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СИСТЕМ

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PHASE COEXISTENCE IN POLYDISPERSE MULTI-YUKAWA
HARD-SPHERE FLUID

ЛЬВІВ

Співіснування фаз в полідисперсній рідині твердих сфер з багатьма юкавівськими потенціалами

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Анотація. Запропоновано модель рідини полідисперсних твердих сфер з багатьма юкавівськими потенціалами та аналітично описано її термодинамічні властивості в високотемпературному наближенні та в наближенні Ван дер Ваальса. Показано, що в обох наближеннях модель належить до класу так званих моделей з "заокругленою" вільною енергією, тобто моделей, термодинамічні властивості яких (вільна енергія, тиск, хімічний потенціал) визначаються скінченою кількістю узагальнених моментів. Скориставшись цією властивістю, була порахована повна фазова діаграма з бінодалями та кривими співіснування точок роси в наближенні Ван дер Ваальса. Проведено аналіз та порівняння отриманих результатів з відповідними результатами середньо-сферичного наближення, що дозволило встановити межу застосовності наближення Ван дер Ваальса.

Phase coexistence in polydisperse multi-Yukawa hard-sphere fluid

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Abstract. Polydisperse multi-Yukawa hard-sphere fluid model is proposed and analytical description of its thermodynamical properties is developed using van der Waals (vdW) approximation and high temperature approximation (HTA). It is demonstated that in the frames of both approximations the model belongs to the class of the "truncatable free energy models", i.e. the models with thermodynamical properties (Helmholtz free energy, pressure, chemical potential) defined by the finite number of generalized moments. Using this property the complete phase diagram, including binodal curves and cloud and shadow curves, is calculated using vdW approximation. Analysis of our results and their comparison with corresponding results obtained earlier via mean spherical approximation (MSA) is carried out, which allows us to establish the limitations of vdW approach in polydisperse case.

1. Introduction

Using microscopic liquid state theories [1], it has become meanwhile a standard task to determine phase coexistence in two- or even three-component fluid mixtures. However, when proceeding to *polydisperse* liquid mixtures (which can be viewed as a mixture with an infinite number of components), the situation is considerably more complex [2]; methods developed up to now to calculate phase diagrams for such systems have not yet reached the high level of sophistication as in concepts for systems with a *finite* number of components. This is the more deplorable since the (formally) infinite number of components promises a very intriguing phase coexistence behavior with possibly new phases and phase transitions. In addition, phenomena associated to the phase behavior of polydisperse systems, such as fractionation, are also of technological relevance.

Most of the concepts currently used to study polydisperse systems view such a system as a mixture with an infinite number of components, each of them characterized by a continuous variable ξ, which is distributed according to a distribution function $F(\xi)$; it should be noted that ξ can also be a set of variables. The set of concentrations $\{c_i\}$ in a mixture with a finite number of components is replaced by this distribution function, $F(\xi)$, which is positive and normalized, i.e., $\int_0^\infty d\xi \, F(\xi) = 1$. $F(\xi_0)d\xi$ is then the fraction of particles with the parameter ξ located in an infinite interval of width $d\xi$ around ξ_0.

The main problem when dealing with the phase behavior in polydisperse mixtures is the fact that we are now faced with a formally infinite number of coexistence equations for the two daughter phases: e.g. the Helmholtz free energy is now defined in a space of infinite dimensionality, which makes the task of building the common tangent plane construction intractable. On the level of the coexistence equations of equal pressure and chemical potentials of the coexisting phases at fixed temperature T this means that one has to solve the infinitely many equations

$$P^{(1)} = P^{(2)} \qquad \mu^{(1)}(\xi) = \mu^{(2)}(\xi) \quad \text{for all } \xi. \qquad (1)$$

For a given parent distribution $F_0(\xi)$ solution of this set of equations then leads to the unknown daughter distributions $F_1(\xi)$ and $F_2(\xi)$ of the coexisting phases. Solution of this problem for a general system, where P and the $\mu(\xi)$ have to be calculated numerically (with some suitable liquid state theory) remain up to date yet unsolved. However, for a few models it is possible to circumvent this problem successfully: this applies for those systems where the thermodynamic properties can be expressed – within a certain liquid state approximation – by a finite number of generalized moments of the distribution function $F(\xi)$; models that belong to this class are called "truncatable free energy models". In those cases it is then possible to map the phase equilibrium conditions for a polydisperse mixture (1) onto a system of coupled non-linear equations for the corresponding generalized moments of the distribution functions $F^{(\alpha)}(\xi)$ of the coexisting phases. First steps in these directions were made with van der Waals (vdW) models [3,4]; indeed results for complete phase diagrams (i.e. including cloud- and shadow-curves as well as binodals) could be presented. Recently an attempt to go beyond a vdW model has been successfully realized [5] and complete two-phase diagram of the polydisperse one-Yukawa hard-sphere mixture was calculated using mean spherical approximation (MSA).

In this contribution we extend the vdW theory proposed recently [4] to the case of polydisperse hard-sphere Yukawa fluid and compare the numerical results for the complete phase diagram with corresponding results of the MSA [5]. In addition we consider polydisperse version of the multi-Yukawa hard-sphere fluid with each coefficient of the Yukawa potential represented as a sum of arbitrary number of factorized coefficients. It is demonstrated that in the frames of the high temperature approximation (HTA) this model belongs to the class of the truncatable free energy models. The multi-Yukawa version of the model is very flexible and can be used to successfully represent a large variety of the realistic potentials, including Lennard-Jones potential [6,7].

The paper is organized as follows. In the next section we present the phase equilibrium conditions for the multicomponent system and generalize them for polydisperse case. We outlined here the numerical scheme, which is similar to that developed earlier [4] and allows one to solve the corresponding set of equations and calculate the complete two-phase diagram for truncated free energy models. In Section III muti-Yukawa multicomponent hard-sphere model is defined and its thermodynamical properties are presented in terms of the generalized moments of the distribution function using HTA and vdW approximation. Distribution function is discussed in Section IV and in Section V we present our numerical results for the complete two-phase diagram. Finally in Section VI we collect our conclusions.

2. Phase equilibrium conditions

In dealing with polydisperse fluids it is convenient to start with the version of the system with arbitrary but finite number of components

and on the final step switch all the expressions to polydisperse case.

2.1. Multicomponent case

We consider p-component system with q coexisting phases. Each phase consists of $N_i^{(\alpha)}$ particles of species i and occupies the volume $V^{(\alpha)}$, where the upper index α denote the phase. It is assumed that the total number of the particles $N_i^{(0)}$ of species i and total volume $V^{(0)}$ of the system are held constant, i.e.

$$V^{(0)} = \sum_{\alpha=1}^{q} V^{(\alpha)} \tag{2}$$

$$N_i^{(0)} = \sum_{\alpha=1}^{q} N_i^{(\alpha)}, \quad i = 1, \ldots, p. \tag{3}$$

Hereafter the value of the upper index $\alpha = 0$ denotes the properties of the mother phase, which under certain conditions can be separated into q coexisting phases.

Helmholtz free energy A of such system is

$$A = \sum_{\alpha=1}^{q} A^{(\alpha)}\left(T, V^{(\alpha)}, \left\{N_i^{(\alpha)}\right\}\right) \tag{4}$$

where $\left\{N_i^{(\alpha)}\right\}$ denotes the set $N_1^{(\alpha)}, N_2^{(\alpha)}, ..., N_p^{(\alpha)}$. At equilibrium the free energy (4) has its minimum value provided that conditions (2) and (3) are satisfied. To find the minimum under these restrictions we will utilize Lagrange multiplier method. We have

$$
\begin{aligned}
A_{min} &= \sum_{\alpha=1}^{q} A^{(\alpha)}\left(T, V^{(\alpha)}, \left\{N_i^{(\alpha)}\right\}\right) \\
&+ \sum_{i=1}^{q} \lambda_i \left(N_i^{(0)} - \sum_{\alpha=1}^{q} N_i^{(\alpha)}\right) + \delta \left(V^{(0)} - \sum_{\alpha=1}^{q} V^{(\alpha)}\right)
\end{aligned} \tag{5}
$$

where λ_i and δ are Lagrange multipliers. Minimization of the functions A_{min} yield the set of equations for the unknowns λ_i, δ, $N_i^{(\alpha)}$ and $V^{(\alpha)}$

$$\frac{\partial A_{min}}{\partial N_i^{(\beta)}} = \frac{\partial A^{(\beta)}}{\partial N_i^{(\beta)}} - \lambda_i = 0, \quad i = 1, \ldots, p \tag{6}$$

$$\frac{\partial A_{min}}{\partial V^{(\beta)}} = \frac{\partial A^{(\beta)}}{\partial V^{(\beta)}} - \delta = 0 \tag{7}$$

which finally gives the following phase equilibrium conditions for multicomponent system

$$\mu_i^{(1)}\left(T, V^{(1)}, \left\{N_i^{(1)}\right\}\right) = \ldots = \mu_i^{(q)}\left(T, V^{(q)}, \left\{N_i^{(q)}\right\}\right), \quad i = 1, \ldots, p, \tag{8}$$

and

$$P^{(1)}\left(T, V^{(1)}, \left\{N_i^{(1)}\right\}\right) = \ldots = P^{(q)}\left(T, V^{(q)}, \left\{N_i^{(q)}\right\}\right). \tag{9}$$

where $\mu_i^{(\alpha)}$ is the chemical potential of the particles of species i in the phase α and $P^{(\alpha)}$ is the pressure of the phase α. Solution of this set of $(p+1)(q-1)$ equations together with the set of $p+1$ additional conditions (2) and (3) will give us $(p+1)q$ unknowns $N_i^{(\alpha)}, V^{(\alpha)}, \quad i = 1, \ldots, p, \quad \alpha = 1, \ldots, q,$. Note, that each phase will differ not only by its volume, but also by its distribution of the particles of different species.

2.2. Polydisperse case

To extend the phase equilibrium conditions (8) and (9) to the case of polydisperse system it is more convenient to use instead of the set of variables $V^{(\alpha)}$ and $N_i^{(\alpha)}$ the set, which includes the density of the phase α, $\rho^{(\alpha)} = N^{(\alpha)}/V^{(\alpha)}$, and two types of the fractions, i.e.

$$x_i^{(\alpha)} = N_i^{(\alpha)}/N^{(\alpha)} \tag{10}$$

$$x^{(\alpha)} = N^{(\alpha)}/N^{(0)}, \tag{11}$$

where

$$N^{(\alpha)} = \sum_{i=1}^{p} N_i^{(\alpha)}. \tag{12}$$

Now the set of equilibrium conditions (8) and (9) together with additional constrains (2) and (3) can be recast in the following form

$$\mu_i^{(1)}\left(T, \rho^{(1)}, \left\{x_i^{(1)}\right\}\right) = \ldots = \mu_i^{(q)}\left(T, \rho^{(q)}, \left\{x_i^{(q)}\right\}\right), \tag{13}$$

$$P^{(1)}\left(T, \rho^{(1)}, \left\{x_i^{(1)}\right\}\right) = \ldots = P^{(q)}\left(T, \rho^{(q)}, \left\{x_i^{(q)}\right\}\right), \tag{14}$$

$$v^{(0)} = \sum_{\alpha=1}^{q} v^{(\alpha)} x^{(\alpha)}, \tag{15}$$

$$x_i^{(0)} = \sum_{\alpha=1}^{q} x_i^{(\alpha)} x^{(\alpha)}, \tag{16}$$

with the fractions $x_i^{(\alpha)}$ satisfying the following normalizing condition

$$\sum_{i=1}^{p} x_i^{(\alpha)} = 1, \tag{17}$$

where $v^{(0)} = 1/\rho^{(0)}$ and $v^{(\alpha)} = 1/\rho^{(\alpha)}$.

Now extension of the phase equilibrium conditions to the case of polydisperse system is straightforward and can be achieved by switching from discrete species index i to its continuous counterpart ξ via the following substitution rule [8]

$$x_i \rightarrow F(\xi) \, d\xi, \tag{18}$$

with $F(\xi)$ being a positive distribution function normalized to 1. It should be pointed out that ξ can be multidimensional. Due to this substitution, summations over i in (13)-(17) become integrations over ξ and thermodynamic properties become *functionals* of the distribution function $F(\xi)$, which we will indicate by the square brackets. We have

$$\mu^{(1)}\left(\xi, T, \rho^{(1)}, \left[F^{(1)}(\xi)\right]\right) = \ldots = \mu^{(q)}\left(\xi, T, \rho^{(q)}, \left[F^{(q)}(\xi)\right]\right), \tag{19}$$

$$P^{(1)}\left(T, \rho^{(1)}, \left[F^{(1)}(\xi)\right]\right) = \ldots = P^{(q)}\left(T, \rho^{(q)}, \left[F^{(q)}(\xi)\right]\right). \tag{20}$$

$$v^{(0)} = \sum_{\alpha=1}^{q} v^{(\alpha)} x^{(\alpha)}, \tag{21}$$

$$F^{(0)}(\xi) = \sum_{\alpha=1}^{q} F^{(\alpha)}(\xi) x^{(\alpha)}, \tag{22}$$

$$\int F^{(\alpha)}(\xi) \, d\xi = 1. \tag{23}$$

Formally the set of relations (19)-(23) form a closed set of equations for the unknowns $\rho^{(\alpha)}$, $x^{(\alpha)}$ and $F^{(\alpha)}(\xi)$, which can be solved as soon as expressions for the thermodynamical properties of the corresponding polydisperse system at hand will be available.

At present this problem seems to be solvable only for the so-called truncatable free energy models, i.e. these models, for which thermodynamic properties can be represented by a finite number of (generalized) moments of the distribution function $F(\xi)$.

2.3. Two-phase equilibrium conditions for the free energy truncatable models

In this section we will consider two-phase equilibrium conditions specialized to the case of truncatable free energy models. In our consideration we will follow the general scheme developed by Bellier-Castella et al. [4]. We assume that thermodynamical properties of the model depends on $K+1$ generalized moments $m_0, m_1, ..., m_K$, which are defined as follows

$$m_l = \rho \int d\xi \, m_l(\xi) \, F(\xi), \qquad l \neq 0 \tag{24}$$

and $m_0 = \rho$.

Now the set of the conditions (19)– (23) takes the following form

$$\mu^{(1)}\left(\xi, T, \left\{m^{(1)}\right\}\right) = \mu^{(2)}\left(\xi, T, \left\{m^{(2)}\right\}\right), \tag{25}$$

$$P^{(1)}\left(T, \left\{m^{(1)}\right\}\right) = P^{(2)}\left(T, \left\{m^{(2)}\right\}\right). \tag{26}$$

$$\rho^{(2)} F^{(2)}(\xi) = \frac{\rho^{(1)} - \rho^{(2)}}{\rho^{(1)} - \rho^{(0)}} \rho^{(0)} F^{(0)}(\xi) + \frac{\rho^{(2)} - \rho^{(0)}}{\rho^{(1)} - \rho^{(0)}} \rho^{(1)} F^{(1)}(\xi), \tag{27}$$

$$\int F^{(\alpha)}(\xi) \, d\xi = 1. \tag{28}$$

where $\left\{m^{(\alpha)}\right\}$ denotes the set $m_0^{(\alpha)}, m_1^{(\alpha)}, ..., m_K^{(\alpha)}$.

Condition on the equality of the chemical potentials in two phases (25) can be written in terms of the excess values of the chemical potentials $\mu_{ex}^{(\alpha)}$

$$\ln\left(\frac{F^{(1)}(\xi)\,\rho^{(1)}}{F^{(2)}(\xi)\,\rho^{(2)}}\right) = \Delta\mu_{ex}\left(\xi, T, \left\{m^{(1)}\right\}, \left\{m^{(2)}\right\}\right), \tag{29}$$

where

$$\Delta\mu_{ex}\left(\xi, T, \left\{m^{(1)}\right\}, \left\{m^{(2)}\right\}\right) =$$
$$= \mu_{ex}^{(2)}\left(\xi, T, \left\{m^{(2)}\right\}\right) - \mu_{ex}^{(1)}\left(\xi, T, \left\{m^{(1)}\right\}\right). \tag{30}$$

This allows us to relate distribution functions $F^{(\alpha)}(\xi)$ in the two different phases

$$F^{(1)}(\xi) = F^{(2)}(\xi) A_{12}\left(\xi, T, \left\{m^{(1)}\right\}\left\{m^{(2)}\right\}\right), \qquad (31)$$

where

$$A_{12}\left(\xi, T, \left\{m^{(1)}\right\}\left\{m^{(2)}\right\}\right) = \frac{\rho^{(2)}}{\rho^{(1)}} \exp\left[\Delta\mu_{ex}\left(\xi, T, \left\{m^{(1)}\right\}\left\{m^{(2)}\right\}\right)\right], \qquad (32)$$

Taking into account (27), (31) and definition (24) we get

$$F^{(1)}(\xi) = F^{(0)}(\xi) H\left(\xi, T, m_0^{(2)}, \left\{m^{(1)}\right\}\left\{m^{(0)}\right\}\right), \qquad (33)$$

$$m_k^{(2)} = \frac{\rho^{(1)} - \rho^{(2)}}{\rho^{(1)} - \rho^{(0)}} m_k^{(0)} + \frac{\rho^{(2)} - \rho^{(0)}}{\rho^{(1)} - \rho^{(0)}} m_k^{(1)}, \qquad (34)$$

where

$$H\left(\xi, T, m_0^{(2)}, \left\{m^{(1)}\right\}\left\{m^{(0)}\right\}\right) = \qquad (35)$$

$$\frac{\left(\rho^{(1)} - \rho^{(2)}\right) A_{12}\left(\xi, T, m_0^{(2)}, \left\{m^{(1)}\right\}\left\{m^{(0)}\right\}\right)}{\left(\frac{\rho^{(2)}\rho^{(1)}}{\rho^{(0)}} - \rho^{(2)}\right) + \left(\rho^{(1)} - \frac{\rho^{(2)}\rho^{(1)}}{\rho^{(0)}}\right) A_{12}\left(\xi, T, m_0^{(2)}, \left\{m^{(1)}\right\}\left\{m^{(0)}\right\}\right)}.$$

Note that H and A_{12} depend on the all moments of the phases 0 and 1 and only on the zero moment (density) of the phase 2, since all the rest of the moments of the second phase are connected to the moments of the phases 0 and 1 via relation (34)

Now the set of equations (25) and (26) can be solved in terms of the moments of coexisting phases. The corresponding set of equations follows from the definition (24)

$$m_k^{(1)} = m_0^{(1)} \int d\xi\, m_k^{(1)}(\xi)\, F^{(0)}(\xi)\, H\left(\xi, T, m_0^{(2)}, \left\{m^{(1)}\right\}\left\{m^{(0)}\right\}\right) \quad (36)$$

where $k = 1, 2, ..., K$. Equation (36) together with the equation for the equality of the pressure in both phases

$$P^{(1)}\left(\xi, T, \left\{m^{(1)}\right\}\left\{m^{(0)}\right\}\right) = P^{(2)}\left(\xi, T, m_0^{(2)}, \left\{m^{(1)}\right\}\left\{m^{(0)}\right\}\right) \quad (37)$$

and normalizing condition (28) for either $\alpha = 1$ or $\alpha = 2$ form a closed set of equations for $K+2$ unknowns $\left\{m^{(1)}\right\}, m_0^{(2)}$. Thus solution of the set of equations (28), (36), (37) for a given temperature T, density of the parent phase $\rho^{(0)}$, and parent distribution function $F^{(0)}(\xi)$ gives the coexisting

densities $\rho^{(\alpha)}$ of the two daughter phases and corresponding distribution functions $F^{(\alpha)}(\xi)$, $\alpha = 1, 2$. The coexistence densities for different temperatures fix binodals, which are terminated at a temperature for which the density of one of the phases is equal to the density $\rho^{(0)}$ of the parent phase; these termination points form the so-called cloud and shadow curves which thus represent an envelope for the binodals. Cloud and shadow curves intersect at the critical point, which is characterized by the critical temperature T_{cr} and critical density $\rho_{cr} = \rho^{(1)} = \rho^{(2)} = \rho^{(0)}$. Thus only for $\rho^{(0)} = \rho_{cr}$ the two branches of the binodal meet at the critical point.

By definition, states located on the cloud curve are characterized that they coexist with a state (localized on the shadow curve) where an infinitely small amount of the other phase emerges. Thus the cloud and shadow curves can be obtained as special solutions of the general phase coexistence problem, when the properties of one phase are equal to the properties of the parent phase: assuming, e.g., the second phase to be the cloud phase, i.e. $\rho^{(2)} = \rho^{(0)}$, and following the scheme presented above we will end up with the same set of equations, (28), (36), (37), but with $\rho^{(2)}$ and $F^{(2)}(\xi)$ substituted by $\rho^{(0)}$ and $F^{(0)}(\xi)$, respectively. Note that $F^{(2)}(\xi) = F^{(0)}(\xi)$ is now known, but $\rho^{(0)}$ is unknown; it is obtained from the solution of the appropriately modified set of equations (28), (36), (37).

3. Thermodynamical properties of the multi-Yukawa hard-sphere fluid

Let us assume that interparticle interaction in the system is represented by the multi-Yukawa hard-sphere potential

$$V_{ij}(r) = \begin{cases} \infty, & \text{for } r \le \sigma_{ij}, \\ -\frac{1}{r} \sum_n \sum_m A_i^{(nm)} A_j^{(nm)} e^{-z_n(r-\sigma_{ij})} & \text{for } r > \sigma_{ij}, \end{cases} \qquad (38)$$

where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and σ_i is the hard-sphere diameter of the particle of species i.

The form assumed for the pair potential is very flexible and it is possible to model a large variety of the realistic potentials by appropriate choice for the coefficients A_i^{nm} and z_n [6,7].

3.1. High temperature approximation

The high temperature approximation (HTA), applied in this study, will be derived using Gibbs-Bogoliubov inequality [1]. We start with the definition of the Helmholtz free energy A

$$-\beta A = \ln \int d\Gamma e^{-\beta H(\Gamma)}, \tag{39}$$

where $\beta = \frac{1}{k_b T}$ and $H(\Gamma)$ is the system Hamiltonian defined on a phase space Γ. Let us assume, that the Hamiltonian of the corresponding reference system is $H_0(\Gamma)$. Subtracting the free energy of the reference system A_0 from the free energy (39) we have

$$-\beta (A - A_0) = \ln \frac{\int d\Gamma e^{-\beta(H(\Gamma)-H_0(\Gamma))} e^{-\beta H_0(\Gamma)}}{\int d\Gamma e^{-\beta H_0(\Gamma)}} = \ln \left\langle e^{-\beta(H-H_0)} \right\rangle_0, \tag{40}$$

where

$$\langle \ldots \rangle_0 = \ln \frac{\int d\Gamma \left(\ldots \right) e^{-\beta H_0(\Gamma)}}{\int d\Gamma e^{-\beta H_0(\Gamma)}}. \tag{41}$$

Taking into account the convexity property of the logarithm it can be proved that

$$\ln \left\langle e^{-\beta(H-H_0)} \right\rangle_0 \geq \left\langle \ln e^{-\beta(H-H_0)} \right\rangle_0, \tag{42}$$

which gives Gibbs-Bogoliubov inequality

$$A - A_0 \leq \langle (H - H_0) \rangle_0. \tag{43}$$

Using the hard-sphere system as a reference system and choosing the upper limit of this inequality the HTA is recovered

$$\frac{\beta A}{V} = \frac{\beta A_{HS}}{V} + \frac{1}{2} \beta \sum_i \sum_j \rho_i \rho_j \int d\vec{r} 4\pi r^2 V_{ij}(r) g_{ij}^{HS}(r). \tag{44}$$

where $g_{ij}^{HS}(r)$ is the hard-sphere radial distribution function. Substituting into (44) expression for the pair potential (38) we have

$$\frac{\beta A}{V} = \frac{\beta A_{HS}}{V} - 2\pi\beta \sum_i \sum_j \rho_i \rho_j \sum_n \sum_m A_i^{(nm)} A_j^{(nm)} \tilde{G}_{ij}^{HS}(z_n). \tag{45}$$

where $\tilde{G}_{ij}^{HS}(z_n)$ is the Laplace transform of hard-sphere radial distribution function

$$\tilde{G}_{ij}^{(HS)}(z_n) = e^{z_n \sigma_{ij}} \int dr r e^{-z_n r} g_{ij}^{(HS)}(r). \tag{46}$$

We will be using here Percus-Yewick approximation for hard-sphere radial distribution function, since analytical expression for its Laplace transform is known [9, 10]

$$\tilde{G}_{ij}^{(HS)}(z_n) = \frac{\Delta}{z_n^2 \tilde{D}_0^{(n)}} \left\{ z_n \left[\sigma_{ij} + \sigma_i \sigma_j \frac{\pi}{4\Delta} m_2 \right] + 1 + \frac{\pi}{2\Delta} m_3 + \right.$$
$$\left. + \frac{\pi z_n}{2\Delta} \left(m_2^{(n)} - 2\sigma_{ij} m_1^{(n)} + \sigma_i \sigma_j m_0^{(n)} \right) \right\}, \tag{47}$$

where

$$\tilde{D}_0^{(n)} = \Delta^2 - \frac{2\pi}{z_n} \left(\Delta + \frac{1}{2}\pi m_3 \right) \left(m_0^{(n)} + \frac{1}{2} m_2 \right) -$$
$$-2\pi \left\{ \Delta m_1^{(n)} + \frac{1}{4}\pi \left[m_2^{(n)} \left(m_2 + 2m_0^{(n)} \right) - 2 \left(m_1^{(n)} \right)^2 \right] \right\}, \tag{48}$$

$$m_l = \sum_k \rho_k m_l(k); \quad m_l(k) = \sigma_k^l, \tag{49}$$

$$m_l^{(n)} = \sum_k \rho_k m_l^{(n)}(k); \quad m_l^{(n)}(k) = \sigma_k^l \varphi(z_n, \sigma_k), \tag{50}$$

$$\Delta = 1 - \pi m_3 / 6, \tag{51}$$

$$\varphi(z_n, \sigma) = \frac{1}{z_n^2} \left(1 - z_n \sigma - e^{-z_n \sigma} \right) \tag{52}$$

To extend the expressions for thermodynamical properties for polydisperse case it is convenient to represent expression for Helmholtz free energy (45) in terms of the moments. Introducing in addition to already existing moments m_l and $m_l^{(n)}$ one more

$$m_l^{(nm)} = \sum_k \rho_k m_l^{(nm)}(k); \quad m_l^{(nm)}(k) = \sigma_k^l A_k^{(nm)}, \tag{53}$$

we have

$$\frac{\beta A}{V} = \frac{\beta A_{HS}}{V} - 2\pi\beta \sum_{n,m} \frac{Q_0^{(nm)}}{z_n^2 \tilde{D}_0^{(n)}} \tag{54}$$

where

$$Q_0^{(nm)} = z_n \frac{\pi}{2} \left(\frac{m_2}{2} + m_0^{(n)} \right) m_1^{(nm)} m_1^{(nm)} +$$
$$+ z_n \left(\Delta - \pi m_1^{(n)} \right) m_0^{(nm)} m_1^{(nm)} +$$
$$+ \left(\Delta + \frac{\pi}{2} m_3 + \frac{\pi z_n}{2} m_2^{(n)} \right) m_0^{(nm)} m_0^{(nm)}. \tag{55}$$

Differentiating expression for Helmholtz free energy (54) with respect to the density we will have the following expression for the chemical potential

$$\beta\mu_k = \frac{\partial}{\partial\rho_k}\left(\frac{\beta A}{V}\right) =$$

$$\beta\mu_k^{(HS)} - 2\pi\beta\sum_{n,m}\frac{1}{z_n^2\tilde{D}_0^{(n)}}\left(\frac{\partial Q_0^{(nm)}}{\partial\rho_k} - \frac{Q_0^{(nm)}}{z_n^2\tilde{D}_0^{(n)}}\frac{\partial\tilde{D}_0^{(n)}}{\partial\rho_k}\right) \quad (56)$$

where

$$\frac{\partial Q_0^{(nm)}}{\partial\rho_k} = -z_n\left(\frac{\pi}{6}m_3(k) + \pi m_1^{(n)}(k)\right)m_1^{(nm)}m_0^{(nm)} +$$

$$+ z_n\left(\Delta - \pi m_1^{(n)}\right)\left(m_0^{(nm)}m_1^{(nm)}(k) + m_0^{(nm)}(k)m_1^{(nm)}\right) +$$

$$+ z_n\frac{\pi}{4}\left(m_2(k) + 2m_0^{(n)}(k)\right)m_1^{(nm)}m_1^{(nm)} +$$

$$+ z_n\frac{\pi}{2}\left(m_2 + 2m_0^{(n)}\right)m_1^{(nm)}m_1^{(nm)}(k) +$$

$$+ \left(\frac{\pi}{3}m_3(k) + \frac{z_n\pi}{2}m_2^{(n)}(k)\right)m_0^{(nm)}m_0^{(nm)} +$$

$$+ 2\left(\Delta + \frac{\pi}{2}m_3 + \frac{z_n\pi}{2}m_2^{(n)}\right)m_0^{(nm)}m_0^{(nm)}(k) \quad (57)$$

$$\frac{1}{2\pi}\frac{\partial\tilde{D}_0^{(n)}}{\partial\rho_k} = \frac{1}{3}\pi m_3(k)\left[\frac{1}{2}m_1^{(n)} - \frac{1}{z_n}\left(m_0^{(n)} + \frac{1}{2}m_2\right)\right]$$

$$- \Delta\left(\frac{1}{6}m_3(k) + m_1^{(n)}(k)\right) \quad (58)$$

$$- \left(\frac{1}{2}m_2(k) + m_0^{(n)}(k)\right)\left[\frac{1}{z_n}\left(\Delta + \frac{1}{2}\pi m_3\right) + \frac{1}{2}\pi m_2^{(n)}\right]$$

$$- \frac{1}{4}\pi m_2^{(n)}(k)\left(m_2 + 2m_0^{(n)}\right) + \pi m_1^{(n)}m_1^{(n)}(k).$$

The pressure P of the system can be calculated invoking the following general relation

$$\beta P = \beta\sum_k\rho_k\mu_k - \frac{\beta A}{V} \quad (59)$$

Here $\mu_{HS,k}$ and P_{HS} are the hard-sphere chemical potential and pressure, which in this study is represented by the Mansoori-Carnahan-Starling-Leland approximation [11]

$$\mu_{HS,k} = \mu_{id,k} + \mu_{HS,k}^{ex}, \quad (60)$$

where

$$\beta\mu_{HS,k}^{ex} = \frac{\beta A_{cs}^{ex}}{N} + \left(\frac{m_2}{m_3}\right)^2\left[3\sigma_k^2 - \frac{m_2}{m_0 m_3}\left(m_3 + 2m_0\sigma_k^3\right)\right]\ln\Delta -$$

$$-\frac{\pi\sigma_k}{2\Delta}\left[\frac{1}{3}\left(\frac{m_2^3}{m_0 m_3^2} - 1\right)\sigma_k^2 m_0 - m_2 - \sigma_k m_1\right] -$$

$$-\frac{\pi m_2 m_1}{2m_0\Delta^2}\left(\Delta - \frac{\pi}{6}\sigma_k^3 m_0\right) + \frac{\pi\sigma_k^2 m_2^2}{2m_3\Delta^2} + \quad (61)$$

$$+\frac{\pi m_2^3}{6m_3^2 m_0\Delta}\left[\Delta\left(\sigma_k^3 m_0 + m_3\right) - \frac{\pi}{3}m_3 m_0\sigma_k^3\right]$$

and

$$\frac{\beta A_{cs}^{ex}}{N} = \left(\frac{m_2^3}{m_0 m_3^2} - 1\right)\ln\Delta + \frac{\pi}{2\Delta}\frac{m_2}{m_0}\left(m_1 + \frac{1}{3}\frac{m_2^2}{m_3\Delta}\right). \quad (62)$$

$$\beta P_{HS} = \frac{1}{\Delta}\left[m_0 + \frac{\pi}{2\Delta}m_1 m_2 + \frac{\pi^2}{12\Delta^2}m_2^3 - \frac{\pi^3}{216\Delta^2}m_2^3 m_3\right] \quad (63)$$

Expressions for thermodynamical properties (54)-(63) are written in terms of the moments (49)-(53) and their extension to the polydisperse case is straightforward. This goal can be achieved by substituting all the sums with respect to the discrete species index k by integration with respect to the multidimensional species index $\xi = (\sigma, \{A^{nm}\})$. Here $\{A^{(nm)}\}$ represent the set of all coefficients of the Yukawa potential (38). Now for the moments (49)-(53) and for the pressure expression (59) we have

$$m_l = \rho\int d\xi\, m_l(\xi)F(\xi),$$

$$m_l^{(n)} = \rho\int d\xi\, m_l^{(n)}(\xi)F(\xi),$$

$$m_l^{(nm)} = \rho\int d\xi\, m_l^{(nm)}(\xi)F(\xi) \quad (64)$$

and

$$P = \rho\int d\xi\, \mu(\xi)F(\xi) - \frac{A}{V}, \quad (65)$$

where

$$m_l(\xi) = \sigma^l$$

$$m_l^{(n)}(\xi) = \sigma^l \varphi_1(z_n, \sigma)$$

$$m_l^{(nm)}(\xi) = \sigma^l A^{(nm)} \tag{66}$$

One can see, that our multi-Yukawa hard-sphere system treated in the HTA belongs to the class of truncatable free energy model. Thus the formalism developed in the previous section can be used to predict the phase diagrams of the polydisperse version of the model.

3.2. van der Waals approximation

van der Waals approximation can be obtained using Bogoliubov inequality with the following radial distribution function for the reference system

$$g_{ij} = \Theta\left(r - \sigma_{ij}\right), \tag{67}$$

which gives

$$\int dr r e^{-sr} g_{ij}(r) = \left(\frac{\sigma_{ij}}{z_n} + \frac{1}{z_n^2}\right) e^{-z_n \sigma_{ij}}. \tag{68}$$

Now we have

$$
\begin{aligned}
f &= f_R - 2\pi \sum_i \sum_j \sum_n \sum_m \rho_i \rho_j A_i^{(nm)} A_j^{(nm)} \left(\frac{\sigma_{ij}}{z_n} + \frac{1}{z_n^2}\right) = \\
&= f_R - 2\pi \sum_n \sum_m \left(\frac{m_1^{(nm)} m_0^{(nm)}}{z_n} + \frac{m_0^{(nm)} m_0^{(nm)}}{z_n^2}\right),
\end{aligned}
\tag{69}
$$

where

$$f_R = k_b T \sum_i \rho_i \left\{\ln \Lambda_i^3 \rho_i - \ln \Delta - 1\right\}. \tag{70}$$

Similarly for the chemical potentials and pressure we obtain

$$\mu_k = \mu_{R,k} - 4\pi \sum_n \sum_m A_k^{(nm)} \left(\frac{m_1^{(nm)} + \sigma_k m_0^{(nm)}}{2z_n} + \frac{m_0^{(nm)}}{z_n^2}\right), \tag{71}$$

$$P = P_R - 2\pi \sum_n \sum_m \left(\frac{m_1^{(nm)} m_0^{(nm)}}{z_n} + \frac{m_0^{(nm)} m_0^{(nm)}}{z_n^2}\right), \tag{72}$$

where

$$\mu_{R,i} = k_b T \left\{\ln \Lambda_i^3 \rho_i - \ln \Delta + \frac{\pi m_0 \sigma_i^3}{6\Delta}\right\}, \tag{73}$$

$$P_R = k_b T \frac{m_0}{\Delta}. \tag{74}$$

4. The distribution

To illustrate the theory developed above in this study we choose the simplest one-Yukawa version of the model. This version have been studied previously [5] using mean spherical approximation (MSA). According to our choice all the coefficients $A_i^{(nm)}$ are equal zero, except $A_i^{(11)}$, i.e. $A_i^{(11)} = Z_i / \sqrt{\epsilon_0 \sigma_0}$. We will be using here van der Waals approximation and compare its results with results of more advanced MSA.

For the sake of simplicity we have chosen the distribution $F(\sigma, Z)$, which strongly correlate the size σ and the 'charge' parameter Z of the particles

$$F(\sigma, Z) = f(\sigma) \delta\left(Z - Z_0 \frac{\sigma^2}{\langle \sigma^2 \rangle}\right). \tag{75}$$

This choice states that the charge is proportional to the surface of the particles. For $f(\sigma)$ we have chosen the Beta-distribution, given by

$$f(\sigma) = B^{-1}(\alpha, \beta) \left(\frac{\sigma}{\sigma_m}\right)^{\alpha-1} \left(1 - \frac{\sigma}{\sigma_m}\right)^{\beta-1} \Theta(\sigma_m - \sigma) \Theta(\sigma) \tag{76}$$

Here $B(\alpha, \beta)$ is the beta function [12], α and β are related to the first ($\sigma_0 = \langle \sigma \rangle$) and the second ($\langle \sigma^2 \rangle$) moments of $f(\sigma)$ by

$$\alpha = \frac{\sigma_m - \sigma_0 (1 + D_\sigma)}{\sigma_m D_\sigma}; \quad \beta = \left(\frac{\sigma_m - \sigma_0}{\sigma_0}\right) \alpha \tag{77}$$

with $D_\sigma = \langle \sigma^2 \rangle / \sigma_0^2 - 1$.

5. Results and discussion

We now present results for the phase diagram of a system, which is characterized by a mother distribution function $f_0(\sigma)$ represented by the Beta-distribution (76) with $D_\sigma = 0.02$ and $\sigma_m = 2\sigma_0$. The screening length of the Yukawa potential was chosen to be $z\sigma_0 = 1.8$. In what

follows the temperature T and density ρ of the system will be represented by the dimensionless quantities $T^\star = kT/(\epsilon_0 Z_0^2)$ and $\rho^\star = \rho\sigma_0^3$, respectively.

In Figures 1 and 2 we show the phase diagram of the system in the $(T^\star, \rho^\star)$-plane obtained using MSA (Figure 1) and vdW approximation (Figure 2): they contain the cloud- and the shadow-curves, the critical binodals (see below) and in Figure 1 binodal for one selected $\rho_0^\star$-value ($\rho_0^\star = 0.03$). For the critical point MSA gives $T_{cr}^\star = 1.343$ and $\rho_{cr}^\star = 0.3527$. Parameters of the critical point, which follow from vdW are $T_{cr}^\star = 3.195$ and $\rho_{cr}^\star = 0.615$. For reference we have added the phase coexistence curve for a one component system ('oc'), treated as well in the MSA and vdW, characterized by a diameter $\sigma_{oc} = \sigma_0$ and a 'charge' parameter $Z_{oc} = Z_0$; for this system we extract (via extrapolation) the critical point to be located at $T_{cr;oc}^\star = 1.2373$ and $\rho_{cr;oc}^\star = 0.32$ in the case of the MSA and $T_{cr;oc}^\star = 3.075$ and $\rho_{cr;oc}^\star = 2/\pi \approx 0.6366$ in the case of vdW.

Quantitative predictions of the both theories for the critical point and overall position of the phase equilibrium curves are quite different, however there is certain degree of the qualitative similarity. This can be seen in Figure 3, where predictions of both MSA and vdW is plotted in the $(T^\star/T_{cr}^\star, \rho^\star/\rho_{cr}^\star)$ plane. The shape of the cloud and shadow curves are rather similar and the critical binodals almost coincide.

A more specific information about the composition of the coexisting phases can be extracted from the distribution functions of the two daughter phases, which give evidence of possible fractionation effects. For the two selected pairs of points on the phase coexistence curves (C_1, C_2 and E_1, E_2) at $T^\star/T_{cr}^\star = 0.67$ (Figure 3) the daughter distribution functions, $f_1(\sigma)$ and $f_2(\sigma)$, along with the mother distribution function, $f_0(\sigma)$, are shown in Figures 4 and 5, respectively. Points C_1 and C_2 are localized on the critical binodal ($\rho^\star = \rho_{cr}^\star$): while the particles of the fluid phase have – on the average – nearly the same size as in the homogeneous mother phase, the particles in the gas phase are on the average smaller; MSA predict slightly stronger shift in the direction of the smaller particles. Points E_1 and E_2 are localized on the cloud- and and on the shadow-curve: by definition $f_1(\sigma) = f_0(\sigma)$ and we find a remarkable shift of the maximum of $f_2(\sigma)$ towards larger particles in the case of the MSA predictions and much smaller shift in the case of vdW predictions.
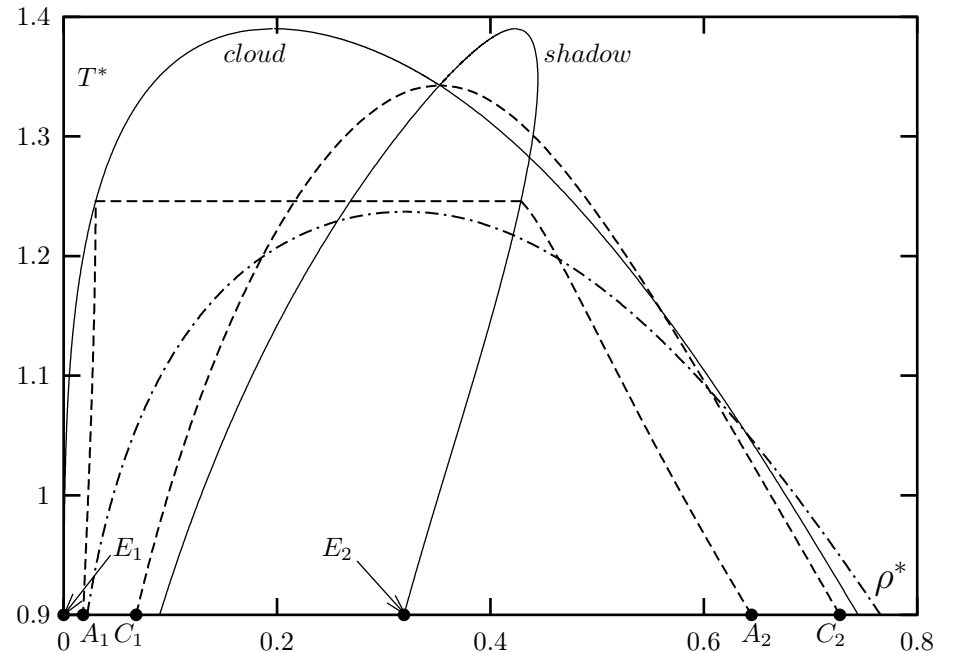

Figure 1. MSA phase diagram. Cloud- and shadow-curves are represented by the solid lines, binodal curves by the broken lines connecting the points, which mark the density of the corresponding mother phase, i.e. $\rho_0^* = 0.03$ (A_1- - -A_2), $\rho_0^* = \rho_c^* = 0.3527$ (C_1- - -C_2); the dash-dotted line denotes the binodal curve for the monodisperse HSY system. Here $T_{cr}^* = 1.343$ and $\rho_{cr}^* = 0.3527$.
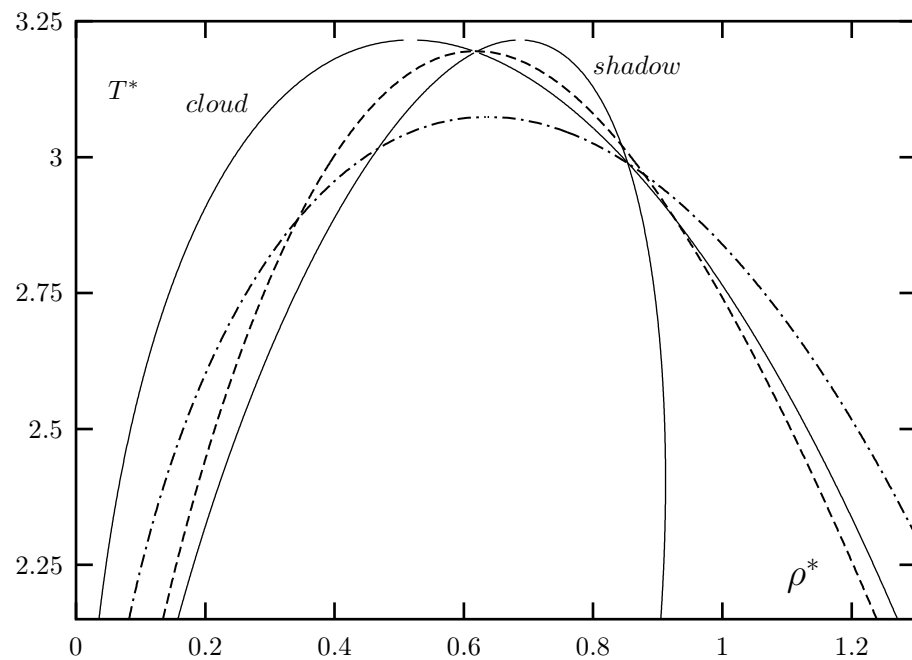
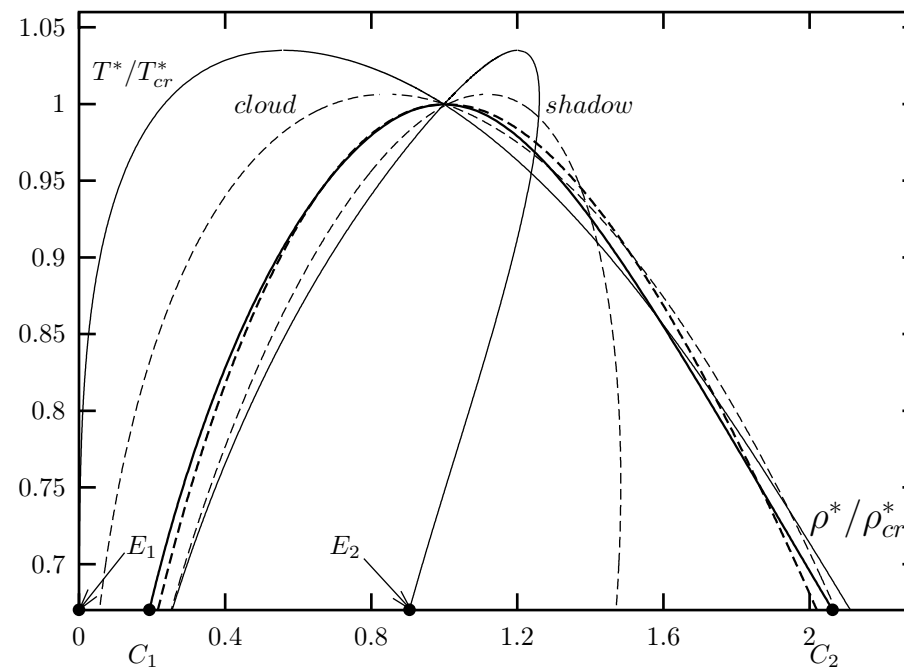Figure 2. vdW phase diagram. Notation is the same as in figure 1.

Figure 3. Comparison of the MSA (solid lines) and vdW (broken lines) predictions for the phase diagram (T^*/T^*_{cr} vs ρ^*/ρ^*_{cr}) of polydisperse HSY fluid.
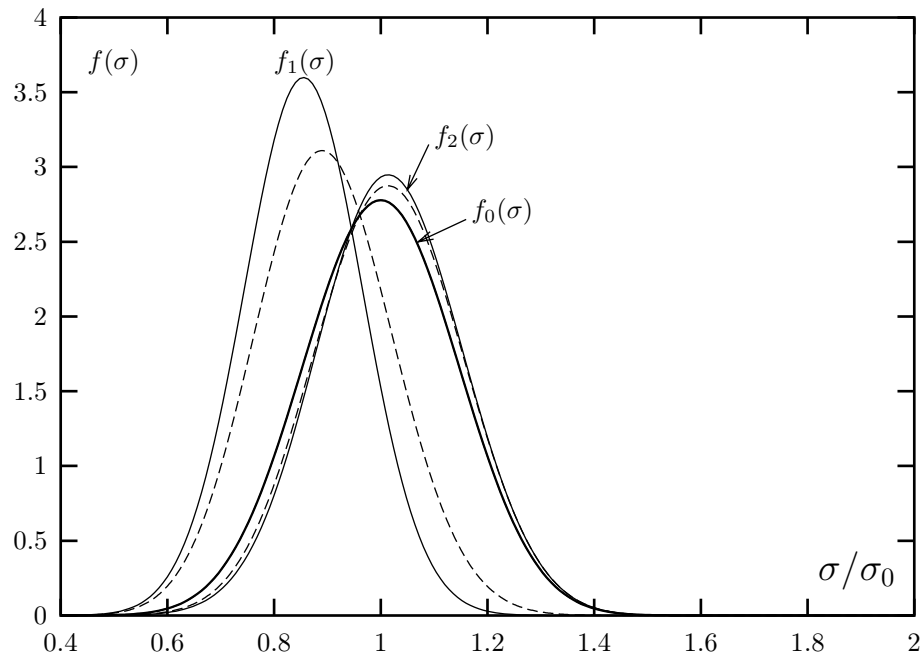
Figure 4. Mother $[f_0(\sigma)]$ and daughter $[f_1(\sigma)$ and $f_2(\sigma)]$ MSA (solid lines) and vdW (broken lines) distribution functions investigated for points C_1 and C_2.
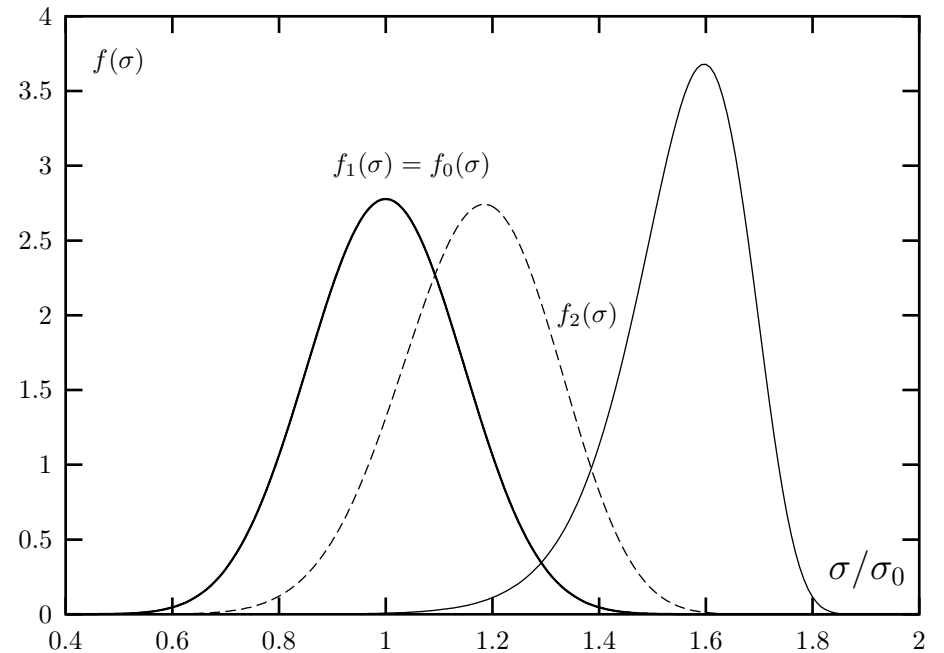

Figure 5. As Figure 4 for points E_1 and E_2.

6. Conclusions

(i) In the frames of the HTA description polydisperse mixture of multi-Yukawa hard-sphere fluids belongs to the class of 'truncatable free energy' models, i.e. thermodynamic functions required to calculate phase equilibria can be expressed by a finite number of generalized moments. As a consequence we could map the coexistence relations that are particularly complex for polydisperse systems onto a coupled set of highly non-linear equations for the unknown moments of the daughter distribution functions.

(ii) vdW approach and MSA theory give rather different quantitative predictions for the phase diagram and fractionation effects of polydisperse one-Yukawa hard-sphere fluid. However both theories give similar qualitative description of the phase diagram and cloud-shadow curves in terms of the reduced temperature T^*/T^*_{cr} and density ρ^*/ρ^*_{cr}.

(iii) Fractionation effects become more pronounced with the decrease

of the temperature and/or decrease of the mother phase density. For the model at hand:

(a) the average size of the particles in the fluid phase is larger than in the gas phase;

(b) the width of both daughter phases distribution functions is smaller than that of the mother phase.

References

1. J.-P. Hansen and I.R. McDonald, *Theory of Simple Liquids*, (Academic, New York, 1986) 2nd edition; C. Caccamo, Phys. Rep. **274**, 1 (1996).
2. P. Sollich, J. Phys. (Condens. Matt.) **14**, R79 (2002).
3. J.A. Gualteri, J.M. Kincaid, and G. Morrison, J. Chem. Phys. **77**, 52 (1982).
4. L. Bellier-Castella, H. Xu, and M. Baus, J. Chem. Phys. **113**, 8337 (2000).
5. Yu.V. Kalyuzhnyi, and G. Kahl, J. Chem. Phys. **119**, 7335(2003).
6. E.N. Rudisill, and P.T. Cummings, Mol. Phys. **68**, 629(1980).
7. Yu.V. Kalyuzhnyi, and P.T. Cummings, Mol. Phys. **87**, 1459(1996).
8. J.J. Salacuse, and G. Stell, J. Chem. Phys. **77**, 3714(1982).
9. J.L. Lebowitz, Phys. Rev. A **133**, 895(1964).
10. L. Blum, and J. Høye, J. Phys. Chem. **81**, 1311(1977).
11. G.A. Mansoori, N.F. Carnahan, K.E. Starling, and T.W. Leland, J. Chem. Phys. **54**, 1523 (1971).
12. M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions*, Applied Mathematical Series, **55** (Washington: National Bureau of Standards) (1964).

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Співіснування фаз в полідисперсній рідині твердих сфер з багатьма Юкавівськими потенціалами