

Structural and thermodynamic properties of a multicomponent freely jointed hard sphere multi-Yukawa chain fluid

YURIJ V. KALYUZHNYI^{1*}, CLARE MCCABE², PETER T. CUMMINGS³
and GEORGE STELL⁴

¹Institute for Condensed Matter Physics, Svientsitskoho 1, 79011 Lviv, Ukraine

²Department of Chemical Engineering, University of Tennessee, TN, Knoxville 37996-2200, USA and Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401, USA

³Departments of Chemical Engineering, Chemistry and Computer Science, University of Tennessee, Knoxville 37996-2200, TN USA and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6110, USA

⁴Department of Chemistry, State University of New York at Stony Brook, New York 11794-3400, USA

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The product–reactant Ornstein–Zernike approach, represented by the polymer mean-spherical approximation (PMSA), is utilized to describe the structure and thermodynamic properties of the fluid of Yukawa hard sphere chain molecules. An analytical solution of the PMSA for the most general case of the multicomponent freely jointed hard sphere multi-Yukawa chain fluid is presented. As in the case of the regular MSA for the hard sphere Yukawa fluid, the problem is reduced to the solution of a set of nonlinear algebraic equations in the general case, and to a single equation in the case of the factorizable Yukawa potential coefficients. Closed form analytical expressions are presented for the contact values of the monomer–monomer radial distribution function, structure factors, internal energy, Helmholtz free energy, chemical potentials and pressure in terms of the quantities, which follows directly from the PMSA solution. By way of illustration, several different versions of the hard sphere Yukawa chain model are considered, represented by one-Yukawa chains of length m , where $m = 2, 4, 8, 16$. To validate the accuracy of the present theory, Monte Carlo simulations were carried out and the results are compared systematically with the theoretical results for the structure and thermodynamic properties of the system at hand. In general it is found that the theory performs very well, thus providing an analytical route to the equilibrium properties of a well defined model for chain fluids.

1. Introduction

The development of accurate molecular based models for the thermodynamic properties of chain-molecule systems is a very important but, as yet, elusive goal. The main approaches being adopted to achieve this aim can be categorized broadly into two major directions: the first technique is based on perturbation theory, and finds its most successful implementation within statistical associating fluid theory (SAFT), which in its numerous forms has been used to model accurately a wide variety of systems [1]; the second approach is based on analytically solved integral equation theories [2], though this field is in a far less developed state than the SAFT approach. The advantage that integral equations can offer over the SAFT equation of

state is that, in its current formulation, the SAFT formalism assumes that the Helmholtz free energy A can be written as a linear sum of separable monomer, chain and association contributions, with no interaction between the terms:

$$\frac{A}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{\text{monomer}}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{association}}}{NkT}. \quad (1)$$

In this equation, N is the number of molecules, k is Boltzmann's constant and T is the temperature. Although proving to be a remarkably useful approximation in applications of SAFT to date [1], in principle one would expect cross interactions between these terms, and integral equation methods provide the possibility for including such nonlinear effects. The challenge for analytically solved integral equation methods, however, is to deal with the considerable algebraic complexity that

* Author for correspondence. e-mail: yukal@icmp.lviv.ua

results when a non-trivial model is employed. The key to a successful integral equation based equation of state for chain fluids is to adopt a model for the chain fluid and an integral equation closure that will result in an accurate theory for chain fluids while keeping the algebraic complexity to a minimum.

Some indication of the choice of chain fluid can be obtained by considering simple fluids, and in this respect the hard core Yukawa fluid model has proved to be very useful in liquid-state theoretical studies. One of the simplest non-trivial versions of the model is the hard sphere Yukawa (HSY) fluid, where the pair potential is given by

$$\beta\Phi^{(\text{HSY})}(r) = \begin{cases} \infty & r < \sigma, \\ -Ke^{-z(r-\sigma)}/r & r > \sigma, \end{cases} \quad (2)$$

where $\beta = 1/kT$, σ is the hard sphere diameter, K is the potential well depth and z is the potential range. This simple model already takes into account the basic elements of the interparticle interaction, i.e., very strong short range repulsion and weaker long-range attraction, and can be used to describe the properties of a simple fluids. For example, a simple generalization of the model potential (2) to a hard sphere core with a linear combination of two Yukawas is able to reproduce the liquid–gas phase diagram of the more realistic Lennard-Jones (LJ) potential [3–5]. Together with the availability of the analytical description via the mean-spherical approximation [6], these are the main reasons for the considerable interest in the HSY fluid model.

The freely jointed hard sphere Yukawa chain (HSYC) fluid is a simple model for chain polymers, constructed by joining hard sphere Yukawa monomers together to form flexible linear chains with a fixed bond length. In spite of its relative simplicity, such a model incorporates the most important characteristics of real polymer chains, i.e., the effects of chain connectivity and excluded volume and the existence of attractive dispersion forces between the chains. Much in the same spirit that the HSY fluid model is used to represent the properties of simple fluids, the freely jointed HSYC fluid model can be used to approximate the properties of a fluid of chain polymers. To achieve this goal, one must have a sufficiently accurate and simple analytical theory describing the equilibrium properties of the freely jointed HSYC fluid model. Recently the so-called product–reactant Ornstein–Zernike approach (PROZA) for polymer fluid models has been formulated [7–10] and the corresponding version of the mean spherical approximation (MSA), the polymer MSA (PMSA) has been proposed [10–13]. The PROZA, based on earlier work of Wertheim [14, 15], is a general statistical-mechanical theory of reacting mixtures in which the product mol-

ecules and the reacting molecules are treated on the same footing. When applied to polymerizing monomers, PROZA yields the mean monomer–monomer pair correlation function, from which the thermodynamics of a fluid of polymerizing molecules can be obtained directly. It is thus a theory of equilibrium polymerization, in which one has a polydisperse mixture of polymer fragments that are polymerizing and breaking up in dynamic equilibrium. In the complete-association limit, the theory becomes the theory for the structure and thermodynamics of a fluid of fully polymerized chains.

A preliminary solution of the PMSA for the one-component multi-Yukawa HSYC fluid model has been derived and compared with the results of Gibbs ensemble and Monte Carlo simulation data in earlier work [16, 17]. In the present paper we extend this solution to the multi-component multi-Yukawa HSYC fluid model. As in the case of the regular MSA for the HSY fluid, we reduce the problem to the solution of a set of nonlinear algebraic equations in the general case [18–21], and to a single equation in the case of factorizable Yukawa potential coefficients [22, 23]. We also present closed form analytical expressions for thermodynamic properties of the system in terms of the quantities, which follow directly from the solution of the PMSA. These expressions are obtained by generalizing the Høye–Stell [24] energy route to MSA thermodynamics within the framework of the present PMSA theory [10, 25]. By way of illustration, we consider several different versions of the HSYC fluid model. To validate the accuracy of the present theory, Monte Carlo (MC) computer simulations were carried out at a range of state points for each chain fluid and the results were systematically compared to the theoretical results for the structure and thermodynamical properties of the system at hand.

2. The model and theory

The model we employed in this study is a multi-component mixture of freely jointed tangent hard sphere multi-Yukawa chain molecules. Each molecule of species a is represented by m_a hard sphere Yukawa sites of size σ_i^a . We denote the molecular species by the small letters a, b, c, \dots , and the site type in a given molecule a by the small letters i, j, k, \dots . Thus the molecular sites have two indices, one denoting the species of the molecule and the other the site type in the molecule. For example, the hard sphere diameter of a site of type i belonging to a molecule of species a is denoted by σ_i^a , and the pair correlation function between the sites of type i and j belonging to molecules of species a and b is denoted by $h_{ij}^{ab}(r)$. The total number density of the system is $\rho = \sum_{a=1}^M \rho_a$, where ρ_a is the number density of the molecules of species a and the number of species is

M . The site-site potential $\Phi_{ij}^{ab}(r)$ between the sites of type i and j belonging to molecules of species a and b is given by

$$\Phi_{ij}^{ab}(r) = \Phi_{ij}^{(hs)ab}(r) + \Phi_{ij}^{(Y)ab}(r), \quad (3)$$

where $\Phi_{ij}^{(hs)ab}(r)$ is a hard sphere potential, and

$$\beta\Phi_{ij}^{(Y)ab}(r) = -\frac{1}{r} \sum_n K_{ij}^{(n)ab} e^{-z_n r}, \quad (4)$$

with $\beta = 1/kT$.

The product-reactant Ornstein-Zernike approach (PROZA), which is utilized in this work, consists of an Ornstein-Zernike-like integral equation,

$$\hat{\mathbf{h}}_{ij}^{ab}(k) = \hat{\mathbf{c}}_{ij}^{ab}(k) + \sum_c \rho_c \sum_l \hat{\mathbf{c}}_{il}^{ac}(k) \hat{\mathbf{a}}_{lj}^{cb}(k), \quad (5)$$

and polymer mean-spherical approximation (PMSA) closure relations [11–13, 10]

$$\begin{cases} \mathbf{c}_{ij}^{ab}(r) = \mathbf{E} \sum_n \frac{K_{ij}^{(n)ab}}{r} e^{-z_n r}, & r > \sigma_{ij}^{ab} = \frac{1}{2}(\sigma_i^a + \sigma_j^b), \\ \mathbf{h}_{ij}^{ab}(r) = -\mathbf{E} + \frac{\mathbf{t}_{ij}^{ab}}{2\pi\sigma_{ij}^{ab}} \delta(r - \sigma_{ij}^{ab}), & r < \sigma_{ij}^{ab}, \end{cases} \quad (6)$$

where $\hat{\mathbf{h}}_{ij}^{ab}(k)$ and $\hat{\mathbf{c}}_{ij}^{ab}(k)$ are matrices with the elements being the Fourier transforms of the elements of the real-space matrices $\mathbf{h}_{ij}^{ab}(r)$ and $\mathbf{c}_{ij}^{ab}(r)$, defined by

$$\mathbf{f}_{ij}^{ab}(r) = \begin{pmatrix} f_{i_0j_0}^{ab}(r) & f_{i_0j_A}^{ab}(r) & f_{i_0j_B}^{ab}(r) \\ f_{i_Aj_0}^{ab}(r) & f_{i_Aj_A}^{ab}(r) & f_{i_Aj_B}^{ab}(r) \\ f_{i_Bj_0}^{ab}(r) & f_{i_Bj_A}^{ab}(r) & f_{i_Bj_B}^{ab}(r) \end{pmatrix},$$

$$\mathbf{f}_{ij}^{ab}(r) = \mathbf{h}_{ij}^{ab}(r), \quad \mathbf{c}_{ij}^{ab}(r).$$

In this equation, the quantities $h_{i_\alpha j_\beta}^{ab}(r)$ and $c_{i_\alpha j_\beta}^{ab}(r)$ appearing in $\mathbf{h}_{ij}^{ab}(r)$ and $\mathbf{c}_{ij}^{ab}(r)$, respectively, represent partial total and partial direct correlation functions. The lower indices 0, A and B denote the bonding states of the corresponding particles [15, 13, 10] and \mathbf{t}_{ij}^{ab} , $\boldsymbol{\alpha}$ and \mathbf{E} are the following matrices

$$t_{i_\alpha j_\beta}^{ab} = \frac{\delta_{ab}}{2\rho_a} \left[\delta_{\alpha A} \delta_{\beta B} \frac{\delta_{i,j+1}}{\sigma_{i,i-1}^{aa}} + \delta_{\alpha B} \delta_{\beta A} \frac{\delta_{i,j-1}}{\sigma_{i,i+1}^{aa}} \right],$$

$$\alpha_{\alpha\beta} = 1 - \delta_{\alpha\beta} + \delta_{\alpha 0} \delta_{\beta 0}, \quad E_{\alpha\beta} = \delta_{\alpha 0} \delta_{\beta 0}$$

with the lower indices α and β each taking the values 0, A and B. The site-site pair distribution function $g_{ij}^{ab}(r)$ is related to the partial distribution functions $g_{i_\alpha j_\beta}^{ab}(r) = h_{i_\alpha j_\beta}^{ab}(r) + \delta_{\alpha 0} \delta_{\beta 0}$ by the relation

$$g_{ij}^{ab}(r) = \sum_{\alpha\beta=0} g_{i_\alpha j_\beta}^{ab}(r). \quad (7)$$

The set of the OZ equations (5) together with the PMSA closure conditions (6) represent a closed set of equations to be solved.

3. General solution of the multi-Yukawa PMSA

Recently the general solution of the PMSA for the one-component multi-Yukawa chain fluid was derived [16, 17]. Here we propose an extension of this solution for the multi-component version of the model. The general scheme of the present solution is quite similar to that obtained earlier [16]. Therefore we shall omit any details and present here only the final expressions, appropriately modified to be suitable for the multi-component system at hand.

The proposed method of the solution is based upon the version of the Baxter factorization technique [26] developed by Blum and coworkers [18–21] for the solution of the regular MSA for the multi-component multi-Yukawa hard sphere fluid. We begin by presenting the set of the OZ equations (5) in a form suitable for factorization:

$$[\mathbf{1} + \hat{\mathbf{h}}(k)\boldsymbol{\rho}][\boldsymbol{\rho}^{-1} - \hat{\mathbf{c}}(k)] = \boldsymbol{\rho}^{-1}, \quad (8)$$

where $\hat{\mathbf{h}}(k)$, $\hat{\mathbf{c}}(k)$, and $\boldsymbol{\rho}$ are the matrices with the elements $\hat{h}_{ij}^{ab}(k)$, $\hat{c}_{ij}^{ab}(k)$ and $\alpha_{\rho_a} \delta_{ab} \delta_{ij}$. Introducing the so-called Baxter factorization \mathcal{Q} function $\mathbf{Q}_{ij}^{ab}(r)$ it is possible to separate the initial set of the OZ equations (8) into two sets of equations in which the functions $\mathbf{h}_{ij}^{ab}(r)$ and $\mathbf{c}_{ij}^{ab}(r)$ are decoupled [26, 18–21]:

$$\begin{cases} \boldsymbol{\rho}^{-1} - \hat{\mathbf{c}}(k) = \hat{\mathbf{Q}}(k)\boldsymbol{\rho}\hat{\mathbf{Q}}^T(-k), \\ \mathbf{1} + \hat{\mathbf{h}}(k)\boldsymbol{\rho} = [\hat{\mathbf{Q}}(k)\boldsymbol{\rho}\hat{\mathbf{Q}}^T(-k)\boldsymbol{\rho}]^{-1}, \end{cases} \quad (9)$$

where $\hat{\mathbf{Q}}(k)$ is the matrix with the elements $\hat{Q}_{ij}^{ab}(k)$. The corresponding set of equations in the real r -space takes the following form:

$$\mathbf{S}_{ij}^{ab}(|r|) = \mathbf{Q}_{ij}^{ab}(r) - \sum_c \rho_c \sum_l \int dr' \mathbf{Q}_{il}^{ac}(r') \boldsymbol{\alpha} [\mathbf{Q}_{jl}^{bc}(r' - r)]^T, \quad (10)$$

$$\mathbf{J}_{ij}^{ab}(|r|) = \mathbf{Q}_{ij}^{ab}(r) + \sum_c \rho_c \sum_l \int dr' \mathbf{J}_{il}^{ac}(|r' - r|) \boldsymbol{\alpha} \mathbf{Q}_{lj}^{cb}(r'), \quad (11)$$

where

$$\mathbf{S}_{ij}^{ab}(r) = 2\pi \int_r^\infty dr' r' \mathbf{c}_{ij}^{ab}(r'), \quad \mathbf{J}_{ij}^{ab}(r) = 2\pi \int_r^\infty dr' r' \mathbf{h}_{ij}^{ab}(r'), \quad (12)$$

and the factor function $\mathbf{Q}_{ij}^{ab}(r)$ is connected to its Fourier transform $\hat{\mathbf{Q}}_{ij}^{ab}(k)$ via the relation

$$\mathbf{Q}_{ij}^{ab}(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \{[\rho^{-1}]_{ij}^{ab} - \hat{\mathbf{Q}}_{ij}^{ab}(k)\} e^{-ikr}. \quad (13)$$

Substituting into equation (13) the expression for $\hat{\mathbf{Q}}_{ij}^{ab}(k)$ obtained from (9), and using the analytical properties of the factor function $\hat{\mathbf{Q}}_{ij}^{ab}(k)$ together with closure relation (6) we have

$$\mathbf{Q}_{ij}^{ab}(r) = [\mathbf{q}_{ij}^{ab}(r) + \mathbf{t}_{ij}^{ab}] \theta(\sigma_{ij}^{ab} - r) + \tilde{\mathbf{E}}^T \sum_n \tilde{\mathbf{D}}_{ij}^{(n)ab} e^{-z_n r} \quad (14)$$

$$r > \lambda_{ji}^{ba} = \frac{1}{2}(\sigma_j^b - \sigma_i^a),$$

where $\tilde{\mathbf{D}}_{ij}^{(n)ab}$ and $\tilde{\mathbf{E}}$ are the row vectors

$$\tilde{\mathbf{D}}_{ij}^{(n)ab} = (D_{i_0 j_0}^{(n)ab}, D_{i_0 j_A}^{(n)ab}, D_{i_0 j_B}^{(n)ab}), \quad \tilde{\mathbf{E}} = (1, 0, 0),$$

and $\tilde{\mathbf{D}}_{ij}^{(n)ab}$ satisfies the following set of algebraic equations

$$\frac{2\pi}{z_n} \tilde{\mathbf{K}}_{ij}^{(n)ab} = \sum_c \rho_c \sum_l \tilde{\mathbf{D}}_{il}^{(n)ac} \alpha [\hat{\mathbf{Q}}_{jl}^{bc}(iz_n)]^T \quad (15)$$

with $\tilde{\mathbf{K}}_{ij}^{(n)ab} = (\tilde{K}_{ij}^{(n)ab}, 0, 0)$. In expression (14) the function $\mathbf{q}_{ij}^{ab}(r)$ is defined in the range $\lambda_{ji}^{ba} < r < \sigma_{ij}^{ab}$ by

$$\mathbf{q}_{ij}^{ab}(r) = \frac{1}{2} \tilde{\mathbf{E}}^T \tilde{\mathbf{A}}_j^b (r - \sigma_{ij}^{ab})(r - \lambda_{ji}^{ba}) + \tilde{\mathbf{E}}^T \tilde{\boldsymbol{\beta}}_j^b (r - \sigma_{ij}^{ab}) + \sum_n \mathbf{C}_{ij}^{(n)ab} (e^{-z_n r} - e^{-z_n \sigma_{ij}^{ab}}). \quad (16)$$

Here

$$\tilde{\boldsymbol{\beta}}_j^b = \frac{\pi}{\Delta} \sigma_j^b \tilde{\mathbf{E}} + \frac{2\pi}{\Delta} \sum_n \tilde{\boldsymbol{\mu}}_j^{(n)b}, \quad (17)$$

$$\tilde{\mathbf{A}}_j^b = \frac{2\pi}{\Delta} \left(\tilde{\mathbf{E}} + \frac{1}{2} \zeta_2 \tilde{\boldsymbol{\beta}}_j^b + \sum_n \tilde{\mathbf{M}}_j^{(n)b} - \tilde{\boldsymbol{\tau}}_j^b \right), \quad (18)$$

$$\mathbf{C}_{ij}^{(n)ab} = \sum_c \sum_l \gamma_{il}^{ac}(z_n) \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{lj}^{(n)cb} - \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{ij}^{(n)ab}, \quad (19)$$

and

$$s\gamma_{ij}^{ab}(s) = 2\pi\rho_b \mathbf{G}_{ij}^{ab}(s) \alpha, \quad (20)$$

$$\tilde{\boldsymbol{\mu}}_j^{(n)b} = \sum_c \rho_c \sum_l \tilde{\mathbf{C}}_l^{(\mu)c}(z_n) \alpha \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{lj}^{(n)cb} e^{-z_n \sigma_{ij}^{cb}}, \quad (21)$$

$$\tilde{\mathbf{M}}_j^{(n)b} = \sum_c \rho_c \sum_l \tilde{\mathbf{C}}_l^{(M)c}(z_n) \alpha \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{lj}^{(n)cb} e^{-z_n \sigma_{ij}^{cb}}, \quad (22)$$

$$\mathbf{G}_{ij}^{ab}(s) = \int_0^{\infty} dr' r' \mathbf{g}_{ij}^{ab}(r') e^{-sr'}, \quad (23)$$

$$\tilde{\mathbf{C}}_l^{(\mu)c}(s) = \sum_d \sum_k \tilde{\mathbf{E}} [\gamma_{lk}^{cd}(s)]^T e^{s\sigma_{ik}^{cd}} s (\sigma_k^d)^3 \phi_1(\sigma_k^d s) + \frac{1}{s^2} \left(1 + \frac{1}{2} s \sigma_l^c \right) \tilde{\mathbf{E}}, \quad (24)$$

$$\tilde{\mathbf{C}}_l^{(M)c}(s) = \sum_d \sum_k \tilde{\mathbf{E}} [\gamma_{lk}^{cd}(s)]^T e^{s\lambda_{ik}^{cd}} (\sigma_k^d)^2 s \varphi_1(-s\sigma_k^d) - \frac{1 + s\sigma_l^c}{s} \tilde{\mathbf{E}}, \quad (25)$$

$$\tilde{\boldsymbol{\tau}}_j^b = \sum_c \rho_c \sum_l \sigma_l^c \tilde{\mathbf{E}} \alpha \mathbf{t}_{ij}^{cb}. \quad (26)$$

Also

$$\phi_1(x) = \frac{1}{x^3} \left[1 - \frac{1}{2}x - \left(1 + \frac{1}{2}x \right) e^{-x} \right],$$

$$\varphi_1(x) = \frac{1 - x - e^{-x}}{x^2}, \quad \zeta_m = \sum_c \rho_c \sum_l \sigma_l^m,$$

and

$$\Delta = 1 - \pi\zeta_3/6.$$

We note in passing that hereafter all the row vectors of the type (A_0, A_A, A_B) are denoted as $\tilde{\mathbf{A}}$.

It can be seen that all the coefficients of the factor function $\mathbf{q}_{ij}^{ab}(r)$ are determined by the set of unknowns $\tilde{\mathbf{D}}_{ij}^{(n)ab}$ and $\gamma_{ij}^{ab}(z_n)$, which follow from the solution of the set of equations (15) and the equations obtained by differentiating relation (11) with respect to r at $\lambda_{ji}^{ba} < r < \sigma_{ij}^{ab}$ and taking the Laplace transform of both sides of the resulting equation. This yields

$$\sum_c \sum_l \gamma_{il}^{ac}(z_n) \hat{\mathbf{Q}}_{lj}^{cb}(iz_n) = \mathbf{f}_{ij}^{ab}(z_n)/z_n, \quad (27)$$

where

$$\mathbf{f}_{ij}^{ab}(s) = \tilde{\mathbf{E}}^T \left[\tilde{\mathbf{A}}_j^b \left(1 + \frac{1}{2} s \sigma_i^a \right) + \tilde{\boldsymbol{\beta}}_j^b s \right] \frac{1}{s^2} e^{-s\sigma_{ij}^{ab}} - \sum_n \frac{z_n}{s + z_n} \mathbf{C}_{ij}^{(n)ab} e^{-(s+z_n)\sigma_{ij}^{ab}} + \mathbf{t}_{ij}^{ab} e^{-s\sigma_{ij}^{ab}}, \quad (28)$$

$$\hat{\mathbf{Q}}_{lj}^{cb}(is) = \frac{\delta_{lj} \delta_{cb}}{\rho_b} \alpha^{-1} - \hat{\boldsymbol{\Omega}}_{lj}^{cb}(s), \quad (29)$$

$$e^{-s\lambda_{ij}^{cb}} \hat{\boldsymbol{\Omega}}_{lj}^{cb}(s) = (\sigma_l^c)^3 \tilde{\mathbf{E}}^T \tilde{\mathbf{A}}_j^b \phi_1(\sigma_l^c s) + (\sigma_l^c)^2 \tilde{\mathbf{E}}^T \tilde{\boldsymbol{\beta}}_j^b \varphi_1(\sigma_l^c s) + \mathbf{t}_{lj}^{cb} \frac{1 - e^{-\sigma_l^c s}}{s} + \sum_n \left\{ \mathbf{C}_{lj}^{(n)cb} \left[\frac{e^{\sigma_l^c z_n} - e^{-\sigma_l^c s}}{z_n + s} + \frac{e^{-\sigma_l^c s} - 1}{s} \right] e^{-z_n \sigma_{ij}^{cb}} + \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{lj}^{(n)cb} \frac{e^{-z_n \lambda_{ji}^{bc}}}{z_n + s} \right\}. \quad (30)$$

The set of equation (15) and (27) have to be solved numerically. This completes our solution of the PMSA for the most general case.

4. Solution of the one-Yukawa PMSA with factorizable coefficients

Further simplification of the final set of algebraic equations (15) and (27) can be carried out in the one-Yukawa case ($n = 1$) with factorizable coefficients [22, 23], i.e.,

$$\beta\Phi_{ij}^{(Y)ab}(r) = -K \frac{d_i^a d_j^b}{r} e^{-zr}. \tag{31}$$

Using the corresponding expression for K_{ij}^{ab} in equation (15), i.e., $K_{ij}^{ab} = K d_i^a d_j^b$, one can see that $\tilde{\mathbf{D}}_{il}^{ac}$ can be written in the form

$$\tilde{\mathbf{D}}_{il}^{ac} = -d_i^a \tilde{\mathbf{a}}_i^c e^{\frac{1}{2}z\sigma_i^c}, \tag{32}$$

which leads to the following expressions for the coefficients \mathbf{C}_{ij}^{ab} , $\tilde{\beta}_j^b$ and $\tilde{\mathbf{A}}_j^b$ entering the expression for the factor function $\mathbf{q}_{ij}^{ab}(r)$ (16):

$$\mathbf{C}_{ij}^{ab} = \left[d_i^a \tilde{\mathbf{E}}^T - \frac{1}{z} (\tilde{\mathbf{B}}_i^a)^T \right] \tilde{\mathbf{a}}_j^b e^{\frac{1}{2}z\sigma_j^b}, \tag{33}$$

$$\tilde{\beta}_j^b = \frac{\pi}{\Delta} \sigma_j^b \tilde{\mathbf{E}} + \Delta_n \tilde{\mathbf{a}}_j^b, \tag{34}$$

$$\tilde{\mathbf{A}}_j^b = \frac{2\pi}{\Delta} \left(1 + \frac{\pi}{2\Delta} \zeta_2 \sigma_j^b \right) \tilde{\mathbf{E}} + \frac{\pi}{\Delta} P \tilde{\mathbf{a}}_j^b - \frac{2\pi}{\Delta} \tilde{\tau}_j^b. \tag{35}$$

Here

$$\tilde{\mathbf{B}}_i^a = z \tilde{\mathbf{E}} \sum_c \sum_l [\gamma_{il}^{ac}(z)]^T d_l^c, \tag{36}$$

$$\begin{aligned} \Delta_n = & -\frac{2\pi}{\Delta} \tilde{\mathbf{E}} \alpha \sum_c \rho_c \sum_l (\sigma_l^c)^2 \left[\phi_1(z\sigma_l^c) \sigma_l^c (\tilde{\mathbf{B}}_l^c)^T e^{\frac{1}{2}z\sigma_l^c} \right. \\ & \left. + \frac{1+z\sigma_l^c/2}{(\sigma_l^c)^2 z^2} d_l^c \tilde{\mathbf{E}}^T e^{-\frac{1}{2}z\sigma_l^c} \right], \end{aligned} \tag{37}$$

$$\begin{aligned} P = & \left(\zeta_2 - \frac{\Delta}{\pi} z \right) \Delta_n + \tilde{\mathbf{E}} \alpha \sum_c \rho_c \sum_l \sigma_l^c [\varphi_0(z\sigma_l^c) \sigma_l^c (\tilde{\mathbf{B}}_l^c)^T e^{\frac{1}{2}z\sigma_l^c} \\ & + d_l^c \tilde{\mathbf{E}}^T e^{-\frac{1}{2}z\sigma_l^c}], \end{aligned} \tag{38}$$

where $\varphi_0(x) = (1 - e^{-x})/x$.

Next we shall make use of the symmetry property of the factor function $\mathbf{Q}_{ij}^{ab}(r)$,

$$\mathbf{Q}_{ij}^{ab}(\lambda_{ji}^{ba}) = [\mathbf{Q}_{ji}^{ba}(\lambda_{ij}^{ab})]^T, \tag{39}$$

which gives

$$(\tilde{\mathbf{X}}_i^a)^T \tilde{\mathbf{a}}_j^b = (\tilde{\mathbf{a}}_i^a)^T \tilde{\mathbf{X}}_j^b, \tag{40}$$

where

$$(\tilde{\mathbf{X}}_i^a)^T = \tilde{\mathbf{E}}^T (\sigma_i^a \Delta_n + d_i^a e^{-\frac{1}{2}z\sigma_i^a}) + \sigma_i^a (\tilde{\mathbf{B}}_i^a)^T \varphi_0(z\sigma_i^a) e^{\frac{1}{2}z\sigma_i^a}. \tag{41}$$

Now we are in a position to introduce Blum's scaling parameter Γ via the relation

$$\tilde{\mathbf{a}}_j^b = \frac{2\Gamma}{D} \tilde{\mathbf{X}}_j^b, \tag{42}$$

where D is a parameter that will be defined later.

Differentiating expression (10) with respect to r and taking the limit of $r \rightarrow 0$ we have

$$\begin{aligned} \tilde{\mathbf{a}}_i^a = & \frac{2}{D} \left[-\tilde{\mathbf{E}} \Delta_n \left(1 + \frac{1}{2} z \sigma_i^a \right) - \tilde{\mathbf{B}}_i^a e^{\frac{1}{2}z\sigma_i^a} - \sigma_i^a \tilde{\mathbf{E}} \eta^B \right. \\ & \left. + \sum_d \rho_d \sum_k \tilde{\mathbf{X}}_k^d \alpha_{ik}^{ad} \right], \end{aligned} \tag{43}$$

where

$$\eta^B = \frac{\pi}{2\Delta} \sum_d \rho_d \sum_k \sigma_k^d \tilde{\mathbf{X}}_k^d \alpha_{ik}^{dT}, \tag{44}$$

and for D we assume

$$D = \sum_d \rho_d \sum_k \tilde{\mathbf{X}}_k^d \alpha(\tilde{\mathbf{X}}_k^d)^T. \tag{45}$$

All the unknowns introduced so far can now be expressed in terms of only one quantity Γ . Let us first express the unknown parameters $\tilde{\mathbf{X}}_i^a$ in terms of Γ , η^B and Δ_n . Using relations (41), (42) and (43), we have

$$\begin{aligned} [1 + \sigma_i^a \varphi_0(z\sigma_i^a) \Gamma] \tilde{\mathbf{X}}_i^a = & \sigma_i^a \varphi_0(z\sigma_i^a) \tilde{\mathbf{T}}_i^a - [(\sigma_i^a)^3 \phi_1(z\sigma_i^a) z^2 \Delta_n \\ & + (\sigma_i^a)^2 \varphi_0(z\sigma_i^a) \eta^B - d_i^a e^{-\frac{1}{2}z\sigma_i^a}] \tilde{\mathbf{E}}, \end{aligned} \tag{46}$$

where $\tilde{\mathbf{T}}_i^a = \sum_k \rho_k \tilde{\mathbf{X}}_k^a \alpha(\mathbf{t}_{ik}^{aa})^T$. The solution of this set of equations for $X_{i_0}^a$ is

$$X_{i_0}^a = \eta_{i_0}^a \Delta_n + \xi_{i_0}^a \eta^B + \lambda_{i_0}^a, \tag{47}$$

where

$$\eta_{i_0}^a = -\frac{(\sigma_{i_0}^a)^3 z^2 \phi_1(z\sigma_{i_0}^a)}{1 + \sigma_{i_0}^a \varphi_0(z\sigma_{i_0}^a) \Gamma},$$

$$\xi_{i_0}^a = -\frac{(\sigma_{i_0}^a)^2 \varphi_0(z\sigma_{i_0}^a)}{1 + \sigma_{i_0}^a \varphi_0(z\sigma_{i_0}^a) \Gamma},$$

$$\lambda_{i_0}^a = \frac{d_{i_0}^a e^{-\frac{1}{2}z\sigma_{i_0}^a}}{1 + \sigma_{i_0}^a \varphi_0(z\sigma_{i_0}^a) \Gamma}.$$

Solving equation (46) with respect to $X_{i_0}^a$ for $\alpha \neq 0$ and substituting into the resulting recurrent relation expression for $x_{i_0}^a$ (equation (47)) we have finally

$$\tilde{\mathbf{X}}_i^a = \tilde{\eta}_i^a \Delta_n + \tilde{\xi}_i^a \eta^B + \tilde{\lambda}_i^a, \tag{48}$$

where

$$\tilde{\eta}_i^a = \left(\eta_{i_0}^a, (1 - \delta_{il}) \sum_{l=2}^i \eta_{(l-1)_0}^a 2^{1-l+i} \prod_{k=i}^l \chi_k^a \sigma_{k,k-1}^{aa}, \right. \\ \left. (1 - \delta_{in}) \sum_{l=i}^{n-1} \eta_{(l+1)_0}^a 2^{1-l+i} \prod_{k=i}^l \chi_k^a \sigma_{k,k+1}^{aa} \right), \quad (49)$$

$$\tilde{\xi}_i^a = \left(\xi_{i_0}^a, (1 - \delta_{il}) \sum_{l=2}^i \xi_{(l-1)_0}^a 2^{1-l+i} \prod_{k=i}^l \chi_k^a \sigma_{k,k-1}^{aa}, \right. \\ \left. (1 - \delta_{in}) \sum_{l=i}^{n-1} \xi_{(l+1)_0}^a 2^{1-l+i} \prod_{k=i}^l \chi_k^a \sigma_{k,k+1}^{aa} \right), \quad (50)$$

$$\tilde{\lambda}_i^a = \left(\lambda_{i_0}^a, (1 - \delta_{il}) \sum_{l=2}^i \lambda_{(l-1)_0}^a 2^{1-l+i} \prod_{k=i}^l \chi_k^a \sigma_{k,k-1}^{aa}, \right. \\ \left. (1 - \delta_{in}) \sum_{l=i}^{n-1} \lambda_{(l+1)_0}^a 2^{1-l+i} \prod_{k=i}^l \chi_k^a \sigma_{k,k+1}^{aa} \right), \quad (51)$$

and

$$\chi_i^a = \frac{\sigma_i^a \varphi_0(z\sigma_i^a)}{1 + \sigma_i^a \varphi_0(z\sigma_i^a) \Gamma}. \quad (52)$$

The unknowns η^B and Δ_n follow from the solution of the set of two linear equations formed by the expressions for η^B (equation (44)) and for Δ_n

$$\Delta_n = -\frac{4\eta^B}{z^2} \left(\Gamma + \frac{\pi}{2\Delta} \zeta_2 + \frac{1}{2}z \right) \\ - \frac{2\pi}{\Delta z^2} \sum_c \rho_c \sum_l \tilde{\mathbf{X}}_l^c \alpha [\tilde{\mathbf{E}}^T + (\tilde{\boldsymbol{\tau}}_l^c)^T], \quad (53)$$

in which $X_{i_0}^a$ is substituted for by equation (48). Here the expression for Δ_n is obtained by combining relations (37), (41), (42) and (43). Solving the resulting set of the equations we have

$$\eta^B = \frac{\Theta^\lambda (z^2 + \Omega^\eta) - \Theta^\eta \Omega^\lambda}{\left(4\Gamma + \frac{2\pi}{\Delta} \zeta_2 + 2z + \Omega^\xi \right) \Theta^\eta + (z^2 + \Omega^\eta)(1 - \Theta^\xi)}, \quad (54)$$

$$\Delta_1 = \frac{\Omega^\lambda (\Theta^\xi - 1) - \left(4\Gamma + \frac{2\pi}{\Delta} \zeta_2 + 2z + \Omega^\xi \right) \Theta^\lambda}{\left(4\Gamma + \frac{2\pi}{\Delta} \zeta_2 + 2z + \Omega^\xi \right) \Theta^\eta + (z^2 + \Omega^\eta)(1 - \Theta^\xi)} \quad (55)$$

where

$$\Omega^y = \frac{2\pi}{\Delta} \sum_c \rho_c \sum_l [y_{l_0}^c (1 + \tau_{l_A}^c + \tau_{l_B}^c) + y_{l_A}^c (1 + \tau_{l_B}^c) \\ + y_{l_B}^c (1 + \tau_{l_A}^c)], \quad (56)$$

$$\Theta^y = \frac{2\pi}{\Delta} \sum_c \rho_c \sum_l \sigma_l^c (y_{l_0}^c + y_{l_A}^c + y_{l_B}^c). \quad (57)$$

Finally, the nonlinear algebraic equation for the parameter Γ follows from expression (15). Using equations (29), (32)–(38) and (41), equation (15) can be written in terms of the unknowns $\tilde{\mathbf{a}}_j^b$ and $\tilde{\mathbf{X}}_j^b$ as follows

$$\frac{2\pi}{z} K d_j^b e^{-z\sigma_j^b/2} \tilde{\mathbf{E}} + \sum_c \sum_l \tilde{\mathbf{a}}_l^c \left\{ \delta_{lj} \delta_{cb} - \frac{2\pi}{\Delta} \phi_1(z\sigma_j^b) (\sigma_j^b)^3 \right. \\ \times \left[\rho_c \left(1 + \frac{\pi \zeta_2}{2\Delta} \sigma_l^c \right) \alpha \tilde{\mathbf{E}}^T + \rho_c \alpha (\tilde{\boldsymbol{\tau}}_l^c)^T \right] \tilde{\mathbf{E}} \\ \left. - \frac{\pi}{\Delta} \varphi_0(z\sigma_j^b) \rho_c \sigma_l^c (\sigma_j^b)^2 \alpha \tilde{\mathbf{E}}^T \tilde{\mathbf{E}} - \varphi_0(z\sigma_j^b) \rho_c \sigma_j^b \alpha (\mathbf{t}_{jl}^{bc})^T \right\} \\ + \left\{ \frac{1}{2z} d_j^b e^{-z\sigma_j^b/2} \tilde{\mathbf{E}} + \frac{1}{2} \varphi_0(z\sigma_j^b) \tilde{\mathbf{X}}_j^b - \frac{\pi}{\Delta} \phi_1(z\sigma_j^b) (\sigma_j^b)^3 \right. \\ \left. \times \sum_d \rho_d \sum_l \sigma_l^d \tilde{\mathbf{X}}_l^d \alpha \tilde{\mathbf{E}}^T \tilde{\mathbf{E}} \right\} \sum_c \rho_c \sum_l \tilde{\mathbf{a}}_l^c (\tilde{\mathbf{a}}_l^c)^T = \tilde{\mathbf{0}}. \quad (58)$$

Using equations (42)–(45) and (53) this set of equations can be presented as only one equation for the unknown scaling parameter Γ

$$\Gamma^2 + z\Gamma + \pi KD = 0. \quad (59)$$

Thus the solution of the one-Yukawa AMSA with factorizable coefficients has been reduced to the solution of one nonlinear algebraic equation.

5. Structure and thermodynamics

5.1. Structural properties

An important advantage of the analytical solution of the PMSA is that it enables us to give the structural and thermodynamic properties of the system directly in terms of the Hamiltonian parameters upon solution of the set of equations we shall now obtain.

The expression for the contact value of the non-singular part of the partial correlation functions $\bar{\mathbf{h}}_{ij}^{ab} = \bar{\mathbf{h}}_{ij}^{ab}(\sigma_{ij}^{ab})$ follows from (11) by differentiating with respect to r at $r = \sigma_{ij}^{ab}$ +

$$\sigma_{ij}^{ab} \bar{\mathbf{h}}_{ij}^{ab} = \tilde{\mathbf{E}}^T \sum_c \rho_c \sum_l \sigma_l^c \left[\frac{1}{2} \tilde{\mathbf{A}}_j^b \psi_{ijl}^{(acb)}(\sigma, \lambda) + \tilde{\boldsymbol{\beta}}_j^b v_{ijl}^{(acb)}(\sigma, \lambda) \right] \\ + \mathbf{E} \alpha \sum_c \rho_c \sum_l \sum_n \mathbf{C}_{lj}^{(n)cb} \left\{ \left[\frac{1}{z_n} \left(\lambda_{il}^{ac} - \frac{1}{z_n} \right) \right. \right. \\ \left. \left. + \frac{1}{2} \sigma_i^a \sigma_l^c \right] e^{-z_n \sigma_{ij}^c} + \frac{1}{z_n} \left(\frac{1}{z_n} - \sigma_{il}^{ac} \right) e^{-z_n \lambda_{ij}^{bc}} \right\} \\ + \frac{1}{2\pi} \sum_c \rho_c \sum_l \mathbf{t}_{il}^{ac} \alpha \left[\mathbf{t}_{lj}^{cb} - \tilde{\mathbf{E}}^T \tilde{\boldsymbol{\beta}}_j^b \sigma_l^c + \tilde{\mathbf{D}}_{lj}^{(n)cb} e^{-z_n \lambda_{ij}^{bc}} \right]$$

$$\begin{aligned}
& + \sum_n \mathbf{C}_{ij}^{(n)cb} (e^{-z_n \lambda_{ij}^{bc}} - e^{-z_n \sigma_{ij}^{cb}}) \Big] \\
& - \tilde{\mathbf{E}}^T \sum_c \rho_c \sum_l \sum_n \frac{1}{z_n} \left(\sigma_{il}^{ac} - \frac{1}{z_n} \right) \tilde{\mathbf{D}}_{lj}^{(n)cb} e^{-z_n \lambda_{ij}^{bc}} \\
& - \frac{1}{2\pi} \sum_n \mathbf{C}_{ij}^{(n)ab} z_n e^{-z_n \sigma_{ij}^{ab}} - \frac{1}{2} \sigma_i^a \tilde{\mathbf{E}}^T \tilde{\boldsymbol{\tau}}_j^b, \quad (60)
\end{aligned}$$

where

$$\begin{aligned}
\psi_{ij}^{(acb)}(\sigma, \lambda) &= \frac{1}{4} \sigma_j^b [(\sigma_{ij}^{cb})^2 + (\lambda_{ij}^{bc})^2] \\
& - \frac{1}{3} [\sigma_{ij}^{cb} \sigma_j^b + (\lambda_{ij}^{bc})^2] (\sigma_{ij}^{ab} + \sigma_j^b) \\
& + \frac{1}{2} \sigma_{ij}^{ab} (\sigma_j^b)^2 - \frac{1}{2} \lambda_{ij}^{bc} \sigma_{ij}^{cb} \sigma_i^a, \\
v_{ij}^{(acb)}(\sigma, \lambda) &= \frac{1}{3} [\sigma_{ij}^{cb} \sigma_j^b + (\lambda_{ij}^{bc})^2] + \frac{1}{2} (\sigma_{ij}^{ab} \sigma_i^c - \sigma_{ij}^{cb} \sigma_j^b).
\end{aligned}$$

In order to calculate the pressure we also need the expression for the derivative of the pair correlation function $\bar{\mathbf{h}}_{ij}^{ab}(r)$ with respect to r at $r = \sigma_{ij}^+$. This expression follows similarly from equation (11) differentiated twice

$$\begin{aligned}
\sigma_{ij}^{ab} \partial \bar{\mathbf{h}}_{ij}^{ab} &= -\bar{\mathbf{h}}_{ij}^{ab} + \tilde{\mathbf{E}}^T \sum_c \rho_c \sum_l \frac{1}{2} \sigma_l^c \left[\frac{1}{6} (\sigma_l^c)^2 \tilde{\mathbf{A}}_j^b - \sigma_l^c \tilde{\boldsymbol{\beta}}_j^b \right] \\
& + \frac{1}{2\pi} \sum_n z_n^2 \mathbf{C}_{ij}^{(n)ab} e^{-z_n \sigma_{ij}^{ab}} \\
& + \mathbf{E} \boldsymbol{\alpha} \sum_c \rho_c \sum_l \sum_n \mathbf{C}_{ij}^{(n)cb} \\
& \times \left[\left(\lambda_{li}^{ca} + \frac{1}{z_n} \right) e^{-z_n \sigma_{ij}^{cb}} + \left(\sigma_{il}^{ac} - \frac{1}{z_n} \right) e^{-z_n \lambda_{ij}^{bc}} \right] \\
& + \sum_c \rho_c \sum_l \sigma_{il}^{ac} \bar{\mathbf{h}}_{il}^{ac} \boldsymbol{\alpha} \\
& \times \left[-\tilde{\mathbf{E}}^T \tilde{\boldsymbol{\beta}}_j^b \sigma_l^c + \sum_n \mathbf{C}_{lj}^{(n)cb} (e^{-z_n \lambda_{ij}^{bc}} - e^{-z_n \sigma_{ij}^{cb}}) \right. \\
& \left. + \tilde{\mathbf{E}}^T \sum_n \tilde{\mathbf{D}}_{lj}^{(n)cb} e^{-z_n \lambda_{ij}^{bc}} \right] \\
& + \tilde{\mathbf{E}}^T \sum_c \rho_c \sum_l \sum_n \left(\sigma_{il}^{ac} - \frac{1}{z_n} \right) \tilde{\mathbf{D}}_{lj}^{(n)cb} e^{-z_n \lambda_{ij}^{bc}} \\
& + \sum_c \rho_c \sum_l (\sigma_{il}^{ac} \bar{\mathbf{h}}_{il}^{ac} - \lambda_{li}^{ca} \mathbf{E}) \boldsymbol{\alpha}_{lj}^{cb} \\
& - \frac{1}{2\pi} \sum_c \rho_c \sum_l \boldsymbol{\tau}_{il}^{ac} \boldsymbol{\alpha} \left[\frac{1}{2} \tilde{\mathbf{E}}^T \sigma_l^c \tilde{\mathbf{A}}_j^b - \tilde{\mathbf{E}}^T \tilde{\boldsymbol{\beta}}_j^b \right. \\
& \left. + \sum_n z_n (\mathbf{C}_{lj}^{(n)cb} + \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{lj}^{(n)cb}) e^{-z_n \lambda_{ij}^{bc}} \right], \quad (61)
\end{aligned}$$

where

$$\partial \mathbf{h}_{ij}^{ab} = \frac{\partial \mathbf{h}_{ij}^{ab}(r)}{\partial r} \Big|_{r \rightarrow \sigma_{ij}^+}.$$

Knowledge of the Q function enables one to calculate the structural properties of the system. To obtain $\mathbf{g}_{ij}^{ab}(r)$ for $r > \sigma_{ij}^{ab}$ one may either apply the iteration scheme of Perram [27] or utilize the general expression

$$\begin{aligned}
g_{i\alpha j\beta}^{ab}(r) &= [1 - \beta \Phi_{ij}^{(Y)ab}(r)] \delta_{\alpha 0} \delta_{\beta 0} \\
& + \frac{1}{2\pi^2 r} \int_0^\infty dk k \sin(kr) \{ [\boldsymbol{\rho} \hat{\mathbf{Q}}(k) \boldsymbol{\rho} \hat{\mathbf{Q}}^T(-k) \boldsymbol{\rho}]^{-1} \\
& + \hat{\mathbf{Q}}(k) \boldsymbol{\rho} \hat{\mathbf{Q}}^T(-k) - 2\rho^{-1} \}_{i\alpha j\beta}^{ab}, \quad (62)
\end{aligned}$$

which follows from expression (9). In the present study, Fourier transform (62) has been used.

The structure factor $\hat{\mathbf{S}}_{ij}^{ab}(k) = \delta_{ab} \delta_{ij} + \sqrt{\rho_a \rho_b} \hat{h}_{ij}^{ab}(k)$ can be also obtained from expression (9):

$$\hat{\mathbf{S}}_{ij}^{ab}(k) = \frac{1}{\sqrt{\rho_a \rho_b}} \{ [\hat{\mathbf{Q}}(k) \boldsymbol{\rho} \hat{\mathbf{Q}}^T(-k)]^{-1} \}_{i\alpha j\beta}^{ab}, \quad (63)$$

where $\hat{\mathbf{Q}}(k)$ follows from equation (29) at $s = -ik$.

5.2. Thermodynamic properties

Using standard expressions for the excess internal energy ΔE in terms of site-site probability distribution functions we have

$$-\beta \frac{\Delta E}{V} = \sum_{ab} \rho_a \sum_{ij} \sum_n z_n K_{ij}^{(n)ab} \sum_\alpha \gamma_{i\alpha 0}^{ab}(z_n). \quad (64)$$

Since our approach is based on PROZA this expression also includes the part of the intramolecular internal energy $\Delta E_{\text{intra}}^{(\delta)}$ due to the Yukawa interaction between the nearest neighbours forming the chain. It can be calculated separately:

$$-\beta \frac{\Delta E_{\text{intra}}^{(\delta)}}{V} = - \sum_a \rho_a \sum_{i=1}^{m_a-1} \sum_n \frac{K_{ii+1}^{(n)aa}}{\sigma_{ii+1}^{aa}} e^{-z_n \sigma_{ii+1}^{aa}}. \quad (65)$$

The other thermodynamic properties of the system in question can be calculated following the method developed earlier [10]. This method generalizes the Høye–Stell MSA energy route to thermodynamics [24] within the framework of the present PMSA approach. Originally this generalization was developed for the one-component case. Extension of the method to the multicomponent case yields the following expressions for the Helmholtz free energy A , pressure P and chemical potential μ_α^a in excess to their reference system values [25]

$$\begin{aligned}
-\beta \frac{A - A^{(\text{ref})}}{V} &= J + \frac{1}{2} \sum_{ab} \rho_a \rho_b \sum_{ij} \{ \alpha [\hat{\mathbf{c}}_{ij}^{\text{ab}} \\
&\quad - \hat{\mathbf{c}}_{ij}^{(0)\text{ab}}] \alpha \}_{00} - \beta \frac{\Delta E}{V} \\
&\quad + \frac{1}{3} \pi \sum_{ab} \rho_a \rho_b \sum_{ij} (\sigma_{ij}^{\text{ab}})^3 \\
&\quad \times \text{Tr} [\bar{\mathbf{g}}_{ij}^{\text{ab}} \alpha \bar{\mathbf{g}}_{ji}^{\text{ba}} \alpha - \bar{\mathbf{g}}_{ij}^{(0)\text{ab}} \alpha \bar{\mathbf{g}}_{ji}^{(0)\text{ba}} \alpha] \\
&\quad - \frac{1}{3} \sum_{ab} \rho_a \rho_b \sum_{ij} (\sigma_{ij}^{\text{ab}})^2 \\
&\quad \times \text{Tr} \{ \mathbf{t}_{ij}^{\text{ab}} \alpha [\partial \bar{\mathbf{h}}_{ij}^{\text{ab}} - \partial \bar{\mathbf{h}}_{ij}^{(0)\text{ab}}] \alpha \}, \quad (66)
\end{aligned}$$

$$\begin{aligned}
\beta(P - P^{(\text{ref})}) &= -\beta \frac{A - A^{(\text{ref})}}{V} - \frac{1}{2} \sum_{ab} \rho_a \rho_b \sum_{ij} \\
&\quad \times \{ \alpha [\hat{\mathbf{c}}_{ij}^{\text{ab}} - \hat{\mathbf{c}}_{ij}^{(0)\text{ab}}] \alpha \}_{00} + \beta \frac{\Delta E}{V}, \quad (67)
\end{aligned}$$

$$\begin{aligned}
-\beta \rho_a (\mu_i^a - \mu_i^{(\text{ref})a}) &= \frac{1}{2} \rho_a \sum_b \rho_b \sum_j \{ \alpha [\hat{\mathbf{c}}_{ij}^{\text{ab}} - \hat{\mathbf{c}}_{ij}^{(0)\text{ab}}] \alpha \}_{00} \\
&\quad - \beta \frac{\Delta E_i^a}{V}, \quad (68)
\end{aligned}$$

where the quantities with the superscript (ref) denote the reference system quantities, the quantities with superscript (0) denote the corresponding PMSA quantities with $K_{ij}^{(n)an} = 0$, $\hat{\mathbf{c}}_{ij}^{\text{ab}} = \hat{\mathbf{c}}_{ij}^{\text{ab}} (k=0)$, $\bar{\mathbf{g}}_{ij}^{\text{ab}} = \bar{\mathbf{h}}_{ij}^{\text{ab}} + \mathbf{E}$,

$$\frac{\Delta E_i^a}{V} = 2\pi \rho_a \sum_b \rho_b \sum_j \int_0^\infty r^2 g_{ij}^{\text{ab}}(r) \Phi_{ij}^{(Y)\text{ab}}(r) dr, \quad (69)$$

and

$$J = -\frac{1}{6} \beta \sum_{ab} \rho_a \rho_b \sum_{ij} \int_{r > \sigma_{ij}^{\text{ab}}} g_{ij}^{\text{ab}}(r) \mathbf{r} \nabla \Phi_{ij}^{(Y)\text{ab}}(r) d\mathbf{r}. \quad (70)$$

The reference system is represented by the multi-component mixture of hard sphere chain molecules with $K_{ij}^{(n)ab} = 0$. Expressions (66), (67) and (68) are quite general and apply for any type of potential outside the hard core. The quantities, that enter these expressions can be written in terms of the present solution of the PMSA for the model at hand. We have

$$-\beta \frac{\Delta E_i^a}{V} = \rho_a \sum_b \sum_j \sum_n z_n K_{ij}^{(n)ab} \sum_\alpha \gamma_{i\alpha 0}^{\text{ab}}(z_n), \quad (71)$$

$$J = \frac{1}{3} \sum_{ab} \rho_a \sum_{ij} K_{ij}^{(n)ab} z_n^2 \sum_\alpha \partial \gamma_{i\alpha 0}^{(n)ab}, \quad (72)$$

$$\begin{aligned}
\sum_{ab} \rho_a \rho_b \sum_{ij} [\alpha \hat{\mathbf{c}}_{ij}^{\text{ab}} \alpha]_{00} &= - \sum_{ab} \rho_a \rho_b \sum_{ij} \{ \alpha [(\mathbf{M}_{ij}^{\text{ba}})^{\text{T}} \\
&\quad + \mathbf{M}_{ij}^{\text{ab}} + \sum_c \rho_c \sum_l \mathbf{M}_{il}^{\text{ac}} \\
&\quad \times \alpha (\mathbf{M}_{jl}^{\text{bc}})^{\text{T}}] \alpha \}_{00}, \quad (73)
\end{aligned}$$

where

$$\begin{aligned}
\mathbf{M}_{ij}^{\text{ab}} &= \frac{1}{12} (\sigma_i^a)^3 \tilde{\mathbf{E}}^{\text{T}} \tilde{\mathbf{A}}_j^{\text{b}} + \frac{1}{2} (\sigma_i^a)^2 \tilde{\mathbf{E}}^{\text{T}} \tilde{\boldsymbol{\beta}}_j^{\text{b}} \\
&\quad + \sum_n \mathbf{C}_{ij}^{(n)\text{ab}} \left[\left(\frac{1}{z_n} + \sigma_i^a \right) e^{-z_n \sigma_{ij}^{\text{ab}}} - \frac{1}{z_n} e^{-z_n \lambda_{ij}^{\text{ba}}} \right] \\
&\quad - \sigma_i^a \mathbf{t}_{ij}^{\text{ab}} \quad (74)
\end{aligned}$$

and $\partial \gamma_{i\alpha j\beta}^{(n)ab} = \partial \gamma_{i\alpha j\beta}^{(n)ab}(z_n) / \partial z_n$. Expression for $\partial \gamma_{i\alpha j\beta}^{(n)ab}$ follows from the relation (27) differentiated with respect to z_n

$$\begin{aligned}
z_n^2 \partial \gamma_{ij}^{(n)ab} &= - \sum_c \sum_l [\mathbf{f}_{il}^{\text{ac}}(z_n) - z_n \partial \mathbf{f}_{il}^{\text{ac}} \\
&\quad + z_n^2 \sum_k \gamma_{ik}^{\text{ad}}(z_n) \partial \hat{\boldsymbol{\Omega}}_{kl}^{(n)dc}] [\hat{\mathbf{Q}}^{-1}(iz_n)]_{lj}^{\text{cb}}, \quad (75)
\end{aligned}$$

where

$$\begin{aligned}
\partial \mathbf{f}_{ij}^{(n)ab} &= \tilde{\mathbf{E}}^{\text{T}} \{ \tilde{\mathbf{A}}_j^{\text{b}} \left[\frac{1}{2} \sigma_i^a - \left(1 + \frac{1}{2} z_n \sigma_i^a \right) \left(\frac{2}{z_n} + \sigma_{ij}^{\text{ab}} \right) \right] \\
&\quad - \tilde{\boldsymbol{\beta}}_j^{\text{b}} (1 + z_n \sigma_{ij}^{\text{ab}}) \} \frac{1}{z_n^2} e^{-z_n \sigma_{ij}^{\text{ab}}} \\
&\quad + \sum_m \mathbf{C}_{ij}^{(m)\text{ab}} \frac{z_m}{z_m + z_n} \left(\frac{1}{z_n + z_m} + \sigma_{ij}^{\text{ab}} \right) e^{-(z_n + z_m) \sigma_{ij}^{\text{ab}}} \\
&\quad - \sigma_{ij}^{\text{ab}} \mathbf{t}_{ij}^{\text{ab}} e^{-z_n \sigma_{ij}^{\text{ab}}}, \quad (76)
\end{aligned}$$

$$\begin{aligned}
e^{-z_n \lambda_{ij}^{\text{ab}}} \partial \hat{\boldsymbol{\Omega}}_{ij}^{(n)ab} &= (\sigma_i^a)^3 \tilde{\mathbf{E}}^{\text{T}} \left[\sigma_i^a \tilde{\mathbf{A}}_j^{\text{b}} \frac{\partial \phi_1(\sigma_i^a z_n)}{\partial z_n} + \tilde{\boldsymbol{\beta}}_j^{\text{b}} \frac{\partial \varphi_1(\sigma_i^a z_n)}{\partial z_n} \right] \\
&\quad - \frac{1 - (1 + \sigma_i^a z_n) e^{-z_n \sigma_i^a}}{z_n^2} \mathbf{t}_{ij}^{\text{ab}} \\
&\quad + \sum_m \left\{ \mathbf{C}_{ij}^{(m)\text{ab}} \left[\frac{(1 + \sigma_i^a (z_m + z_n)) e^{-\sigma_i^a z_n} - e^{\sigma_i^a z_m}}{(z_m + z_n)^2} \right. \right. \\
&\quad \left. \left. + \frac{1 - (1 + z_n \sigma_i^a) e^{-\sigma_i^a z_n}}{z_n^2} \right] e^{-z_m \sigma_{ij}^{\text{ab}}} \right. \\
&\quad \left. - \tilde{\mathbf{E}}^{\text{T}} \tilde{\mathbf{D}}_{ij}^{(m)\text{ab}} \frac{e^{-z_m \lambda_{ji}^{\text{ba}}}}{(z_m + z_n)^2} \right\} + \lambda_{ij}^{\text{ab}} \hat{\boldsymbol{\Omega}}_{ij}^{\text{ab}}(z_n) e^{-z_n \lambda_{ij}^{\text{ab}}}. \quad (77)
\end{aligned}$$

Here expression (73) is obtained by differentiating equation (11) twice and considering the limit of $r \rightarrow \sigma_{ij}^{\text{ab}}+$,

and expression (74) follows from the first of equations (8) at $k \rightarrow 0$.

Finally, for the sake of completeness we also present the expression for the pressure obtained from the virial route

$$\begin{aligned} \frac{\beta P}{\rho} = & 1 + \frac{2\pi}{3} \sum_{ab} \frac{\rho_a \rho_b}{\rho} \sum_{ij} (\sigma_{ij}^{ab})^3 e^{-\beta \Phi_{ij}^{(Y)ab}(\sigma_{ij}^{ab})} \sum_{\alpha\beta} y_{i\alpha j\beta}^{ab} (\sigma_{ij}^{ab} + \\ & - \sum_a \frac{\rho_a}{\rho} \sum_{i=1}^{m_a-1} \sigma_{i+1}^{aa} \frac{\partial h_{i_0, (i+1)_0}^{aa}}{3g_{i_0, (i+1)_0}^{aa}} \\ & + \frac{1}{3} \sum_{ab} \frac{\rho_a}{\rho} \sum_{ij} \sum_n K_{ij}^{(n)ab} z_n^2 \sum_{\alpha} \partial \gamma_{i\alpha j_0}^{(n)ab} \\ & + \frac{1}{3} \sum_a \frac{\rho_a}{\rho} \sum_{i=1}^{m_a-1} \sum_n \left(\frac{1}{\sigma_{i+1}^{aa}} + z_n \right) K_{i+1}^{(n)aa} e^{-z_n \sigma_{i+1}^{aa}}. \quad (78) \end{aligned}$$

6. Monte Carlo Simulations

We have calculated the PVT behaviour and structure of the dimer, tetramer, 8-mer and 16-mer single-Yukawa HSYC fluids using isothermal-isobaric (NpT) Monte Carlo simulation. We used NpT (thus calculating density) rather than using NVT (thus calculating pressure) since the calculation of the pressure for the HSYC fluid is non-trivial, involving extrapolation of correlation functions to contact, and other technical details. This difficulty is avoided in NpT simulations in which the number of molecules N , pressure p and temperature T are fixed during the simulation. All the simulations were performed with systems of $N = 256$ particles and at state points, ensuring a wide range of temperatures and pressures were examined.

Initial configurations were generated at low pressure by arranging the molecules on a face-centred cubic (fcc) lattice. Simulations at higher pressures, and hence densities, were then started from this equilibrated initial configuration and allowed to re-equilibrate to the corresponding density. The usual periodic boundary conditions and minimum image convention were applied, with the potential being truncated beyond 3σ . One simulation cycle consisted of N attempted displacement, reorientation and reptation moves (i.e., the same number of displacements as the total number of molecules in the system), one attempted volume change, and a specific number of attempted re-growths of randomly selected molecules using continuum configurational bias sampling (CCB) [28]. CCB was used in the reptation and re-growth moves for N -mers greater than $N = 4$.

In all the simulations the maximum displacement and volume changes were adjusted to give an acceptance ratio of between 30% and 40%, and the number of re-

growths was controlled so that between 1% and 3% of the molecules were re-grown each cycle.

The thermodynamic properties of the system were obtained as ensemble averages and the errors estimated by determining the standard deviation. An initial simulation of 50 000–200 000 cycles was performed to equilibrate the system, depending upon pressure and chain length, before averaging for between 200 000 and 500 000 cycles.

7. Results and discussion

In this section we present MC and PMSA results for the structure and thermodynamic properties of the one-component HSYC fluid with one Yukawa tail. For the sake of simplicity we assume the same site–site potential between any pair of beads i and j , i.e.,

$$\Phi_{ij}(r) = \Phi^{(hs)}(r) + \Phi^{(Y)}(r), \quad (79)$$

where $\sigma_i = \sigma = 1$ for all values of i and

$$\beta \Phi^{(Y)}(r) = -\frac{K}{r} e^{-zr}. \quad (80)$$

Instead of explicitly specifying the values of K and molecular number density ρ it is more convenient to use the dimensionless quantities T^* and η , i.e., $T^* = e^z/K$ and $\eta = \pi\rho\sigma^3/6$. Once the values of these quantities, together with the values for the chain length m and Yukawa exponent z are given, the equilibrium properties of the system can be calculated as discussed in the previous sections.

In this study we considered the HSYC fluid model of four different chain lengths $m = 2, 4, 8, 16$ with a fixed value of the Yukawa exponent $z = 1.8$ at various thermodynamic states (T^*, η).

7.1. Structure properties

Usually the structural properties of a fluid of chain molecules are described in terms of the average intermolecular and intramolecular site–site radial distribution functions (RDF) $g^{(inter)}(r)$ and $\omega(r)$, respectively, which are related to the individual intermolecular and overall RDFs $g_{ij}^{(inter)}(r)$ and $g_{ij}(r)$ as follows:

$$\begin{aligned} g^{(inter)}(r) &= \frac{1}{m^2} \sum_{ij} g_{ij}^{(inter)}(r), \\ \omega(r) &= 4\pi\rho m r^2 [g(r) - g^{(inter)}(r)], \quad (81) \end{aligned}$$

where the overall RDF $g(r)$ is defined by the relation (similar to expression (81))

$$g(r) = \frac{1}{m^2} \sum_{ij} g_{ij}(r). \quad (82)$$

Here $g_{ij}(r)$ are the individual overall RDFs, which contain contributions from both intermolecular and intramolecular correlations. Within the framework of PROZA, these RDFs follow directly from the solution of the present PMSA theory and have been calculated using Fourier transforms via equation (62). To separate intra- and intermolecular parts of the correlation from the overall RDF $g_{ij}(r)$ we use the method proposed in [9]. We treat the original one-component system as a two-component equimolar mixture of identical molecules of species 1 and 2. The site-site RDF between the sites of molecules of different species $g_{ij}^{12}(r)$ represents an intermolecular part of the overall RDF of the one-component system in question, i.e. $g_{ij}^{(inter)}(r) = g_{ij}^{12}(r)$. We note, however, that calculation of the thermodynamic properties requires the overall

RDF $g(r)$ rather than the separate intermolecular and intramolecular RDFs, $g^{(inter)}(r)$ and $\omega(r)$. Therefore in addition to intermolecular and intramolecular RDFs we present also the overall RDFs.

Comparisons of the structures predicted by the present theory with those obtained from the MC simulation method for low, intermediate and high packing fractions η and at different values of the temperature T^* for the HSYC fluid of three different chain lengths $m = 2, 4$ and 8 are given in figures 1–8. In the case of the dimer Yukawa fluid the agreement between the theoretical and computer simulation results for $g(r)$ is very good at all values of the temperature T^* and packing fraction η studied, except for distances in the vicinity of contact (figures 1–3). It can be seen that our theory slightly underpredicts the contact values of the RDFs. As the

Figure 1. Average radial distribution function $g(r)$ of the hard sphere Yukawa dimers ($m = 2$) at $(T^*, \eta) = (1.8, 0.082)$ (triangles), $(1.8, 0.307)$ (squares) and $(1.8, 0.393)$ (circles). The corresponding solid lines are theoretical results and the symbols are results of Monte Carlo simulations.

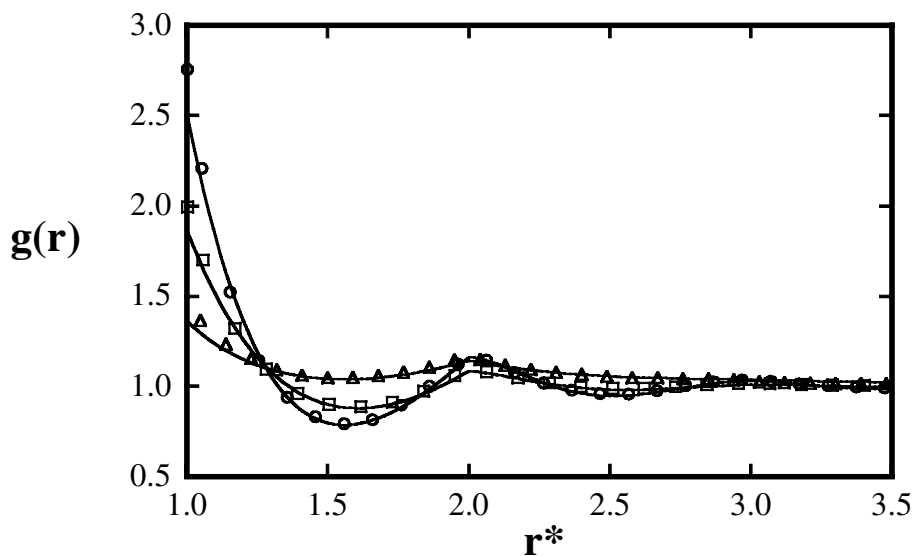
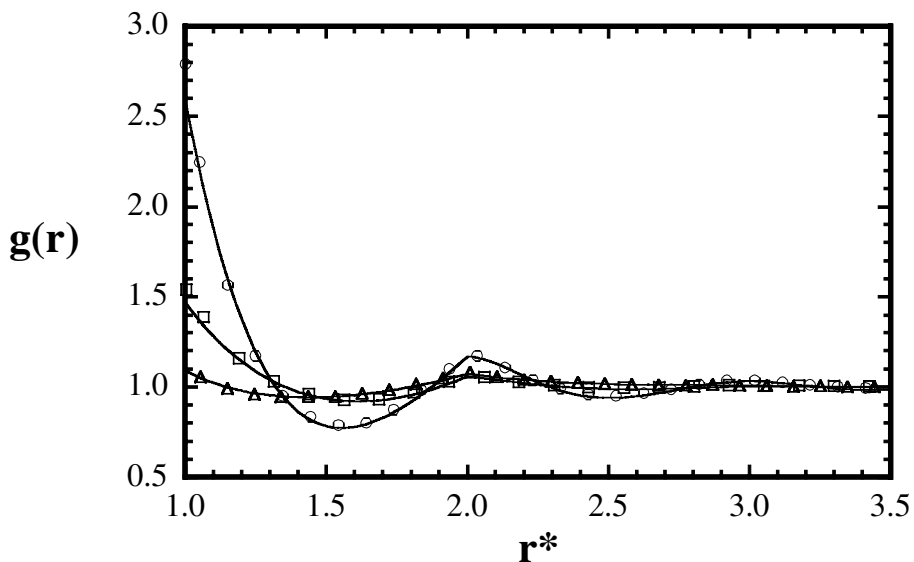


Figure 2. As for figure 1 at $(T^*, \eta) = (2.8, 0.088)$ (triangles), (squares) and $(2.8, 0.404)$ (circles).



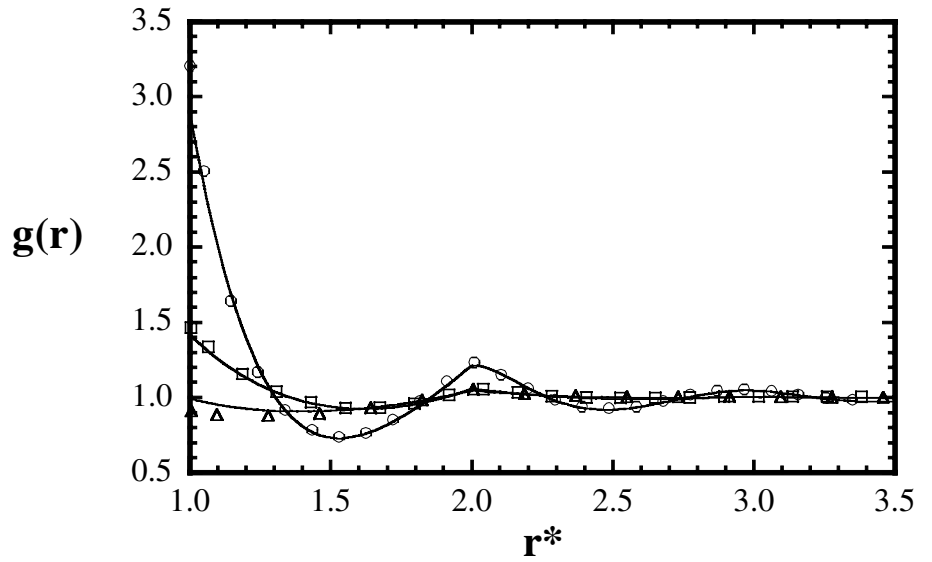


Figure 3. As for figure 1 at $(T^*, \eta) = (5, 0.088)$ (triangles), $(5, 0.251)$ (squares) and $(5, 0.432)$ (circles).

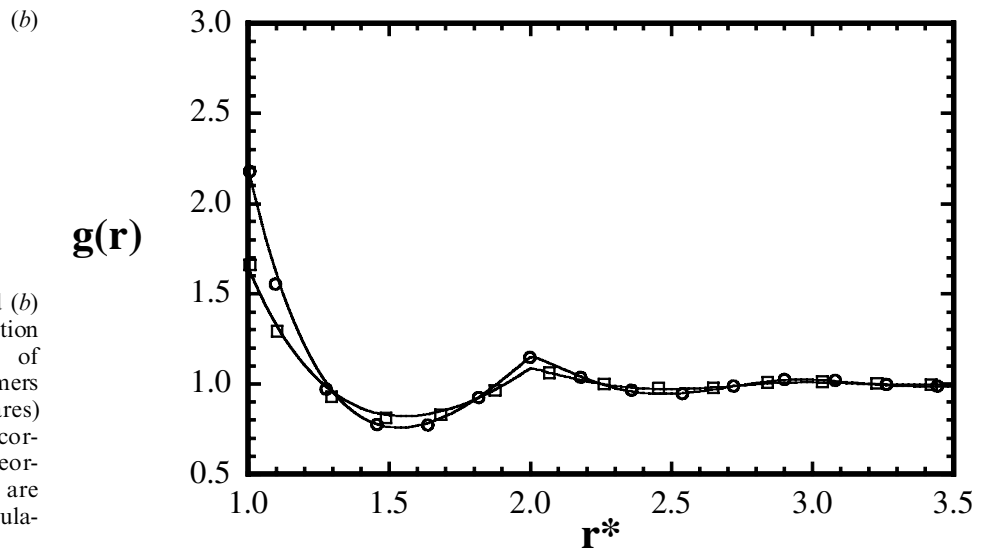
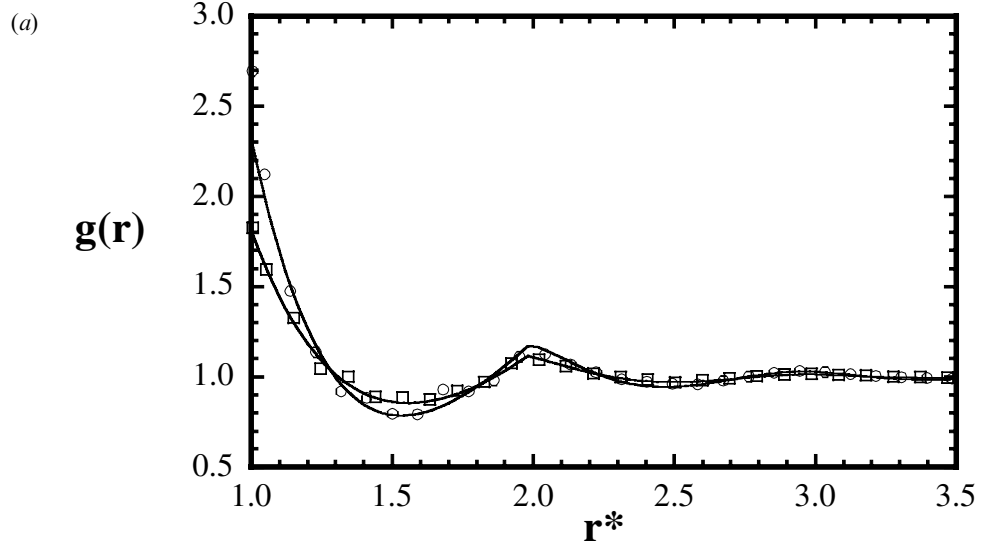


Figure 4. Average (a) overall and (b) intermolecular radial distribution functions $g(r)$ and $g^{(\text{inter})}(r)$ of the hard sphere Yukawa tetramers at $(T^*, \eta) = (1.8, 0.331)$ (squares) and $(1.8, 0.401)$ (circles). The corresponding solid lines are theoretical results and the symbols are results of Monte Carlo simulations.

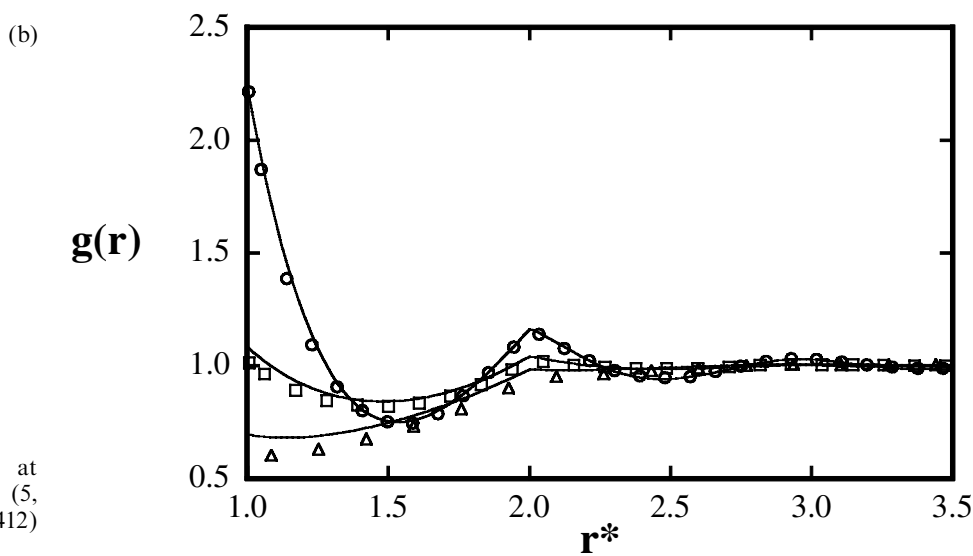
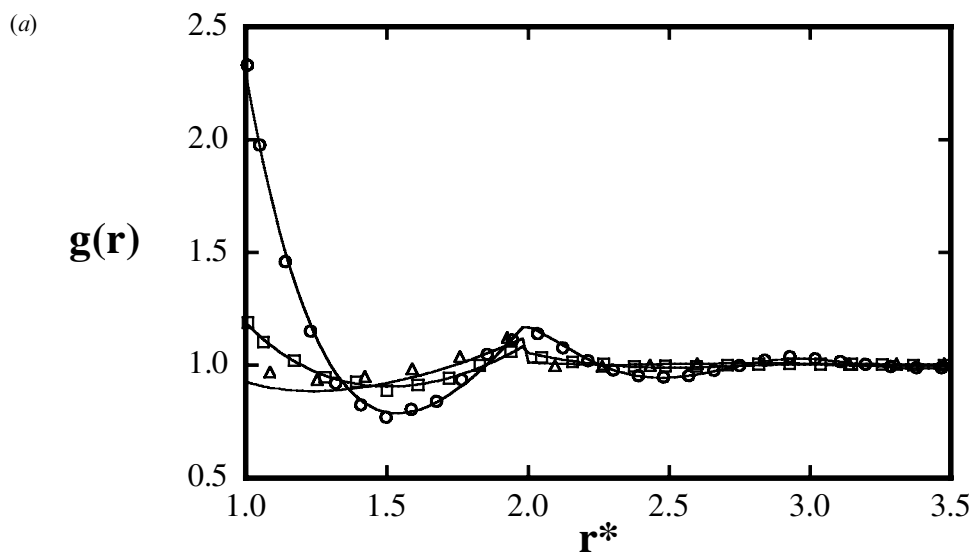


Figure 5. As for figure 4 at $(T^*, \eta) = (5, 0.09)$ (triangles), $(5, 0.248)$ (squares) and $(5, 0.412)$ (circles).

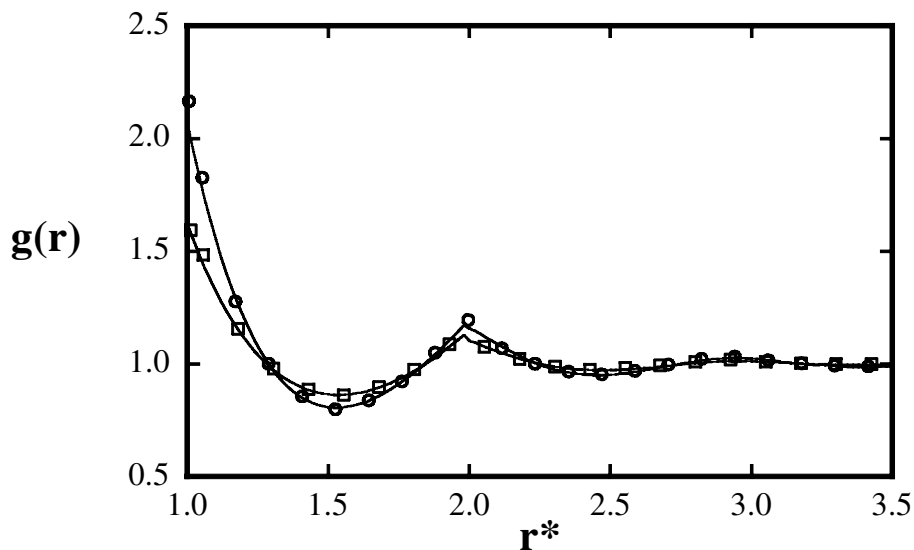
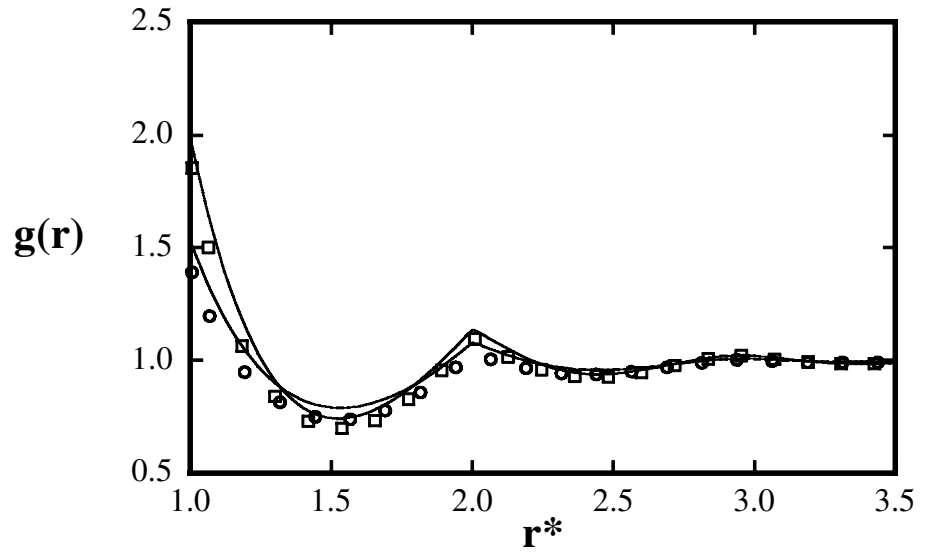
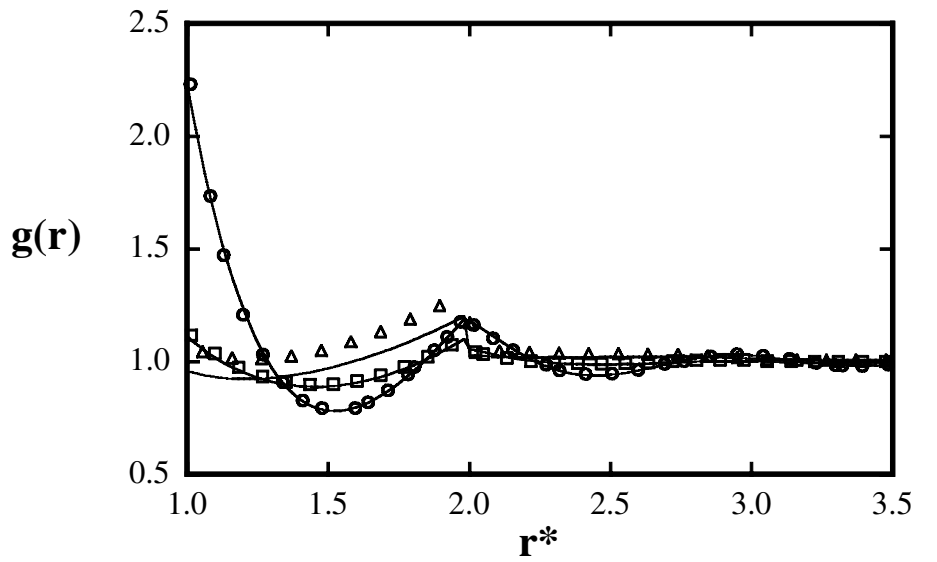


Figure 6. (a) Average overall radial distribution functions $g(r)$ and $g^{(inter)}(r)$ of the hard sphere Yukawa 8-mers at $(T^*, \eta) = (2.3, 0.348)$ (squares) and $(2.3, 0.404)$ (circles). The corresponding solid lines are theoretical results and the symbols are results of Monte Carlo simulations.

Figure 6. (b) Average intermolecular (radial distribution functions $g(r)$ and $g^{(inter)}(r)$ of the hard sphere Yukawa 8-mers at $(T^*, \eta) = (2.3, 0.348)$ (squares) and $(2.3, 0.404)$ (circles). The corresponding solid lines are theoretical results and the symbols are results of Monte Carlo simulations.



(a)



(b)

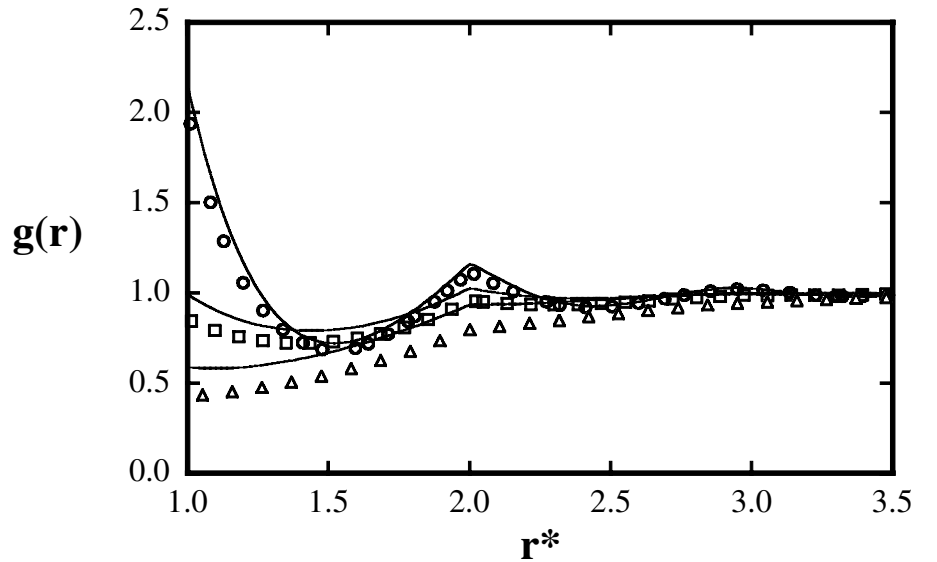


Figure 7. As for figure 6 at $(T^*, \eta) = (5, 0.085)$ (triangles), $(5, 0.264)$ (squares) and $(5, 0.423)$ (circles).

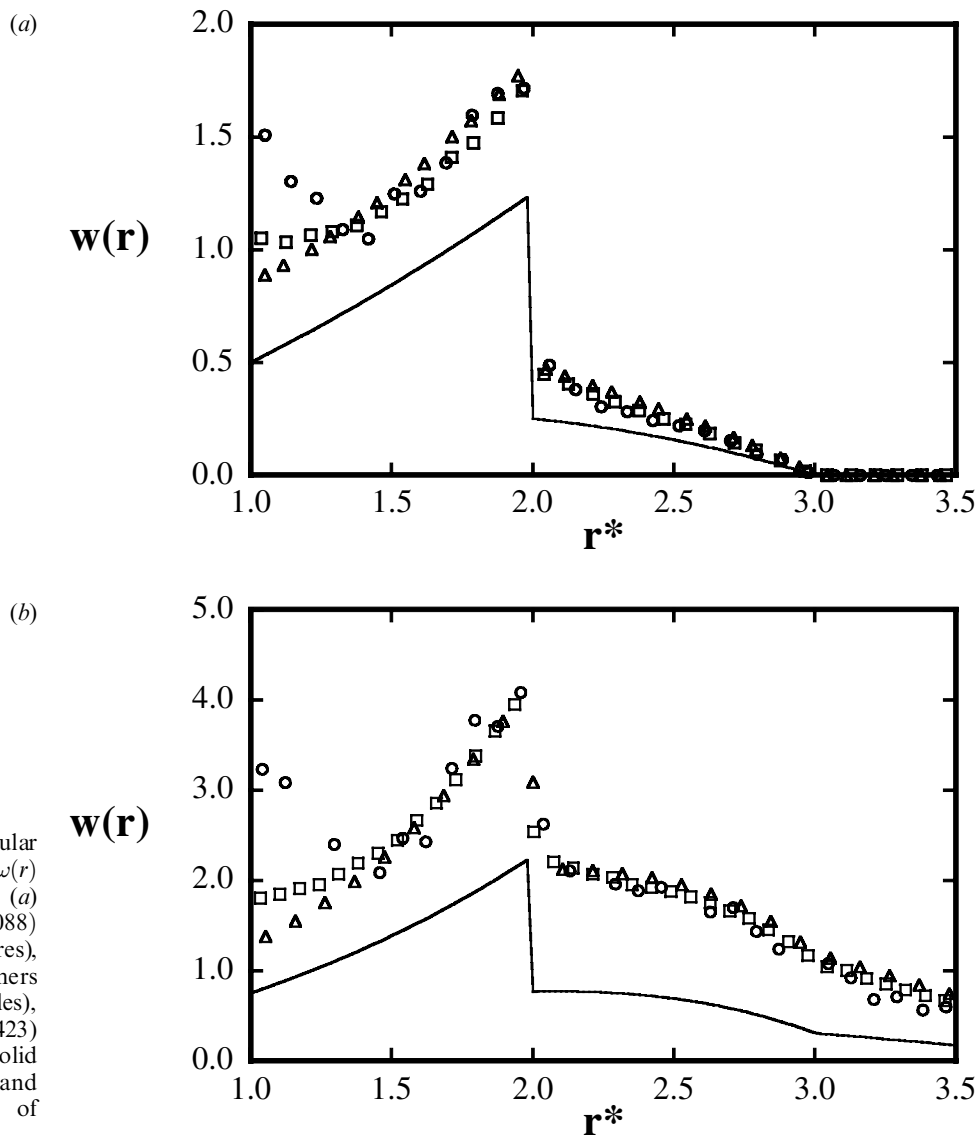


Figure 8. Average intramolecular radial distribution function $\omega(r)$ of the hard sphere Yukawa (a) tetramers at $(T^*, \eta) = (5, 0.088)$ (triangles), $(5, 0.248)$ (squares), $(5, 0.412)$ (circles) and (b) 8-mers at $(T^*, \eta) = (5, 0.085)$ (triangles), $(5, 0.264)$ (squares) and $(5, 0.423)$ (circles). The corresponding solid lines are theoretical results and the symbols are the results of Monte Carlo simulation.

chain length is increased the agreement at intermediate and high values of η is still good, while for low values of η the predictions of the present theory become slightly less accurate. Figure 8 presents the results for the intramolecular RDF $\omega(r)$. As was observed in the case of the hard sphere chain fluid [9], the agreement with the computer simulation results is only qualitative, and the theoretical $\omega(r)$ do not exhibit any dependence on the density and temperature. The corresponding MC simulation results demonstrate only a weak dependence of $\omega(r)$ on T^* and η , which is seen in the distance range $1 < r < 1.5$.

In general the overall RDFs are predicted more accurately than the corresponding intermolecular and intramolecular RDFs. This is reflected in the higher accuracy of the theoretical results for the thermodynamic properties, which are discussed in the next section.

7.2. Thermodynamic properties

The NpT simulation results for the dimer along isotherms of $T^* = 1.8, 2.8$ and 5 and a range of pressures are reported in table 1. The results are presented in figure 9 along with the corresponding PMSA predictions. We note in passing that the reference system properties are described hereafter using dimer thermodynamic perturbation theory [29]. We see excellent agreement between the results of the NpT Monte Carlo simulations and the theoretical predictions for all the state points studied. In figure 10 we compare the theoretical predictions and NpT simulation results for the tetramer fluid, again over a range of temperatures and pressures, in order to test the accuracy of the theory under different state conditions. The corresponding simulation data are detailed in table 2. As can be seen from the figure we see very good agreement

Table 1. Isothermal–isobaric Monte Carlo and PMSA results for the hard core single-Yukawa dimer fluid. The fixed variables during the simulation are the number of particles $N = 256$, the reduced pressure $p^* = p\sigma^3/\varepsilon$, and the reduced temperature $T^* = kT/\varepsilon$, where $\varepsilon = kTK e^{-z}$. The packing fraction is given by η and the reduced energy per segment $E^* = E/\varepsilon m$; the uncertainties correspond to one standard deviation.

| T^* | p^* | $\eta(\text{MC})$ | $E^*(\text{MC})$ | $\eta(\text{PMSA})$ | $E^*(\text{PMSA})$ |
|-------|--------|-------------------|------------------|---------------------|--------------------|
| 1.8 | 0.055 | 0.039 ± 0.004 | -0.43 ± 0.06 | 0.041 | -0.67 |
| 1.8 | 0.099 | 0.082 ± 0.010 | -0.90 ± 0.11 | 0.091 | -1.04 |
| 1.8 | 0.124 | 0.113 ± 0.013 | -1.21 ± 0.14 | 0.132 | -1.47 |
| 1.8 | 0.842 | 0.307 ± 0.010 | -3.42 ± 0.13 | 0.317 | -3.66 |
| 1.8 | 1.588 | 0.350 ± 0.010 | -3.91 ± 0.12 | 0.358 | -4.24 |
| 1.8 | 2.908 | 0.393 ± 0.009 | -4.55 ± 0.10 | 0.398 | -4.84 |
| 2.8 | 0.100 | 0.038 ± 0.003 | -0.36 ± 0.04 | 0.037 | -0.39 |
| 2.8 | 0.245 | 0.088 ± 0.007 | -0.86 ± 0.07 | 0.091 | -0.94 |
| 2.8 | 0.380 | 0.126 ± 0.009 | -1.23 ± 0.11 | 0.131 | -1.37 |
| 2.8 | 1.353 | 0.248 ± 0.010 | -2.57 ± 0.12 | 0.253 | -2.78 |
| 2.8 | 2.480 | 0.301 ± 0.008 | -3.25 ± 0.11 | 0.307 | -3.50 |
| 2.8 | 4.145 | 0.347 ± 0.007 | -3.90 ± 0.10 | 0.351 | -4.14 |
| 2.8 | 7.656 | 0.404 ± 0.006 | -4.66 ± 0.08 | 0.405 | -4.94 |
| 5.0 | 0.220 | 0.041 ± 0.003 | -0.36 ± 0.04 | 0.042 | -0.40 |
| 5.0 | 0.565 | 0.090 ± 0.006 | -0.81 ± 0.07 | 0.090 | -0.89 |
| 5.0 | 1.019 | 0.134 ± 0.007 | -1.26 ± 0.08 | 0.136 | -1.36 |
| 5.0 | 3.655 | 0.251 ± 0.008 | -2.59 ± 0.10 | 0.253 | -2.76 |
| 5.0 | 10.103 | 0.350 ± 0.006 | -3.89 ± 0.09 | 0.351 | -4.13 |
| 5.0 | 14.548 | 0.386 ± 0.006 | -4.50 ± 0.09 | 0.387 | -4.66 |
| 5.0 | 22.906 | 0.432 ± 0.005 | -5.08 ± 0.08 | 0.432 | -5.36 |

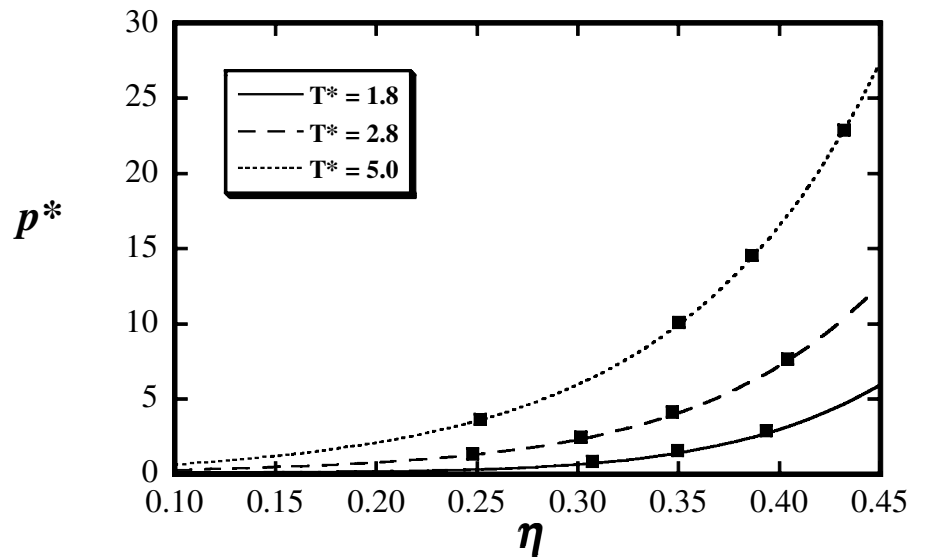


Figure 9. Isotherms for the hard core single-Yukawa dimer fluid. The squares represent the results of isothermal–isobaric Monte Carlo simulations and the lines correspond to the PMSA predictions.

between the simulation data and the PMSA theory for the tetramer fluid at all the state points examined. In figures 11 and 12 we present similar results for the 8-mer and 16-mer fluids, respectively, with the corresponding data being given in tables 3 and 4. Excellent agreement at each state point studied is again achieved between the simulation data and the theoretical predic-

tions, as was observed for the shorter chains. Finally, in figure 13 we compare simulation results at $T^* = 5$ for the dimer, tetramer, and octamer fluids at low pressure in order to examine the accuracy of the theory in predicting the low density behaviour of the fluids. Again, in all cases, good agreement is seen between the theoretical results and the NpT simulations.

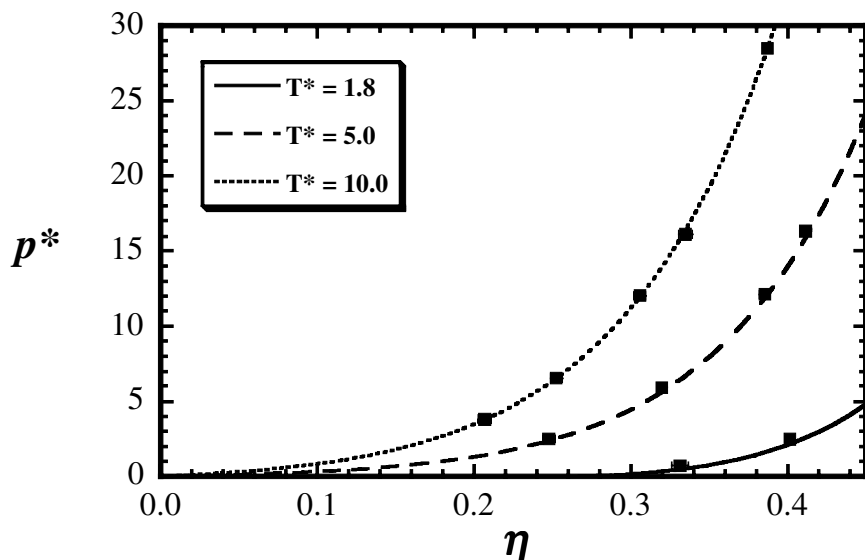


Figure 10. Isotherms for the hard core single-Yukawa 4-mer fluid. The squares represent the results of isothermal-isobaric Monte Carlo simulations and the lines correspond to the PMSA predictions.

Table 2. Isothermal-isobaric Monte Carlo and PMSA results for the hard core single-Yukawa 4-mer fluid. The fixed variables during the simulation are as for table 1.

| T^* | p^* | $\eta(\text{MC})$ | $E^*(\text{MC})$ | $\eta(\text{PMSA})$ | $E^*(\text{PMSA})$ |
|-------|--------|-------------------|------------------|---------------------|--------------------|
| 1.8 | 0.730 | 0.341 ± 0.005 | -3.65 ± 0.07 | 0.349 | -3.91 |
| 1.8 | 2.490 | 0.405 ± 0.004 | -4.48 ± 0.05 | 0.410 | -4.79 |
| 5.0 | 0.100 | 0.037 ± 0.002 | -0.45 ± 0.05 | 0.039 | -0.45 |
| 5.0 | 0.292 | 0.088 ± 0.004 | -0.84 ± 0.04 | 0.091 | -0.90 |
| 5.0 | 0.563 | 0.133 ± 0.005 | -1.22 ± 0.05 | 0.136 | -1.32 |
| 5.0 | 0.909 | 0.169 ± 0.004 | -1.56 ± 0.05 | 0.172 | -1.68 |
| 5.0 | 2.520 | 0.250 ± 0.005 | -2.49 ± 0.05 | 0.253 | -2.61 |
| 5.0 | 5.930 | 0.323 ± 0.003 | -3.32 ± 0.04 | 0.324 | -3.55 |
| 5.0 | 12.130 | 0.388 ± 0.003 | -4.23 ± 0.04 | 0.387 | -4.45 |
| 5.0 | 16.340 | 0.412 ± 0.003 | -4.66 ± 0.03 | 0.414 | -4.85 |
| 10.0 | 3.830 | 0.207 ± 0.004 | -1.91 ± 0.05 | 0.208 | -2.05 |
| 10.0 | 6.550 | 0.252 ± 0.004 | -2.43 ± 0.05 | 0.253 | -2.59 |
| 10.0 | 12.040 | 0.306 ± 0.004 | -3.09 ± 0.05 | 0.307 | -3.29 |
| 10.0 | 16.140 | 0.335 ± 0.004 | -3.47 ± 0.06 | 0.336 | -3.67 |
| 10.0 | 28.510 | 0.387 ± 0.003 | -4.20 ± 0.04 | 0.387 | -4.45 |

8. Conclusions

In this work a theoretical and computer simulation study of the structure and thermodynamic properties of the freely jointed hard sphere single-Yukawa chain fluid is presented. The theory is based on the PMSA version of the product-reactant Ornstein-Zernike approach [7–13]. An analytical solution of the PMSA for the multicomponent freely jointed hard sphere multi-Yukawa chain fluid is presented and closed form analytical expressions for the structure (contact values of the monomer–monomer radial distribution functions, structure factors) and thermodynamic (internal energy, Helmholtz free energy, chemical potentials and pressure) properties of the system at hand are derived. Iso-

thermal-isobaric Monte Carlo computer simulations are carried out for the dimer, tetramer, 8-mer and 16-mer versions of the one-Yukawa hard sphere chain fluid. From a comparison of the results of the theory and computer simulations we find that in general the theory accurately describes the overall and intermolecular radial distribution functions at high and intermediate densities. The PMSA predictions for the intramolecular radial distribution function $\omega(r)$ (equation (81)) of the present model is only qualitatively correct, as was the case of the freely jointed hard sphere chain fluid [9]. This discrepancy results in slightly less accurate results for the overall and intermolecular radial distribution function for the longer chains and/or at

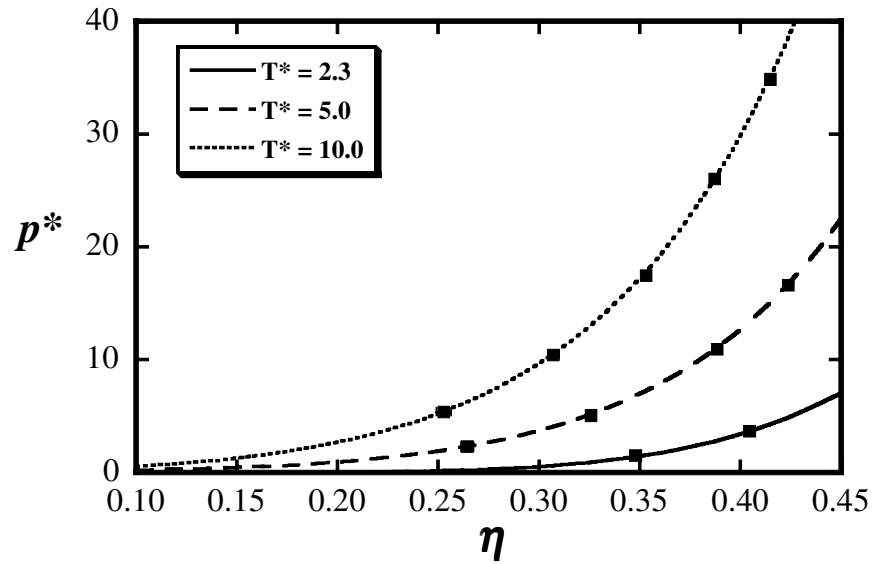


Figure 11. Isotherms for the hard core single-Yukawa 8-mer fluid. The squares represent the results of isothermal-isobaric Monte Carlo simulations and the lines correspond to the PMSA predictions.

Table 3. Isothermal-isobaric Monte Carlo and PMSA results for the hard core single-Yukawa 8-mer fluid. The fixed variables during the simulation are as for table 1.

| T^* | p^* | $\eta(\text{MC})$ | $E^*(\text{MC})$ | $\eta(\text{PMSA})$ | $E^*(\text{PMSA})$ |
|-------|--------|-------------------|------------------|---------------------|--------------------|
| 2.3 | 1.480 | 0.349 ± 0.002 | -3.60 ± 0.03 | 0.352 | -3.84 |
| 2.3 | 3.670 | 0.405 ± 0.002 | -4.36 ± 0.03 | 0.405 | -4.62 |
| 5.0 | 2.300 | 0.264 ± 0.003 | -2.50 ± 0.03 | 0.265 | -2.68 |
| 5.0 | 5.060 | 0.326 ± 0.002 | -3.28 ± 0.03 | 0.324 | -3.45 |
| 5.0 | 10.920 | 0.388 ± 0.002 | -4.10 ± 0.03 | 0.387 | -4.34 |
| 5.0 | 16.590 | 0.424 ± 0.002 | -4.65 ± 0.03 | 0.423 | -4.88 |
| 10.0 | 5.380 | 0.253 ± 0.004 | -2.39 ± 0.03 | 0.253 | -2.51 |
| 10.0 | 10.430 | 0.307 ± 0.003 | -3.02 ± 0.03 | 0.307 | -3.20 |
| 10.0 | 17.500 | 0.353 ± 0.002 | -3.62 ± 0.03 | 0.351 | -3.82 |
| 10.0 | 26.050 | 0.387 ± 0.001 | -4.13 ± 0.03 | 0.387 | -4.34 |
| 10.0 | 34.880 | 0.415 ± 0.002 | -4.51 ± 0.02 | 0.414 | -4.74 |

Table 4. Isothermal-isobaric Monte Carlo and PMSA results for the hard core single-Yukawa 16-mer fluid. The fixed variables during the simulation are as for table 1.

| T^* | p^* | $\eta(\text{MC})$ | $E^*(\text{MC})$ | $\eta(\text{PMSA})$ | $E^*(\text{PMSA})$ |
|-------|--------|-------------------|------------------|---------------------|--------------------|
| 2.3 | 1.110 | 0.346 ± 0.002 | -3.51 ± 0.03 | 0.345 | -3.71 |
| 2.3 | 4.295 | 0.420 ± 0.001 | -4.52 ± 0.01 | 0.420 | -4.78 |
| 5.0 | 2.180 | 0.269 ± 0.003 | -2.53 ± 0.04 | 0.271 | -2.71 |
| 5.0 | 5.527 | 0.339 ± 0.002 | -3.39 ± 0.03 | 0.338 | -3.59 |
| 5.0 | 9.759 | 0.384 ± 0.001 | -4.01 ± 0.02 | 0.383 | -4.22 |
| 5.0 | 16.730 | 0.423 ± 0.001 | -4.54 ± 0.01 | 0.428 | -4.89 |
| 10.0 | 4.507 | 0.250 ± 0.003 | -2.32 ± 0.05 | 0.248 | -2.42 |
| 10.0 | 8.129 | 0.294 ± 0.004 | -2.84 ± 0.05 | 0.293 | -2.98 |
| 10.0 | 14.061 | 0.339 ± 0.002 | -3.40 ± 0.02 | 0.338 | -3.58 |
| 10.0 | 23.600 | 0.384 ± 0.001 | -4.00 ± 0.02 | 0.383 | -4.22 |
| 10.0 | 38.797 | 0.422 ± 0.001 | -4.53 ± 0.01 | 0.428 | -4.89 |

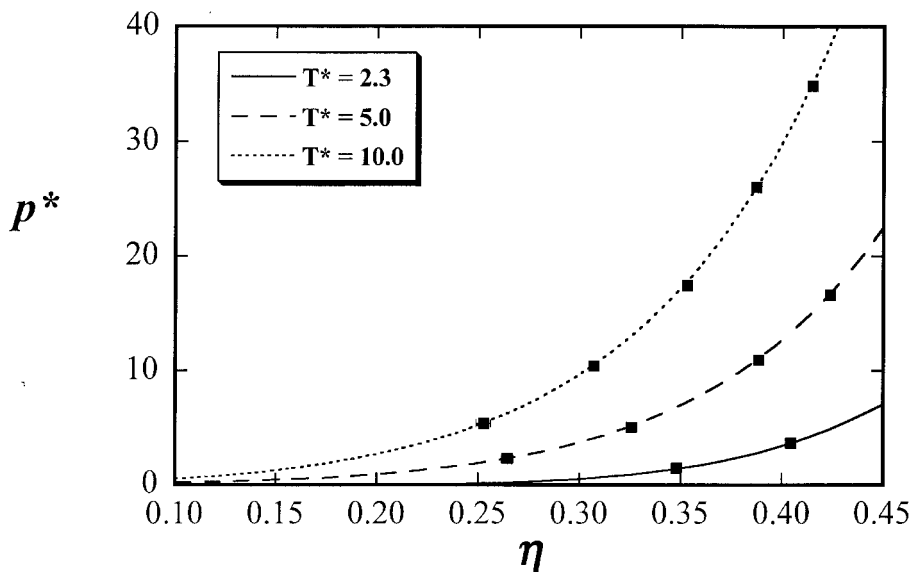


Figure 12. Isotherms for the hard core single Yukawa 16-mer fluid. The squares represent the results of isothermal-isobaric Monte Carlo simulations and the lines correspond to the PMSA predictions.

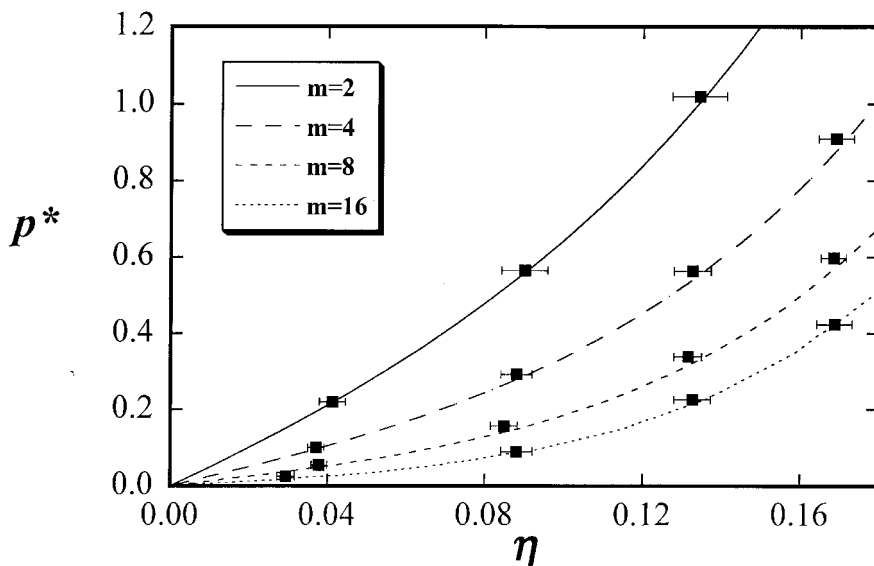


Figure 13. Isotherms at $T^* = 5$ for the hard core dimer (solid line), 4-mer (long dashed line), 8-mer (short dashed line), and 16-mer (dotted line) single-Yukawa fluid. The squares represent the results of isothermal-isobaric Monte Carlo simulations and the lines correspond to the PMSA predictions.

lower densities. However, the agreement is still quite reasonable, especially in the case of the overall radial distribution functions. This is reflected in the higher accuracy of the theoretical results for thermodynamics, which are calculated using as an input the overall radial distribution functions. For each N -mer fluid studied the theoretical predictions for the PVT properties over a range of state points are in very good agreement with the NpT Monte Carlo simulations performed to test the theoretical approach. The latter finding is not unexpected, since quite reasonable thermodynamics can be predicted using the Flory approach with a far worse ideal gas approximation for the structure, i.e. $g(r) = 1$.

In summary, the theory presented provides a quantitatively reliable analytical route to the structure and thermodynamic properties for a well defined model of chain fluids. In future applications we are planning to perform a detailed theoretical and computer simulation study of the equilibrium properties of the multi-Yukawa chain mixtures, in particular focusing on their phase behaviour.

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