA theory only. Nevertheless, it is quite consistent with our earlier findings for the Y0 reference decay parameter within the framework of the Yukawa based van der Waals theory for the simple fluids [7, 13–16]. First of all, there is a requirement for
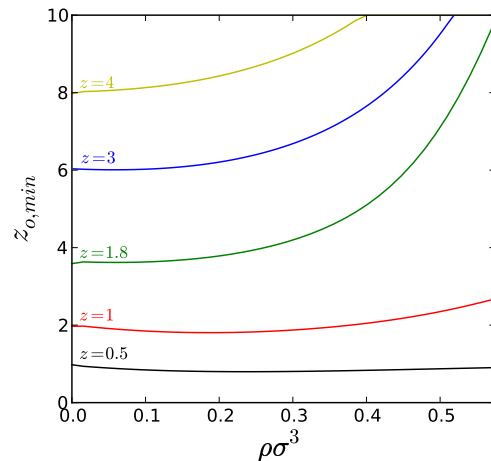

Figure 1. Density dependence of the Y0 reference decay parameter $z_{\mathrm{o,min}}$ that minimizes the free energy for Yukawa fluid models with different value of the decay exponent z as it is specified for each curve. One can see that at low density $z_{\mathrm{o,min}} \to 2z$.

$z_{o,min}$ to be larger than z providing in this way the range of the reference attraction which will be shorter than that in the parent fluid. Secondly, it is obvious that the reference fluid should be in a one-phase region for the set of density and temperature parameters used in the studies of the parent fluid. In the case of a hard sphere reference, this requirement is satisfied since HS fluid does not exhibit the liquid/vapor transition. By adding an attraction one provides the possibility for the phase coexistence. However, the critical temperature is always getting lower if the range of attraction is shorter. In [14] we presented a collection of the Monte Carlo generated liquid/vapor envelopes for Yukawa fluid with different values of the decay parameter (see figure 1 in [14]) from which it follows that the values $3 < z_o\sigma < 6$ can be used as a reference decay for the Lennard-Jones-like Yukawa fluid ($z\sigma = 1.8$) since the critical point temperature in such a reference fluid will always be lower than the triple point temperature in parent fluid.

On the other hand, analyzing the dependence of the critical point coordinates of the Lennard-Jones-like Yukawa fluid ($z\sigma = 1.8$) on the reference system decay parameter z_o, in [13] we have shown that the best agreement with computer simulation data can be reached if $3 < z_o\sigma < 4$. Thus, the result $z_o = 2z$ agrees with these findings and in all our subsequent calculations for the Lennard-Jones-like Yukawa fluid we impose $z_o\sigma = 3.6$, making it independent of the fluid density.

4.2. Comparison between FMSA/HS and FMSA/Y0 solutions

To illustrate the improvements that the FMSA/Y0 theory yields over the conventional FMSA/HS theory, we compare the predictions made up by these two theoretical approaches for compressibility factor and vapor/liquid phase diagram of the most popular Yukawa fluid model defined by the decay parameter $z\sigma = 1.8$.
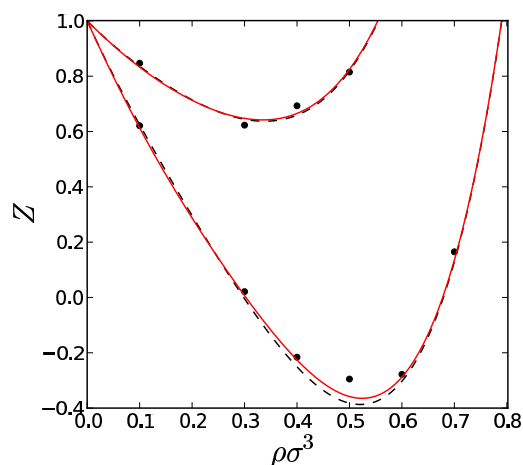

Figure 2. Isotherms $T^* = 1.5$ and $T^* = 1$ (from the top to the bottom) for compressibility factor, $Z = PV/NkT$, of the Yukawa fluid with $z\sigma = 1.8$ as obtained from the conventional FMSA/HS theory (black dashed lines) and from the improved FMSA/Y0 theory with $z_o\sigma = 3.6$ (red solid lines). The symbols denote computer simulation data by Schukla [19].
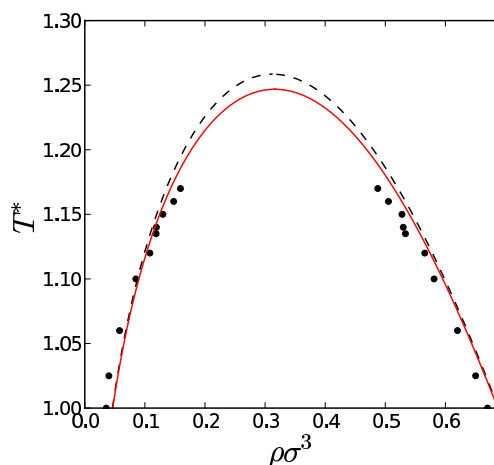
Figure 3. Vapor-liquid phase diagram of the Yukawa fluid with $z\sigma = 1.8$. The notations are the same as in figure 2.

The compressibility factors, $Z = PV/NkT$, of the Yukawa fluid with $z\sigma = 1.8$ and for two temperatures, $T^* = 1.5$ and 1, that result from both FMSA approaches are presented in figure 2. To estimate the effectiveness of the theory, the computer simulation data due to Schukla [19] are shown as well. As it was already pointed out by Tang [6], the conventional FMSA/HS theory does a good job in predicting the compressibility factor of the Yukawa fluid. Nevertheless, the proposed

FMSA/Y0 theory shows to be even more accurate, especially at lower temperature and in the region of intermediate densities.

While the enhancement may seem to be minor in the case of compressibility factor, it is more pronounced for the vapor/luqiud phase diagram shown in figure 3. The results of the FMSA/Y0 theory lead to the shrinkage of coexisting densities envelope in the region near the critical point, approaching the computer simulation data. The estimated improvement in comparison with the FMSA/HS predictions is around 30%.

5. Conclusions

Being compared with computer simulation data for the Lennard-Jones-like Yukawa fluid ($z\sigma = 1.8$), the first order mean-spherical approximation (FMSA/HS) due to Tang et Lu has shown to be only slightly less accurate in the calculations of the thermodynamics and liquid/vapor phase coexistence than the full MSA theory (details of this comparison and a corresponding discussion can be found in the [6]). At the same time, the FMSA/HS is a much simpler theory. Abbreviation HS underlines here that the theory is based on the hard-sphere reference system. In the present study we reported a further improvement of this approach, which we called a conventional FMSA/HS theory by introducing the short-ranged Yukawa fluid (with decay parameter $z_o = 2z$) as a new reference system. Consequently, we are referring to this theory as the FMSA/Y0 theory. Numerical calculations that we performed for the same model discussed by Tang [6] showed that the proposed modifications of the reference system make the first order mean-spherical approximation even more accurate.

It is important that in order to treat the novel reference we are employing the conventional FMSA/HS approach. Due to this, the level of simplicity and transparency of the improved FMSA/Y0 theory is kept at the same level as that of the conventional FMSA/HS theory. In particular, it is easy to see that the resulting new expressions for main ingredients of the FMSA ideology – the Laplace transforms of the radial distribution function, equation (17), and the Baxter factorization function, equation (18), of the new reference system, as well as the equation (20) for the correction term – are only slightly longer than their original counterparts [see equations (4), (5) and (13)] and both being composed of the same variables, functions and model parameters. Only the parameter of the FMSA/Y0 theory appears to be the decay parameter z_o, for which in the case of Yukawa fluid we obtained $z_o = 2z$, and which determines an amount of the out-of-core attraction that should be attributed to the Y0 reference system.

Acknowledgement

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Удосконалене середньосферичне наближення першого порядку для простих рідин

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Пропонується новий підхід теорії збурень на основі середньосферичного наближення першого порядку (ССНПП). Він полягає у використанні твердосферної (ТС) рідини Юкави в якості базисної системи, на основі якої розв'язується рівняння Орнштейна-Церніке в рамках теорії збурень. У роботі обговорюється вибір оптимального параметра притягальної далекодії базисної системи. Результати порівнюються зі звичайною теорією ССНПП/ТС та моделюванням Монте-Карло, для коефіцієнта стисливості і фазової діаграми рідини Юкави. Запропонована теорія зберігає попередній рівень простоти та прозорості як і звичайне ССНПП/ТС, але є більш точною.

Ключові слова: *рідина Юкави, середньосферичне наближення, теорія збурень, моделювання Монте-Карло*