

Self-consistent Ornstein–Zernike approximation for the Sogami–Ise fluid

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We generalize the self-consistent Ornstein–Zernike approximation (SCOZA) to a fluid of particles with a pair potential consisting of a hard-core repulsion and a linear combination of Sogami–Ise tails, $w(r) = -\epsilon\sigma\sum_{\nu}(K_{\nu}/r + L_{\nu}z_{\nu})e^{-z_{\nu}(r-\sigma)}$. The formulation and implementation of the SCOZA takes advantage of the availability of semianalytic results for such systems within the mean-spherical approximation. The predictions for the thermodynamics, the phase behavior and the critical point are compared with optimized random phase approximation results; further, the effect of thermodynamic consistency is investigated. © 2004 American Institute of Physics.

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I. INTRODUCTION

One of the most frequently used liquid-state theories is the mean-spherical approximation (MSA)¹ whose wide-spread use is due to the availability of semianalytic results for the structural and thermodynamic properties of various model systems: They are available in (nearly) closed form for charged hard-spheres (HS),² dipolar HSs,³ sticky HSs,⁴ HS Yukawa fluids,⁵ systems with a generalized HS Yukawa potential,⁶ and HS Yukawa mixtures.⁷ In a recent series of papers^{8–12} the semi-analytic formalism of the MSA has been generalized to a multicomponent fluid of particles interacting via a Sogami–Ise (SI)¹³ pair potential and a generalized form of this potential.

Comparison with simulations^{14–16} showed that the MSA—despite its inherent thermodynamic inconsistency—yields accurate thermodynamic properties for hard-core (HC) systems with purely attractive adjacent interaction tails in large parts of the phase diagram. However, being mean-field like in nature its accuracy decreases as one approaches the critical region. A theoretical approach that goes beyond the MSA is the so called self-consistent Ornstein–Zernike approximation (SCOZA). It is based on a generalized mean-spherical ansatz, introducing in the MSA relation one or more density- and temperature-dependent functions which are determined by enforcing consistency between two or three different thermodynamic routes. Although the SCOZA was proposed already more than 20 years ago by Stell and Høye^{17,18} (in the latter work for a HS Yukawa system) and reformulated in different versions in subsequent work, practical applications remained for a long time rather scarce; its real breakthrough came in 1996¹⁹ when a reformulation of the SCOZA partial differential equation (PDE) made access to subcritical temperatures possible. Since then, the SCOZA has been applied to various discrete systems^{19–25} and continuum systems^{26–29} and the results showed in an impressive way—when compared with computer simulations—that, in contrast to conventional integral equation and perturbation

theories, the theory remains successful as one leaves the fluid-state regions and approaches the liquid–gas coexistence curve and the critical region. In these parts of the phase diagram conventional theories encounter typically the following problems:³⁰ The shape of the coexistence curve is not reproduced correctly, sometimes its two branches are left unconnected so that critical points have to be estimated via extrapolation, the critical point is not located correctly, and critical exponents do not agree with the exact ones. In contrast, SCOZA applications have shown that this theory is able to localize the liquid–vapor coexistence curve and the critical point very accurately (within 1% to 2% of the best numerical estimates). Further, no extrapolation of the coexistence branches towards the critical point is necessary, since the theory allows one to locate the critical point with any desired accuracy. In addition, various effective critical exponents, that are defined as the slopes of curves of logarithmic plots, were investigated: Above the critical temperature the theory yields the same critical exponents as the spherical model but this regime is very narrow, so that thermodynamics and effective exponents are in good agreement with the true critical behavior until the temperature differs from its critical value by less than 1%.^{20,21,27} On the other hand, an analytic study of SCOZA's subcritical exponents by Høye *et al.*³¹ showed that on the coexistence curve, the exponents turn out to be very accurate: e.g., the curvature of the coexistence curve is described by $\beta=0.35$ which is close to the exact value of $\beta\sim 0.326$.³²

For a long time, in the case of continuum fluids, applications of the SCOZA were restricted to the one-component case and to hard-core (HC) interactions with one or two adjacent Yukawa tails (with the possibility of approximating a Lennard-Jones potential rather accurately²⁸). Only recently, when the SCOZA was reformulated on the basis of the more elegant and more flexible Wertheim–Baxter factorization technique^{33,34} to solve the MSA for a HS Yukawa system a broader applicability of the theory came within reach: It became possible to extend the SCOZA to HC systems with a formally arbitrary number of Yukawa tails. As a test system a linear combination of Yukawas was chosen to approximate

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the sphericalized Girifalco potential that describes the interaction between the model fullerenes (C_{60} to C_{96}).³⁵ Furthermore, the SCOZA was extended to binary mixtures of HC Yukawa systems.^{36,37}

In this contribution we present the generalization of the SCOZA to HC systems with a tail that is built up by a linear combination of a Coulomb potential plus a constant that are both exponentially damped (including the HC Yukawa fluid as a special case) and give a detailed presentation of the formalism. We show that, taking benefit of the availability of the MSA solution for this system, a PDE for the internal energy can be derived; its solution fixes the yet undetermined function in the MSA type closure relation, guaranteeing thus thermodynamic consistency between the energy and compressibility route. Compared to the HS Yukawa fluid the formalism is now more complex and cumbersome. As a testing case, the theory has been applied to a few model systems and results for the thermodynamic properties and the phase behavior have been compared with results from the lowest-order gamma ordered approximation (LOGA),³⁸ also known as the optimized random phase approximation (ORPA)³⁹ to study the effect of thermodynamic consistency. For the one-Yukawa system it has been shown⁴⁰ that SCOZA results are in excellent agreement with computer simulations, at least for not too narrow interaction ranges. In this respect, at the moment, SCOZA can be viewed as the best semianalytic method to study the HC Yukawa system and we assume that this is also the case for the Sogami–Ise system considered here.

This paper is organized as follows: In Sec. II we describe the theory and present in detail the formulation of the SCOZA for the system under investigation, in Sec. III the theory is applied to study the thermodynamic properties and the phase behavior of various model systems and a comparison with LOGA/ORPA results is made. In Sec. IV our conclusions are drawn. Details of the semianalytic MSA results on which the SCOZA formulation is based are summarized in Appendices A–D.

II. FORMULATION OF THE THEORY

We consider a fluid of particles interacting via a spherically symmetric Sogami–Ise type pair potential $\phi(r)$ given by

$$\phi(r) = \begin{cases} +\infty & r \leq \sigma \\ w(r) & r > \sigma \end{cases} \quad (1)$$

where the repulsion is characterized by the hard-sphere diameter σ and the attractive tail $w(r)$ is given by a linear combination of a Coulomb potential plus a constant that are both screened with an exponential

$$w(r) = -\epsilon\sigma \sum_{\nu=2}^n \left(\frac{K_{\nu}}{r} + L_{\nu}z_{\nu} \right) e^{-z_{\nu}(r-\sigma)}. \quad (2)$$

The z_{ν} are the screening lengths, the K_{ν} and L_{ν} are the coefficients of the linear combination and chosen so that the minimum of the function $-\sigma \sum_{\nu=2}^n (K_{\nu}/r + L_{\nu}z_{\nu}) e^{-z_{\nu}(r-\sigma)}$ on the interval $[\sigma, \infty)$ is -1 , and ϵ is the depth of the potential. Greek indices are used to designate the different

Sogami–Ise tails and summations—unless otherwise stated—will be extended over n tails. Here the summation starts at $\nu=2$ since the first Sogami–Ise tail is reserved for the description of the HC reference system (see below).

The version of the SCOZA considered here²⁷ is based on the OZ equation

$$h(r) = c(r) + \rho \int d^3r' c(r') h(|\mathbf{r}-\mathbf{r}'|), \quad (3)$$

supplemented with the following closure relation

$$g(r) = 0 \quad \text{for } r \leq \sigma, \\ c(r) = c_{\text{HS}}(r) + K(\rho, \beta)w(r) \quad \text{for } r > \sigma. \quad (4)$$

$h(r)$ and $c(r)$ are the total and direct correlation functions, $g(r) = h(r) - 1$ is the pair distribution function, $c_{\text{HS}}(r)$ is the direct correlation function of the hard-sphere (HS) reference system and $K(\rho, \beta)$ is a yet undetermined function depending on the thermodynamic state that is given by the density ρ and the inverse temperature $\beta = 1/k_B T$, k_B being the Boltzmann constant. The closure resembles to the one used in the LOGA/ORPA^{38,39} where $K(\rho, \beta) = -\beta$ is fixed. Here, $K(\rho, \beta)$ is not given *a priori* but is determined so that thermodynamic self-consistency is guaranteed between the compressibility and the energy route to the thermodynamic properties.¹

We recall that, according to the compressibility route the reduced isothermal compressibility via the compressibility route is given by

$$\frac{1}{\chi^{\text{red}}} = \frac{\partial \beta P}{\partial \rho} = 1 - \rho \bar{c}(k=0), \quad (5)$$

where $\bar{c}(k)$ denotes the Fourier transform of $c(r)$

$$\bar{c}(k) = \int c(r) e^{-i\mathbf{k}\mathbf{r}} d^3r. \quad (6)$$

On the other hand the excess (over ideal) internal energy per unit volume calculated via the internal energy route is

$$\frac{U^{\text{ex}}}{V} = u = 2\pi\rho^2 \int_{\sigma}^{\infty} dr r^2 w(r) g(r). \quad (7)$$

If χ^{red} and u are consistent with each other, they must stem from a unique Helmholtz free energy density $F/V = f = f^{\text{id}} + f^{\text{ex}}$, where f^{id} and f^{ex} are the ideal and excess parts of the free energy density. Thus

$$\rho \frac{\partial^2 u}{\partial \rho^2} = \rho \frac{\partial^2}{\partial \rho^2} \frac{\partial \beta f^{\text{ex}}}{\partial \beta} = \frac{\partial}{\partial \beta} \left(\rho \frac{\partial \beta \mu^{\text{ex}}}{\partial \rho} \right) = \frac{\partial}{\partial \beta} \left(\frac{1}{\chi^{\text{red}}} \right), \quad (8)$$

where $\mu^{\text{ex}} = \partial f^{\text{ex}} / \partial \rho$ is the excess chemical potential. For approximate $g(r)$ as obtained, for instance, by conventional integral equation and perturbation theories¹ Eq. (8), where χ^{red} is given by Eq. (5) and u by Eq. (7), is not fulfilled. In the SCOZA, however, this consistency is enforced through an appropriate choice of the yet undetermined function $K(\rho, \beta)$ that is obtained by solving the partial differential equation (PDE) Eq. (8) supplemented by Eqs. (3)–(7). The solution of the SCOZA PDE is simplified by making use of the semianalytic solution of the MSA for Sogami–Ise type potentials^{8,9} that allows one to express χ^{red} as a function of u

thus transforming the PDE (8) into a PDE for u . This will be outlined in the following. So we start by briefly summarizing the semianalytic solution of the MSA.

Following Baxter's factorization method it can be shown that under certain conditions⁴¹ the OZ relation is equivalent to the equations

$$2\pi r c(r) = -Q'(r) + \rho \int_0^\infty Q(t)Q'(r+t)dt,$$

$$2\pi r h(r) = -Q'(r) + 2\pi\rho \int_0^\infty (r-t)h(|r-t|)Q(t)dt, \quad (9)$$

where the factor function $Q(r)$ has been introduced. From Eqs. (9) and from the closure relation

$$h(r) = -1 \quad r \leq \sigma, \\ c(r) = \sum \left(\frac{\tilde{K}_\nu}{r} + \tilde{L}_\nu z_\nu \right) e^{-z_\nu(r-\sigma)} \quad r > \sigma, \quad (10)$$

it follows⁸ that $Q(r)$ must have the form

$$Q(r) = Q^0(r) + \sum \frac{1}{z_\nu} (D_\nu + E_\nu z_\nu r) e^{-z_\nu(r-\sigma)}, \quad (11)$$

where

$$Q^0(r) = \begin{cases} \frac{a}{2}(r-\sigma)^2 + b(r-\sigma) + \sum \frac{1}{z_\nu} (C_\nu + F_\nu)(e^{-z_\nu(r-\sigma)} - 1) + \sum F_\nu(r e^{-z_\nu(r-\sigma)} - \sigma) & 0 < r < \sigma \\ 0 & \text{otherwise} \end{cases}, \quad (12)$$

with yet undetermined coefficients a , b , C_ν , D_ν , E_ν , and F_ν .

One further introduces the quantities

$$G_\nu = z_\nu \hat{g}(z_\nu) e^{z_\nu \sigma} = z_\nu \int_\sigma^\infty r e^{-z_\nu(r-\sigma)} g(r) dr \quad (13)$$

and

$$G_\nu^{(1)} = z_\nu \hat{g}^{(1)}(z_\nu) e^{z_\nu \sigma} = z_\nu \int_\sigma^\infty r^2 e^{-z_\nu(r-\sigma)} g(r) dr, \quad (14)$$

where $\hat{g}(z)$ and $\hat{g}^{(1)}(z)$ denote the Laplace transforms of $rg(r)$ and $r^2g(r)$. The use of G_ν and $G_\nu^{(1)}$ instead of $\hat{g}(z_\nu)$ and $\hat{g}^{(1)}(z_\nu)$ follows the procedure adopted for the HS Yukawa system^{42,43} and is due to numerical reasons since it allows one to reduce the number of evaluations of exponentials when calculating the coefficients of Eqs. (A1)–(A4). Especially, expressions with positive exponentials are avoided. Inserting the form of $Q(r)$ in Eqs. (9) and using the closure relation (10) allows one to express the unknown variables a , b , C_ν , and F_ν as functions of D_ν , E_ν , G_ν , and $G_\nu^{(1)}$ and to derive a system of $4n$ nonlinear equations for the $4n$ unknowns D_ν , E_ν , G_ν , and $G_\nu^{(1)}$. This procedure is a direct extension of Blum and Høye's work for HS Yukawa systems⁷ and is explained in detail by Yasutomi and Ginoza.⁸ This system of $4n$ nonlinear equations can be divided into 4 subsets of n equations and is compiled in Appendix A.

ϵ and β enter the Eqs. (A1)–(A4) only via

$$A_\nu^{(7)} = 2\pi\tilde{L}_\nu, \quad \forall \nu \quad (15)$$

and

$$C_\nu^{(13)} = 2\pi\tilde{K}_\nu, \quad \forall \nu, \quad (16)$$

while the remaining coefficients are temperature independent. Their explicit expressions are given in Appendix B. They are calculated from the system parameters ρ , z_ν , and σ .

Equations (A3) and (A4) are linear in D_ν and E_ν for given G_ν and $G_\nu^{(1)}$ and can be rewritten as

$$\sum_{\tau=1}^n O_{\nu\tau} D_\tau + \sum_{\tau=1}^n P_{\nu\tau} E_\tau = Q_\nu, \\ \sum_{\tau=1}^n R_{\nu\tau} D_\tau + \sum_{\tau=1}^n S_{\nu\tau} E_\tau = T_\nu. \quad (17)$$

The definitions of the coefficients of Eqs. (17) are compiled in Appendix A. Solution of this system of $2n$ linear equations yields D_ν and E_ν as functions of ρ , G_ν , and $G_\nu^{(1)}$. This result can then be inserted into Eqs. (A1) and (A2) which become a set of $2n$ coupled nonlinear equations in the G_ν and $G_\nu^{(1)}$.

Once the D_ν , E_ν , G_ν , and $G_\nu^{(1)}$ are known, thermodynamic properties can be determined as follows. The inverse reduced isothermal compressibility calculated via the fluctuation theorem is found to be

$$\frac{1}{\chi^{\text{red}}} = 1 - \rho \bar{c}(k=0) = \left(\frac{a}{2\pi} \right)^2. \quad (18)$$

The expression for a in terms of the quantities G_ν , $G_\nu^{(1)}$, D_ν , and E_ν is obtained from

$$a = A^0(1+M) - \frac{4}{\sigma^2} B^0 N, \quad (19)$$

with

$$M = -\rho \sum_{\tau=1}^n \left[\left(\frac{M_\tau^{(a)}}{z_\tau^2} - 2\pi\rho \frac{G_\tau}{z_\tau^4} (M_\tau^{(a)} e^{-z_\tau \sigma} - 1) \right) D_\tau \right. \\ \left. + \left(\frac{P_\tau^{(a)}}{z_\tau^2} - 2\pi\rho \frac{G_\tau}{z_\tau^4} (2L_\tau^{(a)} e^{-z_\tau \sigma} - 2) \right. \right. \\ \left. \left. - 2\pi\rho \frac{G_\tau^{(1)}}{z_\tau^3} (M_\tau^{(a)} e^{-z_\tau \sigma} - 1) \right) E_\tau \right], \quad (20)$$

$$N = \rho \sum_{\tau=1}^n \left[\left(\frac{L_{\tau}^{(a)}}{z_{\tau}^3} - 2\pi\rho \frac{G_{\tau}}{z_{\tau}^5} (L_{\tau}^{(a)} e^{-z_{\tau}\sigma} - 1) \right) D_{\tau} + \left(\frac{2Q_{\tau}^{(a)}}{z_{\tau}^3} - 2\pi\rho \frac{G_{\tau}}{z_{\tau}^5} (3O_{\tau}^{(a)} e^{-z_{\tau}\sigma} - 3) - 2\pi\rho \frac{G_{\tau}^{(1)}}{z_{\tau}^4} (L_{\tau}^{(a)} e^{-z_{\tau}\sigma} - 1) \right) E_{\tau} \right], \quad (21)$$

the quantities $M_{\tau}^{(a)}$, $P_{\tau}^{(a)}$, $L_{\tau}^{(a)}$, $Q_{\tau}^{(a)}$, $O_{\tau}^{(a)}$, A^0 , and B^0 are again calculated from ρ , z_{ν} , and σ ; the respective expressions are compiled in Appendix B.

The excess internal energy per unit volume calculated via the internal energy route is found to be

$$u = -2\pi\rho^2 \epsilon \sigma \sum_{\nu=2}^n \left(\frac{K_{\nu}}{z_{\nu}} G_{\nu} + L_{\nu} G_{\nu}^{(1)} \right). \quad (22)$$

Now we have summarized the semianalytic MSA results relevant for SCOZA and we proceed with the formulation of the SCOZA. In order to stay within the framework of the Sogami–Ise type closure we choose the Waisman parametrization for $c_{\text{HS}}(r)$ ^{44,45} which ensures a highly self-consistent description of the thermodynamic properties of the HS part. It assumes a Yukawa form for $c_{\text{HS}}(r)$ outside the hard-core

$$c_{\text{HS}}(r) = K_1(\rho) \frac{e^{-z_1(\rho)(r-\sigma)}}{r} \quad \text{for } r > \sigma, \quad (23)$$

where $K_1(\rho)$ and $z_1(\rho)$ are known functions of the density (see Appendix A of Ref. 27). These expressions guarantee that both compressibility and virial route yield the Carnahan Starling (CS) equation of state⁴⁶ for the HS reference system. Using Eqs. (2) and (23), relation (4) becomes

$$g(r) = 0 \quad \text{for } r \leq \sigma, \\ c(r) = K_1(\rho) \frac{e^{-z_1(\rho)(r-\sigma)}}{r} - K(\rho, \beta) \epsilon \sigma \\ \times \sum_{\nu=2}^n \left(\frac{K_{\nu}}{r} + L_{\nu} z_{\nu} \right) e^{-z_{\nu}(r-\sigma)} \quad \text{for } r > \sigma. \quad (24)$$

We use now the analytic results presented above to derive a relation between χ^{red} and u , leading to a PDE for u . Using Eq. (18), the consistency relation (8) reads

$$2 \frac{a}{(2\pi)^2} \frac{\partial a}{\partial u} \frac{\partial u}{\partial \beta} = \rho \frac{\partial^2 u}{\partial \rho^2}. \quad (25)$$

a is given by Eqs. (19) and (20) as a function of D_{ν} , E_{ν} , G_{ν} , and $G_{\nu}^{(1)}$; inserting the solutions $D_{\nu}(\rho, G_{\nu}, G_{\nu}^{(1)})$ and $E_{\nu}(\rho, G_{\nu}, G_{\nu}^{(1)})$ of the linear system Eq. (17) into Eqs. (19) and (20) yields $a(\rho, G_{\nu}, G_{\nu}^{(1)})$ and thus

$$2 \frac{a}{(2\pi)^2} \sum_{\nu=1}^n \left(\frac{\partial a}{\partial G_{\nu}} \frac{\partial G_{\nu}}{\partial u} + \frac{\partial a}{\partial G_{\nu}^{(1)}} \frac{\partial G_{\nu}^{(1)}}{\partial u} \right) \frac{\partial u}{\partial \beta} = \rho \frac{\partial^2 u}{\partial \rho^2}, \quad (26)$$

or

$$B(\rho, u) \frac{\partial u}{\partial \beta} = \rho \frac{\partial^2 u}{\partial \rho^2}, \quad (27)$$

once that a , $\partial a / \partial G_{\nu}$, $\partial a / \partial G_{\nu}^{(1)}$, $\partial G_{\nu} / \partial u$, and $\partial G_{\nu}^{(1)} / \partial u$ have been determined as functions of ρ and u (see below). $B(\rho, u)$ is given by

$$B(\rho, u) = 2 \frac{a}{(2\pi)^2} \sum_{\nu=1}^n \left(\frac{\partial a}{\partial G_{\nu}} \frac{\partial G_{\nu}}{\partial u} + \frac{\partial a}{\partial G_{\nu}^{(1)}} \frac{\partial G_{\nu}^{(1)}}{\partial u} \right). \quad (28)$$

Thus we now have derived a PDE for $u(\rho, \beta)$.

What remains is to determine a , $\partial a / \partial G_{\nu}$, $\partial a / \partial G_{\nu}^{(1)}$, $\partial G_{\nu} / \partial u$, and $\partial G_{\nu}^{(1)} / \partial u$ as functions of ρ and u . First of all we introduce $2n$ nonlinear equations $F_i(\rho, u, G_{\nu}, G_{\nu}^{(1)}) = 0$, $i = 1, \dots, 2n$; their solution gives $G_{\nu}(\rho, u)$ and $G_{\nu}^{(1)}(\rho, u)$. The first equation is linear and is the energy equation (22)

$$u + 2\pi\rho^2 \epsilon \sigma \sum_{\nu=2}^n \left(\frac{K_{\nu}}{z_{\nu}} G_{\nu} + L_{\nu} G_{\nu}^{(1)} \right) = 0, \quad (29)$$

or formally written as $F_1(\rho, u, G_2, \dots, G_n, G_2^{(1)}, \dots, G_n^{(1)}) = 0$.

To establish the remaining $2n - 1$ nonlinear equations we make use of Eqs. (A1)–(A4) and Eqs. (15) and (16). Expressions for the \tilde{K}_{ν} and \tilde{L}_{ν} in Eqs. (15) and (16) are obtained by comparison of Eq. (10) with the closure relation (24)

$$\tilde{K}_1 = K_1(\rho), \quad (30)$$

$$\tilde{L}_1 = 0, \quad (31)$$

$$\tilde{K}_{\nu} = -K(\rho, \beta) \epsilon \sigma K_{\nu} \quad \text{for } \nu = 2, \dots, n, \quad (32)$$

$$\tilde{L}_{\nu} = -K(\rho, \beta) \epsilon \sigma L_{\nu} \quad \text{for } \nu = 2, \dots, n, \quad (33)$$

and thus

$$A_1^{(7)} = 0, \quad (34)$$

$$C_1^{(13)} = 2\pi K_1(\rho), \quad (35)$$

$$A_{\nu}^{(7)} L_{\mu} = A_{\mu}^{(7)} L_{\nu} \quad \text{for } \nu, \mu = 2, \dots, n, \quad (36)$$

$$C_{\nu}^{(13)} K_{\mu} = C_{\mu}^{(13)} K_{\nu} \quad \text{for } \nu, \mu = 2, \dots, n, \quad (37)$$

$$A_{\mu}^{(7)} K_{\mu} = C_{\mu}^{(13)} L_{\mu} \quad \text{for } \mu = 2, \dots, n. \quad (38)$$

The second nonlinear equation is Eq. (A1) for $\nu = 1$ where the solution $D_{\nu}(\rho, G_{\nu}, G_{\nu}^{(1)})$ and $E_{\nu}(\rho, G_{\nu}, G_{\nu}^{(1)})$ of Eq. (17) and the relation (34) are inserted, formally written as $F_2(\rho, G_{\nu}, G_{\nu}^{(1)}) = 0$. The third equation is Eq. (A2) for $\nu = 1$ where the solution $D_{\nu}(\rho, G_{\nu}, G_{\nu}^{(1)})$ and $E_{\nu}(\rho, G_{\nu}, G_{\nu}^{(1)})$ of Eq. (17) and the relation (35) are inserted. The fourth equation corresponds to Eq. (38) for $\mu = 2$ using Eqs. (A1) and (A2) to eliminate the unknown function $K(\rho, \beta)$.

The remaining $2n - 4$ equations are obtained from Eqs. (A1) and (A2) for $\nu > 1$, inserting the solution of Eq. (17) $D_{\nu}(\rho, G_{\nu}, G_{\nu}^{(1)})$ and $E_{\nu}(\rho, G_{\nu}, G_{\nu}^{(1)})$ and eliminating the unknown function $K(\rho, \beta)$ in the coefficients $A_{\nu}^{(7)}$, $C_{\nu}^{(13)}$ via the relations (36), and (37) (for $\nu = 2, \mu = 3, \dots, n$).

For given ρ and u the G_{ν} and $G_{\nu}^{(1)}$ are determined in the following way: The coupled set of nonlinear equations $F_1 = 0, \dots, F_{2n} = 0$ is solved numerically via a Newton–Raphson technique using explicit expressions for the Jaco-

bian matrix $J = (\partial F_\mu / \partial G_\nu)$. In each step of the iteration the D_ν and E_ν are obtained by numerical solution of the linear system (17).

The partial derivatives $\partial D_\tau / \partial G_\mu$, $\partial E_\tau / \partial G_\mu$, $\partial D_\tau / \partial G_\mu^{(1)}$, and $\partial E_\tau / \partial G_\mu^{(1)}$ required in the Jacobian are obtained by implicit differentiation of Eqs. (17). Solution of the nonlinear equations via the procedure described above yields the G_ν and $G_\nu^{(1)}$ as functions of ρ and u . We now calculate the derivatives $\partial G_\nu / \partial u(\rho, u)$ and $\partial G_\nu^{(1)} / \partial u(\rho, u)$ required in the coefficient $B(\rho, u)$ in Eq. (28). They are determined by implicitly differentiating equations $F_1 = 0, \dots, F_{2n} = 0$ with respect to u

$$\begin{pmatrix} \frac{\partial G_1}{\partial u} \\ \frac{\partial G_2}{\partial u} \\ \vdots \\ \frac{\partial G_n}{\partial u} \\ \frac{\partial G_1^{(1)}}{\partial u} \\ \frac{\partial G_2^{(1)}}{\partial u} \\ \vdots \\ \frac{\partial G_n^{(1)}}{\partial u} \end{pmatrix} = J(\rho, G_\nu(\rho, u), G_\nu^{(1)}(\rho, u))^{-1} \cdot \begin{pmatrix} -1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}. \quad (39)$$

Finally, the $\partial a / \partial G_\nu(\rho, u)$ and $\partial a / \partial G_\nu^{(1)}(\rho, u)$ are obtained from (19) and (20),

$$\begin{aligned} \frac{\partial a}{\partial G_\nu} &= A^0 \frac{\partial M}{\partial G_\nu} - \frac{4}{\sigma^2} B^0 \frac{\partial N}{\partial G_\nu}, \\ \frac{\partial a}{\partial G_\nu^{(1)}} &= A^0 \frac{\partial M}{\partial G_\nu^{(1)}} - \frac{4}{\sigma^2} B^0 \frac{\partial N}{\partial G_\nu^{(1)}}, \end{aligned} \quad (40)$$

where

$$\begin{aligned} \frac{\partial M}{\partial G_\nu} &= -\rho \sum_{\tau=1}^n \left[\left(\frac{M_\tau^{(a)}}{z_\tau} - 2\pi\rho \frac{G_\tau}{z_\tau} (M_\tau^{(a)} e^{-z_\tau\sigma} - 1) \right) \frac{\partial D_\tau}{\partial G_\nu} \right. \\ &\quad + \left(\frac{P_\tau^{(a)}}{z_\tau} - 2\pi\rho \frac{G_\tau}{z_\tau} (2L_\tau^{(a)} e^{-z_\tau\sigma} - 2) \right. \\ &\quad \left. \left. - 2\pi\rho \frac{G_\tau^{(1)}}{z_\tau^3} (M_\tau^{(a)} e^{-z_\tau\sigma} - 1) \right) \frac{\partial E_\tau}{\partial G_\nu} \right] \\ &\quad + 2\pi\rho^2 \frac{1}{z_\nu^4} (M_\nu^{(a)} e^{-z_\nu\sigma} - 1) \\ &\quad + 2\pi\rho^2 \frac{1}{z_\nu^4} (2L_\nu^{(a)} e^{-z_\nu\sigma} - 2), \end{aligned} \quad (41)$$

and similarly for $\partial M / \partial G_\nu^{(1)}$, $\partial N / \partial G_\nu$ and $\partial N / \partial G_\nu^{(1)}$ with $\{D_\mu, E_\mu, \partial D_\mu / \partial G_\nu, \partial E_\mu / \partial G_\nu, \partial D_\mu / \partial G_\nu^{(1)}, \partial E_\mu / \partial G_\nu^{(1)}\}$ as functions of $[\rho, G_\nu(\rho, u), G_\nu^{(1)}(\rho, u)]$.

The PDE (27) is a quasilinear diffusion equation that has been solved numerically by an implicit finite-difference algorithm⁴⁷ described in detail in Ref. 20 in the region $(\beta, \rho) \in [0, \beta_f] \times [0, \rho_0]$. The integration with respect to β starts at $\beta = 0$ and goes down to lower temperatures. At each temperature the set of nonlinear equations $F_1 = 0, \dots, F_{2n} = 0$ is solved giving G_ν and $G_\nu^{(1)}$ as functions of ρ and u : To ensure rapid convergence the values of the G_ν and $G_\nu^{(1)}$ obtained at the previous temperature step in the solution algorithm of the PDE are taken as initial guess for the solution of the system of nonlinear equations. In the next step $\{D_\mu, E_\mu\}(\rho, u)$, $a(\rho, u)$, $\{\partial D_\mu / \partial G_\nu, \partial E_\mu / \partial G_\nu, \partial D_\mu / \partial G_\nu^{(1)}, \partial E_\mu / \partial G_\nu^{(1)}\}(\rho, u)$, $\{\partial a / \partial G_\nu, \partial a / \partial G_\nu^{(1)}\}(\rho, u)$, and $\{\partial G_\nu / \partial u, \partial G_\nu^{(1)} / \partial u\}(\rho, u)$ are determined to calculate the coefficient $B(\rho, u)$.

The boundary conditions are the same as in Ref. 27: For $\rho = 0$ one obtains from Eq. (22)

$$u(\rho = 0, \beta) = 0 \quad \forall \beta. \quad (42)$$

For the boundary condition at high density ρ_0 (we have set $\rho_0^* = \rho_0 \sigma^3 = 1$ in the calculations) we make use of the so-called high temperature approximation

$$\frac{\partial^2 u}{\partial \rho^2}(\rho_0, \beta) = \frac{\partial^2 u}{\partial \rho^2}(\rho_0, \beta = 0) \quad \forall \beta. \quad (43)$$

The initial condition $u(\rho, \beta = 0)$ can be determined by taking into account that for $\beta = 0$ the direct correlation function $c(r)$ coincides with that of the HS gas. For details see Appendix C. The unphysical region inside the spinodal curve is determined as follows: In the forbidden region either a Eq. (19) becomes negative or no longer a solution of the system of the nonlinear Eqs. (A1) and (A2) can be found. The boundary conditions on the spinodal used here are the same as those in Ref. 27

$$u(\rho_{S_i}, \beta) = u_S(\rho_{S_i}) \quad i = 1, 2, \quad (44)$$

where ρ_{S_i} ($i = 1, 2$) are approximates for the spinodal densities on the discrete density grid at a given temperature. Their values are determined by locating the change of sign of a . $u_S(\rho)$ is the value of the excess internal energy per unit volume where $1/\chi^{\text{red}} = 0$. This value is determined by solving the set of equations

$$\begin{aligned} a(\rho, G_\nu, G_\nu^{(1)}) &= 0, \\ F_2(\rho, G_\nu, G_\nu^{(1)}) &= 0, \\ &\vdots \\ F_{2n}(\rho, G_\nu, G_\nu^{(1)}) &= 0, \end{aligned} \quad (45)$$

with respect to the G_ν and $G_\nu^{(1)}$, providing again the analytic Jacobian matrix of this nonlinear system. Inserting the solutions $G_\nu(\rho)$ and $G_\nu^{(1)}(\rho)$ in the energy equation (22) yields $u_S(\rho)$.

Once $u(\rho, \beta)$ has been determined by solving the PDE (27), the pressure P and the chemical potential μ are obtained by integrating $\partial \beta P / \partial \beta$ and $\partial \beta \mu / \partial \beta$ with respect to β from

TABLE I. Parameters of the 4 SI systems investigated in this work. The normalization factors n were chosen so that the minimum of the function $w(r)$ of Eq. (2) on the interval $[\sigma, \infty)$ is -1 .

System	K_2/n	$L_2 z_2/n$	z_2	n
F0	0	1	1.8	1
F1	-1	1.1	1.8	5.187 87
F2	-1	1	1.8	7.190 39
F3	-1	0.9	1.8	10.531 48

$$\frac{\partial \beta P}{\partial \beta} = -u + \rho \frac{\partial u}{\partial \rho}, \quad (46)$$

$$\frac{\partial \beta \mu}{\partial \beta} = \frac{\partial u}{\partial \rho}, \quad (47)$$

where we have taken as integration constants at $\beta=0$ the CS values for βP and $\beta \mu$

$$\beta P(\rho, \beta=0) = \rho \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3},$$

$$\beta \mu(\rho, \beta=0) = \ln \rho + \frac{8\eta - 9\eta^2 - 3\eta^3}{(1 - \eta)^3}. \quad (48)$$

Alternatively, βP and $\beta \mu$ can be obtained by integrating, respectively, $1/\chi^{\text{red}}$ and $1/\rho \chi^{\text{red}}$ with respect to the density from

$$\left(\frac{\partial \beta P}{\partial \rho} \right)_T = \frac{1}{\chi^{\text{red}}},$$

$$\left(\frac{\partial \beta \mu}{\partial \rho} \right)_T = \frac{1}{\rho \chi^{\text{red}}}. \quad (49)$$

Both paths lead to the same thermodynamics due to the thermodynamic consistency enforced by Eq. (8). In the latter route, the high density branch of the subcritical isotherms, that is separated from the low-density branch by the spinodal, can be obtained by integrating along an isotherm starting at the high density side were the high-temperature approximation is accurate.

III. RESULTS

Using the formalism presented in the previous section we have investigated four systems—in the following labeled F0, F1, F2, and F3 whose parameters are summarized in Table I. For the interaction potential of F0 we have chosen $K_2=0$, i.e., we consider a simple exponential potential $w(r) = -\epsilon e^{-z_2(r-\sigma)}$ as shown in Fig. 1. The interaction potentials of F1–F3 correspond to one Sogami–Ise tail consisting of two competing terms: An attractive exponential and a repulsive Yukawa tail. Varying the value of the ratio $-L_2 z_2/K_2$ from 1.1 (F1) to 0.9 (F3) offers a systematic variation of the characteristic properties of the interaction potentials: The location of the minimum of $\phi(r)$ is shifted to larger r values and the contact-value of $\phi(r)$ at the HS diameter varies from negative to positive values as shown in Fig. 1. Hence for F3 a soft repulsive interaction merges into the infinitely steep repulsive HS wall.

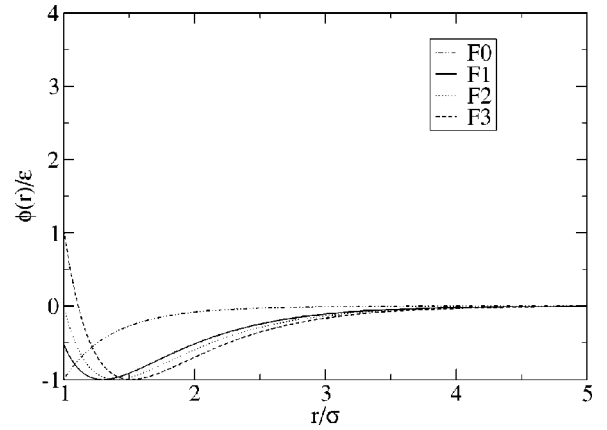


FIG. 1. Sogami–Ise interaction potential of systems F0–F3. Parameters of the systems are given in Table I.

For the four systems characterized above, we have calculated thermodynamic properties and the phase diagrams using the SCOZA as presented above; these results have been compared with results from the LOGA/ORPA approach,^{38,39} according to which in Eq. (24) $K(\rho, \beta) = -\beta$ is fixed. This enables us to investigate the effect of the self-consistency requirement on the thermodynamic properties and on the phase behavior.

The LOGA/ORPA results have been obtained by solving the $4n$ equations (A1)–(A4) in the $4n$ unknowns $\{D_\nu, E_\nu, G_\nu, G_\nu^{(1)}\}$ with a Newton–Raphson technique providing a $4n \times 4n$ analytic Jacobian matrix. In the cases studied here, where the number of Sogami–Ise tails n is equal to 2, the LOGA/ORPA values of $A_\nu^{(7)}$ and $C_\nu^{(13)}$ needed in Eqs. (A1) and (A2) are given by $A_1^{(7)}=0$, $C_1^{(13)}=2\pi K_1(\rho)$, $A_2^{(7)}=2\pi\beta\epsilon\sigma L_2$, and $C_2^{(13)}=2\pi\beta\epsilon\sigma K_2$. Once the $\{D_\nu, E_\nu, G_\nu, G_\nu^{(1)}\}$ are known the excess internal energy via the internal energy route is calculated from Eq. (22), the compressibility from Eqs. (18)–(20), the pressure and the chemical potential via the energy route, P^E and μ^E , from Eqs. (46) and (47), and the corresponding quantities via the compressibility route, P^C and μ^C , from Eqs. (49).

Due to the inbuilt consistency SCOZA provides only two pressures in the following denoted as $P^{E,C}$ (via energy/compressibility route) and P^V (via the virial route). In SCOZA and LOGA/ORPA the virial pressure, P^V , has been obtained as described in detail in Appendix D.

In the following, fluid densities and temperatures are given in reduced units, i.e., $\rho^* = \rho\sigma^3$, $T^* = kT/\epsilon$. In Fig. 2 the pressure obtained from SCOZA via the energy/compressibility route $P^{E,C}$ for system F2 is compared with the pressure calculated within LOGA/ORPA via the three different routes to thermodynamics. The LOGA/ORPA values for P^V and P^C bracket P^E (via LOGA/ORPA) which coincides—within the line thickness—with the SCOZA $P^{E,C}$. In Table II the SCOZA predictions for the pressure and the chemical potential are compared with the LOGA/ORPA results for various thermodynamic states. For the slightly supercritical thermodynamic state of F0 at $\rho^*=0.3$ and $T^*=2$ (see Fig. 3) the agreement is less satisfactory than for the other noncritical states where the SCOZA and the energy route of the LOGA/ORPA provide results that are very close

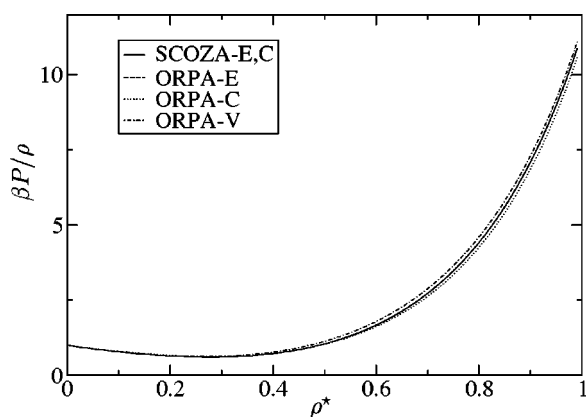


FIG. 2. Pressure of system F2 at temperature $\beta^* = 1/T^* = 0.15$ obtained from SCOZA via energy/compressibility route and from LOGA/ORPA via energy, compressibility and virial route.

together. Within SCOZA discrepancies between pressure values $P^{E,C}$ and P^V are observed which are due to the fact that SCOZA in its present form enforces consistency only between the compressibility and the energy routes, and not with the virial route to thermodynamics. As becomes visible from Table II, SCOZA yields liquid-state pressures from the virial route that are very close to the results for the virial pressure within the LOGA/ORPA approach.

The internal energy per particle u via the energy route and the reduced isothermal compressibility χ^{red} via the compressibility route obtained within the two theoretical approaches are compared in Table III. The agreement in the internal energy is rather good. Again for the supercritical state at $\rho^* = 0.3$ and $T^* = 2$ of system F0 the results—especially of $1/\chi^{\text{red}}$ —differ.

The phase diagram of the system F0 is given in Fig. 3. The SCOZA critical point has been located by the vanishing of $1/\chi^{\text{red}}$. Below T_c^* the spinodal line was determined as described in Sec. II. The coexistence curve was obtained by numerically solving the equilibrium conditions

$$\mu(\rho_g, T) = \mu(\rho_l, T), \quad (50)$$

$$P(\rho_g, T) = P(\rho_l, T), \quad (51)$$

for the two coexisting densities ρ_g and ρ_l of the gas and liquid for a given temperature T . While the coexistence

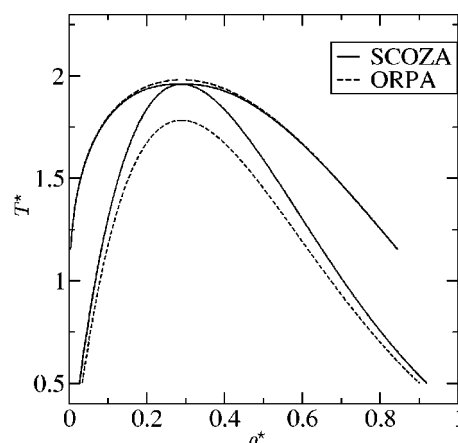


FIG. 3. Phase diagram of system F0 in the $\rho^* - T^*$ plane. Full lines: Coexistence and spinodal curve obtained from the SCOZA. Dashed lines: Coexistence curve obtained from LOGA/ORPA via the energy route and spinodal curve from LOGA/ORPA using the compressibility route.

curve of the SCOZA can be determined up to the critical point, this is not possible for the LOGA/ORPA: Near the critical point no solution of Eqs. (50) and (51) can be found so the two branches remain unconnected. Therefore, the critical point parameters ρ_c^* and T_c^* within the LOGA/ORPA, collected in Table IV, were estimated by extrapolation under the assumption that the coexistence curve can be described by a scaling type law and the law of rectilinear diameters, i.e.,

$$\rho_l - \rho_g = B(T - T_c)^\beta, \quad (\rho_l + \rho_g)/2 = \rho_c + A(T - T_c). \quad (52)$$

Parameters A , B , and β in Eqs. (52) were fitted to the coexistence curves.

In Fig. 3 also the inconsistency of the LOGA/ORPA becomes visible: The curve of diverging compressibility lies well inside the liquid–vapor coexistence curve obtained from the energy route yielding two different critical points from the different routes. The SCOZA value is closer to the one derived from the energy route which is known to yield the most accurate thermodynamic information from the radial distribution function within the LOGA/ORPA approach.

The coexistence curves obtained within SCOZA for the systems F1–F3 are shown in Fig. 4, the corresponding criti-

TABLE II. Pressure and chemical potential for systems F0 and F2 for selected thermodynamic states obtained from SCOZA and from LOGA/ORPA via the different routes.

System	ρ^*	β^*	SCOZA		LOGA/ORPA		
			$\beta P^{E,C}/\rho$	$\beta P^V/\rho$	$\beta P^E/\rho$	$\beta P^C/\rho$	$\beta P^V/\rho$
F0	0.3	0.5	0.357 44	0.257 20	0.354 92	0.465 59	0.250 94
F0	0.8	0.5	2.8874	2.7729	2.8872	3.2168	2.7703
F2	0.3	0.15	0.615 02	0.636 93	0.615 00	0.633 83	0.637 50
F2	0.8	0.15	4.4201	0.461 25	4.4214	4.2573	4.6053
System	ρ^*	β^*	$\beta \mu^{E,C}$		$\beta \mu^E$	$\beta \mu^C$	
F0	0.3	0.5	−2.6379		−2.6365	−2.41 14	
F0	0.8	0.5	0.6155		0.615 82	1.2652	
F2	0.3	0.15	−2.169 45		−2.1690	−2.1124	
F2	0.8	0.15	3.0519		3.0543	2.8984	

TABLE III. Reduced internal energy per particle and isothermal compressibility for systems F0 and F2 for selected thermodynamic states obtained from SCOZA and from LOGA/ORPA.

System	ρ^*	β^*	$U^{ex}/\epsilon N$		$1/\chi^{red}$	
			SCOZA	LOGA/ORPA	SCOZA	LOGA/ORPA
F0	0.3	0.5	-3.2785	-3.2297	0.053 807	0.271 47
F0	0.8	0.5	-8.9067	-8.9062	17.028	17.611
F2	0.3	0.15	-9.1495	-9.1486	0.702 48	0.710 92
F2	0.8	0.15	-23.658	-23.659	21.332	20.617

cal point parameters are listed in Table IV. With increasing integrated strength of the interaction potential (F1–F3) the critical point is shifted to higher temperatures and—less pronounced—to lower densities. As can be seen from Table IV the LOGA/ORPA values of T_c^* are less than 0.5% above those of the SCOZA, also the agreement in the densities ρ_c^* is rather good.

Of special interest is the interaction potential of system F3 that includes, apart from the HC repulsion, a soft repulsive interaction—a case that has not been treated by SCOZA so far and was considered to be out of reach for the study with SCOZA due to substantial numerical problems when solving the SCOZA PDE: In Ref. 48 where HC systems with two competing Yukawa interactions were studied within SCOZA only a rather weak repulsive part in the interaction potential could be considered.

IV. CONCLUSIONS

We have generalized the SCOZA to HC systems with an adjacent tail that is built up by an exponentially damped part and a Yukawa interaction. The theory is based on a LOGA/ORPA like closure relation which involves a state dependent function $K(\rho, \beta)$. In contrast to LOGA/ORPA, $K(\rho, \beta)$ is not fixed *a priori* but is determined by enforcing consistency between the compressibility and the energy route to thermodynamics thus leading to a PDE for the unknown function $K(\rho, \beta)$. Our generalization is based on the availability of the semianalytic MSA solution for Sogami–Ise systems within the Wertheim–Baxter factorization technique. In the first part of this paper we have presented the formalism in detail, we have transformed the consistency PDE for $K(\rho, \beta)$ into a PDE for the internal energy per particle u . In the second part the theory was applied to study the thermodynamics and the phase behavior of various model systems. In order to investigate the effect of the self-consistency require-

TABLE IV. Critical parameters of the fluid systems F0 to F3 investigated in this work obtained from SCOZA and from the LOGA/ORPA via the energy route.

System	SCOZA		LOGA/ORPA	
	T_c^*	ρ_c^*	T_c^*	ρ_c^*
F0	1.960	0.289	1.981	0.290
F1	4.857	0.258	4.882	0.256
F2	5.325	0.250	5.346	0.248
F3	5.744	0.238	5.755	0.230

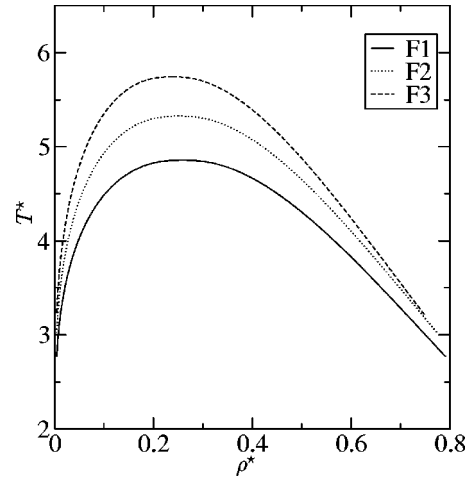


FIG. 4. Phase diagrams of systems F1–F3 obtained within the SCOZA in the $\rho^* - T^*$ plane.

ment we have compared SCOZA and LOGA/ORPA calculations and found that the SCOZA data are close to LOGA/ORPA results obtained within the energy route.

ACKNOWLEDGMENTS

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APPENDIX A: NONLINEAR EQUATIONS

Here we present the coupled set of $4n$ equations that determine the $4n$ unknowns D_ν , E_ν , G_ν , and $G_\nu^{(1)}$. All other quantities that enter the equations are found in Appendix B.

$$\begin{aligned}
 & E_\nu \sum_{\tau=1}^n A_{\tau\nu}^{(1)} G_\tau^{(1)} E_\tau + E_\nu \sum_{\tau=1}^n A_{\tau\nu}^{(2)} G_\tau E_\tau + E_\nu \sum_{\tau=1}^n A_{\tau\nu}^{(3)} G_\tau D_\tau \\
 & + E_\nu \sum_{\tau=1}^n A_{\tau\nu}^{(4)} E_\tau + E_\nu \sum_{\tau=1}^n A_{\tau\nu}^{(5)} D_\tau + E_\nu A_\nu^{(6)} + A_\nu^{(7)} = 0, \\
 & \nu = 1, \dots, n,
 \end{aligned} \tag{A1}$$

$$\begin{aligned}
 & E_\nu \sum_{\tau=1}^n C_{\tau\nu}^{(1)} G_\tau^{(1)} E_\tau + D_\nu \sum_{\tau=1}^n C_{\tau\nu}^{(2)} G_\tau^{(1)} E_\tau \\
 & + E_\nu \sum_{\tau=1}^n C_{\tau\nu}^{(3)} G_\tau E_\tau + D_\nu \sum_{\tau=1}^n C_{\tau\nu}^{(4)} G_\tau E_\tau \\
 & + E_\nu \sum_{\tau=1}^n C_{\tau\nu}^{(5)} G_\tau D_\tau + D_\nu \sum_{\tau=1}^n C_{\tau\nu}^{(6)} G_\tau D_\tau \\
 & + E_\nu \sum_{\tau=1}^n C_{\tau\nu}^{(7)} E_\tau + D_\nu \sum_{\tau=1}^n C_{\tau\nu}^{(8)} E_\tau + E_\nu \sum_{\tau=1}^n C_{\tau\nu}^{(9)} D_\tau \\
 & + D_\nu \sum_{\tau=1}^n C_{\tau\nu}^{(10)} D_\tau + E_\nu C_\nu^{(11)} + D_\nu C_\nu^{(12)} + C_\nu^{(13)} = 0, \\
 & \nu = 1, \dots, n,
 \end{aligned} \tag{A2}$$

$$\begin{aligned}
& G_\nu \sum_{\tau=1}^n B_{\tau\nu}^{(1)} G_\tau^{(1)} E_\tau + G_\nu \sum_{\tau=1}^n B_{\tau\nu}^{(2)} G_\tau E_\tau \\
& + G_\nu \sum_{\tau=1}^n B_{\tau\nu}^{(3)} G_\tau D_\tau + \sum_{\tau=1}^n B_{\tau\nu}^{(4)} G_\tau^{(1)} E_\tau \\
& + \sum_{\tau=1}^n B_{\tau\nu}^{(5)} G_\tau E_\tau + \sum_{\tau=1}^n B_{\tau\nu}^{(6)} G_\tau D_\tau + G_\nu \sum_{\tau=1}^n B_{\tau\nu}^{(7)} E_\tau \\
& + G_\nu \sum_{\tau=1}^n B_{\tau\nu}^{(8)} D_\tau + \sum_{\tau=1}^n B_{\tau\nu}^{(9)} E_\tau + \sum_{\tau=1}^n B_{\tau\nu}^{(10)} D_\tau \\
& + G_\nu B_\nu^{(11)} + B_\nu^{(12)} = 0, \\
\nu = 1, \dots, n,
\end{aligned} \tag{A3}$$

$$\begin{aligned}
& G_\nu^{(1)} \sum_{\tau=1}^n D_{\tau\nu}^{(1)} G_\tau^{(1)} E_\tau + G_\nu^{(1)} \sum_{\tau=1}^n D_{\tau\nu}^{(2)} G_\tau E_\tau \\
& + G_\nu^{(1)} \sum_{\tau=1}^n D_{\tau\nu}^{(3)} G_\tau D_\tau + G_\nu \sum_{\tau=1}^n D_{\tau\nu}^{(4)} G_\tau^{(1)} E_\tau \\
& + G_\nu \sum_{\tau=1}^n D_{\tau\nu}^{(5)} G_\tau E_\tau + G_\nu \sum_{\tau=1}^n D_{\tau\nu}^{(6)} G_\tau D_\tau \\
& + G_\nu^{(1)} \sum_{\tau=1}^n D_{\tau\nu}^{(7)} E_\tau + G_\nu^{(1)} \sum_{\tau=1}^n D_{\tau\nu}^{(8)} D_\tau + G_\nu \sum_{\tau=1}^n D_{\tau\nu}^{(9)} E_\tau \\
& + G_\nu \sum_{\tau=1}^n D_{\tau\nu}^{(10)} D_\tau + \sum_{\tau=1}^n D_{\tau\nu}^{(11)} G_\tau^{(1)} E_\tau + \sum_{\tau=1}^n D_{\tau\nu}^{(12)} G_\tau E_\tau \\
& + \sum_{\tau=1}^n D_{\tau\nu}^{(13)} G_\tau D_\tau + \sum_{\tau=1}^n D_{\tau\nu}^{(14)} E_\tau + \sum_{\tau=1}^n D_{\tau\nu}^{(15)} D_\tau \\
& + G_\nu^{(1)} D_\nu^{(16)} + G_\nu D_\nu^{(17)} + D_\nu^{(18)} = 0, \\
\nu = 1, \dots, n.
\end{aligned} \tag{A4}$$

Equations (A3) and (A4) are linear in D_ν and E_ν for given G_ν and $G_\nu^{(1)}$ and can be rewritten as

$$\begin{aligned}
& \sum_{\tau=1}^n O_{\nu\tau} D_\tau + \sum_{\tau=1}^n P_{\nu\tau} E_\tau = Q_\nu, \\
& \sum_{\tau=1}^n R_{\nu\tau} D_\tau + \sum_{\tau=1}^n S_{\nu\tau} E_\tau = T_\nu,
\end{aligned} \tag{A5}$$

with

$$\begin{aligned}
O_{\nu\tau}(\rho, G_\nu) &= B_{\tau\nu}^{(3)} G_\tau G_\nu + B_{\tau\nu}^{(6)} G_\tau + B_{\tau\nu}^{(8)} G_\nu + B_{\tau\nu}^{(10)}, \\
P_{\nu\tau}(\rho, G_\nu, G_\nu^{(1)}) &= B_{\tau\nu}^{(1)} G_\tau^{(1)} G_\nu + B_{\tau\nu}^{(2)} G_\tau G_\nu + B_{\tau\nu}^{(4)} G_\tau^{(1)} \\
& + B_{\tau\nu}^{(5)} G_\tau + B_{\tau\nu}^{(7)} G_\nu + B_{\tau\nu}^{(9)}, \\
R_{\nu\tau}(\rho, G_\nu, G_\nu^{(1)}) &= D_{\tau\nu}^{(3)} G_\tau G_\nu^{(1)} + D_{\tau\nu}^{(6)} G_\tau G_\nu + D_{\tau\nu}^{(8)} G_\nu^{(1)} \\
& + D_{\tau\nu}^{(10)} G_\nu + D_{\tau\nu}^{(13)} G_\tau + D_{\tau\nu}^{(15)},
\end{aligned} \tag{A6}$$

$$\begin{aligned}
S_{\nu\tau}(\rho, G_\nu, G_\nu^{(1)}) &= D_{\tau\nu}^{(1)} G_\tau^{(1)} G_\nu^{(1)} + D_{\tau\nu}^{(2)} G_\tau G_\nu^{(1)} \\
& + D_{\tau\nu}^{(4)} G_\tau^{(1)} G_\nu + D_{\tau\nu}^{(5)} G_\tau G_\nu + D_{\tau\nu}^{(7)} G_\nu^{(1)} \\
& + D_{\tau\nu}^{(9)} G_\nu + D_{\tau\nu}^{(11)} G_\tau^{(1)} + D_{\tau\nu}^{(12)} G_\tau \\
& + D_{\tau\nu}^{(14)},
\end{aligned}$$

and

$$\begin{aligned}
Q_\nu(\rho, G_\nu) &= -B_\nu^{(11)} G_\nu - B_\nu^{(12)}, \\
T_\nu(\rho, G_\nu, G_\nu^{(1)}) &= -D_\nu^{(16)} G_\nu^{(1)} - D_\nu^{(17)} G_\nu - D_\nu^{(18)},
\end{aligned} \tag{A7}$$

or, in more compact matrix notation as

$$\begin{pmatrix} O & P \\ R & S \end{pmatrix} \begin{pmatrix} \mathbf{D} \\ \mathbf{E} \end{pmatrix} = \begin{pmatrix} Q \\ T \end{pmatrix}, \tag{A8}$$

with $(\mathbf{D}, \mathbf{E})^T = (D_1, \dots, D_n, E_1, \dots, E_n)$, $O = (O_{\nu\tau})$, etc.

APPENDIX B: COEFFICIENTS

In the following we present expressions for the coefficients of Eqs. (A1)–(A4). The following parameters correspond to the hard-sphere case

$$A_0 = 2\pi \frac{1+2\eta}{(1-\eta)^2},$$

$$B_0 = -3\pi \frac{\eta\sigma}{(1-\eta)^2},$$

$$b_0 = 2\pi \frac{\sigma(1+\eta/2)}{(1-\eta)^2}.$$

Further, we introduce the functions

$$\theta_0(x) = 1 - e^{-x},$$

$$\theta_1(x) = 1 - x - e^{-x},$$

$$\theta_2(x) = 1 - x + \frac{x^2}{2} - e^{-x},$$

required in the definition of the coefficients

$$M_\nu^{(a)} = 1 + z_\nu \sigma,$$

$$M_{\nu\mu}^{(b)} = 1 + (z_\nu + z_\mu) \sigma,$$

$$P_\nu^{(a)} = 1 + z_\nu \sigma + (z_\nu \sigma)^2,$$

$$L_\nu^{(a)} = 1 + z_\nu \sigma + \frac{(z_\nu \sigma)^2}{2},$$

$$L_{\nu\mu}^{(b)} = 1 + (z_\nu + z_\mu) \sigma + \frac{((z_\nu + z_\mu) \sigma)^2}{2},$$

$$Q_\nu^{(a)} = 1 + z_\nu \sigma + \frac{(z_\nu \sigma)^2}{2} + \frac{(z_\nu \sigma)^3}{4},$$

$$O_\nu^{(a)} = 1 + z_\nu \sigma + \frac{(z_\nu \sigma)^2}{2} + \frac{(z_\nu \sigma)^3}{6},$$

$$O_{\nu\mu}^{(b)} = 1 + (z_\nu + z_\mu) \sigma + \frac{((z_\nu + z_\mu) \sigma)^2}{2} + \frac{((z_\nu + z_\mu) \sigma)^3}{6},$$

$$\begin{aligned}
 H_\nu^{(a)} &= A_0 \theta_2(z_\nu \sigma) + b_0 z_\nu \theta_1(z_\nu \sigma), \\
 G_\nu^{(a)} &= A_0 z_\nu \theta_1(z_\nu \sigma) - \frac{4}{\sigma^2} B_0 \theta_2(z_\nu \sigma), \\
 H_\nu^{(b)} &= b_0 + \frac{A_0}{z_\nu}, \\
 G_\nu^{(b)} &= A_0 - \frac{4}{\sigma^2} B_0 \frac{1}{z_\nu}, \\
 R_\nu^{(a)} &= [3 \theta_2(z_\nu \sigma) + z_\nu \sigma \theta_1(z_\nu \sigma)] A_0 + z_\nu [2 \theta_1(z_\nu \sigma) \\
 &\quad + z_\nu \sigma \theta_0(z_\nu \sigma)] b_0, \\
 S_\nu^{(a)} &= z_\nu [2 \theta_1(z_\nu \sigma) + z_\nu \sigma \theta_0(z_\nu \sigma)] A_0 - [3 \theta_2(z_\nu \sigma) \\
 &\quad + z_\nu \sigma \theta_1(z_\nu \sigma)] \frac{4}{\sigma^2} B_0, \\
 R_\nu^{(b)} &= \frac{1}{z_\nu} [1 + z_\nu \sigma] b_0 + \frac{1}{z_\nu} [2 + z_\nu \sigma] A_0, \\
 S_\nu^{(b)} &= \frac{1}{z_\nu} [1 + z_\nu \sigma] A_0 - \frac{1}{z_\nu} [2 + z_\nu \sigma] \frac{4}{\sigma^2} B_0, \\
 U_{\nu\mu} &= -\frac{2}{(z_\nu + z_\mu)^3} + \frac{2}{z_\mu^3} e^{-z_\nu \sigma} \\
 &\quad + \left[\frac{2}{(z_\nu + z_\mu)^3} L_{\nu\mu}^{(b)} - \frac{2}{z_\mu^3} L_\mu^{(a)} \right] e^{-(z_\nu + z_\mu) \sigma}, \\
 V_{\nu\mu} &= -\frac{6}{(z_\nu + z_\mu)^4} + \frac{2\sigma}{z_\mu^3} e^{-z_\nu \sigma} \\
 &\quad + \left[\frac{6}{(z_\nu + z_\mu)^4} O_{\nu\mu}^{(b)} - \frac{2\sigma}{z_\mu^3} L_\mu^{(a)} \right] e^{-(z_\nu + z_\mu) \sigma}, \\
 W_{\nu\mu} &= -\frac{1}{(z_\nu + z_\mu)^2} + \frac{1}{z_\mu^2} e^{-z_\nu \sigma} \\
 &\quad + \left[\frac{1}{(z_\nu + z_\mu)^2} M_{\nu\mu}^{(b)} - \frac{1}{z_\mu^2} M_\mu^{(a)} \right] e^{-(z_\nu + z_\mu) \sigma}, \\
 X_{\nu\mu} &= -\frac{1}{(z_\nu + z_\mu)} + \frac{1}{z_\mu} e^{-z_\nu \sigma} - \frac{z_\nu}{z_\mu(z_\nu + z_\mu)} e^{-(z_\nu + z_\mu) \sigma}, \\
 Y_{\nu\mu} &= -\frac{1}{(z_\nu + z_\mu)^2} + \frac{\sigma}{z_\mu} e^{-z_\nu \sigma} \\
 &\quad + \left[\frac{1}{(z_\nu + z_\mu)^2} - \frac{z_\nu \sigma}{z_\mu(z_\nu + z_\mu)} \right] e^{-(z_\nu + z_\mu) \sigma}, \\
 Z_{\nu\mu} &= -\frac{2}{(z_\nu + z_\mu)^3} + \frac{\sigma}{z_\mu^2} e^{-z_\nu \sigma} \\
 &\quad + \left[\frac{2}{(z_\nu + z_\mu)^3} L_{\nu\mu}^{(b)} - \frac{\sigma}{z_\mu^2} M_\mu^{(a)} \right] e^{-(z_\nu + z_\mu) \sigma}, \\
 A_\mu^{(7)} &= 2\pi \tilde{L}_\mu,
 \end{aligned}$$

$$\begin{aligned}
 A_\mu^{(6)} &= -1 + \rho \frac{H_\mu^{(a)}}{z_\mu^3}, \\
 A_{\nu\mu}^{(5)} &= \rho^2 \frac{1}{z_\mu^3 z_\nu^3} [L_\nu^{(a)} G_\mu^{(a)} - z_\nu M_\nu^{(a)} H_\mu^{(a)}] \\
 &\quad + \rho \frac{1}{z_\mu z_\nu} \left[1 - \frac{z_\nu}{z_\nu + z_\mu} e^{-z_\mu \sigma} \right], \\
 A_{\nu\mu}^{(4)} &= \rho^2 \frac{1}{z_\mu^3 z_\nu^3} [2Q_\nu^{(a)} G_\mu^{(a)} - z_\nu P_\nu^{(a)} H_\mu^{(a)}] \\
 &\quad + \rho \frac{\sigma}{z_\mu} \left[1 - \left(\frac{z_\nu}{z_\nu + z_\mu} - \frac{z_\mu}{\sigma(z_\nu + z_\mu)^2} \right) e^{-z_\mu \sigma} \right], \\
 A_{\nu\mu}^{(3)} &= 2\pi \rho^3 \frac{1}{z_\mu^3 z_\nu^5} ([G_\mu^{(a)} - z_\nu H_\mu^{(a)}] \\
 &\quad - [L_\nu^{(a)} G_\mu^{(a)} - z_\nu M_\nu^{(a)} H_\mu^{(a)}] e^{-z_\nu \sigma} - 2\pi \rho^2 \frac{X_{\nu\mu}}{z_\nu^3}, \\
 A_{\nu\mu}^{(2)} &= 2\pi \rho^3 \frac{1}{z_\mu^3 z_\nu^5} ([3G_\mu^{(a)} - 2z_\nu H_\mu^{(a)}] \\
 &\quad - [(L_\nu^{(a)} + 2Q_\nu^{(a)}) G_\mu^{(a)} - z_\nu (M_\nu^{(a)} + P_\nu^{(a)}) H_\mu^{(a)}] e^{-z_\nu \sigma} \\
 &\quad - 2\pi \rho^2 \frac{1}{z_\nu^3} (X_{\nu\mu} + z_\nu Y_{\nu\mu}), \\
 A_{\nu\mu}^{(1)} &= z_\nu A_{\nu\mu}^{(3)}, \\
 C_\mu^{(13)} &= 2\pi \tilde{K}_\mu, \\
 C_\mu^{(12)} &= A_\mu^{(6)}, \\
 C_\mu^{(11)} &= -C_\mu^{(12)} + \rho \frac{R_\mu^{(a)}}{z_\mu^3}, \\
 C_{\nu\mu}^{(10)} &= A_{\nu\mu}^{(5)}, \\
 C_{\nu\mu}^{(9)} &= -C_{\nu\mu}^{(10)} + \rho^2 \frac{1}{z_\mu^3 z_\nu^3} [L_\nu^{(a)} S_\mu^{(a)} - z_\nu M_\nu^{(a)} R_\mu^{(a)}] \\
 &\quad + \rho \frac{z_\mu}{z_\nu} \left[\frac{1}{z_\mu^2} + \left(\frac{M_{\nu\mu}^{(b)}}{(z_\nu + z_\mu)^2} - \frac{M_\mu^{(a)}}{z_\mu^2} \right) e^{-z_\mu \sigma} \right], \\
 C_{\nu\mu}^{(8)} &= A_{\nu\mu}^{(4)}, \\
 C_{\nu\mu}^{(7)} &= -C_{\nu\mu}^{(8)} + \rho^2 \frac{1}{z_\mu^3 z_\nu^3} [2Q_\nu^{(a)} S_\mu^{(a)} - z_\nu P_\nu^{(a)} R_\mu^{(a)}] \\
 &\quad + \rho z_\mu \left[\frac{\sigma}{z_\mu^2} + \left(\frac{2}{(z_\nu + z_\mu)^3} L_{\nu\mu}^{(b)} - \frac{\sigma}{z_\mu^2} M_\mu^{(a)} \right) e^{-z_\mu \sigma} \right], \\
 C_{\nu\mu}^{(6)} &= A_{\nu\mu}^{(3)}, \\
 C_{\nu\mu}^{(5)} &= -C_{\nu\mu}^{(6)} + 2\pi \rho^3 \frac{1}{z_\mu^3 z_\nu^5} ([S_\mu^{(a)} - z_\nu R_\mu^{(a)}] \\
 &\quad - [S_\mu^{(a)} L_\nu^{(a)} - z_\nu R_\mu^{(a)} M_\nu^{(a)}] e^{-z_\nu \sigma} \\
 &\quad - 2\pi \rho^2 \frac{1}{z_\nu^3} z_\mu W_{\nu\mu}),
 \end{aligned}$$

$$\begin{aligned}
C_{\nu\mu}^{(4)} &= A_{\nu\mu}^{(2)}, \\
C_{\nu\mu}^{(3)} &= -C_{\nu\mu}^{(4)} + 2\pi\rho^3 \frac{1}{z_\mu z_\nu^5} ([3S_\mu^{(a)} - 2z_\nu R_\mu^{(a)}] \\
&\quad - [S_\mu^{(a)}(L_\nu^{(a)} + 2Q_\nu^{(a)}) - z_\nu R_\mu^{(a)}(M_\nu^{(a)} + P_\nu^{(a)})]) \\
&\quad \times e^{-z_\nu\sigma} + 2\pi\rho^2 \frac{z_\mu}{z_\nu^3} (-z_\nu Z_{\nu\mu} - W_{\nu\mu}), \\
C_{\nu\mu}^{(2)} &= A_{\nu\mu}^{(1)}, \\
C_{\nu\mu}^{(1)} &= z_\nu C_{\nu\mu}^{(5)}, \\
B_\mu^{(12)} &= \frac{H_\mu^{(b)}}{2\pi}, \\
B_\mu^{(11)} &= A_\mu^{(6)}, \\
B_{\nu\mu}^{(10)} &= \frac{\rho}{2\pi} \frac{1}{z_\nu^3} [L_\nu^{(a)} G_\mu^{(b)} - z_\nu M_\nu^{(a)} H_\mu^{(b)}] + \frac{z_\mu}{2\pi(z_\nu + z_\mu)}, \\
B_{\nu\mu}^{(9)} &= \frac{\rho}{2\pi} \frac{1}{z_\nu^3} [2Q_\nu^{(a)} G_\mu^{(b)} - z_\nu P_\nu^{(a)} H_\mu^{(b)}] \\
&\quad + \frac{1}{2\pi} \frac{z_\nu z_\mu}{(z_\nu + z_\mu)^2} M_{\nu\mu}^{(b)} - \frac{1}{2\pi} \frac{z_\mu}{z_\nu + z_\mu}, \\
B_{\nu\mu}^{(8)} &= A_{\nu\mu}^{(5)}, \\
B_{\nu\mu}^{(7)} &= A_{\nu\mu}^{(4)}, \\
B_{\nu\mu}^{(6)} &= \rho^2 \frac{1}{z_\nu^5} ([G_\mu^{(b)} - z_\nu H_\mu^{(b)}] - [G_\mu^{(b)} L_\nu^{(a)} \\
&\quad - z_\nu H_\mu^{(b)} M_\nu^{(a)}] e^{-z_\nu\sigma}) - \rho \frac{z_\mu e^{-z_\nu\sigma}}{z_\nu^2(z_\nu + z_\mu)}, \\
B_{\nu\mu}^{(5)} &= \rho^2 \frac{1}{z_\nu^5} ([3G_\mu^{(b)} - 2z_\nu H_\mu^{(b)}] - [G_\mu^{(b)}(L_\nu^{(a)} + 2Q_\nu^{(a)}) \\
&\quad - z_\nu H_\mu^{(b)}(M_\nu^{(a)} + P_\nu^{(a)})] e^{-z_\nu\sigma}) \\
&\quad - \rho \frac{z_\mu e^{-z_\nu\sigma}}{z_\nu(z_\nu + z_\mu)^2} M_{\nu\mu}^{(b)}, \\
B_{\nu\mu}^{(4)} &= B_{\nu\mu}^{(6)} z_\nu, \\
B_{\nu\mu}^{(3)} &= A_{\nu\mu}^{(3)}, \\
B_{\nu\mu}^{(2)} &= A_{\nu\mu}^{(2)}, \\
B_{\nu\mu}^{(1)} &= A_{\nu\mu}^{(1)}, \\
D_\mu^{(18)} &= -\frac{R_\mu^{(b)}}{2\pi}, \\
D_\mu^{(17)} &= -\rho \frac{R_\mu^{(a)}}{z_\mu^4}, \\
D_\mu^{(16)} &= -A_\mu^{(6)},
\end{aligned}$$

$$\begin{aligned}
D_{\nu\mu}^{(15)} &= \frac{\rho}{2\pi} \frac{1}{z_\nu^3} [-L_\nu^{(a)} S_\mu^{(b)} + z_\nu M_\nu^{(a)} R_\mu^{(b)}] \\
&\quad - \frac{z_\mu}{2\pi(z_\nu + z_\mu)^2} M_{\nu\mu}^{(b)}, \\
D_{\nu\mu}^{(14)} &= \frac{\rho}{2\pi} \frac{1}{z_\nu^3} [-2Q_\nu^{(a)} S_\mu^{(b)} + z_\nu P_\nu^{(a)} R_\mu^{(b)}] \\
&\quad + \frac{z_\mu}{2\pi(z_\nu + z_\mu)^2} M_{\nu\mu}^{(b)} - \frac{z_\nu z_\mu}{2\pi(z_\nu + z_\mu)^3} 2L_{\nu\mu}^{(b)}, \\
D_{\nu\mu}^{(13)} &= \rho^2 \frac{1}{z_\nu^5} ([z_\nu R_\mu^{(b)} - S_\mu^{(b)}] - [z_\nu R_\mu^{(b)} M_\nu^{(a)} \\
&\quad - S_\mu^{(b)} L_\nu^{(a)}] e^{-z_\nu\sigma}) + \rho \frac{z_\mu e^{-z_\nu\sigma}}{z_\nu^2(z_\nu + z_\mu)^2} M_{\nu\mu}^{(b)}, \\
D_{\nu\mu}^{(12)} &= \rho^2 \frac{1}{z_\nu^5} ([2z_\nu R_\mu^{(b)} - 3S_\mu^{(b)}] - [z_\nu R_\mu^{(b)}(M_\nu^{(a)} + P_\nu^{(a)}) \\
&\quad - S_\mu^{(b)}(L_\nu^{(a)} + 2Q_\nu^{(a)})] e^{-z_\nu\sigma}) \\
&\quad + \rho \frac{z_\mu e^{-z_\nu\sigma}}{z_\nu(z_\nu + z_\mu)^3} 2L_{\nu\mu}^{(b)}, \\
D_{\nu\mu}^{(11)} &= D_{\nu\mu}^{(13)} z_\nu, \\
D_{\nu\mu}^{(10)} &= -(C_{\nu\mu}^{(9)} + C_{\nu\mu}^{(10)})/z_\mu, \\
D_{\nu\mu}^{(9)} &= -(C_{\nu\mu}^{(7)} + C_{\nu\mu}^{(8)})/z_\mu, \\
D_{\nu\mu}^{(8)} &= -A_{\nu\mu}^{(5)}, \\
D_{\nu\mu}^{(7)} &= -A_{\nu\mu}^{(4)}, \\
D_{\nu\mu}^{(6)} &= -(C_{\nu\mu}^{(5)} + C_{\nu\mu}^{(6)})/z_\mu, \\
D_{\nu\mu}^{(5)} &= -(C_{\nu\mu}^{(3)} + C_{\nu\mu}^{(4)})/z_\mu, \\
D_{\nu\mu}^{(4)} &= -(C_{\nu\mu}^{(1)} + C_{\nu\mu}^{(2)})/z_\mu, \\
D_{\nu\mu}^{(3)} &= -A_{\nu\mu}^{(3)}, \\
D_{\nu\mu}^{(2)} &= -A_{\nu\mu}^{(2)}, \\
D_{\nu\mu}^{(1)} &= -A_{\nu\mu}^{(1)}.
\end{aligned}$$

APPENDIX C: INITIAL CONDITIONS FOR THE PDE

In the following we explain the determination of the initial condition of the SCOZA PDE $u(\rho, \beta=0)$. Since for $\beta=0$ the direct correlation function $c(r)$ coincides with that of the HS gas $\tilde{K}_\nu=0$ for $\nu=2, \dots, n$, $\tilde{L}_\nu=0$ for $\nu=1, \dots, n$, yielding $D_\nu(\rho, \beta=0)=0$ for $\nu=2, \dots, n$, and $E_\nu(\rho, \beta=0)=0$ for $\nu=1, \dots, n$. Hence, the first system of linear equations (17) reduces to

$$O_{\nu 1} D_1 = Q_\nu \quad \text{for } \nu=1, \dots, n. \quad (\text{C1})$$

For $\nu=1$ this leads to

$$D_1(\rho, \beta=0) = \frac{Q_1(G_1(\rho, \beta=0))}{O_{11}(G_1(\rho, \beta=0))}, \quad (\text{C2})$$

where $G_1(\rho, \beta=0)$ is obtained from the known quantity $\gamma_1(\rho, \beta=0)$ that was introduced in the Laplace transform technique (see Appendix A of Ref. 27) via

$$G_1(\rho, \beta=0) = \frac{z_1}{4\pi\rho} \frac{A-1}{A\sigma_1 - \tau_1}, \quad (C3)$$

where

$$A = (2 - \sqrt{q} - \gamma_1(\rho, \beta=0)) \frac{2(2+z_1)}{4+2z_1-z_1^2},$$

$$\sigma_1 = \frac{1}{2z_1} \left(\frac{z_1-2}{z_1+2} + e^{-z_1} \right),$$

$$\tau_1 = \frac{1}{2z_1} \left(\frac{z_1^2+2z_1-4}{4+2z_1-z_1^2} + e^{-z_1} \right), \quad (C4)$$

$$q = \frac{(1+2\eta)^2}{(1-\eta)^2},$$

with $\eta = (\pi/6)\rho$ being the packing fraction. From Eq. (C1), for $\nu > 1$, one obtains

$$G_\nu(\rho, \beta=0) = - \frac{D_1(\rho, \beta=0)(B_{1\nu}^{(6)}G_1(\rho, \beta=0) + B_{1\nu}^{(10)}) + B_\nu^{(12)}}{D_1(\rho, \beta=0)(B_{1\nu}^{(3)}G_1(\rho, \beta=0) + B_{1\nu}^{(8)}) + B_\nu^{(11)}}. \quad (C5)$$

The second linear system (17) reduces to

$$R_{\nu 1}D_1 = T_\nu \quad \text{for } \nu = 1, \dots, n, \quad (C6)$$

from which one can eliminate the $G_\nu^{(1)}(\rho, \beta=0)$ once the $G_\nu(\rho, \beta=0)$ are known

$$G_\nu^{(1)}(\rho, \beta=0) = - \frac{D_1(D_{1\nu}^{(6)}G_1G_\nu + D_{1\nu}^{(10)}G_\nu + D_{1\nu}^{(13)}G_1 + D_{1\nu}^{(15)}) + D_\nu^{(17)}G_\nu + D_\nu^{(18)}}{D_1(D_{1\nu}^{(3)}G_1 + D_{1\nu}^{(8)}) + D_\nu^{(16)}}. \quad (C7)$$

Collecting these results one obtains

$$u(\rho, \beta=0) = -2\pi\rho^2\epsilon\sigma \sum_{\nu=2}^n \left(\frac{K_\nu}{z_\nu} G_\nu(\rho, \beta=0) + L_\nu G_\nu^{(1)}(\rho, \beta=0) \right). \quad (C8)$$

APPENDIX D: VIRIAL ROUTE

This Appendix explains the determination of the virial pressure within SCOZA and LOGA/ORPA. P^V is given by

$$\frac{\beta P^V}{\rho} = 1 - \frac{2}{3}\pi\beta\rho \int_0^\infty \frac{d\phi(r)}{dr} g(r)r^3 dr$$

$$= 1 + \frac{2}{3}\pi\rho\sigma^3 g(\sigma) + J, \quad (D1)$$

where

$$J = -\frac{2}{3}\pi\beta\rho \int_\sigma^\infty \frac{dw(r)}{dr} g(r)r^3 dr$$

$$= -\frac{2}{3}\pi\beta\rho\epsilon\sigma \sum_{\nu=2}^n \left(\frac{K_\nu G_\nu}{z_\nu} + K_\nu G_\nu^{(1)} + L_\nu z_\nu G_\nu^{(2)} \right), \quad (D2)$$

with $G_\nu^{(2)}$ being defined as

$$G_\nu^{(2)} = z_\nu \int_\sigma^\infty r^3 e^{-z_\nu(r-\sigma)} g(r) dr = -z_\nu e^{z_\nu\sigma} \frac{dg^{(1)}(z_\nu)}{dz_\nu}. \quad (D3)$$

The $G_\nu^{(2)}$, defined by Eqs. (D3), are determined as follows: By taking the derivative of Eq. (15b) of Ref. 8 with respect to z_n one obtains

$$2\pi G_\nu^{(2)}(1 - \rho\hat{Q}(z_\nu)) = 4\pi\rho G_\nu^{(1)}\hat{Q}^{(1)}(z_\nu)$$

$$+ 2\pi\rho G_\nu\hat{Q}^{(2)}(z_\nu)$$

$$+ \frac{6+4z_\nu\sigma+(z_\nu\sigma)^2}{z_\nu^3} a$$

$$+ \frac{2+2z_\nu\sigma+(z_\nu\sigma)^2}{z_\nu^2} b$$

$$+ \sum_\mu \frac{-2z_\nu}{(z_\mu+z_\nu)^3} L_{\nu\mu}^{(b)} C_\mu$$

$$+ \sum_\mu \frac{-6z_\nu z_\mu}{(z_\mu+z_\nu)^4} O_{\nu\mu}^{(b)} F_\mu.$$

a , b , C_ν , and F_ν are given by

$$a = A^0(1+M) - \frac{4}{\sigma^2} B^0 N, \quad (D4)$$

$$b = b^0(1+M) + A^0 N, \quad (D5)$$

$$C_\nu = -D_\nu + E_\nu + 2\pi\rho \left(\frac{D_\nu G_\nu}{z_\nu^2} e^{-z_\nu\sigma} + \frac{E_\nu G_\nu^{(1)}}{z_\nu} e^{-z_\nu\sigma} \right), \quad (D6)$$

$$F_\nu = -E_\nu + 2\pi\rho \frac{E_\nu G_\nu}{z_\nu^2} e^{-z_\nu\sigma}, \quad (D7)$$

with M and N defined in Eq. (20). $\hat{Q}(z)$, $\hat{Q}^{(1)}(z)$, and $\hat{Q}^{(2)}(z)$ are defined as Laplace transforms

$$\hat{Q}(z) = \int_0^\infty Q(t) e^{-zt} dt, \quad (D8)$$

$$\hat{Q}^{(1)}(z) = \int_0^\infty Q(t) t e^{-zt} dt = -\frac{d\hat{Q}(z)}{dz}, \quad (\text{D9})$$

$$\hat{Q}^{(2)}(z) = \int_0^\infty Q(t) t^2 e^{-zt} dt = \frac{d^2\hat{Q}(z)}{dz^2}, \quad (\text{D10})$$

and are given by

$$\begin{aligned} \hat{Q}(z_\mu) = & a \frac{\theta_2(z_\mu \sigma)}{z_\mu^3} + b \frac{\theta_1(z_\mu \sigma)}{z_\mu^2} \\ & + \sum_\nu D_\nu \left[\frac{1}{z_\mu z_\nu} \left[1 - \frac{z_\nu}{z_\nu + z_\mu} e^{-z_\mu \sigma} \right] \right. \\ & \left. - 2\pi\rho X_{\nu\mu} \frac{G_\nu}{z_\nu^3} \right] \\ & + \sum_\nu E_\nu \left[\frac{\sigma}{z_\mu} \left[1 - \left(\frac{z_\nu}{z_\nu + z_\mu} \right. \right. \right. \\ & \left. \left. - \frac{z_\mu}{\sigma(z_\nu + z_\mu)^2} \right) e^{-z_\mu \sigma} \right] \right. \\ & \left. - 2\pi\rho (X_{\nu\mu} + z_\nu Y_{\nu\mu}) \frac{G_\nu}{z_\nu^3} - 2\pi\rho X_{\nu\mu} \frac{G_\nu^{(1)}}{z_\nu^2} \right], \\ \hat{Q}^{(1)}(z_\mu) = & a \left(\frac{3\theta_2(z_\mu \sigma)}{z_\mu^4} + \frac{\sigma\theta_1(z_\mu \sigma)}{z_\mu^3} \right) + b \left(\frac{2\theta_1(z_\mu \sigma)}{z_\mu^3} \right. \\ & + \frac{\sigma\theta_0(z_\mu \sigma)}{z_\mu^2} \left. \right) + \sum_\nu D_\nu \left[\frac{1}{z_\nu} \left[\frac{1}{z_\mu} \right. \right. \\ & \left. \left. + \left(\frac{M_{\nu\mu}^{(b)}}{(z_\nu + z_\mu)^2} - \frac{M_\mu^{(a)}}{z_\mu^2} \right) e^{-z_\mu \sigma} \right] \right. \\ & \left. - 2\pi\rho W_{\nu\mu} \frac{G_\nu}{z_\nu^3} \right] + \sum_\nu E_\nu \left[\frac{\sigma}{z_\mu} \right. \\ & \left. + \left(\frac{2}{(z_\nu + z_\mu)^3} L_{\nu\mu}^{(b)} - \frac{\sigma}{z_\mu^2} M_\mu^{(a)} \right) e^{-z_\mu \sigma} \right. \\ & \left. - 2\pi\rho (W_{\nu\mu} + z_\nu Z_{\nu\mu}) \frac{G_\nu}{z_\nu^3} - 2\pi\rho W_{\nu\mu} \frac{G_\nu^{(1)}}{z_\nu^2} \right], \\ \hat{Q}^{(2)}(z_\mu) = & a \left(\frac{12\theta_2(z_\mu \sigma)}{z_\mu^5} + \frac{6\sigma\theta_1(z_\mu \sigma)}{z_\mu^4} + \frac{\sigma^2\theta_0(z_\mu \sigma)}{z_\mu^3} \right) \\ & + b \left(\frac{6\theta_1(z_\mu \sigma)}{z_\mu^4} + \frac{4\sigma\theta_0(z_\mu \sigma)}{z_\mu^3} - \frac{\sigma^2}{z_\mu} e^{-z_\mu \sigma} \right) \\ & + \sum_\nu D_\nu \left[\frac{1}{z_\nu} \left[\frac{2}{z_\mu^3} + \left(\frac{2L_{\nu\mu}^{(b)}}{(z_\nu + z_\mu)^3} \right. \right. \right. \\ & \left. \left. - \frac{2L_\mu^{(a)}}{z_\mu^3} \right) e^{-z_\mu \sigma} \right] - 2\pi\rho U_{\nu\mu} \frac{G_\nu}{z_\nu^3} \right] \\ & + \sum_\nu E_\nu \left[\frac{2\sigma}{z_\mu^3} + \left(\frac{6}{(z_\nu + z_\mu)^4} O_{\nu\mu}^{(b)} \right. \right. \end{aligned}$$

$$\begin{aligned} & \left. - \frac{2\sigma}{z_\mu^3} L_\mu^{(a)} \right) e^{-z_\mu \sigma} - 2\pi\rho (U_{\nu\mu} + z_\nu V_{\nu\mu}) \frac{G_\nu}{z_\nu^3} \\ & \left. - 2\pi\rho U_{\nu\mu} \frac{G_\nu^{(1)}}{z_\nu^2} \right]. \end{aligned}$$

The coefficients required in the evaluation of the expressions above are defined in Appendix B.

The contact value $g(\sigma)$ that is required in Eq. (D2) and related to the discontinuity of $Q'(r)$ at $r=\sigma$ is given by

$$g(\sigma) = \frac{1}{2\pi\sigma} \left[b - \sum_{\nu=1}^n (C_\nu + F_\nu z_\nu \sigma) \right]. \quad (\text{D11})$$

Expressions for b , C_ν , and F_ν are given in Eqs. (D5)–(D7).

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