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Self-consistent Ornstein-Zernike approximation for molecules with soft cores

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The self-consistent Ornstein-Zernike approximation (SCOZA) is an accurate liquid state theory. So far it has been tied to interactions composed of hard core repulsion and long-range attraction, whereas real molecules have soft core repulsion at short distances. In the present work, this is taken into account through the introduction of an effective hard core with a diameter that depends upon temperature only. It is found that the contribution to the configurational internal energy due to the repulsive reference fluid is of prime importance and must be included in the thermodynamic self-consistency requirement on which SCOZA is based. An approximate but accurate evaluation of this contribution relies on the virial theorem to gauge the amplitude of the pair distribution function close to the molecular surface. Finally, the SCOZA equation is transformed by which the problem is reformulated in terms of the usual SCOZA with fixed hard core reference system and temperature-dependent interaction. © *2006 American Institute of Physics*.
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I. INTRODUCTION

The self-consistent Ornstein-Zernike approximation (SCOZA) has been found to give very accurate results for the equation of state for fluids and lattice gases. This approximation was proposed by Høye and Stell.[1,2] Some preliminary results were obtained for supercritical temperatures.[2,3]

However, for subcritical temperatures there were numerical problems connected to the singular behavior along the spinodal curve and the no-solution region inside it. The first successful subcritical solution was made by Dickman and Stell for the Ising model or the lattice gas case.[4] It turned out that results were very accurate.

Borge and Høye made a more general numerical investigation of the SCOZA equation of state in the critical region.[5] Clearly scaling was not fulfilled very close to the critical point. But apart from that the critical behavior was close to that of real fluids. It was especially noted that the critical exponent β for the curve of coexistence was equal or close to 0.35. This value was subsequently confirmed by numerical evaluations by others.[6]

Also Borge and Høye compared SCOZA results with experimental data on CO_2 in the critical region.[7] By closer study of these data on a scaling plot it was realized that they did not collapse onto a single scaling curve but gave a series of close-lying curves instead, and the SCOZA results were consistent with such deviations from scaling.[5]

Høye *et al.* then made a closer investigation of the critical region of SCOZA.[8] Their analysis showed that SCOZA fulfills a generalized kind of scaling instead of the usual one, and they obtained the value of 0.35 for the critical exponent β.

SCOZA was then applied to continuum fluids, and Pini *et al.* considered the hard sphere fluid with interaction of Yukawa form.[9] The results agreed well with simulation data. Furthermore, interactions using more Yukawa terms were also considered.[10] This allowed approximations to the Lennard-Jones (LJ) potential of realistic fluids to be studied.[10] Accurate results were also obtained for the more short-ranged fullerene interactions.[11,12]

So far SCOZA has been applied to continuum systems with hard cores perturbed by an attractive interaction only. Real molecules, on the other hand, have soft cores. In order to obtain more accurate results, this should therefore be taken into account. To do so we use hard spheres with an effective diameter d. In combination with the self-consistency requirement of SCOZA, however, the use of an effective diameter turns out to become a nontrivial problem. This is connected to the necessity of properly taking into account the contribution to the internal energy due to the repulsive interaction. Furthermore, a numerical procedure using the semianalytical solution of the Ornstein-Zernike (OZ) equation becomes more problematic as a grid of fixed densities ρ implies varying packing fractions $\eta=(\pi/6)\rho d^3$ when the effective diameter d changes. While a fully numerical solution of the OZ relation is possible[13] and sidesteps this particular problem, it entails a huge increase in computational complexity and cost.

In the present work, on the other hand, we avoid the need for heavy numerics. Instead we opt for a more conceptual approach to the introduction of soft cores into SCOZA by means of effective hard cores. In doing so we prefer here a prescription for the hard core diameter d that depends only upon temperature (Sec. II). It turns out that an accurate evaluation of the reference system contribution to the configurational internal energy plays an important role. This

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quantity can be linked to the pressure and hence to the virial theorem (Sec. III) and must be taken into account for the energy route part of the SCOZA self-consistency problem (Sec. IV). A further refinement uses the virial theorem once more, this time to gauge the amplitude of the pair distribution function close to the core (Sec. V). We conclude with a formal mapping of the soft-core SCOZA for fixed interaction onto the usual SCOZA with fixed hard core and a temperature-dependent potential. This essentially eliminates any softness and so provides a way of avoiding the complexities associated with it (Sec. VI).

II. INTERACTION AND EFFECTIVE HARD CORES

The pair interaction for real atoms that are neutral is typically given by the LJ interaction,

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right],$$

with length and energy scales of σ and ϵ, respectively. (From now on we will use units where $\sigma=\epsilon=1$.) In approximations, the repulsive part of this interaction where $\phi(r)>0$ is commonly replaced by a hard core. This has also been done in earlier SCOZA computations where the hard core diameter d was kept fixed.

State-dependent effective hard cores have been used earlier to evaluate the equilibrium properties of fluids, and there exist various recipes; see Ref. 14 for a recent compilation and comparison in the context of thermodynamic perturbation theory. The simplest schemes such as the Barker-Henderson prescription[15] use an effective diameter d that depends on temperature only, whereas more advanced recipes include a density dependence, too.[16]

In the present work we limit ourselves to a d that depends only upon temperature. The main reason for this is the added complexity of the problem when combining it with the self-consistency of SCOZA. In particular, the latter requires that the reference system internal energy becomes part of the thermodynamic self-consistency and must be properly accounted for. This inclusion of the contribution of the soft cores in the self-consistency problem is the fundamental difference between this method and another one which is a combination of SCOZA and a first order perturbation theory proposed as a way of handling soft repulsive cores[17] and studied recently.[18]

Another reason for the use of a d that depends only upon temperature is the connection to the hard sphere equation of state that becomes unique. In other words, both the virial theorem and the compressibility theorem will remain consistent if they are consistent for the reference system with temperature independent d.

The importance of d for quantitative accuracy is seen from the fact that the mean-field critical temperature and density vary with d as d^3 and d^{-3}, respectively, when the interaction $\psi(r)$ is held constant. From the second virial coefficient of the repulsive part of the LJ interaction one will find roughly $d^3 \sim 0.92$ at the critical temperature if $\phi(r)$ for $r<1$ is replaced by an effective hard core. This is in satisfactory agreement with the SCOZA result with fixed d when compared with simulations. With temperature independent $d=1$ SCOZA yields the value $T_c=1.245$ with a three-Yukawa fit to the Lennard-Jones interaction for $r>1$, cf. Fig. 4.3 of Ref. 19. For simulations performed for the full LJ interaction, one has found $T_c=1.310$ (Ref. 20) and 1.313 (Ref. 21) by molecular dynamics, and $T_c=1.3120(7)$ (Ref. 22) and 1.326(2) (Ref. 23) by Monte Carlo methods. Previous SCOZA evaluations but with temperature independent $d=1$, however, yielded values $T_c=1.304$, 1.293 (Ref. 10), and 1.305 (Ref. 19) of the critical temperature. But these values are based on two-Yukawa fits to the LJ interaction with a compensation for the soft core such that the right second virial coefficient is reproduced. The variations in these latter numbers are due to the precise potential fit and the detailed form of the direct correlation function used with respect to the reference system hard cores.

Without thermodynamic self-consistency, results for isotherms at different temperatures are independent. The effective d for a given temperature then determines the equation of state for that temperature. This is the case for common fluid theories. For SCOZA, on the other hand, this is no longer true. But away from the critical region this coupling cannot be important as other theories are accurate there, too. One approximate way to implement SCOZA with temperature-dependent d can then be to solve the equations with the same d at all temperatures but to use the results only for the isotherm corresponding to the chosen d. Repeated evaluations with different d will then give the full phase diagram. This approach bears some resemblance to the SCOZA-based perturbation theory mentioned above.[18] Just as the latter, however, such a procedure is only approximate, and compiling a full phase diagram requires substantial computer resources far in excess of those needed for a single run of the SCOZA program.

The division of the pair interaction $\phi(r)$ into a reference system part $\phi_0(r)$ and a perturbing part $\psi(r)$ can be performed in various ways. As suggested above, one can use the repulsive part where $\phi(r)>0$ as the reference system interaction,[15]

$$\phi_0(r) = \begin{cases} \phi(r), & r<1 \\ 0, & r>1. \end{cases}$$

With this the perturbing interaction is

$$\psi(r) = \begin{cases} 0, & r<1 \\ \phi(r), & r>1. \end{cases} \tag{1}$$

However, there are more choices for this splitting of the interaction, and an alternative is to use[24] ($r_m=2^{1/6}$)

$$\phi_0(r) = \begin{cases} \phi(r)-\phi(r_m), & r<r_m \\ 0, & r>1 \end{cases}$$

$$\psi(r) = \begin{cases} \phi(r_m), & r<r_m \\ \phi(r), & r>r_m. \end{cases}$$

As was verified by Høye and Borge, SCOZA requires a perturbing interaction that is mainly attractive, or else the equations cannot be solved.[25] Clearly, the above suggested splittings of the potential fulfill this condition.

Furthermore, in order to keep the numerical implementation less demanding it is desirable to approximate the interaction outside the effective hard core as a sum of Yukawa terms. This allows the OZ equation to be solved in a semianalytic way. For a potential such as the LJ one, such a multi-Yukawa form of $\phi(r)$ outside the core is easily found. For example, a simple nonlinear least-squares fit of a sum of three Yukawa terms constrained to reproduce $\phi(1)=0$ converges rapidly and gives a result that is essentially indistinguishable from the original LJ form for $r>1$.[19] When $d<1$, however, this fit is certainly not constant for $d<r<1$ as mandated by the two types of splitting mentioned above. For instance, one can then add one more Yukawa term to approximate the desired form; this will generally be a rather short-ranged function that hardly contributes beyond $r=1$. For prescription (1) both the range and the amplitude of the additional Yukawa term can be fixed by imposing, e.g., $\psi(d)=\psi'(d)=0$. At any rate, any remainder of $\psi(r)$ not accounted for by this sum of Yukawa terms is added to $\phi_0(r) \equiv \phi(r)-\psi(r)$ and so enters the computation through the evaluation of the effective diameter.

In solving SCOZA, the reference system is used as a boundary condition at temperature $T\to\infty$, or $\beta=0$ where $\beta=1/(k_BT)$ and k_B is Boltzmann's constant. Strictly speaking, the reference system becomes the ideal gas in this limit for a soft core, i.e., $d\to 0$ which is far from unity. However, use of the ideal gas as reference system may give rise to additional problems, especially in the numerical implementation. So we have not tried to investigate this possibility further. Instead we have focused upon the situation with an effective hard core diameter d near 1. The justification for this lies in our arguments above. They mean that different temperatures and densities do not couple significantly away from the critical point anyway. We can therefore start at $\beta=0$ with a nonvanishing value of d corresponding to, say, twice the critical temperature, and start to vary d only at lower temperatures for which SCOZA values then will be valid.

III. REFERENCE SYSTEM AND REPULSIVE INTERNAL ENERGY

In approximating a soft repulsive core by an effective hard core, the simplest prescription is to let the diameter d depend only upon temperature. One possibility is to define d such that the second virial coefficient for the soft particles coincides with that of the effective hard cores,

$$\frac{4\pi}{3}d^3 = \int (1-e^{-\beta\phi_0(r)})d\mathbf{r}. \tag{2}$$

The prescription of Ref. 15 is slightly different from this in that it replaces the three-dimensional integral (2) with a one-dimensional one. However, the result will be the same to leading order in the difference $1-d$ which is considered small. In this connection, it can be mentioned that the precise prescription is not crucial since both give a d that depends only upon β, and the SCOZA problem needs only $d(\beta)$ as input, not its prescription.

At high density there are better approximations with density dependence, but we expect the deviations of such choices from Eq. (2) to be small when the soft potential can be considered steep at the molecular surface.

In contrast to strict hard spheres, a soft repulsive potential implies that the reference system also contributes to the configurational internal energy. This can be related to the pressure and ultimately to the virial theorem. The equation of state can be written as

$$\beta p = \rho + \left(1-\rho\frac{\partial}{\partial\rho}\right)I_0, \tag{3}$$

where p is the pressure, $I_0=-\beta\rho f_0$, and f_0 is the excess (beyond the ideal gas) Helmholtz free energy per particle. For effective hard cores, I_0/ρ only depends on the packing fraction η,

$$I_0 = \rho y(\eta).$$

Insertion into Eq. (3) thus gives

$$\beta p = \rho\left(1-\eta\frac{\partial y}{\partial\eta}\right). \tag{4}$$

The configurational or excess internal energy u_0 per particle of the reference system is now

$$\rho u_0 = -\frac{\partial I_0}{\partial\beta} = -\rho\frac{\partial y}{\partial\eta}\frac{\partial\eta}{\partial\beta} = -\rho\eta\frac{\partial y}{\partial\eta}\frac{\partial \ln d^3}{\partial\beta},$$

and finally, using Eq. (4) for $\partial y/\partial\eta$,

$$\rho u_0 = (\beta p - \rho)\frac{\partial \ln d^3}{\partial\beta}.$$

The virial theorem for hard spheres implies

$$\beta p - \rho = \frac{2\pi}{3}d^3\rho^2 n_0(d+)$$

and so connects the above internal energy to the contact value $n_0(d+)$ of the pair distribution function,

$$\rho u_0 = \frac{2\pi}{3}d^3\rho^2 n_0(d+)\frac{\partial \ln d^3}{\partial\beta}. \tag{5}$$

To gain some intuition for the consistency of this result, we can insert the definition (2) for the effective diameter. This yields

$$\frac{\partial \ln d^3}{\partial\beta} = \frac{1}{d^3}\frac{\partial d^3}{\partial\beta} = \frac{\int\phi_0(r)e^{-\beta\phi_0(r)}d\mathbf{r}}{(4\pi/3)d^3}$$

and thus finally,

$$\rho u_0 = \frac{1}{2}\rho^2 n_0(d+)\int \phi_0(r)e^{-\beta\phi_0(r)}d\mathbf{r}.$$

This is the low density value of the internal energy, amplified by the contact value $n_0(d+)$ for higher densities. Compared with the exact u_0, the pair distribution function is here approximated by $n_0(d+)e^{-\beta\phi_0(r)}$. Its accuracy increases as the repulsive part of the potential becomes less soft. A different prescription for $d(\beta)$ such as that of Ref. 15 gives different expressions for the above two integrals, but otherwise the precise choice of $d(\beta)$ is of no consequence for the remainder of this work.

IV. SCOZA EQUATIONS

The SCOZA approach is based upon thermodynamic consistency between the energy and compressibility routes to thermodynamics. These routes are connected via the thermodynamic relation

$$\frac{\partial a}{\partial \beta} = \rho \frac{\partial^2 \rho u_t}{\partial \rho^2}, \tag{6}$$

where

$$a = \frac{\partial \beta p}{\partial \rho}$$

is the reduced inverse compressibility and u_t is the total configurational internal energy per particle. Both a and u_t are evaluated from the pair correlation function in different ways, viz. by the compressibility and energy routes to thermodynamics. In general, the pair structure is known only approximately, and a and u_t give different thermodynamics. In SCOZA, on the other hand, consistency between the two routes in the form of Eq. (6) is enforced by adjusting an unknown parameter, usually the amplitude of the direct correlation function $c(r)$ outside the hard core. Specifically, in the mean spherical approximation (MSA) the contribution to $c(r)$ from the perturbing attractive interaction $\psi(r)$ is

$$c(r) = -\beta\psi(r), \quad r > d. \tag{7}$$

SCOZA replaces β in the above relation by an effective value that depends on both temperature and density and is obtained from the solution of Eq. (6). The total correlation function $h(r)=n(r)-1$ is then obtained from the core condition

$$h(r) = -1, \quad r < d,$$

and the OZ equation

$$\tilde{h}(k) = \tilde{c}(k) + \rho\tilde{c}(k)\tilde{h}(k).$$

(The tilde marks Fourier transforms.) One can then evaluate a as well as u, the internal energy contribution from the attractive interaction alone, according to

$$\begin{aligned} a &= 1 - \rho\tilde{c}(0), \\ u &= \frac{1}{2}\rho \int \psi(r)(h(r)+1)d\mathbf{r}. \end{aligned} \tag{8}$$

In this way, both a and u are, in principle, obtained as functions of the effective temperature β_e for any given density and interaction. Consequently, u (or a) can replace β_e as the free parameter so that correspondingly a (or u) can be expressed in terms of the former. Inserting this into Eq. (6) one then obtains the SCOZA partial differential equation (PDE) for u (or a).

V. CONTACT VALUE OF THE PAIR DISTRIBUTION FUNCTION

For soft repulsive interactions the total internal energy u_t to be used in Eq. (6) is the sum of the contributions (5) and (8), i.e.,

$$u_t = u_0 + u. \tag{9}$$

At first sight one might expect u_0 to play a minor role. But a closer investigation shows that it is crucial for obtaining results consistent with a changing diameter d. The reason for this is that the reference system enters primarily as the boundary condition of the PDE at $\beta=0$. For $\beta>0$, a change in d is not "seen" except through u_0 [and a small perturbation of u due to small changes in $h(r)$]. Neglecting u_0 thus means essentially keeping d fixed at its $\beta=0$ value. Our preliminary numerical work strongly indicated this importance of the u_0 term.

Since u_0 plays such an important role, the accuracy of the contact value $n(d+)=1+h(d+)$ becomes of interest. For $\beta>0$, $n(d+)$ deviates from $n_0(d+)$, and clearly the former more accurately describes the energy due to the reference system interaction $\phi_0(r)$. With a direct correlation function of the form (7), however, there is no reason to expect that the $h(r)$ obtained is accurate close to the hard core. In particular, the contact value $h(d+)$ strongly depends on the choice of $\psi(r)$ at $r=d$ and thus on the potential fit with the added Yukawa tails. A more reliable method of obtaining the contact value is thus desirable.

One appealing possibility is provided by the virial theorem that then also, to a certain degree, enters the SCOZA where it has played no role traditionally. Høye and Stell earlier proposed full consistency between the energy, virial, and compressibility routes,[2] but this requires structure functions depending on two free parameters and has not been considered numerically so far, nor will it be considered here. But on the other hand we can still obtain desired information about the contact value $n(d+)$ via the virial theorem using the SCOZA quantities as input.

From the virial theorem for hard cores with attraction, the contact value $n(d+)$ is as follows:

$$\beta p = \rho + \frac{4\pi}{6} d^3 \rho^2 n(d+) + \beta\rho(u - v),$$

where the virial integral is split into two parts, with u given by Eq. (8). The expression for the remainder v then becomes

$$v = u + \frac{1}{6}\rho \int (\mathbf{r}\,\nabla\,\psi(r))n(r)d\mathbf{r} = \frac{1}{6}\rho \int \nabla(\mathbf{r}\psi(r))n(r)d\mathbf{r},$$

with the integrations restricted to $r>d$. Note that v vanishes in the mean field limit as then $n(r)=1$. Expression (5) for u_0 can now be expressed in terms of the new contact value $n(d+)$ instead of the reference system value $n_0(d+)$. With the above relations we find

$$\rho u_0 = (\beta p - \rho - \beta\rho u + \beta\rho v)\frac{\partial \ln d^3}{\partial \beta}. \tag{10}$$

Thus the additional complication of evaluating u_0 is the evaluation of the integral for v.

VI. TRANSFORMATION TO UNIT DIAMETER

With varying d there is an additional problem if the analytic solution of the OZ equation for a sum of Yukawa terms is used. The latter provides a as a function of u only at constant packing fraction and interaction, whereas the PDE requires the temperature derivative to be taken at constant density. When β and thus d change while the density grid in the discretization is kept fixed, the packing fraction also changes and the relation between a and u becomes less direct and more challenging to evaluate numerically.

If now the varying d problem can be transformed into a situation of fixed unit diameter $d=1$, the discrepancy mentioned will not arise and application of the analytic solution of the OZ equation will be simpler. The price to pay is an interaction that varies with β in the transformed problem. As we will se below, this works out nicely and gives equations that can be given a direct physical interpretation.

To obtain the desired transformation we introduce a number of quantities, marking those of the unit diameter problem by a subscript 1,

$$\rho_1 = \rho d^3, \quad \beta_1 = \beta / d^3, \quad p_1 = p d^6,$$

$$u_1 = u d^6, \quad v_1 = v d^3, \quad \phi_1(r_1) = d^3 \phi(r),$$

$$r_1 = r/d, \quad d\mathbf{r}_1 = d\mathbf{r}/d^3, \quad n_1(r_1) = n(r).$$

With Eqs. (6), (9), and (10) we have the SCOZA PDE

$$\frac{\partial a}{\partial \beta} = \rho \frac{\partial^2}{\partial \rho^2}[\rho u + A(p - \rho u + \rho v)],$$

where, for brevity, we put

$$A = \beta \frac{\partial \ln d^3}{\partial \beta} = \frac{\beta}{d^3} \frac{\partial d^3}{\partial \beta}.$$

For a d that depends only on β, the introduction of the new quantities on the right hand side is done in a straightforward way. With $\partial^2/\partial\rho^2 = d^6 \partial^2/\partial\rho_1^2$ we get

$$\frac{\partial a}{\partial \beta} = \frac{1}{d^3} \rho_1 \frac{\partial^2}{\partial \rho_1^2}[\rho_1 u_1 + A(p_1 - \rho_1 u_1 + \rho_1 v_1)]. \tag{11}$$

For a we find likewise

$$a = \frac{\partial(\beta p)}{\partial \rho} = \frac{\partial(\beta_1 p_1)}{\partial \rho_1} = a_1.$$

The derivative with respect to β then becomes

$$\begin{aligned} \frac{\partial a}{\partial \beta} &= \frac{\partial \beta_1}{\partial \beta} \frac{\partial a_1}{\partial \beta_1} + \frac{\partial \rho_1}{\partial \beta} \frac{\partial a_1}{\partial \rho_1} \\ &= \left(\frac{1}{d^3} - \frac{\beta}{d^6} \frac{\partial d^3}{\partial \beta} \right) \frac{\partial a_1}{\partial \beta_1} + \rho d^3 \frac{1}{\beta} A \frac{\partial a_1}{\partial \rho_1} \\ &= \frac{1}{d^3} \left[(1 - A) \frac{\partial a_1}{\partial \beta_1} + \rho_1 A \frac{\partial^2 p_1}{\partial \rho_1^2} \right]. \end{aligned}$$

Upon insertion into Eq. (11) the p_1 terms cancel and we obtain

$$\frac{\partial a_1}{\partial \beta_1} = \rho_1 \frac{\partial^2}{\partial \rho_1^2}[\rho_1 u_1 + A_1 \rho_1 v_1], \tag{12}$$

where

$$A_1 = \beta_1 \frac{\partial \ln d^3}{\partial \beta_1} = \frac{A}{1 - A}.$$

The latter equality follows from

$$\left(\frac{1 - A}{d^3} \right)^{-1} = \frac{\partial \beta}{\partial \beta_1} = d^3 + \beta \frac{\partial d^3}{\partial \beta_1} = d^3 (1 + A_1).$$

The resulting Eq. (12) can be given a direct physical interpretation in terms of the transformed system. The latter consists of hard spheres of fixed diameter ($d_1=1$), where now there is an attractive pair interaction that depends upon the temperature, $\phi_1(r_1) = d^3 \phi(r) = d^3 \phi(r_1 d)$. Furthermore, the soft repulsive interaction is no longer present as the transformed system has hard cores. In the usual virial graph expansion, the Helmholtz free energy per particle at given density will depend only upon the interaction as before (besides temperature and density). This will remain the same even though $\phi_1(r_1)$ depends on the temperature. The total configurational internal energy per particle obtained from the pair distribution function is thus

$$\begin{aligned} u_{1t} &= \frac{\partial(\beta_1 f_1)}{\partial \beta_1} = \frac{1}{2} \rho_1 \int \frac{\partial}{\partial \beta_1} [\beta_1 d^3 \phi(r_1 d)] n_1(r_1) d\mathbf{r}_1 \\ &= \frac{1}{2} \rho \int \left[\phi_1(r_1) + A_1 \left(\phi_1(r_1) + \frac{1}{3} d^3 \frac{\partial \phi(r_1 d)}{\partial d} \right) \right] n_1(r_1) d\mathbf{r}_1 \\ &= \frac{1}{2} \rho \int \left[\phi_1(r_1) + \frac{1}{3} A_1 \nabla (\mathbf{r}_1 \phi_1(r_1)) \right] n_1(r_1) d\mathbf{r}_1 \\ &= u_1 + A_1 v_1, \end{aligned}$$

in accordance with the right hand side of Eq. (12).

VII. CONCLUSION

We have investigated a method to perform SCOZA evaluations for realistic molecules with soft cores. A temperature-dependent effective hard core diameter is then introduced. For thermodynamic self-consistency it turns out that the excess internal energy of the reference system is important and should be treated accurately. For this purpose the contact value of the pair correlation function at the hard sphere surface is needed. Since SCOZA does not give such a reliable contact value, it is instead obtained by use of the virial theorem. In Sec. VI the SCOZA problem with varying d is transformed to a simpler one with fixed $d=1$. This transformation not only eliminates some of the difficulties associated with temperature-dependent diameter but also provides an independent method of evaluation that can be useful as a test of the internal consistency of results.

The results of this work have been obtained along with numerical work to implement and solve new problems when soft cores are considered. So far we have only considered simple test functions $d(\beta)$ to obtain a program that can handle varying d when using analytic expressions. In this respect the transformation to fixed $d=1$ in Sec. VI has been verified numerically by solving SCOZA with both the original and transformed equations by putting for simplicity the virial type integral for v and thus the one for v_1 equal to zero. For explicit evaluations with the LJ interaction it is necessary to evaluate integral (2) for $d(\beta)$ and the less trivial one for v; preliminary computations already including v are encouraging. Furthermore, it will then also be desirable to study the influence of different prescriptions for $d(\beta)$ and for the splitting of the potential into a reference part and a perturbing attractive part. We intend to extend our computations in this way.

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[1] J. S. Høye and G. Stell, J. Chem. Phys. **67**, 439 (1977). See discussion in Sec. IV.

[2] J. S. Høye and G. Stell, Mol. Phys. **52**, 1071 (1984).

[3] J. S. Høye and G. Stell, Int. J. Thermophys. **6**, 561 (1985).

[4] R. Dickman and G. Stell, Phys. Rev. Lett. **77**, 996 (1996).

[5] A. Borge and J. S. Høye, J. Chem. Phys. **108**, 4516 (1998).

[6] D. Pini,G. Stell, and R. Dickman, Phys. Rev. E **57**, 2862 (1998).

[7] M. S. Green, M. Vicentini-Missoni, and J. M. H. Levelt Sengers, Phys. Rev. Lett. **18**, 1113 (1967).

[8] J. S. Høye, D. Pini, and G. Stell, Physica A **279**, 213 (2000).

[9] D. Pini,G. Stell, and J. S. Høye, Int. J. Thermophys. **19**, 1029 (1998).

[10] D. Pini, G. Stell, and N. B. Wilding, J. Chem. Phys. **115**, 2702 (2001).

[11] D. Costa, G. Pellicane, C. Caccamo, E. Schöll-Paschinger, and G. Kahl, Phys. Rev. E **68**, 021104 (2003).

[12] E. Schöll-Paschinger and G. Kahl, Europhys. Lett. **63**, 538 (2003).

[13] E. Schöll-Paschinger, A. L. Benavides, and R. Castañeda-Priego, J. Chem. Phys. **123**, 234513 (2005).

[14] D. Ben-Amotz and G. Stell, J. Phys. Chem. B **108**, 6877 (2004).

[15] J. A. Barker and D. Henderson, J. Chem. Phys. **47**, 4714 (1967).

[16] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).

[17] F. O. Raineri, G. Stell, and D. Ben-Amotz, J. Phys.: Condens. Matter **16**, S4887 (2004).

[18] E. Schöll-Paschinger and A. Reiner, J. Chem. Phys. (submitted).

[19] E. Schöll-Paschinger, Ph.D. thesis, Techinische Universität Wien, 2002.

[20] A. Lotfi, J. Vrabec, and J. Fischer, Mol. Phys. **76**, 1319 (1992).

[21] J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, Mol. Phys. **78**, 591 (1993).

[22] J. J. Potoff and A. Z. Panagiotopoulos, J. Chem. Phys. **109**, 10914 (1998).

[23] J. M. Caillol, J. Chem. Phys. **109**, 4885 (1998).

[24] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).

[25] J. S. Høye and A. Borge, J. Chem. Phys. **108**, 8830 (1998).