Self-consistent Ornstein–Zernike approximation for the Yukawa fluid with improved direct correlation function

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Thermodynamic consistency of the mean spherical approximation as well as the self-consistent Ornstein–Zernike approximation (SCOZA) with the virial route to thermodynamics is analyzed in terms of renormalized γ-ordering. For continuum fluids, this suggests the addition of a short-ranged contribution to the usual SCOZA direct correlation function, and the shift of the adjustable parameter from the potential term to this new term. The range of this contribution is fixed by imposing consistency with the virial route at the critical point. Comparison of the results of our theory for the hard-core Yukawa potential with the simulation data show very good agreement for cases where the liquid-vapor transition is stable or not too far into the metastable region with respect to the solid state. In the latter case for extremely short-ranged interactions discrepancies arise. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2894474]

I. INTRODUCTION

By use of the self-consistent Ornstein–Zernike approximation (SCOZA), very accurate results have been obtained for the equation of state for fluids[1,2] and lattice systems (or the Ising spin system).[3–6] Also, in the critical region, the results are very accurate, showing nonclassical critical behavior,[3] but a form of generalized scaling is obtained in the critical region instead of full scaling.[7]

Looking more closely into the data, one finds that for the lattice gas or nearest neighbor Ising model, results are somewhat better than those for the continuum fluid. The SCOZA critical temperature T_c of the former is about 0.2% away from the best estimates,[8] while this separation is about 0.6% for the commonly considered Yukawa fluid ($z=1.8$) according to recent estimates based on Monte Carlo (MC) computations.[2,9] Here, we will analyze this situation in view of renormalized γ-ordering,[10,11] and we will propose a modified version of SCOZA. A slightly simplified variant of this scheme is implemented and numerically solved, essentially yielding perfect agreement with simulations for potential ranges relevant for the liquid state. For extremely short-ranged potentials where the gas-liquid transition is deeply buried inside the metastable region, however, agreement is less satisfactory, and the numerical procedure may even fail to converge to consistency with the virial pressure.

As SCOZA builds upon the mean spherical approximation (MSA), we can understand that SCOZA is more accurate for lattice gases than for fluids by noting that this is also true for the MSA. Upon further analysis, it is seen that for fluids, a significant contribution to the direct correlation function of short range is missing. When this contribution is included, it enlarges the amplitude of the correlation function and thus amplifies the internal energy due to correlations (which is negative). This further increases the deviation from the corresponding mean field or van der Waals type equation of state (EOS). Since correlations lower the critical temperature, the net result is a further lowering of it. For the Yukawa interaction typically used as a model potential in simulations, we expect this additional lowering to be something like $(0.5 \pm 0.4)\%$ as a crude estimate. An immediate problem here is the determination of the proper range of this short-ranged piece of the direct correlation function. In this respect, we can be guided by considering thermodynamic consistency with the virial theorem to estimate the range mentioned.

In Sec. II, we will investigate the relation between the MSA and renormalized γ-ordering for potentials of long range. Then, in Sec. III, thermodynamic consistency with the virial theorem is considered and applied to SCOZA. A modified theory is then formulated on this basis in Sec. IV, and numerically applied to the one-Yukawa problem in Sec. V. A short summary (Sec. VI) concludes our contribution.

II. RENORMALIZED γ-ORDERING AND MSA

The MSA is the solution of the Ornstein–Zernike (OZ) equation,

$$\widetilde{h}(k) = \frac{\widetilde{c}(k)}{1 - \rho\widetilde{c}(k)},$$

with boundary conditions

$$h(r) = -1 \quad \text{for } r < 1,$$

$$c(r) = -\beta\psi(r) \quad \text{for } r > 1. \tag{1}$$

Here, $h(r)$ is the pair correlation function, $c(r)$ is the direct correlation function, and

$$\psi(r) = -e^{-z(r-1)}/r \quad (r > 1)$$

is the perturbing interaction; the hard-core diameter and the unit of energy are set to unity for simplicity; and a tilde

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denotes Fourier transformation. [It should be noted that $\psi(r)$ is not restricted to interactions of Yukawa form.]

For a lattice gas or an Ising spin system, the boundary conditions become

$$h(0) = -1,$$

$$c(\mathbf{r}) = -\beta\psi(\mathbf{r}) \quad \text{for } \mathbf{r} \neq 0.$$

So, in this case, we have

$$\rho + \rho^2 h(0) = \rho(1-\rho) = \frac{1}{(2\pi)^3} \int \frac{\rho}{1-\rho\tilde{c}(k)} d^3k \tag{2}$$

for lattice cells of unit volume. (To keep the notation simple, we do not explicitly indicate that k and similar arguments are necessarily vectors in the lattice case, nor do we explicitly point out restriction to the Brillouin zone, i.e., $-\pi \leq k_i \leq \pi$ with $i = x, y, z$.) Defining $\tilde{v}(k) = -\beta\tilde{\psi}(k)$, we can now write

$$\tilde{c}(k) = c_0 + \tilde{v}(k),$$

where c_0 is determined by Eq. (2). For the reference system alone, we then have $[\tilde{\psi}(k) = 0$ by which $h(0) = \tilde{h}(k)]$

$$\mu = \rho + \rho^2\tilde{h}(k) \equiv \rho(1-\rho) = \frac{\rho}{1-\rho c_0}. \tag{3}$$

More generally for $\tilde{\psi}(k) \neq 0$, we can define

$$\mu_c = \frac{\rho}{1-\rho c_0},$$

and the core condition (2) becomes

$$\mu = \mu_c + \mu_c^2 K \tag{4}$$

with

$$K = \frac{1}{(2\pi)^3} \int \frac{\tilde{v}(k)}{1-\mu_c\tilde{v}(k)} d^3k.$$

With μ given by Eq. (3), relation (4) can also be written as

$$\mu = \mu_c\left(1 - \tfrac{1}{2}\mu''\mu_c K\right), \tag{5}$$

where a prime denotes differentiation with respect to ρ. In this form, we can recognize the relation obtained by the resummation or renormalization process to obtain the equation of state for fluids when the inverse range of the attractive interaction γ is used as a perturbing parameter[10,11] [see Eqs. (26) and (36) of Ref. 11]. In Eq. (5), μ_c represents the renormalized hypervertex μ when graph expansion in terms of γ-ordering is considered.[12,13] The μ follows from the reference system, e.g., hard spheres, by use of the compressibility relation as

$$\mu = \rho\left(\frac{\partial\beta p_0}{\partial\rho}\right)^{-1} = \rho + \rho^2\tilde{h}_0(0), \tag{6}$$

where p_0 and $h_0(r)$ are the pressure and the correlation function of the reference system. Thus, μ represents the Mayer graphs of the correlation function of the reference system. For small γ, they are regarded as δ-functions of relative dis-

tance r so that only integral (6) is needed as a leading order approximation.

Now with renormalization [Eq. (5)], the EOS becomes more consistent, with better agreement between the energy and compressibility routes and essentially common critical point *via* the two routes.[10] However, the remaining thermodynamic inconsistency prevents well-defined isotherms near the critical point, which is also the situation of the MSA for the lattice gas or Ising model.

In contrast to the MSA for lattice systems, the MSA for continuum fluids is not consistent with Eq. (5) and therefore farther away from thermodynamic self-consistency. In fact, for interactions of very long range, i.e., small γ, the MSA for continuum fluids also fulfills Eq. (4) but not Eq. (5). This is due to the difference in reference systems. For a Percus–Yevick hard sphere reference system, one has

$$\mu = \frac{(1-\eta)^4}{(1+2\eta)^2},$$

instead of expression (3), where $\eta = (\pi/6)\rho$ for spheres of unit diameter. From this, $\mu'' = \partial^2\mu/\partial\rho^2$ can be evaluated at the critical density, i.e., $\rho_c \approx 0.3$ or $\eta_c \approx 0.15$ for interactions of realistic range. (In mean field, $\eta_c = 0.129$.) With $\eta = 0.15$, we find

$$\tfrac{1}{2}\mu'' = -0.53\cdots \approx -0.5, \tag{7}$$

which is only one half of the "MSA value" that follows from Eq. (4).

Compared with the mean field, the finite range of interaction lowers the critical temperature T_c, and we have

$$T_c \approx \frac{\mu_c}{\mu} T_c^{\text{MF}}, \tag{8}$$

where T_c^{MF} is the mean field value. [The spinodal curve and thus T_c follow from the denominator of the integrand of integral (4) being zero at $k = 0$.] In view of this, it is clear that the MSA compressibility critical point is lowered too much so that the more accurate energy route gives a classical critical point well above the former. For interactions of shorter range where details of the core condition and hard-core correlations become more important, the above results will be modified, but the qualitative features of the MSA inconsistency will remain.

III. SCOZA EVALUATIONS

The SCOZA differs from the MSA in its imposition of thermodynamic consistency between the energy and compressibility routes to thermodynamics: A state-dependent free parameter is introduced into the pair structure and determined in such a way that the consistency condition

$$\frac{\partial a}{\partial\beta} = \rho\frac{\partial^2\rho u}{\partial\rho^2}, \tag{9}$$

holds. Here,

$$u = \frac{1}{2}\rho \int \psi(r)(h(r)+1)d^3r \tag{10}$$

is the configurational part of the internal energy per particle as computed from the energy route, and

$$a = 1 - \rho\tilde{c}(0) \tag{11}$$

is the reduced inverse compressibility as obtained from the compressibility route.

In earlier SCOZA evaluations, the MSA form [Eq. (1)] of the direct correlation function has been used with β replaced by an effective value β_e. The contribution to the internal energy per particle u_1 from correlations is then given by integral (4) as

$$-\rho u_1 = \frac{1}{2\beta_e}\mu_c K, \tag{12}$$

with $\tilde{v}(k) = -\beta_e\tilde{\psi}(k)$. [Note that a "self-energy" term $-\rho\psi(0)$ is included in Eq. (12), but it will not contribute in Eq. (9) anyway.] In addition, one has the mean field term $u_0 = \rho^2\tilde{\psi}(0)/2$ such that $u = u_0 + u_1$. For continuum fluids, μ_c should also depend on k, i.e., $\mu_c = \tilde{\mu}_c(k)$, which we disregard here to simplify the argument. Now at the critical point, $1 - \mu_c\beta_{ec}(-\tilde{\psi}(0)) = 0$ is valid for both MSA and SCOZA that directly builds upon MSA via Eq. (1). For the former $\beta_e = \beta$ so that $\beta_{ec} = \beta_c$, but one notes that both MSA and SCOZA have the same configurational internal energy at the critical point just as in the lattice case.

Now with relation (5), the internal energy u_1 can no longer be equal to the MSA one at the critical point since the vertex function μ_c is different. According to the relation

$$1 - \mu_c\beta_{ec}(-\tilde{\psi}(0)) = 0,$$

a change in μ_c means a change in β_{ec} while $\mu_c K$ in Eq. (12) remains unchanged. The change in μ_c thus has the consequence that the internal energy contribution from u_1 at the critical point, $u_{1c} \propto 1/\beta_{ec} = \mu_c$, is also modified.

In SCOZA computations, the shift in T_c relative to the mean field value T_c^{MF} is determined by Eq. (5) to leading order and not by the MSA μ_c from Eq. (4) since the former is closer to thermodynamic consistency. At the same time, the SCOZA energy u_1 is dictated by the MSA μ_c. Thus, there results an inaccuracy in the SCOZA u_1 with a corresponding inaccuracy in the SCOZA T_c. The reason is that to leading order the shift down in T_c relative to T_c^{MF} is proportional to u_1. In terms of u_1, Eq. (5) is ($\beta_e = \beta$)

$$\mu = \mu_c(1+A), \quad A = -\mu''\beta u_1/\rho. \tag{13}$$

However, by solving SCOZA, u_1 is changed into the MSA value that follows from the $\mu_c = \mu_c^{MSA}$ of Eq. (4) instead of Eqs. (5) or (13),

$$u_1^{MSA} = \frac{\mu_c^{MSA}}{\mu_c}u_1.$$

This new value modifies Eq. (13) into

$$\mu = \mu_c\left(1 + A\frac{\mu_c^{MSA}}{\mu_c}\right).$$

When inserted into Eq. (8), this gives an additional shift in T_c compared with the use of Eq. (13), viz.,

$$\Delta T_c = \left(\frac{1}{1+A} - \frac{1}{1+A\dfrac{\mu_c^{MSA}}{\mu_c}}\right)T_c^{MF}$$

$$\approx -\left(1 - \frac{\mu_c^{MSA}}{\mu_c}\right)AT_c^{MF}. \tag{14}$$

Now with Eq. (4), we approximate

$$\mu \approx \mu_c^{MSA}(1 + \mu_c K) \approx \mu_c^{MSA}(1 + 2A),$$

where the last relation follows from comparison with Eq. (5) and using the numerical value [Eq. (7)] for μ''. When inserted into Eq. (14) and expanded, this means

$$\Delta T_c \approx -A^2 T_c^{MF}. \tag{15}$$

Evaluations for the Lennard–Jones (LJ) interaction gave[10,11]

$$A = 1 - \frac{\mu_c}{\mu} = 1 - \frac{T_c}{T_c^{MF}} = 1 - \frac{0.2545 \times 4}{0.272 \times 4} = 0.064$$

so that

$$\Delta T_c \approx -4.2 \times 10^{-3}T_c^{MF} \approx -4.5 \times 10^{-3}T_c. \tag{16}$$

IV. MODIFIED SCOZA DIRECT CORRELATION FUNCTION

The lowering on T_c given by Eq. (15) can be understood in terms of a graph expansion. There is a significant contribution of short range to $h(r)$ and the direct correlation function $c(r)$ that is not properly taken care of by previous SCOZA computations. To leading order it is connected to the μ'' term of Eq. (5). In terms of graphs, μ represents the hypervertex where the graphs are those of the reference system correlation function plus $\delta(\mathbf{r})$, i.e., $\rho\delta(\mathbf{r}) + \rho^2 h_0(r)$. On two ρ vertices of these graphs, a chain bond K with endpoints or vertices μ that can be replaced by μ_c to leading order and a symmetry factor $\frac{1}{2}$ are added. This contribution is then added to the reference system correlation function or vertex μ to obtain the renormalized vertex μ_c.[10,11]

For lattice gases, however, we do not need to explicitly consider this term as the core condition [Eq. (4)] is then equivalent to Eq. (5). To fulfill the former, a constant c_0 is added to the direct correlation function $c(r)$ at $\mathbf{r} = 0$. This can also be regarded as a short-ranged piece of the perturbing potential such that $\tilde{v}(k)$ in expression (4) is replaced by $c_0 + \tilde{v}(k)$. The consequence of this is that the chain bond integral (4) becomes zero and renormalization [Eq. (5)] drops out as c_0 has already taken care of it.

For continuum fluids, however, Eq. (5) cannot be replaced by a $c_0(r)$ only inside hard cores if the core condition is to be kept; the short-ranged part of it goes outside the core in contrast to the lattice gas system. Thus, $c(r)$ must have a contribution of short range outside the hard core [beyond that of the hard sphere reference system, $c_{HS}(r)$]. This term will

have both an amplitude and a range. In a SCOZA scheme, this means there are two unknown parameters if now the remaining part of $c(r)$ is just its MSA form outside the core, i.e., the new term replaces the earlier need for an effective temperature.

Assuming the added short-ranged piece to the direct correlation is also of Yukawa form, the SCOZA direct correlation function for the one-Yukawa potential now becomes

$$c(r) = K_1 \frac{e^{-z_1(r-1)}}{r} + K_2 \frac{e^{-z_2(r-1)}}{r} + c_{HS}(r), \quad r > 1. \quad (17)$$

The first term can be treated as in MSA, i.e., its amplitude can be identified with the inverse temperature, $K_1 \equiv \beta$, while its form coincides with that of the interaction, $z_1 \equiv z$; this also means that $c(r)$ asymptotically coincides with $-\beta\psi(r)$ for large r as it should except at the critical point. K_2 and z_2, on the other hand, are the two unknown parameters of the added short-ranged piece to $c(r)$. Obviously, conventional SCOZA is recovered when setting $z_2 = z_1 = z$, with $K_1 + K_2$ playing the role of the effective inverse temperature β_e.

The use of an effective parameter β_e is common to conventional SCOZA problems. So the differences between various SCOZA problems lie in the actual equations used. These again depend on whether continuum fluids or lattice gases are considered, and further they depend on the pair interaction used. However, in the present case, this conventional scheme is modified by which we have two unknown parameters present in Eq. (17). As only one parameter can be determined in "standard" SCOZA, an option is to keep the range fixed and to make evaluations for various values of z_2 to see how the estimated change in T_c comes out. Furthermore, SCOZA allows the contact value of $h(r)$ at the hard-core surface to be obtained so that we can also check consistency with the virial theorem. Alternatively, the range parameter z_2 can also be adjusted alongside K_2 as a function of β and ρ so that consistency between all three of the energy, virial, and compressibility routes is obtained throughout the temperature-density plane. In this more ambitious SCOZA evaluation first proposed by Høye and Stell,[14] both unknown parameters, K_2 and z_2, are supposed to be simultaneously determined. This scheme thus bears some resemblance to the version of the generalized MSA studied in Ref. 15 that did not, however, take into account $c_{HS}(r)$ outside the core.

Yet another possibility is to keep z_2 fixed for all densities and temperatures, choosing it in such a way that consistency with the virial theorem is achieved at the critical point. This has the advantage over full consistency of being much easier to implement while it can be expected that this simpler version already incorporates most of the effect of full consistency with the virial route, at least when using the location of the critical point and the phase boundary to gauge the relative accuracy and performance of various liquid state theories as we will do here.

V. NUMERICAL RESULTS

In our computations, we found it advantageous to adopt the Waisman recipe for the direct correlation function $c_{HS}(r)$ of the hard sphere reference system, i.e.,

$$c_{HS}(r) = K_{HS} \frac{e^{-z_{HS}(r-1)}}{r}, \quad r > 1,$$

with density dependent parameters K_{HS} and z_{HS} that reproduce the Carnahan Starling equation of state.[2,16] Just as in conventional SCOZA, the direct correlation function outside the hard core is then just a sum of Yukawa terms for which the solution of the OZ equation together with the core condition, $h(r) = -1$ for $r < 1$, is semianalytically known by way of a Wiener–Hopf factorization and Eqs. (10) and (11) can be evaluated efficiently.[17,18]

The main change required vis-à-vis the conventional theory is the shift from K_1, which acquires an explicit temperature dependence, to K_2 as the adjustable parameter; also, it becomes necessary to implement the virial route expressions[19] that are not normally featured in SCOZA computations but already appeared in the preliminary evaluation of our recent adaptation of SCOZA to molecules with soft cores.[20]

For an interaction composed of a hard core of unit diameter with a perturbing tail $\psi(r)$, the virial theorem,

$$\frac{\beta P}{\rho} = 1 + \frac{2\pi}{3}\rho\left[1 + h(1+) - \beta\int_1^\infty r^3(h(r)+1)\psi'(r)dr\right],$$

relates the pressure P both to the contact value $h(1+)$ of the pair correlation function and to an averaged interparticle force away from the contact. In the case of a direct correlation function of multi-Yukawa form outside the core, the same steps that lead to the energy route u and the compressibility route a, Eqs. (10) and (11), also provide us with explicit expressions for the Laplace transform $G(s)$ of $r + rh(r)$ (Ref. 17) from which the contact value can be worked out.[18] If, on the other hand, the interaction is a sum of Yukawa terms with inverse length scale parameters z_i, it is easily seen that the integral on the right-hand side of the relation above reduces to a sum of linear combinations of $G(s)$ and $dG(s)/ds$ with s set to each of the z_i. As both conditions are met in our case, the virial pressure can be numerically evaluated no less efficiently than the other thermodynamic quantities commonly entering SCOZA.

Implementation of the theory outlined in Sec. IV started from our reimplementation of conventional SCOZA, which has been developed with a view to great conceptual simplicity, modularity, and flexibility and has turned out to be a convenient test bed for modifications of both the theory and its numerical realization. Methodically, it largely follows the work of Schöll-Paschinger;[21] the main differences are the avoidance of general nonlinear solving routines through the systematic use of linearizations (which also eliminate the need for cumbersome implicit differentiations and incidentally brings about a significant speed advantage) and an improved implementation of the artificial spinodal boundary condition (see below) that is more computationally efficient

and does not restrict the estimated spinodal to the discretization grid, nor does it use the ill-founded criterion of minimal width of the spinodal.

For the computations below, we solved the SCOZA partial differential equation (PDE) [Eq. (9)] by an iterated predictor-corrector method on density grids of $N_\rho = 10^3$ density steps spanning the range $0 \leqslant \rho \leqslant \rho_{max} = 1$ with the ideal gas $(u = 0)$ and the MSA $(K_2 = 0)$ as boundary conditions at $\rho = 0$ and $\rho = \rho_{max}$, respectively. The inverse temperature β was turned on from $\beta = 0$, where the hard sphere reference fluid provided the initial conditions, down to the critical point with temperature steps decreasing upon approaching the critical point in approximate proportionality to $\min_\rho \sqrt{a(\beta, \rho)}$. Below the critical point, the temperature steps again increased in such a way that the shift of the spinodal per integration step was limited to less than one density step. Below the critical point, there is a region where the analytical solution of the OZ equation becomes invalid,[22] and even a fully numerical procedure[6] that does not rely on the analytical result eventually runs into problems of numerical convergence.[23] Either way, it proves necessary to remove part of the solution from the PDE's domain through the imposition of an artificial boundary condition at the spinodal. In our implementation we do so by estimating its location at the new temperature from the solution of the PDE at the previous temperature on nearby grid points and forcing the internal energy there to be compatible with $a = 0$. Pressure and chemical potential are obtained by thermodynamic integration at fixed density, starting from the hard-core reference fluid at $\beta = 0$. This allows the binodal to be found by locating densities $\rho_v(\beta)$ and $\rho_l(\beta)$ of the coexisting vapor and liquid phases of equal pressure, $P(\rho_v, \beta) = P(\rho_l, \beta)$, and chemical potential, $\mu(\rho_v, \beta) = \mu(\rho_l, \beta)$. The critical point is identified with the locus where the liquid and vapor branches of the spinodal and the binodal meet.

This computation is then repeated for different values of z_2. To illustrate the dependency of the critical parameters on z_2, let us consider the potential with $z = 1.8$ that is known to exhibit thermodynamics roughly equivalent to the LJ interaction. As can be seen from Fig. 1, the critical temperature obtained with $z_2 > z_1 = z$ is indeed a bit lower than that for conventional SCOZA $(z_2 = z_1 = z)$, and typical shifts are comparable to the estimate [Eq. (16)] obtained using results for the LJ interaction.

As we solve the SCOZA PDE, we compare the pressure obtained from thermodynamic integration to the virial route result. In general, for every value of z_2 there will be lines along which consistency between SCOZA and the virial theorem occurs; this is illustrated, again for the case of $z = 1.8$, in Fig. 2. As can be seen, the geometry of these lines is rather complex, especially below the critical point. We expect this distribution of z_2 values to quite closely resemble the function $z_2(\beta, \rho)$ that would be obtained with the more general version of the theory imposing consistency with the virial route throughout the PDE's domain (cf. Sec. IV).

In the present contribution, however, we consider a simpler version of SCOZA, where z_2 is determined from consistency at the critical point only. Numerically, the search for this optimal value of z_2 calls for repeated solutions of the
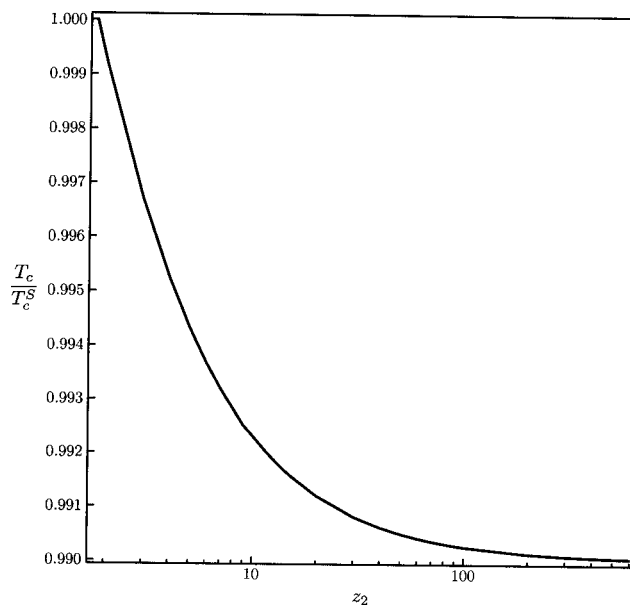

FIG. 1. Variation of the critical temperature T_c with the inverse range parameter z_2 of the adjustable part of the direct correlation function for the potential with $z = 1.8$. The z_2 is varied from $z_2 = z$, corresponding to conventional SCOZA $(T_c = T_c^S)$, up to $z_2 = 600$.

SCOZA PDE and might thus seem to be exceedingly burdensome. In contrast, e.g., to Ref. 24 where this is indeed a concern, however, we can use the semianalytic solution of the OZ equation. In combination with a very small number of Yukawa terms in Eq. (17), the integration of the PDE down to the critical temperature is sufficiently fast so that the search for z_2 does not constitute a problem.
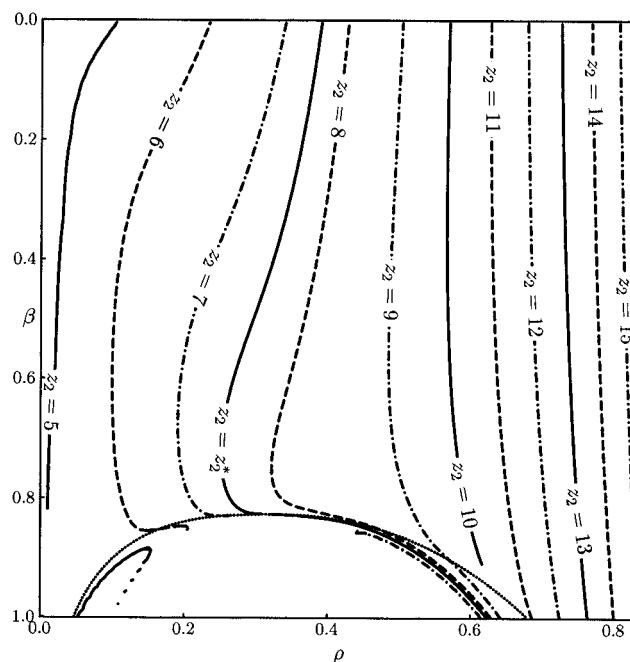

FIG. 2. Loci of consistency with the virial route for the hard-core Yukawa potential with $z = 1.8$ and various values of z_2. Consistency is achieved at the critical point for $z_2 = z_2^* = 7.571\,45$. The binodal obtained in this case is shown by the dotted line. This figure combines the results of several runs of our SCOZA implementation during each of which z_2 was kept fixed as opposed to a more general version of the theory where z_2 would be adjusted during a single run.

TABLE I. Comparison of the critical temperatures and densities for hard-core Yukawa fluids of various inverse range parameters z. SCOZA results were obtained as described in Sec. V, with z_2 determined from consistency with the virial route as proposed in Sec. IV, or set equal to z as in conventional SCOZA. The simulation results are taken from the literature.

z	T_c	ρ_c	Method
1	2.518 14	0.279	SCOZA, $z_2=z$
	2.513 88	0.279	SCOZA, $z_2=5.955\ 60$
1.8	1.218 69	0.3145	SCOZA, $z_2=z$
	1.212(2)	0.312(2)	GCMC, FSS (Ref. 2)
	1.210 13	0.312	SCOZA, $z_2=7.571\ 45$
	1.177(5)	0.313(13)	GEMC ($N=108$, Ref. 9)
2	1.088 11	0.323	SCOZA, $z_2=z$
	1.078 77	0.320	SCOZA, $z_2=8.033\ 31$
3	0.740 25	0.359	SCOZA, $z_2=z$
	0.728 60	0.352	SCOZA, $z_2=10.561\ 67$
	0.715(11)	0.375(27)	GEMC ($N=108$, Ref. 9)
3.9	0.602 00	0.387	SCOZA, $z_2=z$
	0.589 80	0.373	SCOZA, $z_2=13.085\ 09$
	0.571 4	$\cdots$	MC ($N=108$, Ref. 25)
	0.549(3)	0.37(2)	GEMC ($N=216$, Ref. 26)
4	0.591 08	0.390	SCOZA, $z_2=z$
	0.578 89	0.375	SCOZA, $z_2=13.377\ 49$
	0.576(6)	0.377(21)	GEMC ($N=108$, Ref. 9)
5	0.508 85	0.415	SCOZA, $z_2=z$
	0.496 78	0.392	SCOZA, $z_2=16.430\ 66$
6	0.456 24	0.437	SCOZA, $z_2=z$
	0.443 90	0.402	SCOZA, $z_2=19.758\ 02$
7	0.418 81	0.454	SCOZA, $z_2=z$
	0.411(2)	0.50(2)	GEMC ($N=216$, Ref. 26)
	0.405 30	0.403	SCOZA, $z_2=23.440\ 57$
	0.400 0	$\cdots$	MC ($N=108$, Ref. 25)
8	0.389 77	0.463	SCOZA, $z_2=z$
	0.374 46	0.397	SCOZA, $z_2=27.544\ 52$
9	0.365 74	0.465	SCOZA, $z_2=z$
	0.348 42	0.386	SCOZA, $z_2=32.093\ 89$
10	0.344 97	0.462	SCOZA, $z_2=z$
	0.325 78	0.372	SCOZA, $z_2=37.081\ 03$
25	0.235 3	$\cdots$	MC ($N=108$, Ref. 25)
	0.187 06	0.307	SCOZA, $z_2=z$
	0.158 29	0.170	SCOZA, $z_2=165.804\ 99$
100	0.153 8	$\cdots$	MC ($N=108$, Ref. 25)
	0.060 59	0.07	SCOZA, $z_2=z$

FIG. 3. Critical temperatures T_c for hard-core Yukawa potentials with varying inverse length scale z as computed by conventional SCOZA (dashed line) and by various simulations relative to the prediction T_c^* of our modified version of SCOZA. For the simulations, the crosses mark the value of T_c, the vertical bars indicate the uncertainties where available, and the labels identify the source: A—GCMC, FSS (Ref. 2); B—GEMC ($N=108$, Ref. 9); C—MC ($N=108$, Ref. 25); D—GEMC ($N=216$, Ref. 26); cf. Table I.

In Table I, we list the results both of the version of SCOZA outlined in Sec. IV ($z_2 > z_1 = z$) and for conventional SCOZA ($z_2 = z_1 = z$) for various potentials, and we compare them to moderately recent simulations: MC results obtained with $N=108$ particles for $z \in \{3.9, 7, 25, 100\}$;[25] Gibbs ensemble MC (GEMC) data for $z \in \{1.8, 3, 4\}$ ($N=108$) (Ref. 9) and for $z \in \{3.9, 7\}$ ($N=216$);[26] as well as the results of grand canonical MC (GCMC) simulations in combination with finite size scaling (FSS) analysis for $z=1.8$ (Ref. 2). The same
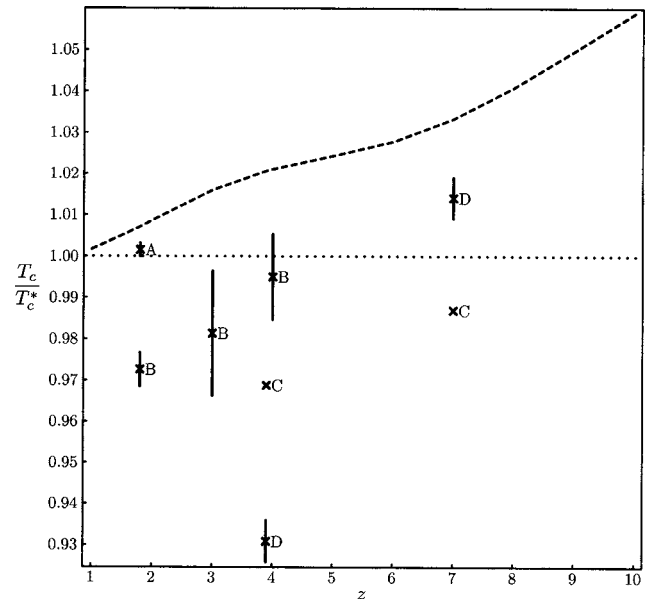
data are also displayed in Fig. 3. It should be noted that the liquid-gas transition considered here is metastable with respect to the solid for rather short-ranged potentials, viz., for $z \gtrsim 6$;[26] in particular, the highest z values for which simulations are available, viz., $z \in \{25, 100\}$ correspond to interactions for which the fluid-fluid transition is buried deep inside the metastable region.[25]

First limiting ourselves to moderately short-ranged potentials ($z \lesssim 10$), a comparison of conventional SCOZA ($z_2 = z_1 = z$) and of our modified SCOZA proposed here ($z_2 \neq z_1 = z$) shows two general trends: As expected, the critical temperature is shifted to lower values; for the LJ value of $z = 1.8$ this difference is about 0.7% and thus well compatible with the estimate [Eq. (16)]. Furthermore, the shift in critical temperature is also accompanied by a small decrease of the critical density. Both effects become more pronounced as z becomes larger. The available simulations confirm that the shift in T_c is certainly in the right direction, and the agreement is excellent considering the uncertainties of the simulation studies that generally cite nonoverlapping confidence intervals for the same interaction. For some values of z, the prediction of our modified SCOZA falls right into the confidence interval of some study, as is the case for $z=1.8$ and the sophisticated analysis of Ref. 2 or for $z=4$ and the GEMC result of Ref. 9. For the nearby value of $z=3.9$ deemed relevant to the fullerene C_{60}, on the other hand, two different studies[25,26] agree that our T_c is too high, if by significantly different amounts, whereas our prediction is right between the results of the same two references for $z=7$. For $z=3$, our modified SCOZA is marginally compatible with the GEMC results. By way of contrast, conventional SCOZA ($z_2 = z_1 = z$) yields too high a critical temperature in all cases. This

situation is graphically summarized in Fig. 3; to judge by T_c, the variant of SCOZA studied in the present contribution thus constitutes a genuine progress over its conventional form, and the available simulations are not sufficiently accurate to point out systematic deficiencies in the critical temperatures predicted. As for the critical density, both old and new SCOZA are well compatible with the results for $z \in \{3, 3.9, 4\}$. Only for $z = 1.8$ are we able to differentiate between the two versions of the theory: The modified SCOZA is in perfect agreement with the extremely narrow confidence interval obtained by way of GCMC and FSS methods whereas conventional SCOZA lies somewhat outside this range, thus also hinting at the superiority of our modifications for the critical density.

As the potential becomes more and more short ranged, however, discrepancies start to appear. For one, our modifications always bring about a shift of the critical density to lower values, but at $z = 7$, the GEMC ρ_c is already higher than that of conventional SCOZA. Similarly, the critical temperature is always lowered, but the MC simulations for the two highest values of z listed in Table I, viz., $z \in \{25, 100\}$ yield critical temperatures that are far greater than those of conventional SCOZA; furthermore, consistency with the virial theorem does not seem achievable at all for $z = 100$, presumably due to numerical difficulties with the evaluation of the virial pressure (Ref. 19). Clearly, more work is needed to clarify the situation at these extremely high values of z that are, however, far outside the range of stability of the liquid-vapor transition and thus of limited interest for a liquid state theory.

VI. SUMMARY

In the present contribution, we have considered in some depth the question of thermodynamic consistency between MSA and SCOZA (that builds upon MSA but incorporates consistency between the energy and compressibility routes) on the one hand, and the virial route on the other hand. The basis for our investigations is formed by an analysis of the solution of the MSA closure in the presence of the core condition in the light of renormalized γ-ordering that highlights a crucial difference between the lattice and the continuum cases. For the latter it is seen that a short-ranged piece must be added to the direct correlation function, and it is this term that we propose to be adjusted instead of the usual potential term. This scheme has been numerically implemented in a simplified version where only the amplitude of this contribution to $c(r)$ is varied throughout the (β, ρ) plane according to the usual SCOZA procedure implementing consistency between the energy and compressibility routes only whereas its range is fixed by imposing consistency with the virial route at the critical point only. Comparison with the results of various simulation studies shows that these modifications bring about significant improvements over conventional SCOZA; particularly encouraging is the perfect agreement with a sophisticated and extremely accurate study combining GCMC simulations with FSS analysis for $z = 1.8$ (Ref. 2).

If all of our evaluations have been restricted to the hard-core Yukawa class of interactions, the question naturally arises whether this approach can also be applied to other types of potentials. In this respect, it is clear that nothing prevents us from adding some Yukawa term to the MSA direct correlation function for, say, a LJ potential and using the same strategies for evaluating its range parameter and solving the modified SCOZA PDE. At the same time, however, the form of the Yukawa potential is special in that it is most attractive right at the core whereas more realistic interactions reach the maximum of the depth of the potential only at greater distances. For these a contribution of Yukawa form to the direct correlation function hardly seems appropriate. So clearly more work is needed before the results presented here can be transferred to other cases. Nevertheless, we expect the strategy of using the virial theorem (that is not traditionally featured in SCOZA at all) as a means of gauging the fluid structure close to the repulsive core to remain the key for fixing the form of the adjustable part of the direct correlation function. This strategy, it should be noted, was also prominently featured in our earlier work on SCOZA for molecules with soft cores.[20]

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