Integral-equation theories of fluids interacting through short-range forces: I. Thermodynamic and structural properties

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PACS classification: 61.20.Gy, 61.20.Ja

Abstract

Thermodynamic and structural properties of a system of hard-sphere particles interacting through an attractive Yukawa tail are investigated in the context of the Modified Hypernetted Chain (MHNC) approximation, a Generalized Mean Spherical Approximation (GMSA), a Self-Consistent Ornstein Zernike Approximation (SCOZA), the Hierarchical Reference Theory (HRT), and through extensive Monte Carlo (MC) simulations.

The GMSA solution is implemented through a numerically `iterative` procedure which embodies the fulfilment of entirely internal thermodynamic consistency constraints, thus avoiding recourse to any external set of data. We use the schemes of solution of the other theories that have been established elsewhere by other authors.

We investigate different Yukawa-tail screening lengths λ, ranging from $\lambda = 1.8$ (a value appropriate to approximate the shape of the Lennard-Jones `potential`) to $\lambda = 9$ (suitable for a simple one-body modelization of complex fluids like colloidal suspensions and globular protein solutions).

We find that at $\lambda = 1.8$ the MHNC, and the versions of the GMSA, SCOZA and HRT used here all provide rather accurate estimates of the various quantities of interest. At higher λ's the MHNC remains, on the whole, reasonably accurate and better than the other theories as far as the energy and the contact value of the radial distribution function are concerned. On the other hand the SCOZA predictions of the compressibility factor (i.e., the pressure) are the most accurate for the higher values of λ, especially at low temperatures and high density. Except for this, the predictions of all the theories tend to slightly worsen at low temperatures and high density. Versions of the GMSA, SCOZA and HRT that can be expected to be more accurate for interactions with extremely short-ranged attractions are identified.

I. INTRODUCTION

The hard-core Yukawa fluid (HCYF) has been the object of a rather intense investigation in the most recent years (see ref. 1 for a review). One reason for such an interest is that for this model one has available analytic and semi-analytic theories ([1–6] and references therein quoted) which allow one a rapid investigation of its physical properties; on the other hand, the potential parameters can easily be adjusted so to mimic more realistic interactions as, for instance, the Lennard-Jones potential [7]; the two circumstances allow then one to predict in a fairly easy, albeit approximate, manner the properties of a number of real fluids.

The simplicity of the model has also prompted the assessment of the performances of several theories against computer simulation data. Such comparisons have mainly concerned thermodynamic properties [8,9], with estimates of phase coexistence conditions and predictions of critical behavior [10–13]. These studies have however been restricted to some specific cases, and no systematic investigation of the accuracy of different theories over wide ranges of temperatures, densities and Yukawa screening parameters, λ, has hitherto been performed. In particular, an assessment of the accuracy of various theoretical approaches at high λ is still lacking; such a parameter regime is worth investigating since it corresponds to very short-ranged potentials, a situation in which the phase diagram of the fluid undergoes profound modifications, with the disappearence of a stable liquid phase (see [14] and references therein, and [10,11]). As documented in the current literature, a phase portrait of this kind is of peculiar interest for the description of complex fluids like colloidal suspensions and protein solutions [14].

In view of the above considerations, we have undertaken an extensive investigation of the performances of several theoretical approaches as applied to the HCYF, `supplemented` by the production of a number of new simulation data for this same model.

We report the related results in two joint papers, the first of which (present work) reports the comparison between theories and simulation results for thermodynamic and structural quantities. We start from low λ values ($\lambda \simeq 2$), roughly corresponding to the Lennard-Jones

fluid, and go up to $\lambda \simeq 9$, a realistic screening length for HCYF modelizations of colloidal suspensions and protein solutions [15].

We implement here a numerical solution procedure of a comprehensive form of the Generalized Mean Spherical Approximation (GMSA, [2,16–18]), which also embodies, as additive equations, the thermodynamic consistency constraints descending from all the three routes connecting structure to thermodynamics in liquid state theories. The consistency is thus achieved only in terms of internal conditions.

We also apply the Modified Hypernetted Chain (MHNC, [19]) theory, as well as a simple version of the Self-Consistent Ornstein-Zernike Approximation (SCOZA, [4,5,20]) and the Hierarchical Reference Theory (HRT, [21–23]), developed elsewhere by other authors.

In the second paper (hereafter referred to as II) we address the calculation of the phase diagram of the HCYF. We determine both the liquid-vapor and the freezing line of the fluid, the latter being estimated via a one-phase freezing criterion recently proposed by other authors [24]. Comparison is made, whenever possible, with phase diagrams obtained through computer simulation [10,11,20,25]. We refer the reader to paper II for the status of the investigation of the HCYF's phase diagram, and for the related bibliography.

Theories and simulation procedures in use are described in Sec. II. The results are reported and discussed in Sec. III. Sec. IV contains our conclusions.

II. MODEL, THEORIES AND SIMULATION PROCEDURES

We consider a fluid composed of hard-sphere particles of diameter σ, interacting through an attractive Yukawa tail; the interparticle potential is thus written as

$$\begin{aligned} v(r) &= \infty & r < \sigma \\ v(r) &= -\sigma\epsilon \exp[-\lambda(r-\sigma)]/r & r \geq \sigma \, . \end{aligned} \tag{1}$$

The properties of this model fluid are calculated in the context of the MHNC approximation, and versions of the GMSA, the SCOZA, and the HRT, all of which are defined below.

As is well known, in the MHNC scheme [19], the Ornstein-Zernike equation

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|)h(r')d\mathbf{r}' \ , \tag{2}$$

where $g(r)$ is the radial distribution function (rdf) and $h(r) = g(r) - 1$ and $c(r)$ are the pair and direct correlation function, respectively, is solved by means of the formally exact closure

$$g(r) = \exp[-\beta v(r) + h(r) - c(r) + B(r)] \ . \tag{3}$$

Here $B(r)$ is the bridge function of the system under study and $\beta = 1/k_B T$.

We shall assume that the bridge function for the HCYF can be approximated by those of a hard-sphere fluid in the Percus-Yevick approximation. As usual in the MHNC scheme, we choose the hard-core diameter entering the definition of the PY bridge function so as to impose a (partial) thermodynamic consistency constraint on the theory.

Specifically, we require the equality of the isothermal compressibilities as calculated according to the virial and compressibility route, that is:

$$\left(\beta \frac{\partial P}{\partial \rho}\right)_{T,\rho}^{vir} = 1 - \rho \tilde{c}(q = 0) \ . \tag{4}$$

Here $\tilde{c}(q = 0)$ is the $q = 0$ limit of the Fourier transform of $c(r)$. The solution of the system of equations (2)-(3) is obtained through the well known Gillan's algorithm [26].

In the GMSA [2,16–18] a closure to eq. (2) is obtained by observing that, because of (1), one has

$$g(r) = 0 \qquad r < \sigma \ , \tag{5}$$

and by assuming

$$c(r) = -\beta v(r) + K \exp[-z(r - \sigma)]/r \qquad r \geq \sigma \tag{6}$$

where $v(r)$ is given by (1) while K and z entering the Yukawa function in eq. (6), are used as adjustable parameters in order to impose the internal thermodynamic consistency of the theory. Specifically, we impose in the GMSA the satisfaction of condition (4) and also

$$-\left(\frac{\partial F}{\partial V}\right)_T^U = P^{vir}\,, \tag{7}$$

where the left-hand side of (7) is the pressure obtained from the energy route by differentiating the Helmholtz free energy F, whose excess part with respect to the hard-sphere fluid F^{ex} is in turn obtained from the configurational energy through standard thermodynamic integration along an isochore path, that is

$$\beta F^{ex}(\rho) = \int_0^\beta U^{ex}(\beta', \rho) d\beta' \,. \tag{8}$$

The isochore path integration starts from infinite temperature ($\beta = 0$), corresponding to the hard-sphere limit of the HCYF. The hard-sphere fluid free energy is in turn obtained by integrating the equation of state along an isothermal path at infinite temperature starting from zero density up to the density of interest; the Yukawa parameters K and z are progressively adjusted along the path so to reproduce the Carnahan-Starling (CS, [27]) pressure and compressibility at each thermodynamic point. The hard-sphere Helmholtz free energy has thus the CS value.

We have implemented the solution of the GMSA, under the conditions (4) and (7), in a fully numerical manner. Specifically, we have used eq. (6) as a closure relation in an iterative solution procedure of the integral equation (2); the rationale for such a choice, which does not make use of any of the more direct semi-analytic solution schemes of equations (2) and (6) available in the literature, is that conditions (4) and (7) require in any case a numerical search of the consistency parameters; we have then found it advantageous to incorporate their fulfilment in the same numerical procedure which solves eqs. (2) and (6).

It is worthwhile at this point to note that Stell, Høye and their coauthors have used the term GMSA in a generic sense, applied to a family of approximations, all of which have the common feature of supplementing the $-\beta v$ term appearing in a direct correlation function $c(\mathbf{r})$ outside the core with Yukawa terms. In some versions of the GMSA (for example those that have already been used to describe fluids of charged spheres and dipolar spheres [16,28]) the amplitudes and ranges of the Yukawa terms are adjusted to yield self-

consistency with thermodynamics given by prescribed equations of state that have been predetermined, rather than by equations of state that are determined through the imposition of self consistency, as is the case here. This latter form of the GMSA (which can also be regarded as a SCOZA, as noted below) is more demanding computationally, especially in the version used here that requires self-consistency among the energy, virial, and compressibility routes to thermodynamics. The work reported here is the first quantitative study of this particular version for the HCYF. An alternative version, introduced in ref. [4], that also involves consistency among the same three routes, has not yet been assessed.

The term SCOZA is also used by Høye and Stell in a generic sense to apply to approximations in which one or more state-dependent parameters are introduced into the relation between $c(\mathbf{r})$ and $-\beta v(\mathbf{r})$ in such a way that thermodynamic self-consistency gives rise to a differential equation for one of the parameters, the solution of which yields the thermodynamics of the system. In the version of SCOZA used here, there is only one parameter A, multiplying the $-\beta v(r)$ term outside the core, but there is a second term, also of Yukawa form, that represents the contribution to $c(r)$ outside the core from the hard-sphere core itself

$$c(r) = -A\beta v(r) + K_{\rm HS} \exp[-z_{\rm HS}(r-\sigma)]/r \qquad r \geq \sigma \ , \tag{9}$$

where we use the subscript HS to signify that $K_{\rm HS}$ and $z_{\rm HS}$ depend only on the presence of the hard-sphere core, independent of $v(r)$. The $K_{\rm HS}$ and $z_{\rm HS}$ are predetermined by setting $v(r) = 0$ in (9) and requiring that both the compressibility and the virial route to thermodynamics yield the Carnahan-Starling equation of state for a hard-sphere fluid. The A in (9) is then obtained by requiring that the compressibility and energy routes yield the same thermodynamics, which requires the consistency condition

$$-\frac{\partial}{\partial\beta}\tilde{c}(q=0) = \frac{\partial^2}{\partial\rho^2}\left(\frac{U^{ex}}{V}\right)_T \ . \tag{10}$$

This in turn induces a consistency condition upon $A(\rho,\beta)$ in the form of a partial differential equation which must be solved numerically. For the Yukawa fluid considered

here, this is made simpler by the fact that within the closure (9) the relation between the inverse reduced compressibility $1-\rho\tilde{c}(q=0)$ and the excess internal energy U^{ex} can be determined analytically [2,3]. The solution procedure has been described in detail in Ref. [20].

The designations SCOZA and GMSA as used by Høye and Stell are not mutually exclusive. In fact the GMSA investigated here is identical to the more comprehensive version of the SCOZA developed by Høye and Stell in ref. [5] that ensures self-consistency with respect to the virial equation as well as the energy and compressibility equations.

For the sake of a more complete overview of theoretical results, we also include the results of some calculations performed within the HRT; this approach, which does not have the structure of the other liquid-state integral-equation theories embodies the correct renormalization group behaviour as the liquid-vapor critical point is approached. In the HRT the interparticle potential is first split into a short-range, repulsive contribution $v_R(r)$ and a longer-ranged, attractive one $w(r)$. For the hard-core plus tail interaction considered here this is done trivially. The attractive part is then turned on in a gradual fashion by introducing a modified interaction $w_Q(r)$, such that its Fourier components with wavevectors smaller than a certain cutoff Q are vanishing. In the resulting Q-*system* long-range fluctuations with characteristic length $L > 1/Q$ are then strongly inhibited. As Q evolves from $Q = \infty$, the interaction takes on its components of longer and longer wavelengths, until in the limit $Q \to 0$ the fully interacting system is recovered. The corresponding evolution of the Helmholtz free energy is described by the exact equation

$$\frac{\partial}{\partial Q}\left(\frac{\beta\mathcal{F}_Q}{V}\right) = \frac{Q^2}{4\pi^2}\log\left(1+\frac{\beta\tilde{w}(Q)}{\tilde{C}_Q(Q)}\right), \tag{11}$$

where $\tilde{w}(k)$ is the Fourier transform of the attractive interaction, and $\mathcal{F}_Q$ and $\tilde{C}_Q(k)$ are straightforwardly related to the Helmholtz free energy F_Q and

to the direct correlation function in momentum space $\tilde{c}_Q(k)$ of the Q-system. Eq. (11) is closed by resorting to an approximation similar to Eq. (9). Specifically, we assume

$$\begin{aligned} g_Q(r) &= 0 \qquad\qquad r < \sigma \\ \tilde{C}_Q(k) &= B_Q \beta \tilde{w}(k) + \tilde{c}_R(k) \qquad r \geq \sigma \,, \end{aligned} \tag{12}$$

where c_R is the direct correlation function of the hard-sphere fluid as given, for instance, by the Verlet-Weis parametrization [29], and B_Q is determined so to satisfy the compressibility sum rule

$$\tilde{C}_Q(k=0) = \frac{\partial^2}{\partial \rho^2} \left(-\frac{\beta \mathcal{F}_Q}{V} \right) . \tag{13}$$

This can be regarded as a consistency condition between the compressibility route and a route (different from all the above-mentioned ones) in which the thermodynamics is determined from the Helmholtz free energy as obtained from Eq. (11). The latter yields then a partial differential equation for $\mathcal{F}_Q$, which is integrated numerically starting from $Q = \infty$ down to $Q \to 0$. We refer the reader to the related literature for more details [21--23].

Finally, a number of conventional constant-temperature, constant-volume Monte Carlo simulations [30], have been performed. As detailed in the next section, quite large system samples, enclosed in cubic boxes with periodic boundary conditions, are employed in this context, in order to get accurate estimates of various thermodynamic quantities of interest. Whenever necessary long-range corrections have been adopted in order to correct for truncation effects at the box boundaries on the radial distribution function.

The isothermal compressibility is also calculated by generating the equation of state of the fluid through a series of constant volume simulations along an isotherm, with an accurate sampling centered at the density of interest.

Calculations of the chemical potential at several thermodynamic state points have also been performed, through the Widom test-particle method [30].

III. RESULTS AND DISCUSSION

In what follows we shall measure the distance r in σ units and the temperature T, the density ρ and the pressure P in ϵ/k_B, σ^{-3} and ϵ/σ^3 units, respectively.

For clarity sake, we also divide this section into three subsections, according to the different λ's investigated.

A. $\lambda = 1.8$

The GMSA, MHNC, SCOZA [20] and HRT predictions are compared with one another and with MC results obtained with the use of 2000 particles. Comparison with previous **computer simulation data [8,31]** obtained with a few hundred particles is also reported.

Three different temperatures, $T = 1.00$, 1.50 and 2.0 have been investigated along the same isochore $\rho = 0.80$. As documented in paper II, the first state point falls deep inside the liquid pocket of the system; at $T = 1.50$ the system is instead already in a supercritical dense phase. Thermodynamic results are collected in Table I (restricted to the two lowest temperatures) and fully visualized in Fig. 1.

It appears that the SCOZA, the HRT and the MHNC reproduce to a remarkable accuracy the MC energy value. The GMSA is instead superior in reproducing the pressure, **(accurately predicted also in the SCOZA and in the HRT)**, and even better, the contact $g(\sigma)$. The compressibility is practically exact in the MHNC, the SCOZA **and the HRT**.

Radial distribution functions are shown in Fig. 2. The MHNC results appear quantitatively accurate. The SCOZA is also remarkably good; **the GMSA and the HRT are also good; the latter theories show however a small dephasing with respect to the MC pattern.**

B. $\lambda = 4$

Several comparisons between all the four theories and simulation have been performed along the isochore $\rho = .816$, a density which falls just before the freezing line [11] (see also paper II) and at temperatures ranging from inside the liquid pocket of the phase diagram ($0.5 < T < 0.625$) up to a supercritical state ($T = 1.0$). MC simulations are performed on a sample composed of 1500 atoms. Results are collected in Table II and visualized in Fig. 3.

As in the $\lambda = 1.8$ case, the MHNC predictions of the energy are quantitatively accurate against simulation; the GMSA and the HRT systematically underestimate this quantity while the SCOZA slightly overestimates it.

The GMSA lacks quantitative accuracy with regard to $\beta P/\rho$, for which the SCOZA values are particularly accurate. The SCOZA and the HRT compressibilities are the most accurate on the whole, followed closely by the MHNC. Note that, as it results from the phase diagram reported in paper II, at $\lambda = 4$ the thermodynamic point ($\rho = .816$, $T = 0.5$) falls on the coexistence line, if not inside the coexistence region. Under these conditions the HRT yields a vanishing value for $\partial P/\partial\rho$, and hence a diverging compressibility (see also Sec. II of paper II).

As far as the structural quantities are concerned the MHNC and GMSA $g(\sigma)$ remain reasonably accurate; the SCOZA is fairly good except at very low temperatures. The rdfs. shown in Fig. 4 confirm the great accuracy of the MHNC structural predictions; the GMSA and the SCOZA are also good but show a trend to lose the main features' position and the oscillatory phase at intermediate distances, an effect also visible in the structure factor (which we have calculated but do not report here), whose first peak in the two latter theories turns out to be slightly overestimated with respect to the MHNC.

C. $\lambda = 9$

More extensive investigations have been performed for $\lambda = 9$. MHNC predictions are assessed against MC data along two isotherms, $T = 0.80$ well above the sublimation line (as estimated by other authors [10]), and $T = 0.45$, and over a wide density range.

MC simulations have been performed for a sample of 400 particles. Results are displayed in Table III and visualized in Fig. 5.

As for the other λ's investigated, the energy predictions of the MHNC are very accurate even to high densities and irrespective of the temperature. The pressure estimates are good at low densities, but tend to worsen at high densities with a maximum discrepancy of approximately 25% at low temperatures. The contact value $g(\sigma)$ appears quite good in comparison, with a maximum discrepancy of 3%. The chemical potential may become wrong by a factor of two at low temperatures.

A comparison between GMSA, SCOZA, MHNC and MC along two isochores is then reported in Table IV and visualized in Fig. 6. The MHNC energy is still quantitatively accurate, and the overall compressibility, the pressure and the contact rdf estimates are also fairly good. The SCOZA energy is fairly good only at high temperatures, whilst the compressibility and the chemical potential are rather satisfactory for all the thermodynamic state investigated. The SCOZA pressure is particularly good — far better than that given by the other theories. The SCOZA contact values, however, are particularly poor. The GMSA performance, on the whole, only qualitatively reproduces the MC data.

The GMSA and SCOZA rdfs. shown in Fig. 7 exhibit now significant discrepancies with respect to the MC results reproduced instead quite well by the MHNC, especially beyond the first minimum.

The body of the results presented here puts in evidence the accuracy of the MHNC approach in the prediction of both thermodynamic and structural quantities of the HCYF on a very wide range of Yukawa screening parameters. It seems remarkable that such a good

performance can be obtained by imposing a single thermodynamic consistency constraint.

The SCOZA also appears remarkably good for the thermodynamic quantities, especially with regard to pressure at the higher values of λ at low temperatures and high densities, where the other theories are, for the most part, at their worst. The main deficiency of SCOZA is its relatively poor estimate of the contact rdf at high λ. In relation to this point, it is to be noted that although this theory embodies an accurate representation of the hard-sphere fluid properties at the level of the Carnahan-Starling equation of state, thermodynamic consistency is imposed only between fluctuation and energy pressures, without any explicit control on the virial (a quantity directly related to the contact rdf). This perhaps accounts for the poor $g(\sigma)$ estimates at high λ's.

The GMSA embodies in principle a full thermodynamic consistent treatment; it does not seem however that this is sufficient to **make the theory accurate** at all λ's. The fact that the energy and compressiblity predictions are relatively less accurate than the pressure and the contact rdf, together with the increasingly poor representation of $g(r)$ at large r, indicate that, despite the link to two consistency constraints, the adopted closure is not able to entirely cope with the interplay between short- and long-range effects in the interaction potential. This is perhaps not surprising in light of the fact that the two parameters K and z of the GMSA shown in Eq. (6) are being asked to play an even more comprehensive thermodynamic role than the three SCOZA parameters A, K_{HS} and z_{HS}, in Eq. (9). In the SCOZA, the K_{HS} and z_{HS} are dedicated to accurately and self-consistently taking into account the hard-core contribution to the thermodynamics so that A need only accommodate itself to the energy-compressibility self-consistency of the thermodynamics that results from the additional presence of the soft tail of the pair potential. In the GMSA, on the other hand, the K and z must assure that the thermodynamics of both the hard-core contribution to $v(r)$ and its soft Yukawa tail together yield full virial-energy-compressibility self-consistency. This appears to be too demanding a task to be met with high accuracy by the simple form of the single Yukawa term in (6).

The HRT, finally, is accurate in the prediction of thermodynamic quantities up to $\lambda = 4$.

We have verified however that beyond this value its results tend to get worse, as we shall discuss in paper II, where other HRT results will be reported. Since Eq. (11) is exact, this must be regarded as a consequence of the approximation intrinsic in the closure relation (12). The latter appears then to become less and less accurate as λ increases.

IV. CONCLUSIONS

Thermodynamic and structural properties of the HCYF have been investigated for different values of the Yukawa screening parameter λ. Calculations performed in the MHNC, in the GMSA with consistency constraints from all the three routes (fluctuations, virial and energy) from structure to thermodynamics, in the SCOZA, and in the HRT, have been compared with one another and with new and accurate computer simulation data obtained for high λ's.

The MHNC, which in our scheme is implemented with the use of PY bridge function, turns out to be able to reproduce in a practically quantitative manner the simulation data for the energy at all the λ's investigated, and on a very wide range of temperatures and densities. The same theory is slightly less accurate in predicting the pressure, the compressibility and the contact values of the radial distribution function.

The SCOZA, on the other hand, is the best of the theories for directly predicting the equation of state, and it turns out to retain its accuracy in this regard at the larger λ's, even at high density and low temperature, which the other theories do not.

The GMSA turns out to be reasonably accurate for the thermodynamic quantities and for $g(\sigma)$ only at low λ's. The HRT appears to be on a comparable level of accuracy.

The MHNC also appears to predict in a fairly quantitative manner the overall pattern of the radial distribution function. The GMSA, SCOZA **and HRT** $g(r)$ are reasonably good at low densities, but show a trend to overestimate the amplitude of the large r oscillations, and also to moderately lose the phase, especially when the density increases. The SCOZA

and the HRT $g(\sigma)$'s are too low for all states sampled, especially for higher λ's, and are poorer than the GMSA or MHNC.

We finally note that the implementation of the thermodynamic consistency constraint turns out to be non-trivial within either the GMSA or the MHNC. Actually, the calculation turns out to be more demanding within the GMSA, since in this theory we impose a double thermodynamic consistency constraint, a condition which is obtained through the use of two adjustable parameters rather than one as in the MHNC.

A further examination of the performances of the theories considered here with respect to their predictions of the phase diagram, is certainly in order at this stage, and will form the content of the following paper. It is also natural to try to use what we have learned from our results here to develop improved variants of the approximations we have studied.

In view of the good performances of the MHNC it seems worth trying to use more accurate bridge functions as those, for instance, obtainable from the bridge-functional approach based on the fundamental measure theory recently proposed by Rosenfeld [32]. Calculations in this direction are in progress.

The success of SCOZA in predicting the equation of state despite its relative lack of contact-value accuracy is also quite striking. The fact that the GMSA has not represented an overall improvement as a result of its more accurate $g(\sigma)$ via imposition of virial-theorem self-consistency suggests that one should consider other means of incorporating that theorem. One way of doing this is to let the range as well as the amplitude in the term relating $c(r)$ and $v(r)$ differ from that of the $v(r)$, as discussed in Section IV of [4]. Another way to do this is suggested by the observation [33] that the function

$$c(r) + \beta v(r) = h(r) - \ln g(r) + B(r) \tag{14}$$

for a Lennard-Jones type fluid has the exact large-r form $Kh^2(r)$, which suggests using

$$c(r) = -\beta v(r) + K_1 h^2(r) + B_{\rm HS}(r) \tag{15}$$

with K_1 and the diameter of the hard-sphere bridge function $B_{\rm HS}(r)$ adjusted to yield

compressibility-energy-virial self-consistency. This scheme could equally well be regarded as an alternative version of the GMSA.

Although the HRT does not impose self-consistency among any of the three routes considered here, in its current implementation it resorts to a closure relation for the direct correlation function similar to that used in SCOZA (See Eqs. (9) and (12)), the main difference being the way in which the amplitude of the interaction contribution to $c(r)$ is determined. In particular, in both theories the profile of the ''excess'' direct correlation function $c(r) - c_{\rm HS}(r)$ outside the core is forced to follow $v(r)$ at large as well as at small r's. Using an expression for $c(r)$ more suited to deal with the interplay between the short- and the long-range structure appears to be a possible way of obtaining improved results also bridge functions as those, for instance, obtainable from the bridge-functional approach based on the fundamental measure theory recently proposed by Rosenfeld [32]. Calculations in this

ACKNOWLEDGMENTS

D.P. acknowledges the support of the National Science Foundation for his work while at Stony Brook. G.S. acknowledges support by the Division of Chemical Sciences, Office of Science, Office of Energy Research, U.S. Department of Energy. D.C. acknowledges the support of the project on protein crystallization PROCRY of the Istituto Nazionale Fisica della Materia. C.C., D.C. and G.P. wish to thank the Istituto Tecniche Spettroscopiche of CNR in Messina for making available local computing facilities.

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TABLES

TABLE I. HCYF with $\lambda = 1.8$, at fixed density $\rho = 0.8$. The internal energy per particle $-\beta U^{ex}/N$, the compressibility factor $\beta P/\rho$, the isothermal compressibility χ_T and the contact value of the pair distribution function $g(\sigma)$ are shown. †: MC simulation of ref. [8]; §: MD simulation of ref. [31]; ‡: MC simulations performed in this work. Error bars of the MC results refer to the last figures of the related quantities.

	$-\beta U^{ex}/N$	$\beta P/\rho$	χ_T	$g(\sigma)$
	$\underline{T = 1.0}$			
GMSA	5.663	1.234	0.1533	4.468
HRT	5.644	1.158	0.1032	4.132
MHNC	5.641	0.995	0.1026	4.315
SCOZA	5.631	1.145	0.1024	4.153
MC†	5.635	1.29		4.490
MD§	5.638	1.17		4.382
MC‡	5.639(1)	1.179(8)	0.102	4.423(5)
	$\underline{T = 1.50}$			
GMSA	3.765	3.357	0.06406	4.287
HRT	3.755	3.311	0.04860	4.095
MHNC	3.754	3.193	0.04908	4.18
SCOZA	3.749	3.333	0.04820	4.107
MC†	3.753	3.31		4.257
MD§	3.755	3.37		4.261
MC‡	3.752(1)	3.355(2)	0.0483	4.279(3)

TABLE II. Comparison between theoretical predictions *vs.* MC results for the HCYF with $\lambda = 4$; the density is fixed at $\rho = 0.816$. Error bars as in Table I.

	$-\beta U^{ex}/N$	$\beta P/\rho$	χ_T	$g(\sigma)$
	$T = 0.50$			
GMSA	6.155	0.444	0.7862	6.466
HRT	6.223	0.0434		4.610
MHNC	5.960	-0.159	0.3067	5.937
SCOZA	5.913	0.0164	0.4522	4.913
MC	6.006(1)	0.134(8)	0.420	6.149(5)
	$T = 0.625$			
GMSA	4.825	1.820	0.2996	5.821
HRT	4.803	1.458	0.1770	4.501
MHNC	4.712	1.364	0.1608	5.452
SCOZA	4.669	1.542	0.1855	4.708
MC	4.722(1)	1.608(5)	0.1830	5.604(3)
	$T = 1.0$			
GMSA	2.944	4.035	0.09436	5.049
HRT	2.943	3.901	0.06868	4.366
MHNC	2.900	3.803	0.06712	4.878
SCOZA	2.882	3.961	0.06923	4.485
MC	2.901(1)	3.997(7)	0.06840	4.989(4)

TABLE III. HCYF with $\lambda = 9$ along the isotherms $T = 0.45$ and $T = 0.80$. Comparison between MC data (first column of each entry) and MHNC (second column). The excess chemical potential μ^{ex} is in ϵ units.

ρ	$-\beta U^{ex}/N$		$\beta P/\rho$		$g(\sigma)$		$-\mu^{ex}$	
	$T = 0.45$							
0.50	2.557(5)	2.574	0.791(16)	0.703	8.400(17)	8.357	0.254(12)	0.319
0.60	3.069(6)	3.069	0.888(16)	0.758	8.506(28)	8.388	0.224(5)	0.317
0.70	3.630(5)	3.620	1.078(12)	0.894	8.755(15)	8.595	0.133(2)	0.268
0.80	4.269(3)	4.261	1.479(14)	1.172	9.228(7)	9.018	0.067(3)	0.143
	$T = 0.80$							
0.50	1.096(1)	1.105	1.914(8)	1.872	4.611(9)	4.597	1.196(2)	1.148
0.60	1.395(1)	1.404	2.377(7)	2.307	5.049(6)	5.016	1.722(1)	1.650
0.70	1.738(1)	1.749	3.055(10)	2.941	5.614(6)	5.558	2.484(1)	2.353
0.80	2.143(1)	2.156	4.144(22)	3.927	6.403(18)	6.299		3.396
0.90	2.621(1)	2.640	5.847(34)	5.449	7.471(18)	7.292		4.954

TABLE IV. HCYF with $\lambda = 9$: comparison between MHNC, GMSA and SCOZA predictions *vs.* MC results. Error bars over MC results are obtained as r.m.s. over the block averages; see also text.

	$-\beta U^{ex}/N$	$\beta P/\rho$	χ_T	$g(\sigma)$	μ^{ex}
	$T = 0.50,\ \rho = 0.50$				
GMSA	2.235	1.160	2.5853	7.67	-0.028
MHNC	2.158	1.068	2.2985	7.24	-0.094
SCOZA	1.963	1.097	2.3821	4.65	0.012
MC	2.146(2)	1.067(10)	2.3630	7.30(1)	-0.039(2)
	$T = 0.50,\ \rho = 0.70$				
GMSA	3.364	1.849	0.9340	8.62	0.320
MHNC	3.134	1.354	0.5823	7.76	0.117
SCOZA	2.949	1.547	0.6729	5.30	0.282
MC	3.128(2)	1.544(23)	0.666	7.89(1)	0.238(4)
	$T = 0.80,\ \rho = 0.50$				
GMSA	1.169	1.975	0.8062	4.90	1.223
MHNC	1.105	1.872	0.6554	4.60	1.146
SCOZA	1.046	1.919	0.6593	3.54	1.220
MC	1.095(1)	1.903(13)	0.670	4.60 (1)	1.196(2)
	$T = 0.80,\ \rho = 0.70$				
GMSA	1.861	3.221	0.2858	6.00	2.562
MHNC	1.749	2.941	0.1935	5.56	2.353
SCOZA	1.679	3.058	0.1998	4.40	2.503
MC	1.737(1)	3.057(32)	0.205	5.62(3)	2.484(1)

FIGURES

FIG. 1. Equation of state (top) and $g(\sigma)$ (bottom) for the HCYF with $\lambda = 1.8$. Symbols: circles=MHNC; triangles=GMSA; squares=SCOZA; diamonds=HRT; crosses=MC simulations.

FIG. 2. Radial distribution function for the HCYF with $\lambda = 1.8$; state points $T = 1.0$, $\rho = 0.8$ (top) and $T = 1.5$, $\rho = 0.8$ (bottom). Symbols are listed in the figures.

FIG. 3. Equation of state (top) and $g(\sigma)$ (bottom) for the HCYF with $\lambda = 4$. Symbols as in Fig. 1.

FIG. 4. Radial distribution function for the HCYF with $\lambda = 4$; $T = 0.50$, $\rho = 0.816$ (top) and $T = 1.00$, $\rho = 0.816$ (bottom). Symbols: see figures.

FIG. 5. Equation of state (top) and $g(\sigma)$ (bottom) for the HCYF with $\lambda = 9$; data for the isotherms $T = 0.45$ and $T = 0.80$ are displayed. Symbols are listed in figures.

FIG. 6. Equation of state (top) and $g(\sigma)$ (bottom) for the HCYF with $\lambda = 9$ along the isochore $\rho = 0.7$. Symbols as in Fig. 1.

FIG. 7. Radial distribution function for the HCYF with $\lambda = 9$; $T = 0.45$, $\rho = 0.70$ (top) and $T = 0.80$, $\rho = 0.706$ (bottom). Symbols: see figures.