Thermodynamically self-consistent liquid state theories for systems with bounded potentials

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The mean spherical approximation (MSA) can be solved semi-analytically for the Gaussian core model (GCM) and yields – rather surprisingly – exactly the same expressions for the energy and the virial equations. Taking advantage of this semi-analytical framework, we apply the concept of the self-consistent Ornstein-Zernike approximation (SCOZA) to the GCM: a state-dependent function $K$ is introduced in the MSA closure relation which is determined to enforce thermodynamic consistency between the compressibility route and either the virial or energy route. Utilizing standard thermodynamic relations this leads to two different differential equations for the function $K$ that have to be solved numerically. Generalizing our concept we propose an integro-differential-equation based formulation of the SCOZA which, although requiring a fully numerical solution, has the advantage that it is no longer restricted to the availability of an analytic solution for a particular system. Rather it can be used for an arbitrary potential and even in combination with other closure relations, such as a modification of the hypernetted chain approximation.

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I. INTRODUCTION

It is meanwhile well-known and widely documented that conventional integral equation theories – such as the Percus-Yevick (PY), the hypernetted chain (HNC), or the mean spherical (MSA) approximation – are thermodynamically inconsistent, which means that the various thermodynamic routes to calculate the dimensionless equation of state lead to significantly different results. Over the past decades considerable effort has been devoted to the formulation of thermodynamically self-consistent liquid state theories, which, in turn, have led to an improved description of the structural and thermodynamic properties of liquids with harshly repulsive potentials. In the first generation of these concepts, such as the Rogers-Young (RY), the modified hypernetted chain (MHNC), or the Zerah-Hansen approach, simple functions were introduced in the respective closure relations to the Ornstein-Zernike (OZ) equation which use a pointwise adjustable but not explicitly state-dependent parameter to interpolate between the conventional closures. Since self-consistency was enforced for each state point independent of the neighboring ones, we shall call this approach locally self-consistent. The concepts of the second generation of the self-consistent liquid state theories were based on more sophisticated ideas: the SCOZA scheme introduced an explicitly state-dependent function in the MSA closure relation to the OZ-equation in order to enforce thermodynamic self-consistency between different thermodynamic routes; the hierarchical reference theory (HRT), on the other hand, successfully merged ideas of microscopic liquid state theory and renormalization group concepts. In both these advanced liquid state approaches thermodynamic consistency was enforced in the entire space of system parameters, which we shall call global self-consistency.

In recent years, increasing effort has been devoted to investigations of the structural and thermodynamic properties of soft matter systems. The interactions in such systems either diverge weakly or even remain finite (“bounded”) at short distances, i.e., when particles overlap. These potentials are commonly referred to as soft potentials. Initially, they were investigated by means of conventional and, more recently, by means of locally self-consistent integral-equation theories. However, the advanced liquid state theories mentioned above have not been generalized to systems with soft potentials so far. The HRT concept, for instance, relies on the known properties of a suitable reference system. While for systems with strongly repulsive interactions the hard-core (HC) liquid represents an obvious and very successful choice, no such reference system can be identified for liquids with soft potentials. We therefore have to rule out HRT, at least for the time being.

On the other hand, applications of the SCOZA-concept to liquid systems were up to now restricted to those cases where the respective interactions can be expressed as a combination of HC potentials with an adjacent linear combination of Yukawa-tails (HCY-systems). This restriction can be traced back to the fact that the rather elaborate SCOZA-formalism is intricately linked to the availability of the analytic solution of the MSA for such a system. From this point of view the obvious counterpart of HCY systems in soft matter is the Gaussian core model (GCM). For this system the pair potential is given by

$$\Phi(r) = \epsilon \exp[-(r/\sigma)^2],$$

where $\epsilon$ is an energy- and $\sigma$ a length-parameter.
Within the framework of the MSA (in the case of soft potentials sometimes also termed random phase approximation), the structural and thermodynamic properties of the GCM can to a large extent be expressed semi-analytically. In this contribution we extend the SCOZA formalism to the GCM.

The GCM can be interpreted as a simple model to describe soft matter. It has been pointed out that, for example, the effective (coarse-grained) interaction between two isolated non-intersecting polymer chains or dendritic macromolecules can, to a very good approximation, be represented by the GCM potential. It is for two reasons that this potential represents an ideal candidate to apply the concept of global thermodynamic self-consistency to systems with soft potentials: (i) as we will show, two of the three traditional thermodynamic routes, i.e., the energy and the virial route, coincide exactly for the GCM within the MSA, a fact that, to the best of our knowledge, has not been documented in literature so far; there is even evidence that this also holds true for other systems with soft potentials. Therefore, thermodynamic self-consistency has to be enforced between two routes only, which considerably facilitates the theory. (ii) Using the analytic expressions given by the MSA to enforce thermodynamic consistency for the GCM it is possible to derive, via standard thermodynamic relations, either an ordinary (ODE) or a partial (PDE) differential equation for the state-dependent function introduced in the closure relation of the SCOZA. The ODE results from combining the virial and compressibility route and can be solved for each isothermal line independently. The PDE enforces consistency between the energy and compressibility route and relates both density- and temperature-derivatives. These two differential equations, although of different complexity, have to be solved numerically and lead within numerical accuracy to consistent results. In addition, we propose an equivalent, integro-differential-equation (IDE) based formulation of the SCOZA, which also has to be solved numerically. This latter approach has the advantage that it can be used for an arbitrary (soft) potential and in combination with closure relations other than the MSA, such as e.g. a HNC-based SCOZA ansatz; thus, it is no longer restricted to systems where semi-analytic solutions of liquid state theories are known.

The rest of the paper is organized as follows: in Sec. [II] we re-visit the MSA for the GCM, providing thus the basis for the (semi-)analytic formulation of the SCOZA. In Sec. [III] we present the ideas of SCOZA and derive the two differential equations and the IDE that impose self-consistency and in Sec. [IV] we present details about the numerical solution strategies. Sec. [V] is devoted to a detailed discussion of the SCOZA results and a comparison with MC simulation data. Finally, in Sec. [VI] we summarize and draw our conclusions.

II. MSA

For the GCM, semi-analytic expressions for the static and thermodynamic properties can be derived within the MSA. Here we add a few details that have not been documented yet.

The MSA closure relation to the Ornstein-Zernike (OZ) equation,

\[
h(r) = c(r) + g \int \, dr' \, h(|r - r'|) \, c(r'), \quad (2)
\]

where \( h(r) \) and \( c(r) \) are the total and the direct correlation functions and \( g \) is the number density of the system, was originally proposed for systems for which the pair potential consists of a HC interaction with diameter \( \sigma \) plus a tail that can take different functional forms. For such potentials, the MSA consists of an ansatz for \( c(r) \),

\[
c(r) = -\beta \Phi(r) \quad \text{for } r > \sigma, \quad (3)
\]

where \( \beta = (k_B T)^{-1} \), \( T \) is the temperature and \( k_B \) Boltzmann’s constant, along with the so-called core condition that expresses the impenetrability of the particles

\[
g(r) = 0 \quad \text{for } r < \sigma. \quad (4)
\]

Here, \( g(r) = h(r) + 1 \) is the radial distribution function (RDF).

As soft potentials lack a hard core, Eq. (4) cannot be applied anymore and the MSA reduces to

\[
c(r) = -\beta \Phi(r) \quad \text{for all } r. \quad (5)
\]

For the specific case of the GCM, where \( \Phi(r) \) is a simple Gaussian, this immediately leads to an analytic expression for the static structure factor, \( S(q) \),

\[
S(q) = [1 - q \hat{c}(q)]^{-1} = \frac{1}{1 + \alpha \exp[-(q^2 \sigma^2/4)]} \quad (6)
\]

where the hat denotes a Fourier transform, \( q \) is the wave vector, and \( \alpha = \pi^{3/2} \sigma^{3} \beta \epsilon \). For the RDF we find

\[
g(r) = 1 - \frac{\alpha}{q} \frac{1}{8 \pi^3} \int dq \, e^{-iqr} \frac{1}{e^{q^2 \sigma^2/4} + \alpha}; \quad (7)
\]

in particular

\[
g(0) = 1 + \frac{\beta \epsilon}{\alpha} \text{Li}_{3/2}(-\alpha). \quad (8)
\]

Here, \( \text{Li}_n(x) \) is the polylogarithm of order \( n \) which is discussed in detail in the Appendix.
Further, the thermodynamic properties of the GCM can be calculated semi-analytically using one of the usual three thermodynamic routes. The results for the dimensionless equation of state, \( \beta P/\rho \), where \( P \) is the pressure, obtained via the compressibility route ('C')

\[
\left( \frac{\beta P}{\rho} \right)_C^\alpha = 1 + \frac{1}{2} \alpha
\]

(9)

and the virial route ('V')

\[
\left( \frac{\beta P}{\rho} \right)_V^\alpha = 1 + \frac{1}{2} \alpha - \beta \varepsilon N(\alpha),
\]

(10)

where

\[
N(\alpha) = \frac{1}{2} \left[ \text{Li}_{3/2}(\alpha) - \text{Li}_{1/2}(\alpha) \right]
\]

(11)

have already been reported in.\(^9\)\(^6\)\(^3\)

The energy route ('E') has not been considered in the literature so far. To obtain \( \beta P/\rho \) we first calculate the excess (over ideal gas) internal energy per particle, \( U^\text{ex}/N \),

\[
\frac{\beta U^\text{ex}}{N} = 2\pi \int_0^\infty dr \Phi(r) g(r) r^2 = \frac{\alpha}{2} \frac{\beta \varepsilon}{2\alpha} \left[ \alpha + \text{Li}_{3/2}(\alpha) \right],
\]

(12)

from which we obtain the excess free energy per particle, \( F^\text{ex}/N \),

\[
\frac{\beta F^\text{ex}}{N} = \int_0^\beta \frac{\beta U^\text{ex}(\beta', \rho)}{N} = \frac{\alpha}{2} \frac{\beta \varepsilon}{2\alpha} \left[ \alpha + \text{Li}_{5/2}(\alpha) \right],
\]

(13)

and, finally, the equation of state

\[
\left( \frac{\beta P}{\rho} \right)_E^\alpha = 1 + \rho \frac{\partial}{\partial \rho} \left( \frac{\beta F^\text{ex}}{N} \right) = 1 + \frac{1}{2} \alpha - \beta \varepsilon N(\alpha).
\]

(14)

Thus we find that virial and energy route lead exactly to the same expressions for the dimensionless equation of state. This is certainly an unexpected and atypical result. In fact, in our numerical investigations of similar bounded systems in combination with other closure relations, we have observed an analogous, remarkable coincidence of the virial and the energy route. To what extent this behavior is a general feature of soft systems remains to be investigated. For those systems where virial and energy route do coincide, this greatly facilitates the formulation of thermodynamically self-consistent integral equation theories, since consistency has to be enforced only either between the virial and the compressibility or between the energy and the compressibility route.

### III. SCOZA

The original formulation of the SCOZA for HC systems\(^6\) is based on the MSA. It enforces the RDF to vanish inside the core and for distances larger than the core diameter sets the direct correlation function proportional to the potential; the proportionality factor contains a state-dependent function that imposes thermodynamic consistency. Following the same scheme used to generalize the MSA to soft potentials (cf. Sec. III), we modify the original SCOZA ansatz:

\[
c(r) = \beta K(\rho, \beta) \Phi(r) \quad \text{for all } r,
\]

(15)

where \( K(\rho, \beta) \) is an as yet undetermined, state-dependent function. As the MSA is recovered for \( K(\rho, \beta) \equiv -1 \), the present formulation of the SCOZA takes advantage of the availability of the semi-analytic solution of the MSA for the GCM presented in the preceding subsection.

Thus, closed expressions can be derived for the thermodynamic properties within the SCOZA. To simplify the notation we introduce a function \( \hat{\alpha}(\rho, \beta) = \pi^{3/2} / \rho \alpha^3 \beta \varepsilon K(\rho, \beta) = \alpha K(\rho, \beta) \), which is explicitly state-dependent, but for simplicity suppress the arguments of \( \hat{\alpha} \) in the following.

According to the compressibility route the density derivative of the equation of state is given by

\[
(\chi^\text{C}_{\text{red}})^{-1} = (\rho k_B T \chi^\text{C}_T)^{-1} = 1 - \rho \hat{c}(0) = 1 - \hat{\alpha},
\]

(16)

where \( \chi^\text{C}_T \) is the isothermal compressibility and the reduced isothermal compressibility \( \chi^\text{C}_{\text{red}} \) is the zero wavevector value of the structure factor \( S(q) \).

Further, following the virial route one finds the following expression for the dimensionless equation of state

\[
\left( \frac{\beta P}{\rho} \right)_V^\alpha = 1 - \frac{2\pi}{3} \rho \int_0^\infty dr r^2 \frac{d\Phi(r)}{dr} g(r)
\]

\[
= 1 + \frac{1}{2} \alpha - \frac{\beta \varepsilon}{2\alpha} \left[ \text{Li}_{3/2}(\hat{\alpha}) - \text{Li}_{3/2}(\hat{\alpha}) \right]
\]

(17)

Finally, according to the energy route the dimensionless excess energy per particle is given by

\[
\frac{\beta U^\text{ex}}{N} = \frac{1}{2} \alpha + \frac{\beta \varepsilon}{2\alpha} \left[ \text{Li}_{3/2}(\hat{\alpha}) - \hat{\alpha} \right].
\]

(18)

The energy and the virial route already coincide within the MSA and this also holds for the SCOZA. We are therefore left with one single inconsistency, which can be removed either via the virial/compressibility or via the energy/compressibility route; both possibilities will be considered in the following subsections.
A. Virial- and compressibility-route

We start by calculating the compressibility via the virial route, \( \chi_T^V \), which is achieved by differentiating Eq. (17) with respect to \( \varrho \),

\[
\left( \frac{\partial \beta P}{\partial \varrho} \right)^V = 1 + \alpha - \frac{1}{2\sigma^3\pi^{3/2}K(\varrho, \beta)^2} \left\{ \begin{array}{c}
K(\varrho, \beta) \left[ \operatorname{Li}_{3/2}(\tilde{\alpha}) - \operatorname{Li}_{1/2}(\tilde{\alpha}) \right] \\
+ \frac{\partial K(\varrho, \beta)}{\partial \beta} \left[ 2\operatorname{Li}_{3/2}(\tilde{\alpha}) - \operatorname{Li}_{5/2}(\tilde{\alpha}) - \operatorname{Li}_{1/2}(\tilde{\alpha}) \right] \end{array} \right\}.
\]

Equating this result with the compressibility as obtained via the compressibility route \( \Rightarrow \) leads to the following ODE for the unknown function \( K(\varrho, \beta) \):

\[
\frac{\partial K(\varrho, \beta)}{\partial \varrho} = \frac{K(\varrho, \beta) \left\{ 2\pi^3 \beta \varrho^2 \sigma^6 K(\varrho, \beta) \left[ K(\varrho, \beta) + 1 \right] - \left[ \operatorname{Li}_{3/2}(\tilde{\alpha}) - \operatorname{Li}_{1/2}(\tilde{\alpha}) \right] \right\}}{\varrho \left[ 2\operatorname{Li}_{3/2}(\tilde{\alpha}) - \operatorname{Li}_{5/2}(\tilde{\alpha}) - \operatorname{Li}_{1/2}(\tilde{\alpha}) \right]}.
\]

Note that this ODE can be solved for each isothermal line separately.

Analyzing the ODE, we note that the right hand side (RHS) of Eq. (20) contains two singularities. Obviously the denominator vanishes for \( \varrho \to 0 \), but expanding numerator and denominator around \( \varrho = 0 \), we find that

\[
K(\varrho = 0; \beta) = -\frac{4\sqrt{2}}{4\sqrt{2} + \beta \varepsilon}.
\]

Further, the denominator also vanishes at \( \tilde{\alpha} = \tilde{\alpha}_0 \approx -7.7982 \). This, however, turns out to be a removable singularity which can be treated by appropriate means (cf. subsection IV A).

B. Energy- and compressibility-route

To enforce thermodynamic consistency between the energy and compressibility route we utilize the variant of the SCOZA-formalism proposed in\(^19,20\) which brought along a breakthrough of this concept for systems with repulsive potentials. This approach is based on replacing the differential equation for \( K(\varrho, \beta) \) by one for the excess energy density \( u = U^e/V \). To this end, we consider the following thermodynamic relation (see, e.g.,\(^21\))

\[
\frac{\partial}{\partial \beta} \left( \frac{1}{\chi_{\text{red}}(u)} \right) = \varrho \frac{\partial^2 u}{\partial \varrho^2}.
\]

Expressing at constant density \( \chi_{\text{red}}^E \) as a function of \( u \), the left hand side can be rewritten as

\[
\frac{\partial}{\partial \beta} \left( \frac{1}{\chi_{\text{red}}^E(u)} \right) = \frac{\partial}{\partial u} \left( \frac{1}{\chi_{\text{red}}^E(u)} \right) \frac{\partial u}{\partial \beta},
\]

so that finally Eq. (22) becomes

\[
\frac{\partial u}{\partial \beta} = \left[ \frac{\partial}{\partial u} \left( \frac{1}{\chi_{\text{red}}^E(u)} \right) \right]^{-1} \frac{\varrho}{\partial \varrho^2} \frac{\partial^2 u}{\partial \varrho^2}.
\]

In contrast to Eq. (20), this relation contains derivatives with respect to both \( \varrho \) and \( \beta \) and is a PDE of the diffusion type. However, the diffusivity, \( D(\varrho, \beta, \chi_{\text{red}}(u)) = \left[ \frac{\partial}{\partial u} \left( \frac{1}{\chi_{\text{red}}^E(u)} \right) \right]^{-1} \), is state-dependent\(^\circ\) and turns out to be negative which renders the numerical solution extremely intricate. \( \chi_{\text{red}}(u) \) is now identified with the expression obtained by the compressibility route (16)

\[
\left[ \chi_{\text{red}}^C(u) \right]^{-1} = 1 - \tilde{\alpha},
\]

where \( K(u) \) is determined by inverting the result of the energy route

\[
u = \frac{\varrho}{\beta} \left\{ \frac{1}{2} \alpha + \frac{\beta \varepsilon}{2\tilde{\alpha}} \left[ \operatorname{Li}_{3/2}(\tilde{\alpha}) - \tilde{\alpha} \right] \right\}.
\]
C. Integro-differential equation approach

So far, in deducing the SCOZA-ODE \cite{24} and PDE \cite{23}, we have taken advantage of the availability of the semi-analytic framework provided by the MSA for the properties of the GCM. Unfortunately, this represents a rather singular exception. In order to eliminate the restrictions resulting from this fact one may ask whether the SCOZA-concept may be formulated for the general case, i.e., when a semi-analytic solution to the MSA is not at hand. This is indeed possible as we show in the following: let us assume a SCOZA-type closure relation, i.e.,

\[ c(r) = \beta \bar{K} \Phi(r) \quad \text{for all } r. \quad (27) \]

Once \( \bar{K} \) is specified, this leads in combination with the OZ equation directly to the radial distribution function

\[ g(r) = g(r; \varrho, \beta; \bar{K}), \]

which is thus also a function of \( \bar{K} \). If we assume \( \bar{K} \) to be explicitly state-dependent, i.e., \( \bar{K} = \bar{K}(\varrho, \beta) \), the compressibility as determined by the virial route, i.e., differentiating the standard virial equation of state, is

\[
\left[ \frac{\beta \Phi(r)}{3 \varrho} \right]^{-1} = 1 - \frac{4 \pi}{3} \varrho \int_0^\infty dr r^3 \frac{d\beta \Phi(r)}{dr} g(r; \varrho, \beta; \bar{K}) - \frac{2 \pi}{3} \varrho^2 \int_0^\infty dr r^3 \frac{d\beta \Phi(r)}{dr} \frac{\partial g(r; \varrho, \beta; \bar{K})}{\partial \varrho}
\]

\[
- \frac{2 \pi}{3} \varrho^2 \frac{\partial \bar{K}}{\partial \varrho} \int_0^\infty dr r^3 \frac{d\beta \Phi(r)}{dr} \frac{\partial g(r; \varrho, \beta; \bar{K})}{\partial \bar{K}}.
\quad (28)
\]

Thermodynamic self-consistency between the virial and the compressibility route is now enforced by choosing the mixing parameter \( \bar{K} \) such that \( \chi^V_T \) is equal to \( \chi^G_T \), i.e., by finding at fixed temperature \( T \) a root of the function

\[ f(\bar{K}) = \chi^C_T - \chi^G_T. \quad (29) \]

Here, derivatives with respect to \( \varrho \) and \( \bar{K} \) have to be calculated numerically (see below).

It was exactly this idea that was realized in previous applications of parameterized closure relations such as RY, HMSA, or MHNC. However, consistency was then achieved only locally, i.e., considering each state point in isolation and neglecting thus the density dependence of \( \bar{K} \). This corresponds to setting \( \partial \bar{K} / \partial \varrho = 0 \) and dropping the last term in Eq. (28). In the present approach, in contrast, we consider \( \bar{K} \) to be explicitly state-dependent; this term is retained. Thus, the consistency criterion involves not only isolated state points but also via the density derivative nearby state points; therefore, we have chosen to call the criterion a global one. The quantitative difference between the local and the global approaches will be discussed below.

D. HNC-based SCOZA

The above approach to thermodynamic consistency represents an IDE based re-formulation of the SCOZA; it is not only entirely independent of the semi-analytic solution provided by the MSA for the GCM and thus becomes completely general in the sense that in this formulation self-consistency can now be enforced for systems with arbitrary (soft) potentials and in combination with other, parameterized closure relations.

To demonstrate the power of this idea we introduce a HNC-based SCOZA (for clarity we will refer to the SCOZA approach introduced above “conventional SCOZA”). This particular choice is motivated by the fact that the HNC has been found to work very well for the GCM and other soft potentials \cite{9, 16}. For the closure relation of our HNC-based SCOZA we propose

\[ g(r) = \exp(\beta \bar{K}_{\text{HNC}}(\varrho, \beta) \Phi(r) + h(r) - c(r)), \quad (30) \]

where the unknown, state-dependent function \( \bar{K}_{\text{HNC}}(\varrho, \beta) \) is determined such as to make the RHS of the consistency requirement \cite{29}, i.e., the equality between the compressibility and the virial route, vanish. Numerically, this is achieved by solving Eq. (28), where \( g(r; \varrho, \beta; \bar{K}_{\text{HNC}}) \) is now obtained from the solution of the OZ-equation along with the closure relation (30).
generally very well except for those state points where the expression in the square brackets of the denomi-
ator of the RHS of Eq. (20) vanishes. A closer analysis shows that this singularity at \( \dot{\alpha} = \dot{\alpha}_0 \) is removable, since both numerator and denominator vanish simultaneously. In fact, splitting the density range in two regions, de-
pending on whether \( \tilde{\alpha} \) is smaller or larger than \( \dot{\alpha}_0 \), and integrating the ODE “forward” \( \text{starting at } \varrho = 0 \) with initial value \( \varrho = 0 \) in the former and “backward” \( \text{from a sufficiently high density so that } K = -1 \) in the latter, we were able to smoothly join the partial solutions at \( \tilde{\alpha} = \tilde{\alpha}_0 \) and thus to obtain \( K(\varrho, \beta) \) over the entire density range. We point out that reliable solutions of this ODE can only be obtained if an efficient and accurate evaluation of the polylogarithm is guaranteed (see Appendix). \( K(\varrho, \beta) \) as a function of \( \varrho \) and \( \beta \) is displayed in Figure 2; the results will be discussed in Sec. V.

Alternatively, we have also solved this ODE with \textsc{Mathematica} using a Livermore solver for ordinary differential equations with automatic method switching \( \text{(LSODA)} \). The polylogarithms encountered in the RHS of Eq. (20) are evaluated in \textsc{Mathematica} with high accuracy (for details see\textsuperscript{22}). Although the differential-equation-solver package is not able to deal properly with the removable singularity noted above and breaks down for \( \tilde{\alpha} \sim \tilde{\alpha}_0 \), outside this small range, \textsc{Mathematica} provides quasi-exact reference data for the function \( K(\varrho, \beta) \).

### B. PDE approach

From the numerical point of view, solving the diffusion-
type SCOZA-PDE \( \text{(21)} \) is a delicate task. Boundary con-
ditions at \( \varrho = 0 \) and at a large, but finite \( \varrho_{\text{max}} \), as well as an initial condition at \( \beta = 0 \) are required. In par-
ticular the boundary condition at \( \varrho_{\text{max}} \) has to be chosen care-
fully. In contrast to HC systems, where boundary condi-
tions follow naturally from the existence of a max-
imum density, particles that interact via bounded po-
tentials can fully overlap and thus it is possible to com-
press the system to arbitrary high densities. For this re-
region, we know that the MSA becomes exact and thus self-consistent\textsuperscript{16}, i.e., \( K(\varrho = \infty, \beta) = -1 \). In numerical calculations, however, we are forced to set \( K = -1 \) at some finite maximum density \( \varrho_{\text{max}} \). Furthermore, we have to face the problem of a state-dependent diffusivity \( D(\varrho, \beta) \). Since this quantity is even negative, not only the solution to the PDE but any numerical error incurred in obtaining it may be expected to grow exponentially. Among other things, small errors made in the formula-
lation of the boundary conditions and the inversion of the highly non-linear relation \( \text{(26)} \) to determine \( D(\varrho, \beta) \) will eventually get dominant. Together, these difficulties make it practically impossible to reliably solve this PDE. Taking on the other hand \( K(\varrho, \beta) \) as obtained from the ODE \( \text{(20)} \) and inserting it into Eq. \( \text{(24)} \), we find that this relation is fulfilled very accurately, which proves the numerical consistency of the two differential equations approaches to the SCOZA.

### C. IDE approach

The IDE based formulation of the SCOZA, i.e., equations \( \text{(21)} \) along with \( \text{(25)} \), has been solved iteratively using both the conventional \( \text{(24)} \) and the HNC-based closure \( \text{(31)} \). We introduce a density-grid (with spacing \( \Delta \varrho \)) and assume a starting value \( K = -1 \). We solve the OZ equation with the appropriate closure relation using stan-
ard integral-equation solver algorithms for a given state point (i.e., we fix \( \varrho \) and \( \beta \) and the neighboring density-values (i.e., for \( \varrho \pm \Delta \varrho \)). Thus, the derivatives in the RHS of Eq. \( \text{(25)} \) can be calculated numerically. Due to the appearance of the derivative \( \partial K/\partial \varrho \), Eq. \( \text{(25)} \) has to be solved iteratively and leads then to \( K(\varrho, \beta) \) for the entire density range considered. As a consequence of the iterative and purely numerical character of the solution strategy, this approach is more time consuming than the solution of the ODE \( \text{(20)} \).

### D. Monte Carlo simulations

To test the reliability of our integral equation results we have generated reference data for the GCM by means of standard Monte Carlo (MC) simulations in the canoni-
ical ensemble. For each thermodynamic state considered, we started from a random configuration of \( N = 1000 \) particles. The system was at first allowed to equilibrate for 10 000 passes, where a pass consists of \( N \) trial moves, i.e., on average each particle has been subjected to a trial move once. After that, we have carried out production runs of another 150 – 300 000 passes to calculate the de-
sired ensemble averages.

### V. RESULTS

We start the discussion of our results by specifying the range in \( (\varrho, \beta) \)-space where the MSA and the SCOZA provide unphysical results, i.e., where \( g(r) \) is negative (see Figure 1). While this failure of the MSA was briefly addressed in\textsuperscript{16}, we think that a more quantitative analysis is in order, since similar problems might be encountered in applications of the MSA (and of related concepts) to other systems with soft potentials. In fact, also for the SCOZA unphysical results can be obtained for certain system parameter combinations. For the MSA the limits of this range of unphysical behaviour are easily deter-
m\textit{m}ined via Eq. \( \text{(3)} \), and for the SCOZA they are found from the equivalent, generalized expression (i.e., replacing \( \alpha \) by \( \tilde{\alpha} \)). Results are shown in Figure 1, indicating that at low temperatures the MSA and the SCOZA both become unphysical if the density is reduced below some threshold density \( \varrho = \varrho(\beta) \). It is interesting to note that similar problems of unphysical solutions and
becomes exact and thus self-consistent. While in 
16
in
tent. At high densities we confirm earlier results reported
regions where the MSA is thermodynamically inconsis-
stantially from this value at low densities (with a pro-
K
– equivalent results.

Thus restricted applicability have also been reported for
other self-consistent schemes, such as the RY- or the zero-

The state-dependent function \( K(\rho, \beta) \) which guaran-
tees in the SCOZA-scheme full thermodynamic self-
consistency, i.e., between all three thermodynamic routes
is depicted in Figure 2 in a representative part of the pa-
parameter space. Detailed numerical investigations have
shown that all three SCOZA formulations presented in
the previous chapters provide – within numerical accu-
ry and despite different levels of numerical complexity –
equivalent results.

Bearing in mind that the MSA is recovered for
\( K(\rho, \beta) \equiv -1 \), we observe that this function differs sub-
stantially from this value at low densities (with a pro-
nounced temperature-dependence), thus indicating those
regions where the MSA is thermodynamically inconsis-
tent. At high densities we confirm earlier results reported
in \( 9,16 \), which have stated that in this regime the MSA
becomes exact and thus self-consistent. While in \( 16 \) this
conclusion was based on an analysis of the large density-

For the HNC-based SCOZA, the corresponding func-
tion, \( K_{\text{HNC}}(\rho, \beta) \) is shown in Figure 3. Taking the devia-
tion of this function from \(-1\) as a measure of the thermo-
dynamic inconsistency of the simple HNC-approach (sim-
lar to the case of the MSA), we observe that the HNC
is to a large degree self-consistent. It is only at small
densities and low temperatures that \( K_{\text{HNC}}(\rho, \beta) \) slightly
deviates from \(-1\). This large degree of thermodynamic self-consistency of the HNC for systems with bounded
potentials was already observed for selected state points
in \( 9,16 \), but was never demonstrated on a quantitative level
for a wider range of system parameters.

We conclude our discussion of the thermodynamic self-
consistency of the conventional (MSA-based) and the
HNC-based SCOZA concepts by a direct comparison be-
tween local and global self-consistency, as defined in sub-
section III C. Let \( K(\rho, \beta) \) denote the explicitly state-
dependent function \( K(\rho, \beta) \), as introduced to enforce
thermodynamic self-consistency in the IDE formulation of
the (MSA- or HNC-based) SCOZA (cf. Sec. III C);
thus, the subscript ‘g’ stands for global self-consistency.
On the other hand, if the last term in Eq. (28) is ne-
glected thermodynamic self-consistency is only enforced
for a single, isolated state point and in this case we de-
note the function by \( K_{l}(\rho, \beta) \) (local self-consistency). In
Figure 4 we show the relative difference between these
functions for the conventional SCOZA and we observe that
it amounts to a few percent only for small densities,
even down to intermediate temperatures. Figure 5 shows
the same function for the HNC-based SCOZA. Here, the
differences become noticeable only at small densities and
low temperatures. Thus, over a large parameter range lo-
cal consistency is in both cases already a good substitute
for global consistency.

We now turn to the structural properties of the GCM
by comparing the RDFs for two different thermodynamic states. In Figure 6 we have chosen a state-point close to the boundary where the SCOZA becomes unphysical (cf. Figure 4). We observe that compared to the MC reference data, the conventional SCOZA does bring along a slight improvement over the MSA. On the other hand, the results provided by the HNC and the HNC-based SCOZA both reproduce the MC-data perfectly. Figure 7 shows the RDF for the GCM at a low temperature and low density. Here, we are in the regime where both the MSA and the MSA-based SCOZA provide unphysical results. We see that while the conventional HNC results already reproduce the MC data rather well, the HNC-based SCOZA leads to a perfect agreement with the simulations. We conclude, that although the MSA-based SCOZA for the GCM does not bring along the same improvement for the structural properties as documented for HCY-systems, the concept of self-consistency by itself proves to be of great value when used with a closure better adapted to bounded potentials, i.e., a HNC-based closure.

Finally, we examine some thermodynamic properties and start our discussion by presenting a rather surprising result: if we plot the quantity $ω σ^3 / ε$ as a function of the density, then the curves evaluated for different isothermal lines practically coincide (cf. Figure 8); even though we present only the conventional SCOZA, we note that this coincidence is also observed for the MSA, the HNC, and the HNC-based SCOZA. This remarkable scaling behavior might be worth being the subject of future investigations.

We conclude this section with the results for the dimensionless equation of state, $β P / ρ$, for two different temperatures, i.e., $k_B T / ε = 10$ (see Figure 9) and $k_B T / ε = 0.1$ (see Figures 10 and 11). For $k_B T / ε = 10$, we find that the SCOZA-results coincide with high accuracy with the MC-data. For $k_B T / ε = 0.1$ we observe (Figure 10) that the conventional SCOZA provides data that are obviously very close to those obtained by simulations, while the HNC-based SCOZA data fit them perfectly. A more thorough comparison, including this time also other liquid state theories, such as the MSA, the PY, or the HNC approximations, is displayed on an enlarged scale in
Motivated by the success of the SCOZA to describe the properties of HC systems, we have made first steps to extend this concept to systems with soft potentials. The fact that the MSA can be solved semi-analytically for the GCM makes this system an ideal candidate for a first application of the SCOZA.

Due to the fact that virial and energy route happen to yield exactly the same result for the GCM within the MSA (and possibly also for other closure relations), we are left to fix only one inconsistency, namely between one of these two routes and the compressibility route on the other hand side. Introducing a state dependent function $K(\rho, \beta)$ in the MSA closure, we were able to derive three different approaches, namely an ODE, a PDE, and an IDE, that enforce thermodynamic self-consistency. While the ODE and PDE rely on the analytic solution provided by the MSA for this particular system, the IDE formulation is completely independent of this framework and can be applied for arbitrary systems and in combination with...
any closure relation. It remains to be verified whether the IDE approach is also applicable to systems with repulsive potentials.

The three formulations provide results for \( K(\rho, \beta) \) and \( \bar{K}(\rho, \beta) \) that are equivalent within numerical accuracy. In contrast to systems with harshly repulsive potentials the improvement of the conventional SCOZA approach over the MSA data is less spectacular. While it coincides with the MSA results in the limiting case of high densities where the MSA is already self-consistent, the (conventional) SCOZA represents a substantial improvement at small densities and low temperatures where the thermodynamic inconsistency of the MSA is more pronounced. Replacing the conventional SCOZA relation by a HNC-type closure that contains an analogous state-dependent function \( \bar{K}_{\text{HNC}}(\rho, \beta) \), we are able to improve the HNC-data for the structural as well as for the thermodynamic properties of the system. With this generalised approach we have not only demonstrated the flexibility and power of the IDE approach but have also proposed what may turn out to become a reliable liquid state theory for systems with bounded potentials.

VII. APPENDIX

The polylogarithm of order \( n \), \( \text{Li}_n(z) \), also known as Jonquière’s function, is a complex valued function of complex argument \( z \), defined by

\[
\text{Li}_n(z) = \frac{z}{\Gamma(n)} \int_0^\infty dt \frac{t^{n-1}}{e^t - z},
\]

where \( n \) is a positive, real parameter. If \( z \in \mathbb{R} \setminus (1, \infty) \), then the polylogarithm is real-valued. For \( |z| < 1 \) the polylogarithm can be evaluated as a power series

\[
\text{Li}_n(z) = \sum_{k=1}^\infty \frac{z^k}{k^n}.
\]

A relation that turned out to be useful for the present application is

\[
\frac{d}{dz} \text{Li}_n(z) = \frac{1}{z} \text{Li}_{n-1}(z).
\]

A detailed list of additional, helpful relations for this function can be found in.\(^{26}\)

\[
F_n(z) = \frac{1}{\Gamma(n+1)} \int_0^\infty dt \frac{t^n}{e^t - z} = -\text{Li}_{n+1}(-e^z)
\]

along with the accurate and efficient implementation of \( F_n(z) \) via series and asymptotic expansions in combination with Chebyshev fits, as implemented in the GNU Scientific Library\(^{28}\), provided the desired results, which finally brought the solution of the SCOZA differential equations within reach.

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1 J.-P. Hansen and I. R. McDonald, Theory of Simple Liquids, (Academic, New York, 1986) 2nd edition.
2 C. Caccamo, Phys. Rep. 274, 1 (1996).
3 F. J. Rogers and D. A. Young, Phys. Rev. A 30, 999 (1984).
4 Y. Rosenfeld and N. W. Ashcroft, Phys. Rev. A 20, 1208 (1979).
5 J.-P. Hansen and G. Zerah, Phys. Lett. 108, 277 (1985); G. Zerah and J.-P. Hansen, J. Chem. Phys. 84, 2336 (1986).

The polylogarithm was introduced in\(^{26}\) to calculate the thermodynamic properties of the GCM within the MSA where, obviously, expression \( (32) \) was used throughout; this was done even though there was no guarantee that for certain state points the modulus of the respective arguments \( |z| \) does not exceed 1, violating thus the condition for the validity of Eq. \( (22) \). Since this function plays a central role in the formalism of the MSA and the SCOZA (see Sec. III and III), a reliable evaluation of \( \text{Li}_n(z) \) for arbitrary argument \( z \) is indispensable for a successful solution of the SCOZA-ODE and PDE. We therefore provide in the following a more detailed presentation of evaluation schemes and indicate how this function can be calculated in an accurate and efficient way for arbitrary argument \( z \).

In its evaluation of \( \text{Li}_n(z) \), the Mathematica software relies on Euler-Maclaurin summation, expansions in terms of incomplete Gamma functions, and numerical quadrature.\(^{26}\) Efficient and accurate C- or Fortran-based implementations, on the other hand, are more difficult to find. First attempts to evaluate Eq. \( (31) \) directly by various numerical integration schemes turned out to be either too time-consuming or did not provide results of sufficient accuracy. Finally, we found that the following functional relation between the polylogarithm and the complete Fermi-Dirac function, \( F_n(z) \),

\[
\text{Li}_n(z) = \frac{1}{\Gamma(n+1)} \int_0^\infty dt \frac{t^n}{e^t - z} = -\text{Li}_{n+1}(-e^z)
\]
1 J. S. Høye and G. Stell, J. Chem. Phys. 67, 439 (1977); J. S. Høye and G. Stell, Mol. Phys. 52, 1071 (1984).
2 A. Parola and L. Reatto, Adv. Phys. 44, 211 (1995); A. Reiner and G. Kahl, Phys. Rev. E 65, 046701 (2002); A. Reiner and G. Kahl, J. Chem. Phys. 117, 4925 (2002).
3 C. N. Likos, Phys. Rep. 348, 267 (2001).
4 A. Lang, C. N. Likos, M. Watzlawek, and H. Löwen, J. Phys. (Condens. Matter) 12, 5087 (2000).
5 M.-J. Fernaud, E. Lomba, and L. L. Lee, J. Chem. Phys. 112, 810 (2000).
6 E. Schöll-Paschinger, J. Chem. Phys. 120, 11698 (2004).
7 L. Blum and J. S. Høye, J. Stat. Phys. 19, 317 (1978); E. Arrieta, C. Jedrzejek, and K. N. Marsh, J. Chem. Phys. 95, 6806 (1991).
8 C. N. Likos, Phys. Rep. 348, 267 (2001).
9 A. A. Louis, P. G. Bolhuis, J.-P. Hansen, and E. J. Meijer, Phys. Rev. Lett. 85, 2522 (2000).
10 I. O. Götte, H. M. Harreis, and C. N. Likos, J. Chem. Phys. 120, 7761 (2004).
11 A. A. Louis, P. G. Bolhuis, and J.-P. Hansen, Phys. Rev. E 62, 7961 (2000).
12 B. M. Mladek, M.-J. Fernaud, G. Kahl, and M. Neumann, Condens. Matter Phys. 8, 135 (2005).
13 W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in FORTRAN: The Art of Scientific Computing* (Cambridge University Press, Cambridge, 1992) 2nd edition.
14 D. Wood, *The Computation of Polylogarithms* (Technical Report 15-92, University of Kent, Computing Laboratory, Canterbury, 1992).
15 D. Pini, G. Stell, and N. B. Wilding, Mol. Phys. 95, 483 (1998).
16 E. Schöll-Paschinger, *Phase Behaviour of Simple Fluids and Their Mixtures*, PhD Thesis (Technische Universität Wien, 2002, unpublished).
17 M. Galassi et al., GNU Scientific Library Reference Manual (2nd edition), ISBN 0954161734; see also http://www.gnu.org/software/gsl.