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СИСТЕМ

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Розв'язок середньо-сферичного наближення для моделі полідисперсної багатоюкавівської суміші твердих сфер з допомогою ортогональних поліномів

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SOLUTION OF THE MEAN SPHERICAL APPROXIMATION
FOR POLYDISPERSE MULTI-YUKAWA HARD-SPHERE FLUID
MIXTURE
USING ORTHOGONAL POLYNOMIAL EXPANSIONS

ЛЬВІВ

Розв'язок середньо-сферичного наближення для моделі полідисперсної багатоюкавівської суміші твердих сфер з допомогою ортогональних поліномів

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Анотація. У статті узагальнено розв'язок середньо-сферичного наближення для багатокомпонентної багатоюкавівської рідини твердих сфер для полідисперсного випадку. Узагальнення використовує розклад по ортогональних поліномах, застосований у роботах Ладо (*Phys. Rev. E* **54**, 4411(1996)). Представлено замкнуті аналітичні вирази для структурних та термодинамічний властивостей системи, які подані в термінах параметрів, що з'являються підчас розв'язку. Для ілюстрації, з допомогою методу описуються термодинамічні властивості одно та двоюкавівської моделі.

Solution of the mean spherical approximation for polydisperse multi-Yukawa hard-sphere fluid mixture using orthogonal polynomial expansions

Yurij V. Kalyuzhnyi and Peter T. Cummings

Abstract. The Blum-Høye solution of the MSA for multi-component multi-Yukawa hard-sphere fluid is extended to a polydisperse multi-Yukawa hard-sphere fluid. Our extension is based on the application of the orthogonal polynomial expansion method of Lado (*Phys.Rev.E* **54**, 4411(1996)). Closed form analytical expressions for the structural and thermodynamic properties of the model are presented. They are given in terms of the parameters, that follow directly from the solution. By way of illustration the method of solution is applied to describe the thermodynamic properties of one- and two-Yukawa versions of the model.

1. Introduction

Polydispersity is an intrinsic property of a vast majority of colloidal and polymeric materials. In contrast to atomic fluids or fluids of small molecules, most complex fluids consist of the many species of particles, each being unique in its size, charge, shape, or other properties. Understanding of the effects of polydispersity on the structure and thermodynamic properties of such systems, in particular on their phase behavior and fractionation are of crucial importance in numerous technological applications.

Most of the concepts currently used to study polydisperse systems view such systems as a mixture with an infinite number of components, each of them characterized by a continuous variable ξ, which is distributed according to a certain distribution function $f(\xi)$. Theoretical description of the structural and thermodynamic properties of such fluids, using the methods of the modern liquid state theory, represents a nontrivial problem. One of the possibilities in solving the problem is to use an analytical solution of the corresponding integral equation approximation. This possibility was used to describe the properties of polydisperse hard-sphere fluid utilizing Percus-Yewick (PY) approximation [1–4] and polydisperse Yukawa hard-sphere fluid using mean spherical approximation [5–7] (MSA). More recently the MSA was used to study the phase behavior of polydisperse hard-sphere mixtures with Yukawa [8], Coulombic [9–11], and sticky [12] interactions outside the hard core. In the case of Yukawa and sticky potentials application of the MSA is restricted to the systems with factorized version of interaction, i.e. the matrix of the coefficients describing the strength of the corresponding interaction is factorized into the product of two vectors.

In the present study we are removing this restriction for the system with Yukawa interaction. We propose here an extension of the Blum-Høye solution of the MSA [13,14] for multi-component multi-Yukawa hard-sphere fluid to polydisperse multi-Yukawa hard-sphere fluid. To reach the goal we use the orthogonal polynomial expansion method, developed recently [15,16]. The paper is organized as follows: In Section II we introduce the model and MSA closure relations and in Section III we present the solution. Expressions for thermodynamic and structural properties written in terms of the solution obtained in the previous section are derived in Section IV and in Section V we present and discuss numerical results for one- and two-Yukawa versions of the model, which illustrate our solution. Finally our conclusions are collected in Section VI.

2. The model and MSA closure relation

We consider a polydisperse hard-sphere multi-Yukawa fluid mixture at a temperature T $(\beta = 1/k_B T)$ and number density ρ. The pair potential acting between particles of species ξ_1 and ξ_2 is

$$\beta\Phi(r;\xi_1,\xi_2) = \begin{cases} \infty, & 0 \le r \le \sigma(\xi_1,\xi_2), \\ -\frac{1}{r}\sum_n K^{(n)}(\xi_1,\xi_2)e^{-z_n[r-\sigma(\xi_1,\xi_2)]}, & \\ & \sigma(\xi_1,\xi_2) < r \le \infty, \end{cases} \quad (1)$$

where $\sigma(\xi_1,\xi_2) = [\sigma(\xi_1) + \sigma(\xi_2)]/2$, $\sigma(\xi)$ is the hard-sphere diameter of the particles of species ξ, $K^{(n)}(\xi_1,\xi_2) = \beta\sigma_0^{(1)}\epsilon_0^{(n)}A^{(n)}(\xi_1,\xi_2)$, $\epsilon_0^{(n)}$ is the energy parameter, $\sigma_0^{(1)}$ is the average hard-sphere diameter and $A^{(n)}(\xi_1,\xi_2)$ is the dimensionless parameter characterizing the intensity of Yukawa interaction between the particles of species ξ_1 and ξ_2. The particles of species ξ are distributed according to the distribution function $f(\xi)$.

For the present model MSA theory consists of the Ornstein-Zernike (OZ) equation

$$\begin{aligned} h(r_{12};\xi_1,\xi_2) &= c(r_{12};\xi_1,\xi_2) \\ &+ \rho\int_0^\infty d\xi_3 f(\xi_3)\int d\mathbf{r}_3\, c(r_{13};\xi_1,\xi_3)h(r_{32};\xi_3,\xi_2) \end{aligned} \quad (2)$$

and boundary conditions

$$\begin{cases} c(r;\xi_1,\xi_2) &= \frac{1}{r}\sum_n K^{(n)}e^{-z_n[r-\sigma(\xi_1,\xi_2)]}, & \sigma(\xi_1,\xi_2) < r \le \infty \\ h(r;\xi_1,\xi_2) &= -1, & 0 \le r \le \sigma(\xi_1,\xi_2), \end{cases} \quad (3)$$

where $h(r;\xi_1,\xi_2)$ and $c(r;\xi_1,\xi_2)$ are the total and direct correlation functions, respectively. OZ equation (2) together with the MSA closure relation (3) represent closed set of equations to be solved.

3. Solution op the MSA

3.1. Extension of the Blum-Høye solution

Formal solution of the set of equations (2) and (3) can be obtained by generalizing solution of the MSA for the multi-component multi-Yukawa hard-sphere fluid derived by Blum and Høye [13,14]. Their solution is given in terms of the factor correlation Q-function, which is obtained using the Baxter Wiener-Hopf factorization method [17]. Extension of this solution to polydisperse hard-sphere Yukawa fluid is rather straightforward and thus we will present here only the final results. For the model at hand the factor correlation function $Q(r;\xi_1,\xi_2)$ can be written as follows

$$Q(r;\xi_1,\xi_2) = Q^{(0)}(r;\xi_1,\xi_2) + \sum_n D^{(n)}(\xi_1,\xi_2)e^{-z_n[r-\sigma(\xi_1,\xi_2)]}, \quad (4)$$

where in the interval $\lambda(\xi_2,\xi_1) < r < \sigma(\xi_1,\xi_2)$

$$\begin{aligned} Q^{(0)}(r;\xi_1,\xi_2) &= \frac{1}{2}[r - \sigma(\xi_1,\xi_2)][r - \lambda(\xi_2,\xi_1)]A(\xi_2) \\ &+ [r - \sigma(\xi_1,\xi_2)]B(\xi_2) \\ &+ \sum_n C^{(n)}(\xi_1,\xi_2)\left[e^{-z_n[r-\sigma(\xi_1,\xi_2)]} - 1\right]. \end{aligned} \quad (5)$$

Outside this interval $Q^{(0)}(r;\xi_1,\xi_2) = 0$. Here $\lambda(\xi_1,\xi_2) = \frac{1}{2}[\sigma(\xi_1) - \sigma(\xi_2)]$ and Q-function parameters $A(\xi)$, $B(\xi)$ and $C^{(n)}(\xi_1,\xi_2)$ are determined by the unknowns of the problem $G^{(n)}(\xi_1,\xi_2)$ and $D^{(n)}(\xi_1,\xi_2)$, which satisfy the following set of equations

$$D^{(n)}(\xi_1,\xi_2) - \rho\int_0^\infty d\xi_3\, f(\xi_3)D^{(n)}(\xi_1,\xi_3)\tilde{Q}^{(n)}(\xi_2,\xi_3) = \frac{2\pi}{z_n}K^{(n)}(\xi_1,\xi_2)$$

$$\hat{G}^{(n)}(\xi_1,\xi_2) - \rho\int_0^\infty d\xi_3\, f(\xi_3)\hat{G}^{(n)}(\xi_1,\xi_3)\tilde{Q}^{(n)}(\xi_3,\xi_2) = F^{(n)}(\xi_1,\xi_2), \quad (6)$$

where

$$\begin{aligned} F^{(n)}(\xi_1,\xi_2) &= \frac{1}{z_n^2}\left[1 + \frac{1}{2}z_n\sigma(\xi_1)\right]A(\xi_2) + \frac{1}{z_n}B(\xi_2) \\ &\quad - \sum_m \frac{z_m}{z_n + z_m}C^{(m)}(\xi_1,\xi_2), \end{aligned} \quad (7)$$

$$\begin{aligned} \tilde{Q}^{(n)}(\xi_1,\xi_2) &= \psi^{(n)}(\xi_1)A(\xi_2) + \varphi^{(n)}(\xi_1)B(\xi_2) \\ &+ \sum_m \left[C^{(m)}(\xi_1,\xi_2)\Omega^{(m,n)}(\xi_1)\right. \\ &\left. + \frac{1}{z_n+z_m}D^{(m)}(\xi_1,\xi_2)\tilde{e}^{(m)}(\xi_1)\right] \end{aligned} \quad (8)$$

with

$$\psi^{(n)}(\xi) = \frac{1}{z_n^3}\left\{1 - \frac{1}{2}z_n\sigma(\xi) - \left[1 + \frac{1}{2}z_n\sigma(\xi)\right]e^{(n)}(\xi)\right\}, \quad (9)$$

$$\varphi^{(n)}(\xi) = \frac{1}{z_n^2}\left[1 - z_n\sigma(\xi) - e^{(n)}(\xi)\right], \quad (10)$$

$$\Omega^{(m,n)}(\xi) = \frac{1}{z_n + z_m}\left[\tilde{e}^{(m)}(\xi) - e^{(n)}(\xi)\right] - \frac{1}{z_n}\left[1 - e^{(n)}(\xi)\right], \quad (11)$$

$$e^{(n)}(\xi) = \exp\left[-z_n\sigma(\xi)\right], \qquad \tilde{e}^{(n)}(\xi) = \exp\left[z_n\sigma(\xi)\right]. \quad (12)$$

Here $\hat{G}^{(n)}(\xi_1,\xi_2) = G(s;\xi_1,\xi_2)e^{s\sigma(\xi_1,\xi_2)}|_{s=z_n}$ and $G(s;\xi_1,\xi_2)$ is the Laplace transform of the radial distribution function $g(r;\xi_1,\xi_2)$, i.e.

$$G(s;\xi_1,\xi_2) = \int_0^\infty dr\, rg(r;\xi_1,\xi_2)e^{-sr}. \quad (13)$$

Relations between parameters $A(\xi)$, $B(\xi)$, $C^{(n)}(\xi_1,\xi_2)$ and unknowns $\hat{G}^{(n)}(\xi_1,\xi_2)$ and $D^{(n)}(\xi_1,\xi_2)$ are

$$B(\xi) = \frac{\pi}{\Delta}\left[\sigma(\xi) + 2\sum_n N^{(n)}(\xi)\right], \quad (14)$$

$$A(\xi) = \frac{2\pi}{\Delta}\left[1 + \frac{1}{2}\zeta_2 B(\xi) + \sum_n M^{(n)}(\xi)\right], \quad (15)$$

where

$$\Delta = 1 - \frac{\pi}{6}\zeta_3, \quad (16)$$

$$\zeta_m = \rho\int_0^\infty d\xi\, f(\xi)\sigma^m(\xi), \quad (17)$$

$$N^{(n)}(\xi_1) = \rho\int_0^\infty d\xi_2\, f(\xi_2)C^{(n)N}(\xi_2)D^{(n)}(\xi_2) \quad (18)$$

$$M^{(n)}(\xi_1) = \rho\int_0^\infty d\xi_2\, f(\xi_2)C^{(n)M}(\xi_2)D^{(n)}(\xi_2) \quad (19)$$

$$C^{(n)N}(\xi_1) = 2\pi\rho\int_0^\infty d\xi_2\, f(\xi_2)\hat{G}^{(n)}(\xi_1,\xi_2)\psi^{(n)}(\xi_2)$$
$$+ \frac{1}{z_n^2}\left[1 + \frac{1}{2}z_n\sigma(\xi_1)\right], \quad (20)$$

$$C^{(n)M}(\xi_1) = 2\pi\rho\int_0^\infty d\xi_2\, f(\xi_2)\hat{G}^{(n)}(\xi_1,\xi_2)\phi^{(n)}(\xi_2) - \frac{1}{z_n} - \sigma(\xi_1), \quad (21)$$

$$\phi^{(n)}(\xi) = \frac{1}{z_n}\left\{\left[1 + z_n\sigma(\xi)\right]e^{(n)}(\xi) - 1\right\}. \quad (22)$$

Assuming that species variable ξ takes a discrete set of values, i.e. $\xi = 1, 2, \ldots, i, \ldots, M$, we have

$$f(\xi) = \sum_i^M x_i\delta(i - \xi), \quad (23)$$

where $\delta(x)$ is the Dirac delta-function and x_i is the fraction of the particles of species i. In this case solution outlined above reduces to the original solution of Blum and Høye [13,14].

Solution of the set of equations (6) will be obtained using orthogonal polynomial expansion technique developed by Lado [15].

3.2. Orthogonal polynomial expansion method of solution

Following the method of Lado [15] we expand all ξ-dependent functions in terms of the orthogonal polynomials

$$p_a(\xi) = \sum_{p=0}^a c_a^p\xi^p \quad (a = 0, 1, 2\ldots), \quad (24)$$

which are associated with the distribution function $f(\xi)$. For a given functions $x(\xi)$ and $y(\xi_1,\xi_2)$ we have

$$x(\xi) = \sum_{a=0}^\infty x_a p_a(\xi), \quad (25)$$

$$y(\xi_1,\xi_2) = \sum_{a,b=0}^\infty y_{ab}p_a(\xi_1)p_b(\xi_2), \quad (26)$$

where the expansion coefficients x_a and y_{ab} are defined by the following relation

$$x_a = \int_0^\infty d\xi\, f(\xi)x(\xi)p_a(\xi), \quad (27)$$

$$y_{ab} = \int_0^\infty d\xi_1 d\xi_2\, f(\xi_1)f(\xi_2)y(\xi_1,\xi_2)p_a(\xi_1)p_b(\xi_2). \quad (28)$$

Now the set of equations (6) can be written in terms of the expansion coefficients $\hat{G}_{ab}^{(n)}$ and $D_{ab}^{(n)}$, which represent unknowns of the problem $\hat{G}^{(n)}(\xi_1,\xi_2)$ and $D^{(n)}(\xi_1,\xi_2)$

$$\begin{cases} \sum_c D_{ac}^{(n)}\left(\delta_{cb} - \rho\tilde{Q}_{bc}^{(n)}\right) &= \frac{2\pi}{z_n}K_{ab}^{(n)} \\ \sum_c \hat{G}_{ac}^{(n)}\left(\delta_{cb} - \rho\tilde{Q}_{cb}^{(n)}\right) &= \frac{1}{2\pi}F_{ab}^{(n)} \end{cases}, \quad (29)$$

where

$$F_{ab}^{(n)} = \frac{1}{z_n^2} \left(\delta_{a0} + \frac{1}{2} z_n \sigma_a^{(1)} \right) A_b + \frac{1}{z_n} \delta_{a0} B_b - \sum_m \frac{z_m}{z_n + z_m} C_{ab}^{(m)}, \quad (30)$$

$$
\begin{aligned}
\tilde{Q}_{ab}^{(n)} &= \psi_a^{(n)} A_b + \varphi_a^{(n)} B_b \\
&+ \sum_m \sum_{dc} \left[C_{db}^{(m)} \Omega_c^{(m,n)} + \frac{\tilde{e}_c^{(m)}}{z_n + z_m} D_{db}^{(m)} \right] q_a^{dc}
\end{aligned} \quad (31)
$$

with

$$\psi_a^{(n)} = \frac{1}{z_n^3} \left[\delta_{a0} - \frac{1}{2} z_n \sigma_a^{(1)} - \sum_{dc} \left(\delta_{d0} + \frac{1}{2} z_n \sigma_d^{(1)} \right) e_c^{(n)} q_a^{dc} \right], \quad (32)$$

$$\varphi_a^{(n)} = \frac{1}{z_n^2} \left(\delta_{a0} - z_n \sigma_a^{(1)} - e_a^{(n)} \right), \quad (33)$$

$$\Omega_a^{(m,n)} = \frac{1}{z_n + z_m} \left(\tilde{e}_a^{(m)} - e_a^{(n)} \right) - \frac{1}{z_n} \left(\delta_{a0} - e_a^{(n)} \right) \quad (34)$$

and

$$B_a = \frac{\pi}{\Delta} \left(\sigma_a^{(1)} + 2 \sum_n N_a^{(n)} \right), \quad (35)$$

$$A_a = \frac{2\pi}{\Delta} \left(\delta_{a0} + \frac{1}{2} \zeta_2 B_a + \sum_n M_a^{(n)} \right), \quad (36)$$

$$C_{ab}^{(n)} = -D_{ab}^{(n)} + \frac{2\pi}{z_n} \sum_{pcd} \hat{G}_{pc}^{(n)} D_{cb}^{(n)} e_d^{(n)} q_a^{pd} \quad (37)$$

with

$$\zeta_m = \rho \sigma_0^{(m)}, \quad (38)$$

$$N_a^{(n)} = \rho \sum_d C_d^{(n)N} D_{da}^{(n)}, \quad (39)$$

$$M_a^{(n)} = \rho \sum_d C_d^{(n)M} D_{da}^{(n)}, \quad (40)$$

$$C_a^{(n)N} = 2\pi\rho \sum_d \hat{G}_{ad}^{(n)} \psi_d^{(n)} + \frac{1}{z_n^2} \left(\delta_{a0} + \frac{1}{2} z_n \sigma_a^{(1)} \right), \quad (41)$$

$$C_a^{(n)M} = 2\pi\rho \sum_d \hat{G}_{ad}^{(n)} \varphi_d^{(n)} - \frac{1}{z_n} \delta_{a0} - \sigma_a^{(1)}. \quad (42)$$

Here q_a^{bc} are the expansion coefficients of the product $p_b(\xi)p_c(\xi)$, i.e.

$$p_b(\xi)p_c(\xi) = \sum_{d=0}^{b+c} q_d^{bc} p_d(\xi). \quad (43)$$

For these coefficients we have the following recurrent relation

$$q_a^{bc} = \frac{1}{c_a^a} \left(d_a^{bc} - \sum_{p=a+1}^{b+c} q_p^{bc} c_a^p \right) \theta \left(b + c - a \right) \quad (44)$$

with $q_{b+c}^{bc} = d_{b+c}^{bc}/c_{b+c}^{b+c}$ and

$$d_a^{bc} = \theta_1 \sum_{d=0}^{a} c_d^{p_x} c_{a-d}^{p_n} + \theta_2 \sum_{d=a-p_n}^{a} c_d^{p_x} c_{a-d}^{p_n} + \theta_3 \sum_{d=a-p_x}^{a} c_d^{p_x} c_{a-d}^{p_n}, \quad (45)$$

where

$$
\begin{aligned}
\theta_1 &= \theta \left(p_n - a \right), \\
\theta_2 &= \theta(p_x - a)\theta(a - p_n - 1), \\
\theta_3 &= \theta(p_n + p_x - a)\theta(a - p_x - 1),
\end{aligned}
$$

$\theta(x)$ is the Heviside step function

$$\theta(x) = \left\{ \begin{array}{cc} 0, & x < 0 \\ 1, & x \geq 0 \end{array} \right. \quad (46)$$

and $p_n = min(b,c)$, $p_x = max(b,c)$.

Thus the solution of the MSA (3) for polydisperse multi-Yukawa hard-sphere fluid is reduced now to the solution of the set of algebraic equations equations (29) for the unknown coefficients $\hat{G}_{ab}^{(n)}$ and $D_{ab}^{(n)}$. The input parameters of this set of equations involve orthogonal polynomial expansion coefficients for the quantities $K^{(n)}(\xi_1, \xi_2)$, $\sigma(\xi)$, $e^{(n)}(\xi)$ and $\tilde{e}^{(n)}(\xi)$, which define the potentials for the model fluid under consideration. We have

$$K_{ab}^{(n)} = \int_0^\infty d\xi_1 d\xi_2 \ f(\xi_1)f(\xi_2)K^{(n)}(\xi_1, \xi_2)p_a(\xi_1)p_b(\xi_2), \quad (47)$$

$$\sigma_a^{(m)} = \int_0^\infty d\xi \ f(\xi)\sigma^m(\xi)p_a(\xi), \quad (48)$$

$$e_a^{(n)} = \int_0^\infty d\xi \ f(\xi)e^{(n)}(\xi)p_a(\xi), \quad (49)$$

$$\tilde{e}_a^{(n)} = \int_0^\infty d\xi \ f(\xi)\tilde{e}^{(n)}(\xi)p_a(\xi). \quad (50)$$

These coefficients can be easily calculated as soon as the above potential model parameters and distribution function are given as functions of ξ.

4. Thermodynamic and structure properties

Once the coefficients of the factor Q-function are found the thermodynamic and structure properties can be calculated. For the multicomponent multi-Yukawa hard-sphere fluid corresponding expressions in terms of the Q-function coefficients are derived by Blum and Høye [13] and in the form convenient for application presented by Arietta et.al. [18]. Here we will recast the latter version of these expressions in terms of the orthogonal polynomial expansion coefficients of the constants in the factor Q-function.

4.1. Thermodynamics

For the excess internal energy $U^{(ex)}$, inverse isothermal compressibility χ^{-1}, virial pressure P^v, energy pressure $P^{(e)}$, Helmholtz free energy A and chemical potential $\mu(\xi)$ we thus obtain

$$\beta\frac{U^{(ex)}}{V} = -2\pi\rho^2\sum_n\sum_{ab}K_{ab}^{(n)}\hat{G}_{ab}^{(n)}, \tag{51}$$

$$\chi^{-1} = \beta\left(\frac{\partial P}{\partial \rho}\right)_\beta = \frac{1}{4\pi}\sum_a A_a^2, \tag{52}$$

$$\begin{aligned}\beta\left(P^{(v)} - P_{HS}\right) &= \tfrac{1}{3}\pi\rho^2\left\{\sum_{ab}\sigma_a^{(1)}\sigma_b^{(1)}\left[g_{ab}^{(\sigma)}\right.\right.\\ &\quad + \tfrac{1}{2}\sum_c\left(g_{c0}^{(\sigma)} + g_{0c}^{(\sigma)}\right)q_c^{ab}\right]\\ &\quad \left.- \tfrac{1}{\Delta}\left(\zeta_1^2 + \zeta_2^2 + \tfrac{\pi}{4\Delta}\zeta_1^2\zeta_2\right)\right\} + J,\end{aligned} \tag{53}$$

$$\begin{aligned}\beta\left(P^{(e)} - P_{HS}\right) &= \frac{1}{6}\pi\rho^2\left\{\sum_{abc}\sigma_a^{(1)}g_{bc}^{(\sigma)}\sum_d\left(g_{dc}^{(\sigma)}q_d^{ab} + g_{bd}^{(\sigma)}q_d^{ac}\right)\right.\\ &\quad \left.- \frac{1}{\Delta}\left[\frac{\pi}{2\Delta}\zeta_2^3\left(\frac{\pi}{4\Delta}\zeta_3 + 1\right) + \frac{1}{2}\zeta_1\zeta_2\left(\frac{\pi}{\Delta}\zeta_3 + 3\right) + \frac{1}{2}\zeta_3\right]\right\} + J,\end{aligned} \tag{54}$$

$$\beta\frac{A - A_{HS}}{V} = \beta\frac{U^{(ex)}}{V} - \beta\left(P^{(e)} - P_{HS}\right) + \frac{1}{2}\rho\left(\chi^{-1} - \chi_{HS}^{-1}\right), \tag{55}$$

$$\begin{aligned}\beta\left[\mu(\xi) - \mu_{HS}(\xi)\right] = -\rho\sum_a\left\{2\pi\sum_{bcp}\sum_n K_{pb}^{(n)}\hat{G}_{cb}^{(n)}q_a^{pc}\right.\\ + \frac{1}{2}\left[\left(\bar{Q}_{a0} - \bar{Q}_{a0}^{(0)}\right) + \left(\bar{Q}_{0a}^{(0)} - \bar{Q}_{0a}^{(0)}\right)\right]\\ \left.- \rho\sum_c\left(\bar{Q}_{ac}\bar{Q}_{0c} - \bar{Q}_{ac}^{(0)}\bar{Q}_{0c}^{(0)}\right)\right]\right\}p_a(\xi). \tag{56}\end{aligned}$$

Here $g_{ab}^{(\sigma)}$ represent the contact values of the radial distribution function (see below), subscript HS denote the corresponding quantity of polydisperse hard-sphere mixture,

$$\begin{aligned}J &= \frac{2}{3}\pi\rho\sum_n z_n\sum_{ab}\left[K_{ab}^{(n)}\left(\partial\hat{G}_{ab}^{(n)} - \frac{1}{z_n}\hat{G}_{ab}^{(n)}\right)\right.\\ &\quad \left.- \frac{1}{2}\sigma_a^{(1)}\sum_{cd}\hat{G}_{bc}^{(n)}\left(K_{dc}^{(n)}q_b^{ad} + K_{bd}^{(n)}q_c^{ad}\right)\right],\end{aligned} \tag{57}$$

$$\partial\hat{\mathbf{G}}^{(n)} = \left(\frac{1}{2\pi}\partial\mathbf{F}^{(n)} + \rho\hat{\mathbf{G}}^{(n)}\partial\tilde{\mathbf{Q}}^{(n)}\right)\left(\mathbf{1} - \rho\tilde{\mathbf{Q}}^{(n)}\right)^{-1}, \tag{58}$$

$\hat{\mathbf{G}}^{(n)}, \tilde{\mathbf{Q}}^{(n)}, \partial\hat{\mathbf{G}}^{(n)}, \partial\tilde{\mathbf{Q}}^{(n)}, \partial\mathbf{F}^{(n)}$ are the matrices with the elements $\hat{G}_{ab}^{(n)}, \tilde{Q}_{ab}^{(n)}, \partial\hat{G}_{ab}^{(n)}, \partial\tilde{Q}_{ab}^{(n)}, \partial F_{ab}^{(n)}$, respectively,

$$\begin{aligned}\partial F_{ab}^{(n)} &= -\frac{1}{z_n^2}\left(\frac{2}{z_n}\delta_{a0} + \frac{1}{2}\sigma_a^{(1)}\right)A_b - \frac{1}{z_n^2}\delta_{a0}B_b\\ &\quad + \sum_m\frac{z_m}{(z_n + z_m)^2}C_{ab}^{(m)}\end{aligned} \tag{59}$$

$$\partial \tilde{Q}_{ab}^{(n)} = \frac{1}{z_n^3} \left\{ \sigma_a^{(1)} - \frac{3}{z_n}\delta_{a0} + \sum_{cd} \left[\frac{3}{z_n}\delta_{c0} + 2\sigma_c^{(1)} + \frac{1}{2}z_n\sigma_c^{(2)} \right] e_d^{(n)} q_a^{cd} \right\} A_b$$

$$+ \frac{1}{z_n^2} \left[\sigma_a^{(1)} - \frac{2}{z_n}\delta_{a0} + \sum_{cd} \left(\sigma_c^{(1)} + \frac{2}{z_n}\delta_{c0} \right) e_d^{(n)} q_a^{cd} \right] B_b$$

$$+ \sum_m \sum_{cd} \left[C_{cb}^{(m)} \partial\Omega_d^{(m,n)} - \frac{1}{(z_n + z_m)^2} D_{cb}^{(m)} \tilde{e}_d^{(m)} \right] q_a^{cd}, \qquad (60)$$

$$\partial\Omega_a^{(m,n)} = \frac{1}{z_n + z_m} \left[\frac{e_a^{(n)} - \tilde{e}_a^{(m)}}{z_n + z_m} + \sum_{bc} \sigma_b^{(1)}\sigma_c^{(1)} q_a^{bc} \right]$$

$$+ \frac{1}{z_n} \left[\frac{\delta_{a0} - e_a^{(n)}}{z_n} - \sum_{bc} \sigma_b^{(1)} e_c^{(n)} q_a^{bc} \right], \qquad (61)$$

$$\bar{Q}_{ab} = -\frac{1}{12}\sigma_a^{(3)} A_b - \frac{1}{2}\sigma_a^{(2)} B_b \qquad (62)$$

$$- \sum_n \left(\frac{1}{z_n}C_{ab}^{(n)} + \sum_{pc} C_{pb}^{(n)}\sigma_c^{(1)} q_a^{pc} - \frac{2\pi}{z_n^2}\rho \sum_p \hat{G}_{ap}^{(n)} D_{pb}^{(n)} \right)$$

and

$$\bar{Q}_{ab}^{(0)} = -\frac{1}{12}\sigma_a^{(3)} A_b^{(0)} - \frac{1}{2}\sigma_a^{(2)} B_b^{(0)}. \qquad (63)$$

4.2. Structure

Contact values for the radial distribution function $g\left[\sigma^+(\xi_1, \xi_2); \xi_1, \xi_2\right]$ are given by

$$\sigma(\xi_1, \xi_2) g\left[\sigma^+(\xi_1, \xi_2); \xi_1, \xi_2\right] = \sum_{ab} g_{ab}^{(\sigma)} p_a(\xi_1) p_b(\xi_2), \qquad (64)$$

where

$$2\pi g_{ab}^{(\sigma)} = \frac{1}{2}\sigma_a^{(1)} A_b + \delta_{a0} B_b - \sum_n z_n C_{ab}^{(n)}. \qquad (65)$$

For the Laplace transform of the radial distribution function (13) we have

$$G(s; \xi_1, \xi_2) e^{s\sigma(\xi_1, \xi_2)} = \sum_{ab} \hat{G}_{ab}(s) p_a(\xi_1) p_b(\xi_2), \qquad (66)$$

where expressions for the expansion coefficients $\hat{G}_{ab}(s)$ follows from the second of the equations (29) written for $z_n = s$, i.e.

$$2\pi\hat{\mathbf{G}}(s) = \mathbf{F}(s) \left[\mathbf{1} - \rho\tilde{\mathbf{Q}}(is) \right]^{-1}. \qquad (67)$$

Here $\hat{\mathbf{G}}(s)$, $\mathbf{F}(s)$ and $\tilde{\mathbf{Q}}(is)$ are the matrices with the elements $\hat{G}_{ab}(s)$, $F_{ab}(s)$ and $\tilde{Q}_{ab}(is)$ and

$$F_{ab}(s) = \frac{1}{s^2} \left(\delta_{a0} + \frac{1}{2}s\sigma_a^{(1)} \right) A_b + \frac{1}{s}\delta_{a0} B_b - \sum_m \frac{z_m}{s + z_m} C_{ab}^{(m)}, \qquad (68)$$

$$\tilde{Q}_{ab}(is) = \psi_a(s) A_b + \varphi_a(s) B_b + \sum_m \sum_{dc} \left[C_{db}^{(m)} \Omega_c^{(m)}(s) \right.$$

$$\left. + \frac{\tilde{e}_c^{(m)}}{s + z_m} D_{db}^{(m)} \right] q_a^{dc}, \qquad (69)$$

$$\psi_a(s) = \frac{1}{s^3} \left[\delta_{a0} - \frac{1}{2}s\sigma_a^{(1)} - \sum_{bc} \left(\delta_{b0} + \frac{1}{2}s\sigma_b^{(1)} \right) e_c(s) q_a^{bc} \right], \qquad (70)$$

$$\varphi_a(s) = \frac{1}{s^2} \left[\delta_{a0} - s\sigma_a^{(1)} - e_a(s) \right], \qquad (71)$$

$$\Omega^{(m)}(s) = \frac{1}{s + z_m} \left[\tilde{e}_a^{(m)} - e_a(s) \right] - \frac{1}{s} \left[\delta_{a0} - e_a(s) \right], \qquad (72)$$

$$e_a(s) = \int_0^\infty d\xi \, f(\xi) e^{-s\sigma(\xi)} p_a(\xi). \qquad (73)$$

5. Numerical calculations

5.1. Numerical solution of the set of equations for $D_{ab}^{(n)}$ and $G_{ab}^{(n)}$ via iteration

Solution of the set of algebraic equations (29) can be obtained by the standard numerical methods, e.g. Newton-Raphson method. However in the present study we propose an iterative method of solution, which in spite of its simplicity appears to be very efficient. Keeping this goal in mind we recast the set of equations (29) in the matrix form as follows

$$\left\{ \begin{array}{ll} \mathbf{D}^{(n)} & = \frac{2\pi}{z_n}\mathbf{K}^{(n)} \left[\mathbf{1} - \rho\left(\tilde{\mathbf{Q}}^{(n)}\right)^T \right]^{-1} \\ \hat{\mathbf{G}}^{(n)} & = \frac{1}{2\pi}\mathbf{F}^{(n)} \left[\mathbf{1} - \rho\tilde{\mathbf{Q}}^{(n)} \right]^{-1} \end{array} \right. , \qquad (74)$$

where $\mathbf{D}^{(n)}$, $\hat{\mathbf{G}}^{(n)}$, $\tilde{\mathbf{Q}}^{(n)}$ and $\mathbf{F}^{(n)}$ are the matrices with the elements $D_{ab}^{(n)}$, $\hat{G}_{ab}^{(n)}$, $\tilde{Q}_{ab}^{(n)}$ and $F_{ab}^{(n)}$, respectively, and $(\ldots)^T$ denotes matrix transpose.

Our iteration loop consists of two steps. In the first step current values of $\mathbf{F}^{(n)}$ and $\tilde{\mathbf{Q}}^{(n)}$ are used to calculate $\mathbf{D}^{(n)}$ and $\hat{\mathbf{G}}^{(n)}$ via the set of equations (74). On a second step we insert these values of $\mathbf{D}^{(n)}$ and $\hat{\mathbf{G}}^{(n)}$ into the right hand side of relations (30) and (31) to get a new estimate for $\mathbf{F}^{(n)}$ and $\tilde{\mathbf{Q}}^{(n)}$. This iteration loop is repeated until self-consistency of the unknowns $\mathbf{D}^{(n)}$ and $\hat{\mathbf{G}}^{(n)}$ is achieved. For the initial guess we have used the values of $\mathbf{F}^{(n)}$ and $\tilde{\mathbf{Q}}^{(n)}$ calculated in the limit of infinitely high temperature. In this limit $\beta \to 0$ and MSA (3) reduces to Percus-Yewick approximation for polydisperse hard-sphere mixture. Thus

$$F_{ab}^{(n)(0)} = \frac{1}{z_n^2}\left(\delta_{a0} + \frac{1}{2}z_n\sigma_a\right)A_b^{(0)} + \frac{1}{z_n}\delta_{a0}B_b^{(0)}, \qquad (75)$$

$$\tilde{Q}_{ab}^{(n)} = \psi_a^{(n)}A_b^{(0)} + \varphi_a^{(n)}B_b^{(0)} \qquad (76)$$

with

$$A_a^{(0)} = \frac{2\pi}{\Delta}\left(\delta_{a0} + \frac{\pi}{2\Delta}\zeta_2\sigma_a^{(1)}\right), \qquad B_a^{(0)} = \frac{\pi}{\Delta}\sigma_a^{(1)}.$$

Usually we start at relatively high temperature and gradually lower the temperature until the state point of interest is reached. To be sure that our solution is physical we monitor the smoothness of variation of the solution variables $D_{ab}^{(n)}$ and $G_{ab}^{(n)}$ while changing the temperature.

5.2. Gamma distribution

Solution of the MSA derived in Section 3 is quite general and can be used to describe a polydisperse multi-Yukawa hard-sphere fluid with any functional dependence of the potential model parameters $\sigma(\xi)$ and $K^{(n)}(\xi_1, \xi_2)$ on the polydispersity attribute ξ and for any reasonable choice for the distribution function $f(\xi)$. For the sake of simplicity we assume that the hard-sphere size of the particle completely defines its species. i.e. the hard-sphere size takes the role of polydispersity attribute ξ and the energy parameter $K^{(n)}(\sigma_1, \sigma_2)$ and distribution function $f(\sigma)$ become the functions of σ. In this study the particle sizes are assumed to follow the gamma (Schultz) distribution [19]

$$f_\Sigma(\sigma) = A_\Sigma^{(\alpha)}\sigma^\alpha e^{-\alpha_\Sigma\sigma}, \qquad (77)$$

where

$$A_\Sigma^{(\alpha)} = \frac{\alpha_\Sigma^{\alpha+1}}{\Gamma(\alpha+1)}, \qquad \alpha_\Sigma = \frac{\alpha+1}{\sigma_0^{(1)}}.$$

Here $\Gamma(z)$ is the gamma function and α is related to the distribution function width D_σ

$$D_\sigma = \frac{\sigma_0^{(2)}}{\left(\sigma_0^{(1)}\right)^2} - 1 = \frac{1}{1+\alpha}. \qquad (78)$$

Orthogonal polynomials, associated with the gamma distribution are represented by the associated Laguerre polynomials $L_a^{(\alpha)}(x)$, i.e.

$$p_a(\sigma) = P_a^{(\alpha)}L_a^{(\alpha)}(\alpha_\Sigma\sigma), \qquad (79)$$

where

$$P_a^{(\alpha)} = \left[\frac{a!\Gamma(\alpha+1)}{\Gamma(a+\alpha+1)}\right]^{1/2}. \qquad (80)$$

For our choice of the distribution function (77) the orthogonal polynomial expansion coefficients $\sigma_a^{(m)}$, $e_a^{(n)}$ and $\tilde{e}_a^{(n)}$ are

$$\sigma_a^{(m)} = (-1)^a A_\Sigma^{(\alpha)}P_a^{(\alpha)}\alpha_\Sigma^{-(\alpha+m+1)}\frac{m!\Gamma(\alpha+m+1)}{a!\,(m-a)!}, \qquad (81)$$

$$e_a^{(n)} = A_\Sigma^{(\alpha)}P_a^{(\alpha)}\frac{z_n^a\Gamma(a+\alpha+1)}{a!\,(\alpha_\Sigma+z_n)^{\alpha+a+1}}, \qquad (82)$$

$$\tilde{e}_a^{(n)} = (-1)^a A_\Sigma^{(\alpha)}P_a^{(\alpha)}\frac{z_n^a\Gamma(a+\alpha+1)}{a!\,(\alpha_\Sigma-z_n)^{\alpha+a+1}}. \qquad (83)$$

5.3. Numerical results

To illustrate the solution of the MSA developed in the previous sections we present here numerical results for the thermodynamical properties (equation of state and internal energy) of the two versions of polydisperse Yukawa hard-sphere fluid. The first version employs one-Yukawa hard-sphere potential and the second one uses two-Yukawa hard-sphere potential. In all cases orthogonal polynomial expansions of the type represented by the expressions (25) and (26 were terminated at $a = 10$. According to our investigation the contribution from polynomials with $a > 10$ is negligible.

In what follows, the temperature T and the density ρ of the system will be expressed in terms of dimensionless quantities $T^* = kT/\epsilon_0 Z_0^2$ and $\rho^* = \rho(\sigma_0^{(1)})^3$, where ϵ_0 is the depth of the Yukawa potential well between the particles of the size $\sigma_0^{(1)}$ and for the definition of Z_0 see below.

5.3.1. One-Yukawa polydisperse hard-sphere fluid

We have chosen the following one-Yukawa potential

$$\Phi(r;\sigma_1,\sigma_2) = \begin{cases} \infty & 0 \leq r \leq \sigma_{12} \\ -\epsilon_0 \sigma_0^{(1)} \frac{A(\sigma_1,\sigma_2)}{r} e^{-z(r-\sigma_{12})} & \sigma_{12} < r \leq \infty, \end{cases} \quad (84)$$

where

$$A(\sigma_1,\sigma_2) = \frac{Z(\sigma_1)Z(\sigma_2)}{1+\alpha\left(\sigma_1-\sigma_0^{(1)}\right)\left(\sigma_2-\sigma_0^{(1)}\right)/\left(\sigma_0^{(2)}\right)^2} \quad (85)$$

and $Z(\sigma) = Z_0\sigma^2/\left(\sigma_0^{(2)}\right)^2$. Here $z\sigma_0^{(1)} = 1.8$, Z_0 is the average value of $Z(\sigma)$ and parameter α defines degree of departure of the potential (84) from the hard-sphere Yukawa potential with factorizable coefficients; the latter is recovered at $\alpha = 0$. Properties of polydisperse hard-sphere fluid with factorized Yukawa potential have been studied earlier [5–8]. Our choice for the Yukawa potential enables us to study the effects due to the departure of the potential from its factorizable version.

In Fig. 1 we show the behavior of the coefficient $A(\sigma_1,\sigma_2)$ as a function of $\sigma = \sigma_1 = \sigma_2$ at different values of parameter α. With the increase of α the difference between factorizable and non-factorizable versions of the potentials substantially increases for larger hard-sphere sizes and slightly increases for smaller hard-sphere sizes. At the same time interaction between the particles of the sizes close to their mean value $\sigma_0^{(1)}$ is unchanged. The latter feature of the potential (84) is build in to provide a meaningful comparison of the properties of the systems with factorizable and non-factorizable interaction. For the same values of α, as those shown in Fig. 1, in Figs. 2 and 3 we present our results for the pressure $P^* = \frac{\pi}{6}(\sigma_0^{(1)})^3\beta P^{(e)}$ and for the excess internal energy $\beta U^{(ex)}/V$ as a functions of the density ρ^* at $T^* = 1.17$ and gamma distribution width $D_\sigma = 0.02$. For the lower values of α, the pressure isotherms show the presence of thermodynamic instability, i.e. with increasing density the pressure decreases. However with increasing α, contributions from the particles with low strength of Yukawa attraction increase and this instability disappears, reflecting the increasing difference between factorized and non-factorized versions of the Yukawa potentials. For similar reasons, the excess internal energy becomes less negative with the increasing values of α (Fig.3).

5.3.2. Two-Yukawa polydisperse hard-sphere fluid

In the presence of double-layer and depletion interactions effective pair potential between colloidal particles is strongly attractive on short distances and repulsive on long distances. This type of interaction can be described by the two-Yukawa hard-sphere potential of the following form

$$\Phi(r;\sigma_1,\sigma_2) = \begin{cases} \infty, & 0 \leq r \leq \sigma_{12} \\ -\frac{\sigma_0^{(1)}}{r}\left[\epsilon_0^{(1)}A^{(1)}(\sigma_1,\sigma_2)e^{-z_1(r-\sigma_{12})} \right. & \\ \left. + \epsilon_0^{(2)}A^{(2)}(\sigma_1,\sigma_2)e^{-z_2(r-\sigma_{12})}\right], & \sigma_{12} < r \leq \infty \end{cases} \quad (86)$$

where $\epsilon_0^{(2)} = \epsilon_0 - \epsilon_0^{(1)}$, $z_1\sigma_0^{(1)} = 5$, $z_2\sigma_0^{(1)} = 4$ and $A^{(n)}(\sigma_1,\sigma_2) = Z^{(n)}(\sigma_1)Z^{(n)}(\sigma_2)$. To mimic depletion and double-layer interactions we assume, that $\epsilon_0^{(1)} > 0$, $\epsilon_0^{(2)} < 0$ and

$$Z^{(1)}(\sigma) = Z_0\frac{\sigma}{\sigma_0^{(1)}}, \qquad Z^{(2)}(\sigma) = Z_0\frac{\sigma^2}{\sigma_0^{(2)}}. \quad (87)$$

Thus it is assumed that depletion interaction is proportional to the hard-sphere size of the particles [20,21]. For the double-layer interaction the usual assumption on the proportionality of the particle charge to its surface is used.

Figure 4 shows two-Yukawa potential (86) between the pair of the particles of the same size $\sigma_0^{(1)}$ at different values of $\epsilon_0^{(1)}$. With the increase of $\epsilon_0^{(1)}$ one can see the increase of the potential barrier and its shift to shorter distances. These peculiarities of the two-Yukawa potential (86) can substantially affect the phase behavior of the model. In the limiting case of a monodisperse fluid ($D_\sigma = 0$) the critical temperature T_{cr}^* exhibits non-monotonic dependence on the value of $\epsilon_0^{(1)}$ (Fig. 5). In the range of $\epsilon_0^{(1)}$ from 1 to 7 the critical temperature decreases and for $\epsilon_0^{(1)} > 7$ increasing $\epsilon_0^{(1)}$ causes an increase in T_{cr}^*. This effect can be seen also from the behavior of the pressure isotherms, shown in Fig.6. While for the low and high values of $\epsilon_0^{(1)}$ one can observe the existence of a thermodynamic instability, for intermediate values of $\epsilon_0^{(1)}$ it disappears. The excess internal energy (Fig. 7) increases with increasing $\epsilon_0^{(1)}$ and for $\epsilon_0^{(1)} \leq 11$ becomes positive in the whole range of the densities studied. Finally in Figs. 8 and 9 we show the pressure isotherms and excess internal energy for the model at hand at $T^* = 0.298$, $\epsilon_0^{(1)} = 8$ and different values of the polydispersity parameter D_σ. Note that for the

highest values of polydispersity parameter $D_\sigma = 0.021$, 0.025 we were not able to find convergent solutions in a certain range of the densities. For low and high degrees of polidispersity pressure isotherms show the presence of thermodynamic instability, which disappears at intermediate values of D_σ. Due to the increase of $\epsilon_0^{(1)}$ in monodisperse case and D_σ in polydisperse case the role of the particles with higher potential barrier becomes more important, which causes similarity in the behavior of both versions of the model at hand.

6. Conclusions

In this paper we have shown how to extend applicability of the MSA to describe the structure and thermodynamical properties of polydisperse multi-Yukawa hard-sphere fluid by combining the Blum-Høye solution of the MSA for multi-component multi-Yukawa hard-sphere fluid [13,14] and the orthogonal polynomial expansion method of Lado et al. [15,16]. In a subsequent paper we are planning to apply the method developed here to study the effects of polydispersity on the phase behavior and fractionation of polydisperse Yukawa fluids.

7. Acknowledgment

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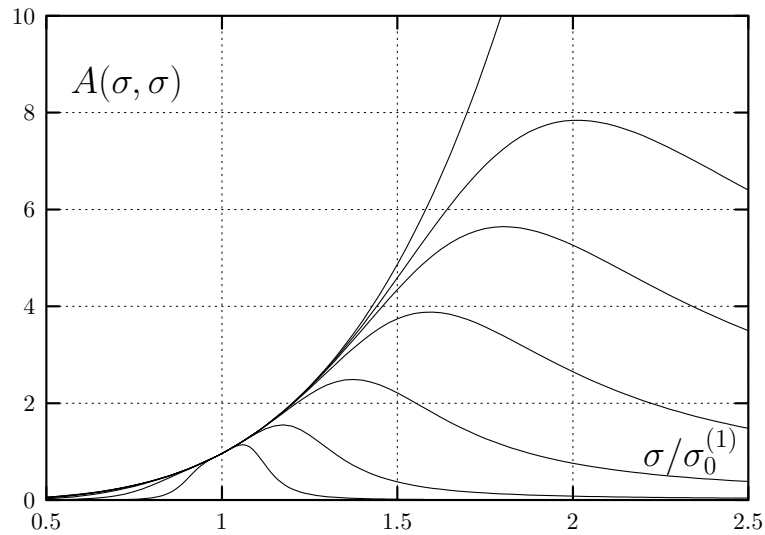21. D. Henderson, A. Trokhymchuk, L. V. Woodcock, and K.-Y. Chan *Molec. Phys.* **103**, 667(2005).

Figure 1.
$A(\sigma_1, \sigma_2)$ versus $\sigma = \sigma_1 = \sigma_2$ at $\alpha = 5000, \ 200, \ 20, \ 5, \ 2, \ 1, \ 0$ from the bottom to the top at $\sigma/\sigma_0^{(1)} = 1.5$
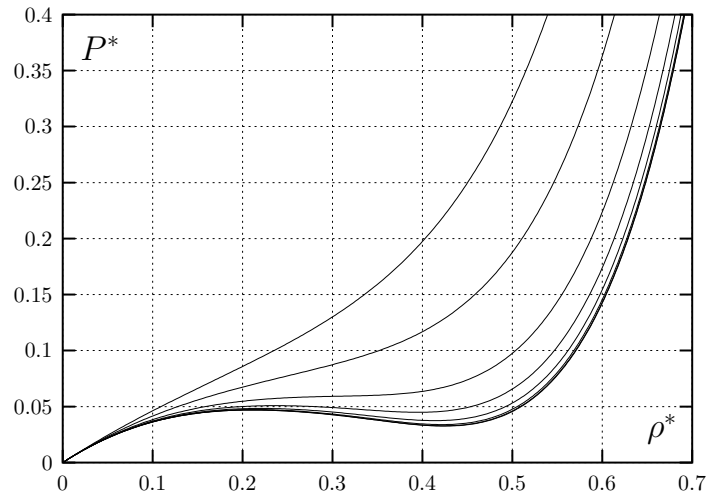

Figure 2.
Pressure isotherms of the one-Yukawa model at $T* = 1.17$, $D_\sigma = 0.02$ and $\alpha = 5000, \ 200, \ 20, \ 5, \ 2, \ 1, \ 0$ from the top to the bottom at $\rho^* = 0.5$
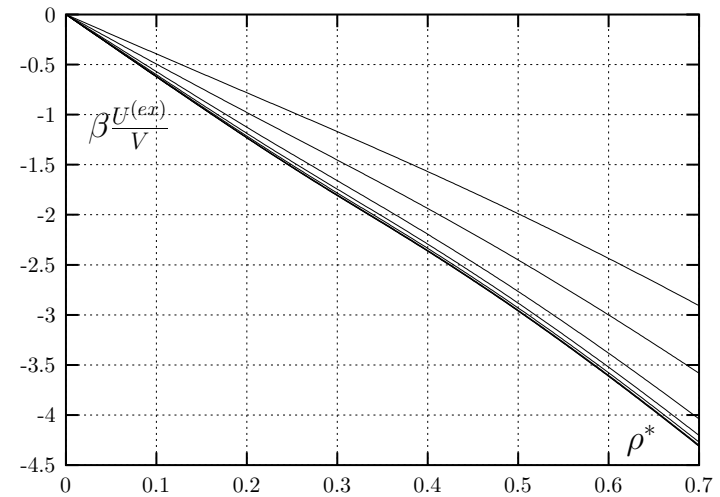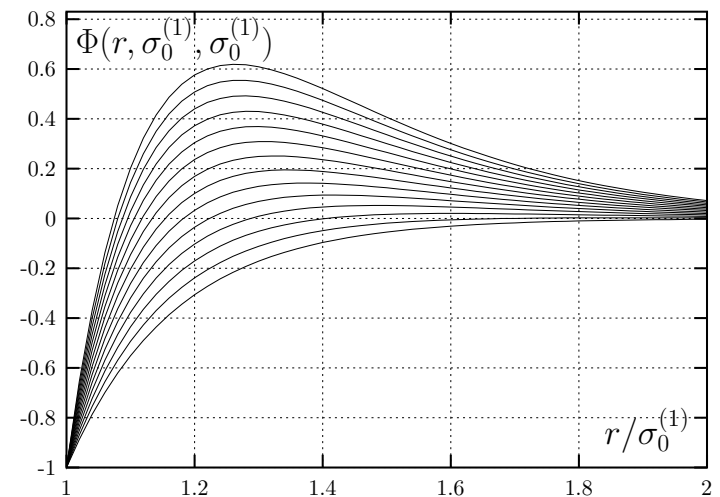

Figure 3.
Excess internal energy of the one-Yukawa model at $T* = 1.17$, $D_\sigma = 0.02$ and $\alpha = 5000, \ 200, \ 20, \ 5, \ 2, \ 1, \ 0$ from the top to the bottom at $\rho^* = 0.5$

Figure 4.
Pair potential $\Phi(r, \sigma_1, \sigma_2)$ of the two-Yukawa model at $\sigma_1 = \sigma_2 = \sigma_0^{(1)}$ and $\epsilon_0^{(1)} = 1, \ 2, \ 3, \ 4, \ 5, \ 6, \ 7, \ 8, \ 9, \ 10, \ 11, \ 12, \ 13, \ 14$ from the bottom to the top at $r/\sigma_0^{(1)} = 1.2$
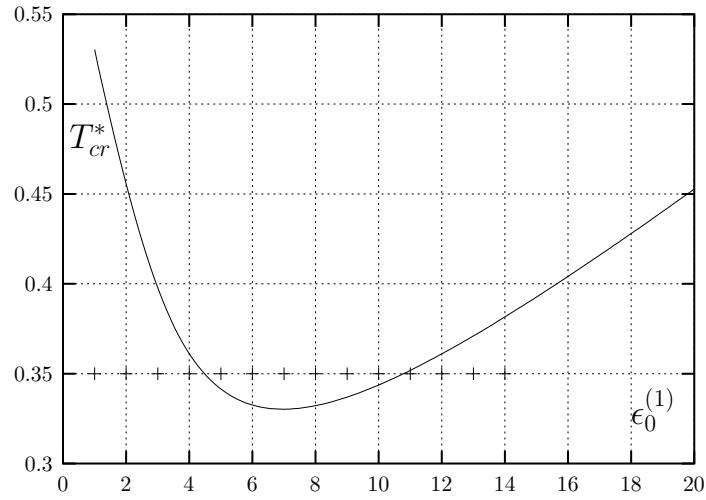
Figure 5.

Critical temperature T_{cr}^* of the two-Yukawa model versus $\epsilon_0^{(1)}$ at $D_\sigma = 0$ (solid line). Crosses denote the values of the temperature T^* and $\epsilon_0^{(1)}$ used to calculate pressure and excess internal energy presented in Figs. 6 and 7

Figure 7.

Excess internal energy of the two-Yukawa model at $T* = 0.35$, $D_\sigma = 0$ and $\epsilon_0^{(1)} = 1$, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 from the bottom to the top at $\rho^* = 0.8$
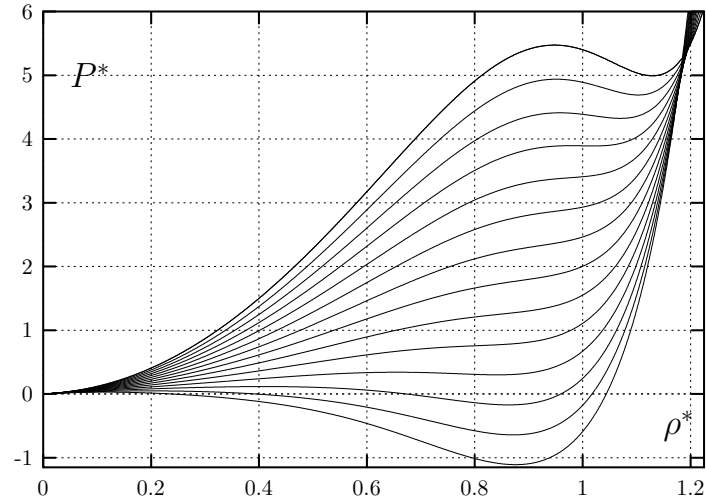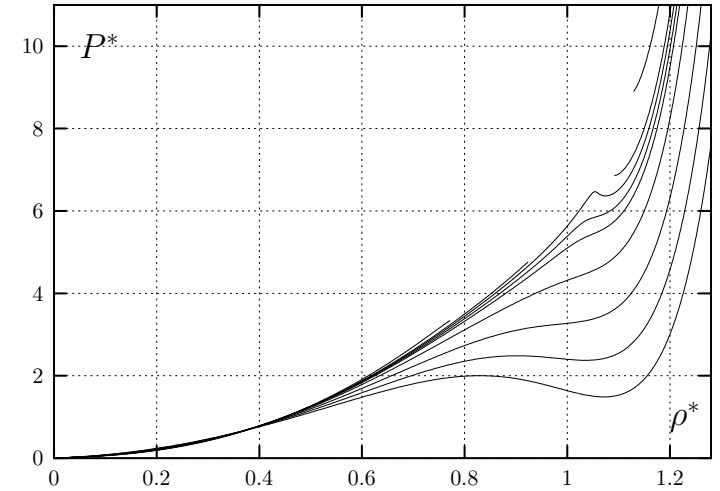
Figure 6.

Pressure isotherms of the two-Yukawa model at $T* = 0.35$, $D_\sigma = 0$ and $\epsilon_0^{(1)} = 1$, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 from the bottom to the top at $\rho^* = 0.8$

Figure 8.

Pressure isotherms of the two-Yukawa model at $T* = 0.298$, $\epsilon_0^{(1)} = 8$ and $D_\sigma = 0$, 0.005, 0.01, 0.015, 0.018, 0.019, 0.02, 0.021, 0.025 from the bottom to the top at $\rho^* = 1$
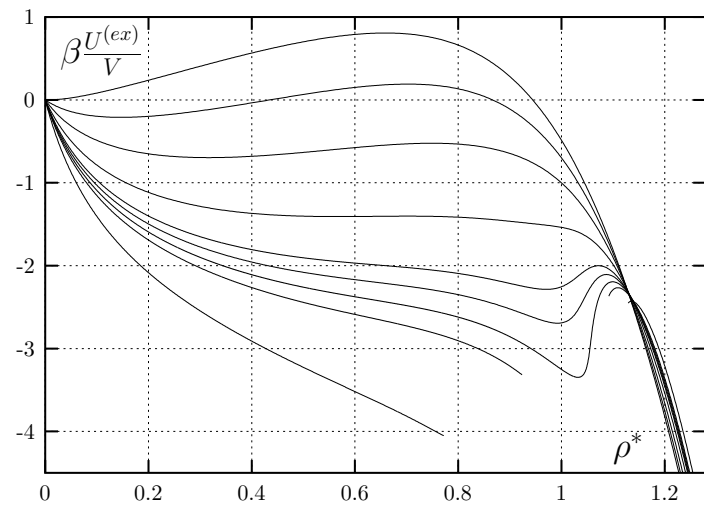
Figure 9.

Excess internal energy of the two-Yukawa model at $T* = 0.298$, $\epsilon_0^{(1)} = 8$ and $D_\sigma = 0$, 0.005, 0.01, 0.015, 0.018, 0.019, 0.02, 0.021, 0.025 from the top to the bottom at $\rho^* = 0.6$

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