



ELSEVIER

Fluid Phase Equilibria 194–197 (2002) 185–196

FLUID PHASE
EQUILIBRIA

www.elsevier.com/locate/fluid

Thermodynamic properties of freely-jointed hard-sphere multi-Yukawa chain fluids: theory and simulation

Clare McCabe^{a,b,*}, Yuriy V. Kalyuzhnyi^c, Peter T. Cummings^{b,d}

^a Department of Chemical Engineering, University of Tennessee, Knoxville, TN 37996-2200, USA

^b Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6268, USA

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

^d Departments of Chemical Engineering, Chemistry and Computer Science, University of Tennessee, Knoxville, TN 37996-2200, USA

Received 18 March 2001; accepted 7 September 2001

Abstract

The hard-sphere Yukawa chain (HSYC) fluid is a simple model for chain fluids and polymers in which each molecule is composed of freely-jointed tangent spheres. The spheres each have a hard core and an attractive interaction, written as a single Yukawa potential or as a sum of Yukawa potentials. We have calculated the phase equilibria and *PVT* behaviour of the HSYC fluid both theoretically and by Monte Carlo simulation. The theoretical approach is based on the analytic solution of the polymer mean spherical approximation for the HSYC fluid. By comparing the theory and simulation we are able to evaluate the accuracy of the theory. We find that in general the theory performs very well, thus, it provides an analytic route to an equation of state for a well-defined model of chain fluids. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hard-sphere; Yukawa chain fluid; Mean spherical approximation; Ornstein-Zernike equation; Simulation

1. Introduction

Much of the success achieved by liquid-state integral-equation theories is due to the availability of analytic solutions for the corresponding integral-equation approximations (IEA) for a number of non-trivial Hamiltonian models of dense fluids and liquids. Historically, the first IEA to be solved analytically was the Percus–Yevick (PY) approximation for the hard-sphere fluid [1,2] almost 40 years ago. Since then analytical solutions have been obtained for a wide variety of model fluid systems, which in addition to the short-ranged repulsive hard-sphere interaction, include both soft repulsive and attractive tails of different types (see [3,4], and references therein). Among the members of the family of analytically solvable models the hard-sphere Yukawa (HSY) fluid has proven to be very useful in theoretical studies

* Corresponding author. Tel.: +1-303-273-3724; fax: +1-303-273-3730.
E-mail address: cmccabe@mines.edu (C. McCabe).

of the liquid-state. For many applications, a sufficiently accurate description of the HSY fluid model can be achieved using the mean spherical approximation (MSA), which can be solved analytically [8]. This simple model takes into account the main elements of the intermolecular interaction between simple fluid molecules, i.e. very strong spherically symmetric short-range repulsion (modeled by a hard-core) and weaker spherically symmetric long-range attraction (modeled by a Yukawa term). As a result, the HSY model can be used to model the properties of simple fluids. For example, a simple generalization of the one-Yukawa hard-sphere potential to a hard-sphere core with a linear combination of two-Yukawas is able to accurately reproduce the liquid–gas phase diagram of the more realistic Lennard–Jones (LJ) potential [5,7]. Similarly, by joining hard-sphere Yukawa monomers together to form flexible linear chains with fixed bond length we obtain a simple model for chain polymers. In spite of its relative simplicity, the freely-jointed hard-sphere Yukawa chain (HSYC) fluid provides a model which incorporates the most important characteristics of real polymer chains, i.e. excluded volume and chain connectivity effects and the existence of the attractive dispersion forces between the chains. In much the same spirit as the HSY fluid is used to model the properties of simple fluids, the freely-jointed HSYC fluid can be used to model the properties of chain molecules. In order to achieve this goal one requires a sufficiently accurate and simple analytical theory to describe the equilibrium properties of freely-jointed HSYC fluids.

Recently, the so-called product–reactant Ornstein–Zernike approach (PROZA) for polymer–fluid models has been formulated [9–12] and the corresponding version of the mean spherical approximation (MSA), the so-called polymer MSA (PMSA) has been proposed [12–15]. The PROZA, based on earlier work of Wertheim [16–19], is a general statistical-mechanical theory of reacting mixtures in which product and reactant 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. Hence, it is 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 limit of complete association, the theory becomes a theory for the structure and thermodynamics of a fluid of fully polymerized chains. It is such a fluid that we are concerned with here.

We should note that there are alternative integral-equation approaches from which one can compute the structure and, from this, calculate thermodynamical properties. These include the polymer reference interaction site model (PRISM) theory [20,21] and its extensions [22–24], multidensity integral-equation theory [25,26], a version of Percus–Yevick (PY) theory for a mixture of associating species that associate into polymer fluids [27,28], theories based on the use of a Born–Green–Ivon-type hierarchy [29–31] or Kirkwood-type hierarchy [32], and Chandler–Silbey–Ladanyi PY theory [33–36]. These theories fall into two categories: those which have a self-contained description of both intermolecular and intramolecular correlations [22–26,31,32] and those which do not have such a description [20,21,27,28,33–36]. Both PRISM and BGY theories require the application of the numerical methods of the solution, while the theories based on the PY-like approximation [25–28] are analytically solvable. In contrast to these other approaches, the theory utilized in the present study has the dual advantage of being analytically solvable as well as having a self-contained description of both intermolecular and intramolecular correlations. Although our approach is formulated for chains formed from tangentially bonded monomers it can be easily reformulated for chains of fused monomers by simply changing the bond length in the PMSA closure conditions.

A preliminary solution of the PMSA for the one-component multi-Yukawa HSYC fluid model has been recently derived [37] and in order to evaluate the theory, in this paper we compare the PMSA predictions

with Monte Carlo (MC) simulations of the PVT properties for the dimer and tetramer HSYC fluids with two-Yukawa tails. We are unaware of any previous simulations, or integral-equation studies of the phase equilibrium and PVT properties of the HSYC fluids in the literature. In Section 2 we discuss the potential model and present the PMSA theory to be utilized and in Section 3 summarize the analytic solution of the PMSA for the one-component multi-Yukawa HSYC fluid and give expressions for the thermodynamic properties. Details of the simulation methods are given in Section 5 and the predictions of the theory for the gas–liquid phase diagram and PVT properties are compared with those obtained from simulation in Section 6.

2. The model and theory

We describe chain molecules as freely-jointed tangent hard-sphere multi-Yukawa chains. Each molecule is represented by m hard-sphere Yukawa sites of hard-core diameter σ . We denote the site type in a given molecule by the small letters i, j, k, \dots , etc. The site–site potential $\Phi_{ij}(r)$ between the sites of type i and j is given by the sum of the hard-sphere potential $\Phi^{(\text{hs})}(r)$ and Yukawa potential

$$\Phi_{ij}(r) = \Phi^{(\text{hs})}(r) + \Phi_{ij}^{(\text{Y})}(r) \quad (1)$$

where the Yukawa term is given by

$$\beta\Phi_{ij}^{(\text{Y})}(r) = -\frac{1}{r} \sum_n K_{ij}^{(n)} e^{-z_n r} \quad (2)$$

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:

$$\hat{h}_{ij}(k) = \hat{c}_{ij}(k) + \rho \sum_l \hat{c}_{il}(k) \alpha \hat{h}_{lj}(k), \quad (3)$$

where ρ is the total number density of the system, and polymer mean spherical approximation (PMSA) closure relations are given by [12,15]

$$\mathbf{c}_{ij}(r) = \mathbf{E} \sum_n \frac{K_{ij}^{(n)}}{r} e^{-z_n r}, \quad r > \sigma; \quad \mathbf{h}_{ij}(r) = -\mathbf{E} + \frac{\mathbf{t}_{ij}}{2\pi\sigma} \delta(r - \sigma), \quad r < \sigma. \quad (4)$$

In Eqs. (3) and (4), $\hat{h}_{ij}(k)$ and $\hat{c}_{ij}(k)$ are matrices with the elements being the Fourier transforms of the elements of the real-space matrices $\mathbf{h}_{ij}(r)$ and $\mathbf{c}_{ij}(r)$, defined by

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

In this equation, the quantities $h_{i_\alpha j_\beta}(r)$ and $c_{i_\alpha j_\beta}(r)$ appearing in $\mathbf{h}_{ij}(r)$ and $\mathbf{c}_{ij}(r)$, respectively, represent partial total and direct correlation functions. The lower indices α and β each take the values 0, A and B and denote the bonding states of the corresponding particles [12,15], i.e. the case of $\alpha = 0$ corresponds

to an unbonded particle, while $\alpha = A$ or $\alpha = B$ to the particle with bonded site A or B , respectively. The quantities t_{ij} , α and E are the following matrices:

$$t_{i\alpha j\beta} = \frac{1}{2\rho\sigma} [\delta_{\alpha A}\delta_{\beta B}\delta_{i,j+1} + \delta_{\alpha B}\delta_{\beta A}\delta_{i,j-1}], \quad \alpha_{\alpha\beta} = 1 - \delta_{\alpha\beta} + \delta_{\alpha 0}\delta_{\beta 0}, \quad E_{\alpha\beta} = \delta_{\alpha 0}\delta_{\beta 0}.$$

To avoid unnecessary repetition, we do not discuss here the derivation of the PMSA closure conditions and the nature of the approximation involved, for details the reader is referred to the original publications [9–15,18,19,25,26].

The set of the Ornstein-Zernike (OZ) equation (3) together with the PMSA closure conditions (4) represent a closed set of equations to be solved.

3. General solution of the multi-Yukawa PMSA

The analytic solution of PMSA for the HSYC fluid is based on the version of the Baxter factorization technique [43] developed by Blum and co-workers [38–40] for the solution of the regular MSA for the multi-component multi-Yukawa hard-sphere fluid. Introducing the so-called Baxter factorization Q -function $Q_{ij}(r)$, it is possible to separate the initial set of the OZ Eq. (3) into two sets of equations in which the functions $h_{ij}(r)$ and $c_{ij}(r)$ are decoupled [38–40,43]:

$$S_{ij}(|r|) = Q_{ij}(r) - \rho \sum_l \int dr' Q_{il}(r') \alpha [Q_{jl}(r' - r)]^T, \quad (5)$$

$$J_{ij}(|r|) = Q_{ij}(r) + \rho \sum_l \int dr' J_{il}(|r' - r|) \alpha Q_{lj}(r'), \quad (6)$$

where

$$S_{ij}(r) = 2\pi \int_r^\infty dr' r' c_{ij}(r'); \quad J_{ij}(r) = 2\pi \int_r^\infty dr' r' h_{ij}(r'). \quad (7)$$

Using analytical properties of the factor function $\hat{Q}_{ij}(k)$ together with the closure relation (4), we have

$$Q_{ij}(r) = [q_{ij}(r) + t_{ij}] \theta(\sigma - r) + \tilde{E}^T \sum_n \tilde{D}_{ij}^{(n)} e^{-z_n r}, \quad r > 0, \quad (8)$$

where $\tilde{D}_{ij}^{(n)}$ and \tilde{E} are the row vectors, $\tilde{D}_{ij}^{(n)} = (D_{i_0 j_0}^{(n)}, D_{i_0 j_A}^{(n)}, D_{i_0 j_B}^{(n)})$, and $\tilde{E} = (1, 0, 0)$, respectively. The quantities $\tilde{D}_{ij}^{(n)}$ satisfy the following set of algebraic equations:

$$\frac{2\pi}{z_n} \tilde{K}_{ij}^{(n)} = \rho \sum_l \tilde{D}_{il}^{(n)} \alpha [\hat{Q}_{jl}(iz_n)]^T, \quad (9)$$

with $\tilde{K}_{ij}^{(n)} = (K_{ij}^{(n)}, 0, 0)$. The function $q_{ij}(r)$ is defined in the range $0 < r < \sigma$ by

$$q_{ij}(r) = \frac{1}{2} \tilde{E}^T \tilde{A}_j(r - \sigma) r + \tilde{E}^T \tilde{\beta}_j(r - \sigma) + \sum_n C_{ij}^{(n)} (e^{-z_n r} - e^{-z_n \sigma}). \quad (10)$$

Here,

$$\tilde{\beta}_j = \frac{\pi}{\Delta} \sigma \tilde{\mathbf{E}} + \frac{2\pi}{\Delta} \sum_n \tilde{\mu}_j^{(n)}; \quad \tilde{A}_j = \frac{2\pi}{\Delta} \left(\tilde{\mathbf{E}} + \frac{1}{2} \zeta_2 \beta_j + \sum_n \tilde{\mathbf{E}}_j^{(n)} - \tilde{\tau}_j \right) \quad (11)$$

$$\mathbf{C}_{ij}^{(n)} = \sum_l \gamma_{il}(z_n) \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{lj}^{(n)} - \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{ij}^{(n)}, \quad (12)$$

where

$$s \gamma_{ij}(s) = 2\pi \rho \mathbf{G}_{ij}(s) \alpha, \quad \tilde{\mu}_j^{(n)} = \rho \sum_l \tilde{\mathbf{C}}_l^{(\mu)}(z_n) \alpha \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{lj}^{(n)} e^{-z_n \sigma}$$

$$\tilde{\mathbf{M}}_j^{(n)} = \rho \sum_l \tilde{\mathbf{C}}_l^{(M)}(z_n) \alpha \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{lj}^{(n)} e^{-z_n \sigma}; \quad \mathbf{G}_{ij}(s) = \int_0^\infty dr' r' \mathbf{g}_{ij}(r') e^{-sr'}$$

$$\tilde{\mathbf{C}}_l^{(\mu)}(s) = \sum_k \tilde{\mathbf{E}} [\gamma_{lk}(s)]^T e^{s\sigma} s \sigma^3 \phi_1(\sigma s) + \frac{1}{s^2} \left(1 + \frac{1}{2} s \sigma \right) \tilde{\mathbf{E}}$$

$$\tilde{\mathbf{C}}_l^{(M)}(s) = \sum_k \tilde{\mathbf{E}} [\gamma_{lk}(s)]^T \sigma^2 s \phi_1(-s\sigma) - \frac{(1 + s\sigma)}{s} \tilde{\mathbf{E}}$$

$$\tilde{\tau}_j = \rho \sum_l \sigma \tilde{\mathbf{E}} \alpha t_{lj}; \quad \phi_1(x) = \frac{1}{x^3} \left[1 - \frac{1}{2} x - \left(1 + \frac{1}{2} x \right) e^{-x} \right]$$

$$\phi_1(x) = \frac{1 - x - e^{-x}}{x^2}; \quad \zeta_p = \rho m \sigma^p; \quad \Delta = \frac{1 - \pi \zeta_3}{6}.$$

It can be seen that all the coefficients of the factor function $\mathbf{q}_{ij}(r)$ are determined by the set of unknowns $\tilde{\mathbf{D}}_{ij}^{(n)}$ and $\gamma_{ij}(z_n)$, which follow from the solution of the set of Eq. (9) and equations obtained by differentiating relation (6) with respect to r at $0 < r < \sigma$ and taking the Laplace transformation of both sides of the resulting equation. This yields:

$$\sum_l \gamma_{il}(z_n) \tilde{\mathbf{Q}}_{lj}(iz_n) = \frac{\mathbf{f}_{ij}(z_n)}{z_n}, \quad (13)$$

where

$$\mathbf{f}_{ij}(s) = \tilde{\mathbf{E}}^T \left[\tilde{A}_j \left(1 + \frac{1}{2} s \sigma \right) + \tilde{\beta}_j s \right] \frac{1}{s^2} e^{-s\sigma} - \sum_n \frac{z_n}{s + z_n} \mathbf{C}_{ij}^{(n)} e^{-(s+z_n)\sigma} + \mathbf{t}_{ij} e^{-s\sigma},$$

$$\hat{\mathbf{Q}}_{lj}(is) = \frac{\delta_{lj}}{\rho} \alpha^{-1} - \sigma^3 \tilde{\mathbf{E}}^T \tilde{A}_j \phi_1(\sigma s) - \sigma^2 \tilde{\mathbf{E}}^T \tilde{\beta}_j \phi_1(\sigma s) - \mathbf{t}_{lj} \frac{1 - e^{-\sigma s}}{s}$$

$$- \sum_n \left\{ \mathbf{C}_{lj}^{(n)} \left[\frac{e^{\sigma z_n} - e^{-\sigma s}}{z_n + s} + \frac{e^{-\sigma s} - 1}{s} \right] e^{-z_n \sigma} + \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{lj}^{(n)} \frac{1}{z_n + s} \right\}$$

The set of Eqs. (9) and (13) have to be solved numerically. This completes our solution of the PMSA for the most general case.

4. Thermodynamics

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

$$-\beta \frac{\Delta E}{V} = \rho \sum_{ij} \sum_n z_n K_{ij}^{(n)} \sum_{\alpha} \gamma_{i\alpha j_0}(z_n). \quad (14)$$

The Helmholtz free energy A , pressure P and chemical potential μ_{α} in excess to their reference system values are given by the expressions [12,41,42]:

$$\begin{aligned} -\beta \frac{(A - A^{(\text{ref})})}{V} &= J + \frac{1}{2} \rho^2 \sum_{ij} \{\alpha [\hat{c}_{ij} - \hat{c}_{ij}^{(0)}] \alpha\}_{00} - \beta \frac{\Delta E}{V} + \frac{1}{3} \pi \rho^2 \sum_{ij} \sigma^3 \text{Tr}[\bar{\mathbf{g}}_{ij} \alpha \bar{\mathbf{g}}_{ji} \alpha - \bar{\mathbf{g}}_{ij}^{(0)} \alpha \bar{\mathbf{g}}_{ji}^{(0)} \alpha] \\ &\quad - \frac{1}{3} \rho^2 \sum_{ij} \sigma^2 \text{Tr}\{t_{ij} \alpha [\partial \bar{\mathbf{h}}_{ij} - \partial \bar{\mathbf{h}}_{ij}^{(0)}] \alpha\}; \\ \beta (P - P^{(\text{ref})}) &= -\beta \frac{A - A^{(\text{ref})}}{V} - \frac{1}{2} \rho^2 \sum_{ij} \{\alpha [\hat{c}_{ij} - \hat{c}_{ij}^{(0)}] \alpha\}_{00} + \beta \frac{\Delta E}{V}; \\ -\beta \rho (\mu_i - \mu_i^{(\text{ref})}) &= \frac{1}{2} \rho^2 \sum_j \{\alpha [\hat{c}_{ij} - \hat{c}_{ij}^{(0)}] \alpha\}_{00} - \beta \frac{\Delta E_i^a}{V}, \end{aligned}$$

where

$$\begin{aligned} \sigma \partial \bar{\mathbf{h}}_{ij} &= \frac{\partial \mathbf{h}_{ij}(r)}{\partial r} \Big|_{r \rightarrow \sigma^+} = -\bar{\mathbf{h}}_{ij} + \frac{1}{2} \tilde{\mathbf{E}}^T \rho \sigma^2 m \left(\frac{1}{6} \sigma \tilde{\mathbf{A}}_j - \tilde{\boldsymbol{\beta}}_j \right) + \frac{1}{2\pi} \sum_n z_n^2 \mathbf{C}_{ij}^{(n)} e^{-z_n \sigma} \\ &\quad + \rho \sigma \sum_l \bar{\mathbf{h}}_{il} \alpha t_{lj} + \mathbf{E} \alpha \rho \sum_{ln} \mathbf{C}_{lj}^{(n)} \left[\frac{1}{z_n} (e^{-z_n \sigma} - 1) + \sigma \right] \\ &\quad + \rho \sigma \sum_l \bar{\mathbf{h}}_{il} \alpha \left[\sum_n \mathbf{C}_{lj}^{(n)} (1 - e^{-z_n \sigma}) + \tilde{\mathbf{E}}^T \left(\sum_n \tilde{\mathbf{D}}_{lj}^{(n)} - \tilde{\boldsymbol{\beta}}_j \sigma \right) \right] + \tilde{\mathbf{E}}^T \rho \sum_{ln} \left(\sigma - \frac{1}{z_n} \right) \tilde{\mathbf{D}}_{lj}^{(n)} \\ &\quad - \frac{1}{2\pi} \rho \sum_l t_{il} \alpha \left[\tilde{\mathbf{E}}^T \left(\frac{1}{2} \sigma \tilde{\mathbf{A}}_j - \tilde{\boldsymbol{\beta}}_j \right) + \sum_n z_n \left(\mathbf{C}_{lj}^{(n)} + \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{lj}^{(n)} \right) \right]. \end{aligned} \quad (15)$$

Here, the quantities with the superscript (ref) denote the reference hard-sphere system's quantities, the quantities with superscript (0) denote the corresponding PMSA quantities with $K_{ij}^{(n)} = 0$, $\hat{c}_{ij} = \hat{c}_{ij}(k=0)$, $\bar{\mathbf{g}}_{ij} = \bar{\mathbf{h}}_{ij} + \mathbf{E}$. Each of the quantities in these equations can be written in terms of quantities derived in

the analytic solution of the PMSA. More explicitly, we have

$$-\beta \frac{\Delta E_i}{V} = \rho \sum_j \sum_n z_n K_{ij}^{(n)} \sum_\alpha \gamma_{i_\alpha j_0}(z_n); \quad J = \frac{1}{3} \rho \sum_{ij} K_{ij}^{(n)} z_n^2 \sum_\alpha \partial \gamma_{i_\alpha j_0}^{(n)};$$

$$\rho^2 \sum_{ij} [\alpha \hat{c}_{ij} \alpha]_{00} = -\rho^2 \sum_{ij} \left\{ \alpha \left[(\mathbf{M}_{ji})^T + \mathbf{M}_{ij} + \rho \sum_l \mathbf{M}_{il} \alpha (\mathbf{M}_{jl})^T \right] \alpha \right\}_{00},$$

$$\mathbf{M}_{ij} = \frac{1}{12} \sigma^3 \tilde{\mathbf{E}}^T \tilde{\mathbf{A}}_j + \frac{1}{2} \sigma^2 \tilde{\mathbf{E}}^T \tilde{\boldsymbol{\beta}}_j + \sum_n \mathbf{C}_{ij}^{(n)} \left[\left(\frac{1}{z_n} + \sigma \right) e^{-z_n \sigma} - \frac{1}{z_n} \right] - \sigma \mathbf{t}_{ij}$$

and $\partial \gamma_{i_\alpha j_\beta}^{(n)} = \partial \gamma_{i_\alpha j_\beta}^{(n)}(z_n) / \partial z_n$. The expression for $\partial \gamma_{i_\alpha j_\beta}^{(n)}$ follows from relation (13) differentiated with respect to z_n :

$$z_n^2 \partial \gamma_{ij}^{(n)} = -\sum_l \left[f_{il}(z_n) - z_n \partial f_{il}^{(n)} + z_n^2 \sum_k \gamma_{ik}(z_n) \partial \hat{\boldsymbol{\Omega}}_{kl}^{(n)} \right] [\hat{\mathbf{Q}}^{-1}(iz_n)]_{lj}, \quad (16)$$

where

$$\partial f_{ij}^{(n)} = \tilde{\mathbf{E}}^T \left\{ \tilde{\mathbf{A}}_j \left[\frac{1}{2} \sigma - \left(1 + \frac{1}{2} z_n \sigma \right) \left(\frac{2}{z_n} + \sigma \right) \right] - \tilde{\boldsymbol{\beta}}_j (1 + z_n \sigma) \right\} \frac{1}{z_n^2} e^{-z_n \sigma}$$

$$+ \sum_m \mathbf{C}_{ij}^{(m)} \frac{z_m}{z_m + z_n} \left(\frac{1}{z_n + z_m} + \sigma \right) e^{-(z_n + z_m) \sigma} - \sigma \mathbf{t}_{ij} e^{-z_n \sigma},$$

$$\partial \hat{\boldsymbol{\Omega}}_{ij}^{(n)} = \sigma^3 \tilde{\mathbf{E}}^T \left[\sigma \tilde{\mathbf{A}}_j \frac{\partial \phi_1(\sigma z_n)}{\partial z_n} + \tilde{\boldsymbol{\beta}}_j \frac{\partial \varphi_1(\sigma z_n)}{\partial z_n} \right] - \frac{1 - (1 + z_n \sigma) e^{-z_n \sigma}}{z_n^2} \mathbf{t}_{ij}$$

$$+ \sum_m \left\{ \mathbf{C}_{ij}^{(m)} \left[\frac{(1 + \sigma(z_m + z_n)) e^{-\sigma z_n} - e^{\sigma z_m}}{(z_m + z_n)^2} + \frac{1 - (1 + z_n \sigma) e^{-\sigma z_n}}{z_n^2} \right] e^{-z_m \sigma} \right.$$

$$\left. - \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{ij}^{(m)} \frac{1}{(z_m + z_n^2)} \right\}.$$

5. Details of the Monte Carlo simulations

We have performed MC simulations of the dimer and tetramer versions of the HSYC fluid. We have examined the gas–liquid phase diagram using the Gibbs ensemble Monte Carlo (GEMC) [44,45] technique and further probed the *PVT* behavior through isothermal–isobaric (*NpT*) Monte Carlo simulations.

In the GEMC method, the coexisting vapor and liquid phases are simulated simultaneously in two distinct regions *a* and *b*, with volumes, V^a and V^b , and molecules, N^a and N^b , respectively. The total volume $V = V^a + V^b$ and total number of molecules $N = N^a + N^b$ are fixed. Three distinct Monte Carlo moves are performed in the GEMC technique in order to satisfy the conditions of phase equilibrium: particle displacements, re-orientations and reptations within either subsystem to reach, and then maintain configurationally equilibrated systems at the same temperature; coupled volume changes, to reach, then

maintain equality of pressure; and particle interchanges between the two subsystems, to reach, and then maintain equality of the chemical potentials. For molecule transfer between subsystems, we use the algorithm originally proposed for mixtures by Panagiotopoulos et al. [45] and the chemical potential was determined with the Widom test particle technique [46], as adapted to the GEMC approach [47] in order to ensure that phase equilibria is achieved. The reader is referred to the original papers for full details [44,45] of the Gibbs ensemble technique.

Initially, the molecules in the vapor subsystem are arranged on a face-centred-cubic (fcc) lattice, while the higher density liquid configurations are obtained by compressing a single subsystem with a standard NpT Monte Carlo technique [51,52]. The usual periodic boundary conditions and minimum image convention are applied [52], with the potential being truncated beyond 2.5σ . Initial guesses for the co-existing densities at each state point are made by using the corresponding theoretical solutions as presented in the preceding section. One simulation cycle consists of N attempted displacement, re-orientation and reptation moves in each box, (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 molecule interchanges. We tested the GEMC code for n -mers by substituting the Yukawa interaction between monomers with the LJ interaction. The results of GEMC simulations of LJ n -mers were found to reproduce those of Dubey et al. [48], Escobedo and de Pablo [50], and Blas and Vega [49] within the statistical uncertainties of the simulations.

In order to obtain PVT results from the simulations to compare with the PMSA predictions, we performed NpT simulations, essentially as a simple modification of the GEMC code (we simply suppress molecule exchanges and fix the pressure externally, using the standard acceptance criterion for constant pressure [51,52]). A cycle in the NpT simulations consists of N attempted displacement, re-orientation and reptation moves and one attempted volume change. We used NpT (thus, calculating density) rather than using NVT (thus, calculating pressure) because 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 all the simulations, the maximum displacement and volume change were adjusted to give an acceptance ratio of between 30 and 40%, and the number of insertions in the GEMC simulations were controlled so that between 1 and 3% of the molecules are interchanged each cycle. The dimer simulations were performed with systems of $N = 28$ particles, while larger system sizes were used for the tetramers ($N = 56$). The thermodynamic properties of the system were obtained as ensemble averages and the errors estimated by determining the standard deviation. For the isothermal isobaric MC simulations the final results were obtained by averaging the values of two independent runs. An initial simulation of 50,000 cycles was performed to equilibrate the subsystems, before averaging for between 100,000 and 250,000 cycles.

6. Results and discussion

We have performed NpT and GEMC simulations for dimer and tetramer HSYC fluids and here we compare the simulation results with theoretical PMSA predictions. The parameters of the two-Yukawa potential $\Phi_{ij}^{(Y)}(r)$ were chosen to be: $z_1/\sigma = 14.808$, $z_2/\sigma = 2.65$, $K_{ij}^{(1)}/\beta^* = -2.0105$, $K_{ij}^{(2)}/\beta^* = 2.006$, where $\sigma = 1.0$ and $\beta^* = \varepsilon\beta$, where ε is the Yukawa potential well depth. Hence, the potential has the form:

$$\frac{\Phi_{ij}^{(Y)}(r)}{kT} = \begin{cases} \infty, & r < 1 \\ \frac{1}{T^*} [2.0105 e^{-14.808(r-1)} - 2.006 e^{-2.65(r-1)}], & r > 1 \end{cases}$$

Table 1
Isothermal–isobaric Monte Carlo simulation results for a hard-core two-Yukawa dimer fluid^a

T^*	p^*	η	E^*
1.6	0.460	0.321 ± 0.010	-3.89 ± 0.14
1.6	0.889	0.348 ± 0.008	-4.28 ± 0.12
1.6	2.059	0.390 ± 0.007	-4.88 ± 0.10
2.5	0.977	0.253 ± 0.010	-2.91 ± 0.14
2.5	3.282	0.349 ± 0.007	-4.24 ± 0.11
2.5	5.576	0.391 ± 0.007	-4.84 ± 0.10
4.0	1.058	0.171 ± 0.009	-1.82 ± 0.11
4.0	2.201	0.239 ± 0.008	-2.69 ± 0.11
4.0	3.990	0.294 ± 0.008	-3.43 ± 0.12

^a The fixed variables during the simulation are the number of particles $N = 128$, the reduced pressure $p^* = p\sigma^3/\varepsilon$, and the reduced temperature $T^* = kT/\varepsilon$. The packing fraction is given by η and the reduced energy per segment $E^* = E/\varepsilon N_s$; the uncertainties correspond to one standard deviation.

where $T^* = \varepsilon/kT = 1/\beta^*$. A slight modification of this potential, of the form

$$\frac{\Phi_{ij}^{(Y-LJ)}(r)}{kT} = \begin{cases} \infty, & r < 0.822 \\ \frac{1}{T^*} [2.0105 e^{-14.808(r-1)} - 2.006 e^{-2.65(r-1)}], & r > 0.822 \end{cases}$$

can be used as a very close approximation to the LJ potential [6], but will not be considered here.

The NpT simulation results for the dimer are reported in Table 1. A range of pressures were examined along three isotherms of the system. The results are presented in Fig. 1 along with the corresponding PMSA predictions. We see excellent agreement between the results of the NpT simulations and the theoretical predictions for all state points studied. In Fig. 2, we compare the theoretical predictions and NpT simulations for the tetramer fluid, the corresponding simulation data is given in Table 2. As can be seen from the figure, we again see very good agreement between the simulation data and the PMSA theory.

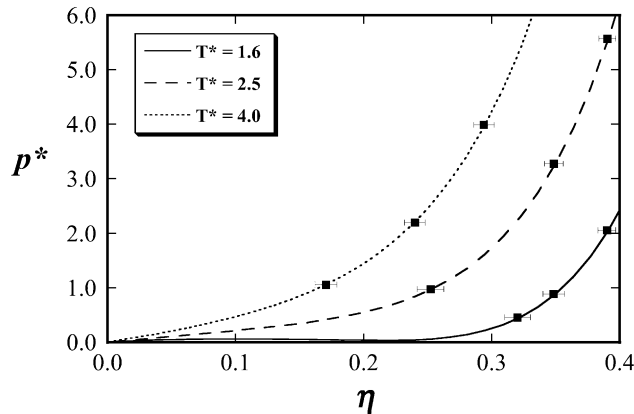


Fig. 1. Isotherms for the hard-core two-Yukawa dimer fluid. The squares represent the results of isothermal–isobaric Monte Carlo simulations and the continuous curves correspond to the PMSA predictions.

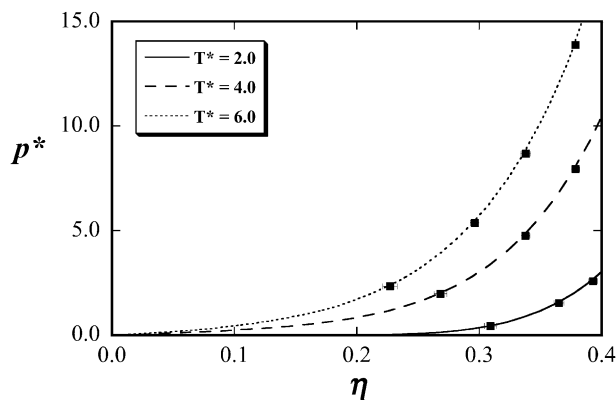


Fig. 2. Isotherms for the hard-core two-Yukawa tetramer fluid. The squares represent the results of isothermal–isobaric Monte Carlo simulations and the continuous curves correspond to the PMSA predictions.

Table 2

Isothermal–isobaric Monte Carlo simulation results for a hard-core two-Yukawa tetramer fluid^a

T^*	p^*	η	E^*
2.0	0.441	0.309 ± 0.005	-3.50 ± 0.07
2.0	1.542	0.365 ± 0.004	-4.27 ± 0.06
2.0	2.595	0.393 ± 0.004	-4.66 ± 0.06
4.0	1.981	0.268 ± 0.005	-2.89 ± 0.07
4.0	4.762	0.338 ± 0.003	-3.83 ± 0.05
4.0	7.947	0.378 ± 0.003	-4.41 ± 0.04
6.0	2.350	0.227 ± 0.006	-2.34 ± 0.08
6.0	5.370	0.296 ± 0.003	-3.24 ± 0.05
6.0	8.685	0.338 ± 0.004	-3.82 ± 0.06
6.0	13.89	0.378 ± 0.003	-4.42 ± 0.04

^a The number of particles $N = 256$. See Table 1 for the definition of the remaining symbols.

In Fig. 3, we present the phase diagram of the dimer HSYC fluid obtained from the PMSA approach and the corresponding GEMC simulation data, which are reported in Table 3. From the figure we see reasonable agreement between the simulation data and the theoretical predictions. The agreement between GEMC and the PMSA is best at the lowest temperatures, away from the critical point of the HSYC dimer

Table 3

Vapour-liquid coexistence data obtained from NVT Gibbs ensemble Monte Carlo simulations for the hard-core two-Yukawa dimer fluid^a

T^*	η_l	η_v	E_l^*	E_v^*	N_l^*	N_v^*
1.25	0.350 ± 0.007	0.008 ± 0.002	-4.35 ± 0.10	-0.16 ± 0.09	235	21
1.30	0.340 ± 0.008	0.012 ± 0.003	-4.19 ± 0.12	-0.22 ± 0.09	225	31
1.40	0.312 ± 0.010	0.023 ± 0.005	-3.80 ± 0.14	-0.41 ± 0.12	204	52
1.50	0.280 ± 0.014	0.048 ± 0.007	-3.38 ± 0.18	-0.77 ± 0.15	161	95

^a The liquid and vapor densities are denoted by v and l , respectively. See Table 1 for the definition of the remaining symbols.

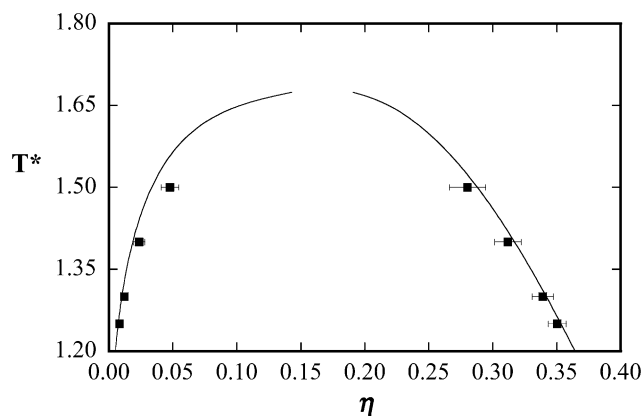


Fig. 3. Vapour-liquid coexistence densities for the hard-core two-Yukawa dimer fluid where $T^* = kT/\varepsilon$, and $\eta = \pi\rho_s\sigma^3/6$ is the packing fraction. The circles correspond to the results of GEMC simulation and the continuous curve represents the PMSA prediction.

fluid. This is to be expected since the PMSA will yield classical critical behavior while the GEMC simulations will exhibit non-classical behavior.

7. Conclusions

In this paper, we have presented a comparison between simulation and the PMSA for the dimer and tetramer HSYC fluids. The *PVT* properties predicted by the PMSA are in good agreement with those obtained by simulation. The agreement between the vapor-liquid phase envelope predicted by the PMSA and that obtained by GEMC simulation was not as good. However, some of the disagreement can be traced to the classical nature of the thermodynamics predicted by the PMSA. More extensive simulations for the tetramer and longer HSYC fluids are currently underway, as well as simulations of mixtures to compare with a recent extension of the PMSA to mixtures [53].

Acknowledgements

The contributions of YVK and PTC were supported by UT-Batelle through the Distinguished Scientist program. The effort of CMC was supported by the National Science Foundation through Grant CTS-9871919.

References

- [1] M.S. Wertheim, Phys. Rev. Lett. 10 (1963) 321.
- [2] E. Theile, J. Chem. Phys. 39 (1963) 474.
- [3] J.P. Hansen, I.R. McDonald, Theory of Simple Fluids, Academic Press, New York, 1986.
- [4] Yu.V. Kalyuzhnyi, P.T. Cummings, in: J.V. Sengers, M.B. Edwin, R.F. Kayser, C.J. Peters (Eds.), IUPAC Volume on Equations of State for Fluids and Fluid Mixtures, Elsevier, Amsterdam, 2000, p. 169.

- [5] C. Jędrzejek, G.A. Mansoori, *Acta Phys. Pol. A* 57 (1980) 107.
- [6] E.N. Rudisill, P.T. Cummings, *Mol. Phys.* 68 (1989) 629.
- [7] Yu.V. Kalyuzhnyi, P.T. Cummings, *Mol. Phys.* 87 (1996) 1459.
- [8] E. Waisman, *Mol. Phys.* 25 (1973) 45.
- [9] Yu.V. Kalyuzhnyi, C.-T. Lin, G. Stell, *J. Chem. Phys.* 106 (1997) 1940.
- [10] C.-T. Lin, Yu.V. Kalyuzhnyi, G. Stell, *J. Chem. Phys.* 108 (1998) 6513.
- [11] Yu.V. Kalyuzhnyi, C.-T. Lin, G. Stell, *J. Chem. Phys.* 108 (1998) 6525.
- [12] Yu.V. Kalyuzhnyi, *Mol. Phys.* 94 (1998) 735.
- [13] M.F. Holovko, Yu.V. Kalyuzhnyi, *Mol. Phys.* 73 (1991) 1145.
- [14] Yu.V. Kalyuzhnyi, M.F. Holovko, *Mol. Phys.* 80 (1993) 1165.
- [15] Yu.V. Kalyuzhnyi, G. Stell, *Chem. Phys. Lett.* 240 (1995) 157.
- [16] M.S. Wertheim, *J. Stat. Phys.* 35 (1984) 19.
- [17] M.S. Wertheim, *J. Stat. Phys.* 35 (1984) 35.
- [18] M.S. Wertheim, *J. Stat. Phys.* 42 (1986) 459.
- [19] M.S. Wertheim, *J. Stat. Phys.* 42 (1986) 477.
- [20] K.S. Schweizer, J.G. Curro, *Phys. Rev. Lett.* 58 (1987) 246.
- [21] J.G. Curro, K.S. Schweizer, *Macromolecules* 20 (1987) 1928.
- [22] K.S. Schweizer, K.G. Honnell, J.G. Curro, *J. Chem. Phys.* 96 (1992) 3211.
- [23] A. Yethiraj, K.S. Schweizer, *J. Chem. Phys.* 97 (1992) 1455.
- [24] J. Melenkevitz, J.G. Curro, K.S. Schweizer, *J. Chem. Phys.* 99 (1993) 5571.
- [25] J. Chang, S.I. Sandler, *J. Chem. Phys.* 102 (1995) 437.
- [26] J. Chang, S.I. Sandler, *J. Chem. Phys.* 103 (1995) 3196.
- [27] Y.C. Chiew, *Mol. Phys.* 70 (1990) 129.
- [28] Y.C. Chiew, *Mol. Phys.* 73 (1991) 359.
- [29] M.P. Taylor, J.E.J. Libson, *J. Chem. Phys.* 102 (1995) 2118.
- [30] M.P. Taylor, J.E.J. Libson, *J. Chem. Phys.* 103 (1995) 6272.
- [31] P. Attard, *J. Chem. Phys.* 102 (1995) 5411.
- [32] H.H. Gan, B.C. Eu, *J. Chem. Phys.* 103 (1995) 2140.
- [33] D. Chandler, R. Silbey, B. Ladanyi, *Mol. Phys.* 46 (1982) 1335.
- [34] P.J. Rossky, Chiles, *Mol. Phys.* 51 (1984) 661.
- [35] Yu.V. Kalyuzhnyi, P.T. Cummings, *J. Chem. Phys.* 105 (1996) 2011.
- [36] Yu.V. Kalyuzhnyi, *Mol. Phys.* 96 (1999) 1289.
- [37] Yu.V. Kalyuzhnyi, C.-T. Lin, G. Stell, A. Yethiraj, *J. Mol. Liq.* 92 (2001) 85.
- [38] L. Blum, J.S. Høye, *J. Stat. Phys.* 16 (1977) 399.
- [39] L. Blum, J.S. Høye, *J. Stat. Phys.* 19 (1978) 317.
- [40] L. Blum, *J. Stat. Phys.* 22 (1980) 661.
- [41] J.S. Høye, G. Stell, *J. Chem. Phys.* 67 (1977) 439.
- [42] Yu.V. Kalyuzhnyi, P.T. Cummings, *J. Chem. Phys.*, 2000, submitted for publication.
- [43] R.J. Baxter, *J. Chem. Phys.* 49 (1968) 2770.
- [44] A.Z. Panagiotopoulos, *Mol. Phys.* 61 (1987) 813.
- [45] A.Z. Panagiotopoulos, N. Quirke, M.R. Stapleton, D.J. Tildesley, *Mol. Phys.* 63 (1988) 527.
- [46] B. Widom, *J. Chem. Phys.* 39 (1963) 2808.
- [47] B. Smit, D. Frenkel, *Mol. Phys.* 68 (1989) 951.
- [48] G.S. Dubey, S.F. O'Shea, P.A. Monson, *Mol. Phys.* 80 (1993) 997.
- [49] F.J. Blas, L.F. Vega, *Mol. Phys.* 92 (1997) 135.
- [50] F.A. Escobedo, J.J. de Pablo, *Mol. Phys.* 87 (1996) 347.
- [51] W.W. Wood, *J. Chem. Phys.* 48 (1968) 415.
- [52] M.P. Allen, D.J. Tildesley, *Computer Simulations of Liquids*, Clarendon Press, Oxford, 1987.
- [53] Yu.V. Kalyuzhnyi, C. McCabe, P.T. Cummings, G. Stell, *Molecular Physics*, 2001, in press.