

Integral-equation theories of fluids interacting through short-range forces: II. Phase diagrams

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Abstract

The Self Consistent Ornstein Zernike Approximation (SCOZA), the Generalized Mean Spherical Approximation (GMSA), the Modified Hypernetted Chain (MHNC) approximation and the Hierarchical Reference Theory (HRT), are applied to the determination of the phase diagram of the Hard Core Yukawa Fluid (HCYF). The liquid-vapor coexistence line and the freezing line are determined for various Yukawa screening parameters λ , which range from $\lambda \approx 2$ when the system reasonably mimics the Lennard-Jones fluid, up to $\lambda = 9$, when the Yukawa tail becomes so short ranged that the interactions can be considered fairly similar to those present between macroparticles in colloidal suspensions and protein solutions.

The comparison of the results obtained with computer simulation data shows that at relatively low λ 's all the theories are fairly accurate, and that the SCOZA and HRT predict the binodal line and the critical parameters in a quantitative manner.

At $\lambda = 4$ some discrepancies begin to emerge in the performances of the different theoretical approaches: the GMSA and the MHNC underestimate and overestimate, respectively, the liquid coexisting density, while the SCOZA and HRT liquid branches fall between the two former theoretical predictions, both appearing to overestimate the critical temperature somewhat. At higher λ 's the GMSA and MHNC binodals further worsen, while the SCOZA remains **qualitatively** predictive.

The determination of the freezing line, performed by means of a one-phase freezing criterion (due to other authors) based on a multiparticle expansion of the excess entropy of the fluid and on structural information at the two particle correlation level, is not particularly satisfactory within either SCOZA, the MHNC, or the HRT; calculations based on these theories do not reproduce in

fact the shift of the binodal line below the sublimation line which is known to take place when the HCYF interaction potential becomes sufficiently short-ranged. The GMSA prediction for the freezing line at $\lambda = 7$ and 9, is instead able to follow in a qualitative manner the evolution of the freezing-sublimation line of the HCYF as determined through computer simulation studies. **Further assessments of the freezing criterion predictions which could be obtained through the use of computer simulation results for the excess entropy and for the two particle distribution functions, seem however necessary before drawing any definite conclusion about the relative accuracy of the various approximations at thermodynamic states near freezing.**

I. INTRODUCTION

As is well known, the hard core Yukawa fluid (HCYF) is one of the simplest model exhibiting a liquid-vapor critical point. There have been several attempts to describe the phase diagram of this system in terms of integral equation of the liquid state; in particular, the Modified Hypernetted Chain (MHNC) approximation [1] and the semi-analytic Self Consistent Ornstein-Zernike Approximation (SCOZA, [2,3]) have been applied in the low-value regime of the Yukawa screening parameter λ [4,5], with a satisfactory reproduction of the liquid-vapor binodal line; the SCOZA also provides a remarkably good description of the critical point region including the nonclassical critical exponent that describes liquid-vapor coexistence [5]. The liquid-vapor coexistence line, including the critical region, is also accurately described by the Hierarchical Reference Theory (HRT, [6]) in terms of the nonclassical critical exponent.

One reason that prompts us to focus on the theoretical investigation of the phase diagram of the HCYF is that when the Yukawa interaction becomes sufficiently short-ranged, the liquid-vapor binodal line shifts beneath the sublimation curve, and hence the liquid-vapor

critical point and phase equilibrium disappears. One has only fluid-solid sublimation. Such behavior, already documented by earlier computer-simulation results [7,8], seems particularly interesting in the case of real systems characterized by very short-ranged interparticle interactions as, for instance, certain colloidal suspensions for which it is not completely clear whether or not stable liquid-vapor coexistence occurs.

Also, it has been argued that the location of the binodal line just below the sublimation line, a configuration in which the metastable critical point is very close to the vapor-solid phase transition boundary, might represent the most favorable condition for a controlled nucleation process in the fluid, and hence for a regular growth of crystals [9]. The latter circumstance is certainly of great interest in protein solutions, systems in which the crystallization procedures do frequently fail to yield crystals of enough large size and good quality so to allow a confident diffraction study of the molecular structure.

Such a state of the art strongly motivates, in our opinion, an extensive investigation of the phase equilibria properties of the HCYF, performed by using the most advanced theories presently available (both semi-analytic and iteratively solvable) and simulation approaches, aimed to cover a range of λ 's much wider than hitherto considered; the analysis should encompass, in particular, λ values high enough so to reproduce the features of the interaction potential typical of complex fluids, such as the previously mentioned colloidal suspensions and protein solutions.

We have extensively examined in the preceding paper (hereafter to be referred to as I) the performances of the SCOZA, the MHNC, the HRT, and the Generalized Mean Spherical Approximation (GMSA, [10]), in predicting the thermodynamic and the structural properties of the HCYF. We have found all the theories are fairly accurate at low λ values, when the potential is sufficiently long-ranged, and tend to worsen in ways that differ in the different theories for very short-ranged interactions. In summary, among the theories we studied, the MHNC was found to have the best overall structural and thermodynamic accuracy while the SCOZA yielded the best equation-of-state predictions, which remained accurate for larger λ 's even at the lowest temperatures and highest densities of our study.

We complete in this paper the above theoretical scenario by undertaking the determination of the binodal liquid-vapor and freezing line of the HCYF over the same extended range of Yukawa screening parameter investigated in paper I. The determination of the binodal is performed according to conventional procedures. The freezing line is determined on the basis of a one-phase freezing criterion proposed by other authors [11]. The phase diagram predicted by different theories, namely the SCOZA, MHNC, GMSA and HRT, are compared with the available computer-simulation studies.

The procedures for determining the lines of coexisting phases and the freezing line are briefly outlined in sec. II. Results are reported and discussed in sect. III. The conclusions follow in sect. IV.

II. THEORETICAL PROCEDURES FOR THE DETERMINATION OF THE PHASE DIAGRAM

The theories and the simulation procedures through which the thermodynamic and structural properties are calculated have been described in detail in paper I, and we refer the reader to that work for the details. **As far as the liquid-vapor coexistence curve is concerned, this is determined straightforwardly in the HRT, since the condition of chemical equilibrium between the two coexisting phases are implemented by the theory itself.** In fact, below the critical temperature this approach yields a diverging compressibility and rigorously flat isotherms in a certain domain of the phase plane, which is then identified with the coexistence region.

In the GMSA, MHNC and SCOZA the determination of the liquid-vapor coexistence line is instead performed by equating the chemical potential at equal temperature and pressures on the liquid and vapor side of the binodal, respectively. The chemical potential is obtained from the Helmholtz free energy calculated either by integrating the pressure along a supercritical isothermal path, or by integrating the configurational energy

with respect to the inverse temperature along an isochore path, starting from a temperature for which the Helmholtz free energy is otherwise known (for instance from the hard-sphere limit).

In implementing such a procedure it happens, as already mentioned in I, that both the MHNC and the GMSA solution algorithms fail to converge to a thermodynamic consistent solution in the critical point region; as a consequence, we cannot display results for the binodal from these two theories on a restricted temperature range close to the critical temperature. In light of earlier results that have already come out of both theoretical and computational studies of HNC-type theories, this difficulty in locating a binodal and critical point may well be intrinsic to such theories rather than an artifact of our numerical procedure. (In the HNC approximation, for example, there appears to be no critical point at which the compressibility computed via the compressibility relation diverges [15,16].) On the other hand, the study of the analytic structure of the GMSA made in [3] strongly suggests that the GMSA is an approximation for which the binodal is well defined in the critical region and at a critical point, which can in principle be located with arbitrarily high precision, just as in the SCOZA.

We also locate the onset of freezing in our HCYF by monitoring the behavior of the multiparticle residual entropy [11], defined as

$$\Delta s \equiv s_{ex} - s_2 , \quad (1)$$

where s_{ex} is the the excess entropy of the system per particle in units of the Boltzmann constant, and

$$s_2 = -\frac{1}{2}\rho \int \{g(r) \ln[g(r)] - g(r) + 1\} dr . \quad (2)$$

Our description of the freezing transition hinges on previous results reported in the literature, from which it turns out [11] that the vanishing of Δs acts as a quite sensitive indicator of the freezing transition in several one-component fluids. The possibility that this same condition can be associated with structural rearrangements that herald other types of phase separations has also been discussed elsewhere [12].

III. RESULTS

The phase diagram at $\lambda = 1.8$ is shown in Fig. 1. As can be seen, all the theories reproduce rather satisfactorily the binodal curve as obtained through finite size scaling computer simulation technique [13].

In particular, as already reported in ref. [4], the liquid branch of the binodal is well predicted by the MHNC; this theory appears fairly accurate at low temperatures, while it tends to slightly overestimate the density of the coexisting liquid phase. The opposite behavior is shown by the GMSA. The results from the SCOZA, previously obtained elsewhere [5] and from the HRT, turn out to be “bracketed” by the two former theories, and appear as the most satisfactory. Both the SCOZA [5] and the HRT yield non-classical critical exponents and in particular yield for the exponent that describes the shape of the binodal curve the values $7/22 (= 0.31)$ and 0.345 respectively. The best renormalization-group estimate of this value is in the neighborhood of 0.332 .

The performances of the different theories on the vapor branch of the binodal are also very accurate, as seen in Fig. 1.

The critical parameters predicted by the various theories at $\lambda = 1.8$ are reported in Table I.

As noted in **section II and also discussed in I**, the MHNC and GMSA iterational algorithms becomes unable to yield a thermodynamic consistent solution for temperatures too close to the critical one. For this reason the GMSA and the MHNC figures are deduced from a power-law interpolation of the available points performed with a non-classical critical exponent, together with the application of the law of rectilinear diameters.

At $\lambda = 1.8$ the SCOZA [5] and the HRT are in quantitative agreement with simulation. The GMSA is also quite accurate. The MHNC [4] is quite good but slightly inferior to the other three theories.

Some of the theoretical trends emerging at $\lambda = 1.8$ herald more pronounced deviations from the simulation results at $\lambda = 4$. This is visible in Fig. 2, where it appears that on

the liquid side of the binodal the MHNC moderately overestimates, and the GMSA sensibly underestimates, respectively, the densities of the coexisting phases. The SCOZA is again in between the two theories; the same is true also for the HRT, but only up to intermediate temperatures. In fact, above $T = 0.55$ the HRT binodal is external to the MHNC one. The critical temperature and density predicted by the different theories are still quite satisfactory (see Table I).

The case with $\lambda = 7$ is now considered. The related results are shown in Fig. 3.

Note that the computer simulation results, known from previous studies, show the shift of the binodal line beneath the sublimation line, a circumstance which implies the metastability of the liquid-vapor equilibrium.

Some of the theories show now considerable discrepancies with respect to the Gibbs ensemble Monte-Carlo (GEMC) data. The GMSA result, in particular, appears poor on both the liquid and the vapor branch of the coexistence line. The MHNC now sensibly overestimates on one side, and undestimates on the other, the coexistence liquid and vapor density, respectively. As a result, the simulation binodal falls well inside the MHNC one.

The SCOZA, as for the other λ 's, is between the MHNC and the GMSA, and maintains a qualitative agreement with the GEMC results.

We now focus our attention on the freezing line. As noted in sec. II, previous studies by other authors indicate that the *locus* of vanishing multiparticle residual entropy, $\Delta s = 0$, corresponds with remarkable accuracy to the freezing line of several model fluids. A detailed discussion of the physical meaning of the $\Delta s=0$ condition in relation to its "coincidence" with the freezing and other coexistence lines, has been provided elsewhere [12]. We here restrict ourselves to examine the related results for the HCYF by performing whenever possible a comparison with the simulation results.

Calculations of the $\Delta s = 0$ *loci* have been performed according to different theories and are reported in Figs. 1-5.

As we can first see in Fig. 1, at $\lambda = 1.8$ the MHNC, GMSA and SCOZA results fall quite

close to each other, and to density functional theory [14]. A calculation of the freezing line performed by using the Hansen-Verlet freezing criterion with SCOZA structural functions as input (whose results are not displayed in the figure), yields a freezing line which descends almost vertical down to a density $\rho = 0.94$.

The triple-point temperature, determined from the intersection of the freezing line with the binodal line, is considerably below the critical one, thus indicating the existence of a very well-defined liquid pocket.

It is interesting to note that on the vapor side of the binodal the MHNC and GMSA $\Delta s = 0$ locus practically falls on the estimated coexisting vapor density line. We could not verify whether anything similar happens for densities close to the liquid branch of the binodal, because of numerical difficulties in that density region. A trend of Δs to vanish seems however conjecturable on the basis of the results shown in Fig. 4 (see ref. [12] for a discussion about the possible meaning of multiple vanishing of the multiparticle residual entropy).

Results for the $\Delta s = 0$ loci at $\lambda = 4$ are shown in Fig. 2.

We can see that the GMSA falls fairly close to the computer simulation line of freezing, by moderately overestimating the freezing density. The MHNC and the SCOZA lines are instead still almost vertical, as in the $\lambda = 1.8$ case. **We have verified** that calculations with the Hansen-Verlet criterion do yield a freezing line hardly different from the one at $\lambda = 1.8$.

Similar remarks as for the $\lambda = 1.8$ case can be made for the vanishing of Δs along the vapor side of the binodal, as obtained within the MHNC and the GMSA.

The MHNC and SCOZA loci at $\lambda = 7$ (see Fig. 3) hardly differ from those at lower λ 's. The GMSA curve, instead, falls now very close to the simulation freezing line although it is not able to follow the trend to flatten of the sublimation curve at low temperatures. It is interesting to note, however, that a portion of the GMSA $\Delta s = 0$ locus can be obtained also in the vapor region, and this is located well above the coexisting vapor density. We could not follow the $\Delta s = 0$ behavior at intermediate densities due to numerical instability problems.

An almost flat interpolation between the two branches could however be reasonably assumed.

Actually, as shown in Fig. 5, the GMSA locus, fully determined at $\lambda = 9$ over the whole density range, has a moderate dependence on the temperature at relatively low densities, so to qualitatively resemble the simulation sublimation line. The MHNC $\Delta s = 0$ locus for comparison stops at considerably higher densities and is located at lower temperatures.

It is also interesting to note that at $\lambda = 7$ the GMSA binodal is located at temperatures which are sensibly smaller than those of the $\Delta s = 0$ locus, in a manner which resembles the relative location of the binodal *vs.* the sublimation lines obtained through simulation.

IV. DISCUSSION AND CONCLUSIONS

It should be noted that all of the integral-equation approximations we have studied here have only been fully defined for the fluid state and not the solid state. As a result, strictly speaking, these approximations are silent as to the location of the triple point and freezing line. They are also silent with regard to the location of the vapor-solid coexistence curve defined for temperatures below the triple-point temperature. Although we believe it is of considerable interest to combine the results of the fluid-state approximations with freezing criteria such as the $\Delta s = 0$ criterion to predict freezing and sublimation lines that can be compared to simulation results, the quality of such predictions clearly cannot be used to rank the relative accuracy of the fluid theories *per se*. For this reason we shall summarize the results for the binodal line before going on to discuss the freezing and sublimation results and ways of going beyond them.

The binodal results extend and add further support to the general conclusion emerging from the results of I that the SCOZA predicts with good accuracy the equation of state over the whole range of potential ranges studied. This turns out to be especially true in the liquid-vapor critical region and leads to the most accurate overall binodals among the theories we have considered.

At low λ 's ($\lambda = 1.8$), that is when the potential is long-ranged, all the theories inves-

tigated reproduce with considerable accuracy the simulation phase diagram; the SCOZA and the HRT, as already known from previous studies, are also able to successfully describe the critical point region and predict non-classical critical exponent. At higher λ 's ($\lambda \geq 4$), that is when the range of the Yukawa tail reduces, significant differences emerge in the performances of the various theories.

The SCOZA is able to maintain good agreement with the computer-simulation binodal, while the GMSA and the MHNC predict a somewhat wider liquid-vapor coexistence curve than simulation. The GMSA and the MHNC somewhat underestimate and overestimate, respectively, the coexistence density on the liquid branch; the HRT also yields too high a critical temperature starting from $\lambda = 4$.

We turn now to the solidification criterion. The freezing line, as determined either according to a criterion based on the vanishing of the residual multiparticle entropy Δs , or according to the Hansen-Verlet criterion, is not as satisfactorily predicted as the binodal line. In fact, the SCOZA, the MHNC and the HRT yield a freezing density which is not significantly sensitive to the variation of the potential range as is known, instead, to be the case; in fact, simulation studies at $\lambda \geq 7$, show that the solid-liquid coexistence line actually becomes a sublimation line running above the (metastable) binodal line, with the liquid-vapor critical point falling just beneath the vapor-solid transition line.

The GMSA $\Delta s = 0$ turns out to be able to follow in a qualitative manner the modification with λ of the freezing line. In particular, at $\lambda = 9$, the locus of vanishing residual multiparticle entropy shifts well above the liquid-vapor coexistence line in a manner which fairly mimics the relative location of the freezing and binodal line in this λ regime.

A natural way of extending the integral-equation theories we consider to the solid phase is to incorporate in the theories the form that one expects of the direct correlation function for the crystal symmetry (or symmetries, if more than one is in contention) associated with the expected solid. One can then find the most stable phase for each ρ and T by comparing the free energy of the solid or solids in contention with the fluid-free energy, and selecting the minimum. This procedure is at the heart of those versions of density-functional theory

that incorporate Ornstein-Zernike formalism.

For the versions of the SCOZA and the GMSA considered here this would entail using in place of the Yukawa of eq. (6) an appropriately parameterized functional form that is consistent with the symmetry of the solid into which the HCYF fluid is expected to freeze. For the modified SCOZA/GMSA given in paper I by its eq. (15), one would instead use a $B_{\text{HS}}(r)$ appropriate to solid symmetry to characterize the solid phase. Similarly, the MHNC can be modified to describe a solid phase through the use of a hard-sphere bridge function appropriate to the solid in eq. (3) of I.

Such generalizations represent a formidable computational challenge. But our results here indicate that on the basis of currently available freezing criteria, fluid-state integral-equation theories cannot give reliable results for phase separation when the attractive term becomes extremely short-ranged.

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REFERENCES

- [1] Y. Rosenfeld and N.W. Ashcroft, *Phys. Rev. A* **20**, 1208 (1979).
- [2] J.S. Høye and G. Stell, *J. Chem. Phys.* **67**, 439 (1977).
- [3] J.S. Høye and G. Stell, *Mol. Phys.* **52**, 1071 (1984).
- [4] C. Caccamo, G. Giunta and G. Malescio, *Mol. Phys.* **84**, 125 (1995).
- [5] D. Pini, G. Stell and N. B. Wilding, *Mol. Phys.* **95**, 483 (1998).
- [6] A. Parola and L. Reatto, *Phys. Rev. Lett.* **53**, 2417 (1984), *Phys. Rev. A* **31** 3309 (1984) and *Advances in Physics* **44**, 211 (1995).
- [7] M.H.J. Hagen and D. Frenkel, *J. Chem. Phys.* **101**, 4093 (1994).
- [8] E. Lomba and N.E. Almarza, *J. Chem. Phys.* **100**, 8367 (1994).
- [9] P.R. ten Wolde and D. Frenkel, *Science* **277**, 1975 (1997).
- [10] J.S. Høye, J.L. Lebowitz and G. Stell, *J. Chem. Phys.* **61**, 3253 (1974).
- [11] P.V. Giaquinta and G. Giunta, *Physica A* **187**, 145 (1992); P.V. Giaquinta, G. Giunta and S. Prestipino Giarritta, *Phys. Rev. A* **45**, 6966 (1992).
- [12] P.V. Giaquinta, G. Giunta and G. Malescio, *Physica A* **250**, 91 (1998).
- [13] N.B. Wilding and A.D. Bruce, *J. Phys. Condens. Matter* **4**, 3087 (1992)
- [14] M. Renkin and J. Hafner, *J. Chem. Phys.* **94**, 541 (1991).
- [15] J.S. Høye, E. Lomba, and G. Stell, *Mol. Phys.* **79**, 523 (1993). Note especially the discussion in Sections 4 and 5 and the references cited therein.
- [16] L. Belloni, *J. Chem. Phys.* **98**, 8080 (1993).
- [17] M. I. Guerrero, G. Saville and L. Rowlinson, *Mol. Phys.* **29**, 1941 (1975); S. M. Foiles and N. W. Ashcroft, *Phys. Rev. A* **24**, 424 (1981).

TABLES

TABLE I. Theoretical and simulation critical point parameters. †: Finite-size scaling Monte-Carlo simulation of ref. [13]; §: Gibbs ensemble Monte-Carlo simulation of ref. [8]; ‡: MHNC calculations with Verlet-Weis bridge functions of ref. [4]

	$\lambda = 1.8$		$\lambda = 4.0$		$\lambda = 7.0$	
	T_{cr}	ρ_{cr}	T_{cr}	ρ_{cr}	T_{cr}	ρ_{cr}
MC	1.212 (2) [†]	0.312 (2) [†]	0.576 (6) [§]	0.377 (21) [§]	0.411 (2) [§]	0.50 (2) [§]
GMSA	1.199	0.312	0.576	0.324		
MHNC	1.193	0.326	0.581	0.412		
MHNC [‡]	1.21	0.28				
HRT	1.214	0.312	0.599	0.394	0.435	0.424
SCOZA	1.219	0.314	0.591	0.3895	0.419	0.4575