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# Self-Consistent Approximation for Fluids and Lattice Gases[1]

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A self-consistent Ornstein–Zernike approximation (SCOZA) for the direct-correlation function, embodying consistency between the compressibility and the internal energy routes to the thermodynamics, has recently been quantitatively evaluated for a nearest-neighbor attractive lattice gas and for a fluid of Yukawa spheres, in which the pair potential has a hard core and an attractive Yukawa tail. For the lattice gas the SCOZA yields remarkably accurate predictions for the thermodynamics, the correlations, the critical point, and the coexistence curve. The critical temperature agrees to within 0.2% of the best estimates based on extrapolation of series expansions. Until the temperature is to within less than 1% of its critical value, the *effective* critical exponents do not differ appreciably from their estimated exact form, so that the thermodynamics deviates from the correct behavior only in a very narrow neighborhood of the critical point. For the Yukawa fluid accurate results are obtained as well, although a comparison as sharp as in the lattice-gas case has not been possible due to the greater uncertainty affecting the available simulation results, especially with regard to the position of the critical point and the coexistence curve.

**KEY WORDS:** coexistence curve; correlation function; critical point; lattice gas; Ornstein–Zernike theory; thermodynamic consistency; Yukawa fluid.

## 1. INTRODUCTION

It is well known that the most popular liquid state theories based on an integral equation for the two-particle correlation function suffer from a lack

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of thermodynamic consistency: that is, different routes to the thermodynamics (typically, the compressibility, the virial, and the internal-energy routes) yield different results [1]. This is quite a serious flaw. It is not surprising, then, that several integral equations have been modified in such a way that consistency between different routes is enforced. The generalized mean spherical approximations (GMSA) of Stell and his colleagues represent one such approach that has proved useful in treating ionic and polar fluid models [2], but it has not been fully developed for simple fluids. For such fluids, self-consistent approaches include the modified hypernetted chain (MHNC) and the Zerah–Hansen (also known as HMSA) integral equation. While yielding remarkably accurate thermodynamics over most of the phase diagram, the latter theories fail nevertheless to converge in the neighborhood of the critical point, so that the top of the coexistence curve is missing [3, 4].

In the present work we show that the requirement of thermodynamic consistency can be used to get a closed theory which gives very good thermodynamics, including an accurate phase diagram. This approach is a self-consistent Ornstein–Zernike approximation (SCOZA) formulated some time ago [5] that has been recently applied to specific systems by solving numerically the resulting partial differential equation (PDE). The systems that have been studied so far are the nearest-neighbor attractive lattice gas (i.e., the ferromagnetic Ising model) and a fluid of particles interacting via a spherically symmetric pair potential consisting of a hard-core repulsive term plus an attractive Yukawa tail. The work on the lattice gas discussed here supplements that already reported in Ref. 6, to which we refer the reader for further details.

## 2. THEORY

The SCOZA deals with a fluid of particles interacting by a two-body potential $v(\mathbf{r})$ that consists of a hard-core repulsion and a longer-ranged attractive contribution $w(\mathbf{r})$. If $g(\mathbf{r})$ is the two-body radial-distribution function at $\mathbf{r}$, $c(\mathbf{r})$ is the Ornstein–Zernike two-body direct-correlation function, and $\sigma$ is the hard-core diameter, the SCOZA in its simplest form amounts to setting

$$\begin{aligned} g(\mathbf{r}) &= 0, & r &< \sigma \\ c(\mathbf{r}) &= A(\rho, \beta)\, w(\mathbf{r}), & r &> \sigma \end{aligned} \tag{1}$$

where $A(\rho, \beta)$ is a function of the density $\rho$ and of the inverse temperature $\beta = 1/(k_B T)$, $T$ being the absolute temperature and $k_B$ the Boltzmann constant. The condition on $g(\mathbf{r})$ (the so-called core condition) is exact and stems from the hard-core repulsion, while the expression of $c(\mathbf{r})$ is clearly an approximation and implies that $c(\mathbf{r})$ always has the same range as the potential: this is usually referred to as the Ornstein–Zernike *ansatz*. Equation (1) resembles the well-known mean-spherical approximation (MSA) [1], except that in the present case the function $A(\rho, \beta)$ is not fixed *a priori* as in the MSA, where one has $A \equiv -\beta$. Instead, it has to be determined in such a way that the compressibility and the internal energy route lead to the same thermodynamics. It is worthwhile stressing that consistency is not enforced *after* the thermodynamics has been obtained through one or the other route; instead, the thermodynamics must be determined self-consistently. The consistency condition can be expressed as

$$\frac{\partial}{\partial \beta}\left(\frac{1}{\chi_{\text{red}}}\right) = \rho \frac{\partial^2}{\partial \rho^2}(\rho u) \tag{2}$$

where $\chi_{\text{red}}$ is the reduced compressibility as given by the zero-wavelength limit of the structure factor, and $u$ is the excess internal energy per particle, obtained by integrating the pair interaction weighted by the radial-distribution function. When Eqs. (1) and (2) are supplemented by the exact Ornstein–Zernike equation connecting $g(\mathbf{r})$ and $c(\mathbf{r})$,

$$g(\mathbf{r}) - 1 = c(\mathbf{r}) + \rho \int d^3\mathbf{r}'\, c(\mathbf{r}')\,[g(\mathbf{r}-\mathbf{r}') - 1] \tag{3}$$

a closed equation for $A(\rho, \beta)$ is obtained. The calculation is considerably simplified in those cases when the link between the quantities $\chi_{\text{red}}$ and $u$ within the Ornstein–Zernike approximation can be written explicitly in closed form. This is actually the case with the lattice gas and the Yukawa fluid considered here. Equation (2) then becomes a nonlinear diffusive PDE that can be integrated numerically.

## 3. LATTICE GAS

In the case of the lattice gas, the interaction potential $v(\mathbf{r})$ is given by

$$v(\mathbf{r}_i - \mathbf{r}_j) = \begin{cases} +\infty, & \mathbf{r}_i = \mathbf{r}_j \\ -w, & i, j \text{ nearest neighbors} \\ 0, & \text{otherwise} \end{cases} \tag{4}$$

where $i$ and $j$ label two generic lattice sites and $w$ is the strength of the nearest-neighbor interaction. According to Eq. (1), the only two nonvanishing values of $c(\mathbf{r})$ for the pair potential [Eq. (4)] are the on-site $c_0$ and the nearest-neighbor $c_1$. The thermodynamics and the correlations can then be conveniently described [7] by the variable $z = qpc_1/(1-\rho c_0)$, $q$ being the coordination number of the lattice, and by the lattice Green's function $P(z)$ [8],

$$P(z) = \int_0^{\pi} \frac{d^3\mathbf{k}}{\pi^3} \frac{1}{1-(z/p)\,\Phi(\mathbf{k})} \tag{5}$$

where $\Phi(\mathbf{k})$ is the Fourier transform of the nearest-neighbor potential and $p$ is a coefficient whose value depends on the particular lattice. If we introduce the quantities $y = [P(z)-1]/[zP(z)]$, $\varphi = \rho(1-\rho)\,y$ and the function $F$ such that $z = F(y)$, we find that Eq. (2) can be cast in the following form:

$$\frac{(1-y)\,F'(y) - F(y)[1-F(y)]}{[1-yF(y)]^2} \frac{\partial\varphi}{\partial\beta} = qw[\rho(1-\rho)]^2 \left(\frac{1}{2}\frac{\partial^2\varphi}{\partial\rho^2} + 1\right) \tag{6}$$

The function $\varphi(\rho, \beta)$ is proportional to the excess contribution to the internal energy per unit volume with respect to the mean-field approximation. The choice of $\varphi(\rho, \beta)$ as the unknown function has been determined by the fact that the resulting Eq. (6) lends itself to numerical integration by an *implicit* method [9] without making the computation very difficult. The use of such a method is highly recommended in the case of the SCOZA PDE, in order to avoid the problem of numerical instability, which would become particularly severe in the critical and subcritical region. To integrate Eq. (6), a set of boundary and initial conditions is also needed. One finds easily that $\varphi(\rho, \beta=0) = \varphi(\rho=0, \beta) = 0$. Moreover, since Eq. (6) preserves particle-hole symmetry, the integration with respect to the density can be carried out in the interval (0, 1/2), with the further boundary condition that $\varphi(\rho, \beta)$ is symmetric with respect to $\rho = 1/2$. Particle-hole symmetry also implies that the correct value of the critical density $\rho_c = 1/2$ is obtained in SCOZA.

The critical temperature predicted by Eq. (6) has been located by the divergence of the isothermal compressibility on the critical isochore. The results are remarkably accurate: for instance, in the case of a simple cubic lattice we obtain $\beta_c w = 0.88503$, while the best estimate obtained by extrapolation of series expansions [10] is $\beta_c w = 0.88662$. The error is less than 0.2%. Similar accuracy is obtained for the body-centered and the face-centered cubic lattices as well [6]. A fit on a log–log plot for the compressibility on the critical isochore and on the critical isotherm shows that the effective critical exponents (the slopes of such plots) approach the mean-spherical values of $\gamma = 2$ and $\delta = 5$, respectively, as the critical point is approached, but they deviate substantially from the true effective exponents only very close to critical, when the reduced temperature,

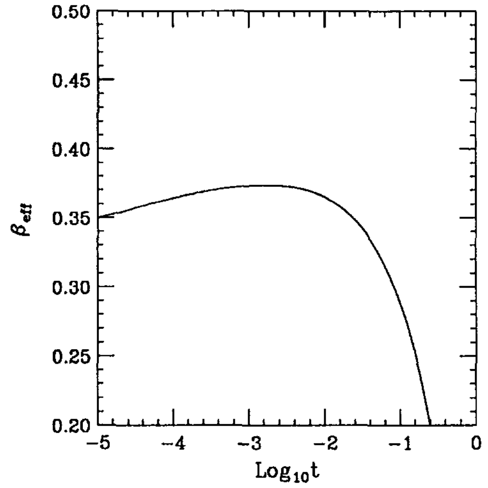

**Fig. 1.** Effective exponent $\beta_{eff}$ for a simple cubic lattice gas with a nearest-neighbor potential as a function of the logarithm of the reduced temperature $t = |T - T_c|/T_c$. $\beta_{eff}$ is defined as the local slope of $\log m$ vs $\log t$, where $m = |\rho - \rho_c|/\rho_c$ is the reduced density.

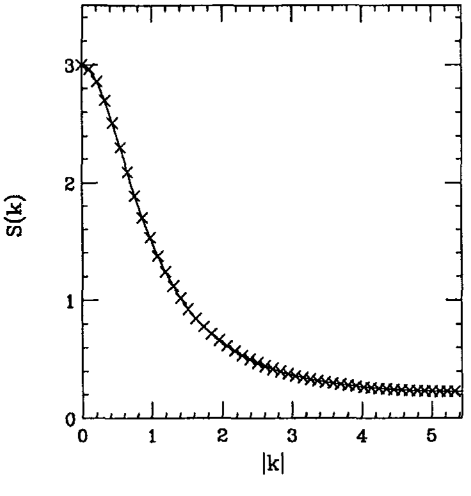

**Fig. 2.** Structure factor $S(\mathbf{k})$ of the simple cubic lattice gas along the direction $k_x = k_y = k_z$ as a function of the norm of $\mathbf{k}$ at the critical density $\rho = 1/2$ and a temperature $k_B T/w = 1.5$, $w$ being the strength of the attractive interaction. (×) SCOZA; (—) approximant [11].

$t = |T - T_c|/T_c$, and density, $m = |\rho - \rho_c|/\rho_c$, are less than $10^{-2}$. Similarly, while the true specific heat at constant volume $c_V$ diverges at critical, the SCOZA $c_V$ takes on a high but finite value. For example, for the simple cubic lattice, it remains a bit higher than the true value until $t \sim 10^{-5}$. Remarkably, for $t$ down to $10^{-5}$ the effective critical exponent $\beta_{\text{eff}}$ describing the coexistence curve shape appears to be approaching a value much closer to the true value of 0.33 than the mean-spherical value of 0.5. This is shown in Fig. 1. (See also the Note Added in Proof.) We also note that both the overall thermodynamics and the correlations are faithfully reproduced. This can be seen, for instance, in Fig. 2, where the structure factor at the critical density $\rho = 1/2$ and a temperature $k_B T/w = 1.5$ is compared with the results from a closed-form approximant [11]; the agreement is very good.

## 4. YUKAWA HARD-CORE FLUID

The pair potential of the Yukawa hard-core fluid considered here is

$$v(r) = \begin{cases} +\infty, & r < 1 \\ -\dfrac{e^{-z(r-1)}}{r}, & r > 1 \end{cases} \tag{7}$$

where $z$ is the inverse range of the interaction and we have set both the hard-sphere diameter $\sigma$ and the strength $\varepsilon$ of the attractive tail equal to unity. This amounts to using the reduced quantities $\rho^* = \rho\sigma^3$ and $T^* = kT/\varepsilon$. It has been shown [12] that for such a potential, *any* closure of the form, Eq. (1), irrespective of the detailed form of the function $A(\rho, \beta)$, allows one to express in closed form the internal energy per particle $u$ as a function of the inverse reduced compressibility $1/\chi_{\text{red}}$. If we regard $1/\chi_{\text{red}}$ as the unknown function $f(\rho, \beta)$, Eq. (2) can then be cast in the form

$$\frac{\partial f}{\partial \beta} = \rho \frac{\partial}{\partial \rho}\left[ C(\rho, f) \frac{\partial f}{\partial \rho} + D(\rho, f) \right] \tag{8}$$

where $C(\rho, f)$ and $D(\rho, f)$ are prescribed functions of $\rho$ and $f$. Equation (8) can be integrated numerically by an implicit algorithm [13] similar to the one used for Eq. (6). The low-density boundary condition corresponds to the perfect gas, so one has $f(\rho = 0, \beta) = 1$. At high density, that is for $\rho^* \simeq 1$, the MSA for the internal energy has been used, and $f$ has then been determined by using Eq. (2) as an evolution equation. It has also been determined that the system is quite insensitive to the specific choice of the high-density boundary condition. Finally, at $\beta = 0$, $f$ must be given by its hard-sphere value. It should be observed that the closure [Eq. (1)]

to the Ornstein–Zernike equation (3) implies that the hard-sphere contribution to $c(r)$ vanishes outside the core, so that the treatment of the hard-sphere gas in the present approximation coincides with the Percus–Yevick (PY) one. While this is exact in the lattice-gas case, it is not fully satisfactory for a continuous fluid, especially at high density. In order to achieve a better description of the hard-sphere system, a further improvement, which the authors have been developing, consists of adding to the expression for $c(r)$ given by Eq. (1) outside the core a nonvanishing contribution $c_{\mathrm{HS}}(r)$. For instance, $c_{\mathrm{HS}}(r)$ can be a second Yukawa tail, with amplitude and range determined in such a way that the resulting thermodynamics of the hard-sphere fluid is given by the Carnahan–Starling equation of state [1]. This generalization appears to be fully feasible, since many of the algebraic manipulations valid for a $c(r)$ with a Yukawa tail still hold when $c(r)$ is a combination of two Yukawas [14]. If one is interested only in the thermodynamics of the fluid rather than its structure, one can estimate the effect of using a more accurate hard-sphere theory by simply replacing the PY hard-sphere contribution by the Carnahan–Starling contribution [1] in the initial condition of Eq. (8) for $\beta = 0$. This is what has been done to obtain the results reported here. Of course, on theoretical grounds, the as-yet-to-be-evaluated version of the SCOZA, which allows for a further contribution $c_{\mathrm{HS}}(r)$ to $c(r)$ for $r > \sigma$ in Eq. (1), will yield the most reliable of our Yukawa-sphere results. (In this connection, see the Note Added in Proof and the results in Ref. 23.)

The critical point has been located by finding the highest temperature at which there is a divergence of the compressibility. For an inverse range $z = 1.8$, we obtain $\rho_c^* = 0.315$ and $T_c^* = 1.216$. Describing the hard-sphere contribution by the PY equation yields $\rho_c^* = 0.308$ and $T_c^* = 1.201$. In Table I the critical density and temperature are compared with the results from different theories [4] and Monte Carlo (MC) simulations [15, 16].

**Table I.** Critical Constants for the Hard-Sphere + Yukawa Fluid ($z = 1.8$)

| | MC[a] | MC[b] | SCOZA[c] | $\mathrm{MSA}_{\mathrm{comp}}$[d] | HMSA[e] | MHNC[e] |
|---|---|---|---|---|---|---|
| $\rho_c^*$ | 0.294 | 0.313 | 0.315 | 0.308 | 0.36 | 0.28 |
| $T_c^*$ | 1.192 | 1.178 | 1.216 | 1.031 | 1.25 | 1.21 |

[a] From Ref. 15.
[b] From Ref. 16.
[c] Using Carnahan–Starling hard-sphere contribution (see text).
[d] This work (from the compressibility route).
[e] From Ref. 4.

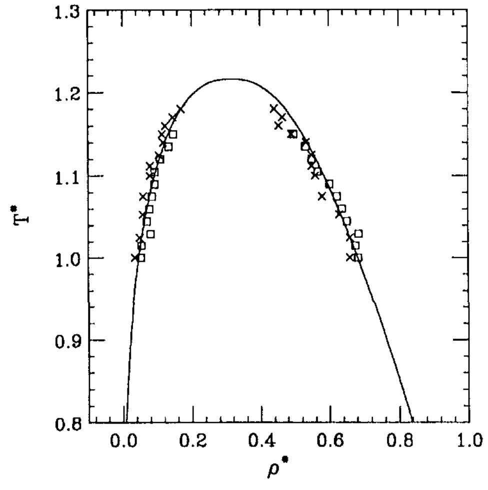

**Fig. 3.** Coexistence curve of the Yukawa fluid in the $\rho^* - T^*$ plane for an inverse range parameter $z = 1.8$. (——) SCOZA with Carnahan Starling reference-system thermodynamics (see text). (×) MC simulation by Smit and Frenkel [15]. (□) MC simulation by Lomba and Almarza [16].

The agreement with the simulation results seems quite satisfactory, although the relatively large discrepancy between the two simulations does not allow for as sharp a comparison as in the lattice-gas case. A similar consideration holds for the coexistence curve, which is reported in Fig. 3, together with the MC results. It is worthwhile observing that the coexistence curve given by the SCOZA extends up to the critical point, which is not the case with other theories [4]. In Table II the compressibility factor

**Table II.** Compressibility Factor $PV/(Nk_BT)$ for the Hard-Sphere + Yukawa Fluid ($z = 1.8$)

| $T^*$ | $\rho^*$ | MC[a] | SCOZA[b] | LOGA/ORPA$_{en}$[c] |
|---|---|---|---|---|
| 2.0 | 0.4 | 1.08 | 1.123 | 1.118 |
| 2.0 | 0.6 | 2.04 | 1.981 | 1.974 |
| 2.0 | 0.8 | 4.27 | 4.436 | 4.432 |
| 1.5 | 0.4 | 0.69 | 0.671 | 0.663 |
| 1.5 | 0.6 | 1.21 | 1.225 | 1.214 |
| 1.5 | 0.8 | 3.31 | 3.336 | 3.330 |

[a] From Ref. 17.
[b] Using Carnahan–Starling (see text).
[c] From Ref. 18 (energy route).

is compared with the results from MC simulations [17] and from a numerical evaluation [18] of a result which is the lowest order gamma-ordered approximation (LOGA) as well as the optimized random-phase approximation (ORPA). The LOGA/ORPA theory is known to be good in the moderate-to-high-density regime sampled in that table [19].

One of the most interesting aspects of the Yukawa hard-core fluid is the effect of the range of the attractive potential [determined by the parameter $z$ in Eq. (7)] upon the thermodynamics of the fluid. This manifests itself in two quite separate ways—the location of the critical point, which shifts to progressively higher densities as $z$ increases, and the behavior of the effective critical exponents. The smaller $z$ is, the closer one expects the critical exponents to approach their mean-field values as one approaches the critical point before crossing over to their limiting values. We observe both effects in our SCOZA results. We intend to give these results in future publications.

## 5. CONCLUSIONS

Results for the nearest-neighbor attractive-lattice gas and preliminary results for the Yukawa fluid suggest that the SCOZA is a quite reliable liquid-state theory, which promises to yield both overall accurate results for the thermodynamics and the correlations and a precise location of the critical point and of the coexistence curve. The spherical-model character of its critical behavior is detectable only in a very narrow region above the critical point. This approach can also be extended to a variety of different models; for instance, the theory has been recently formulated also for a fluid in a porous medium [20] and for the $D$-vector model, i.e., a spin system with spin dimensionality $D$ greater than one [21].

## NOTE ADDED IN PROOF

After this paper was completed we were able to obtain analytically some asymptotic results for the SCOZA critical behavior below $T_c$. They are not spherical-model-like. In particular, $\beta_{\text{coex}} = 7/20$, where $\beta_{\text{coex}} = \lim_{t \to 0} \beta_{\text{eff}}$. Reference 22 includes a brief description of those new results; a report giving their full derivation is in preparation. In Ref. 23 we have also evaluated and described in detail the version of SCOZA mentioned in Section 4, in which $c_{\text{HS}}(r)$ is not set equal to zero for $r > \sigma$. In that same reference, new simulation results of high precision obtained for the hard-core Yukawa fluid using finite-size scaling techniques are presented and compared with our SCOZA results. Finally, for further applications of the SCOZA to several other models, see Refs. 24–26.

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