# Integral equations for dense fluids: *A priori* controllable approximations[a]

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The functional methods developed by Yvon, Bogoliubov, Lebowitz, and Percus in the theory of fluids are applied to the derivation of new integral equations for dense fluids with an *a priori* knowledge of their range of validity in some sense. In particular, we find conditions in order that the resulting radial distribution function contains, at least, all the diagrams in the density ($n$) expansion up to order $n^2$, $n^3$,..., and present a method to obtain systematic corrections to familiar approximations such as the Percus–Yevick and the hypernetted-chains equations.

## I. INTRODUCTION

The study of the static properties of dense fluids rests nowadays upon the theory of nonlinear integral equations for spatial correlation functions.[1] Even though this is still far from a first-principles theory, e.g., it involves some hypothesis remaining unjustified, in general, and usually lacks from any *a priori* criterion for their range of validity, it provides in practice a convenient tool to relate self-consistently interparticle potentials with the static structure or the radial pair distribution functions, for instance. The resulting information may then be compared with the experimental one obtained by producing elastic scattering of electromagnetic waves by the fluid, it may be used to build up macroscopic theory within the realm of thermodynamics and hydrodynamics, both in the case of classical and quantum fluids, etc. [1-3] In fact, their usefulness and versatility has attracted a continuous activity to the field for many years and there is now some revival of interest in nonlinear integral equations focusing on some difficult problems, both numerical and fundamental.[4-7]

The present theory of fluids, including those recent efforts, is mainly centered around the Percus–Yevick (PY) equation.[8] This is a consequence of three facts: The PY equation is simpler than others, it has an exact solution for one- and three- dimensional systems of particles interacting via a hard-core potential,[9-11] and it usually provides a relatively accurate description in the case of systems with more general potentials, e.g., by performing perturbations around the hard-core fluid system state.[12,13] Besides the original deduction,[8] we find most suggestive the functional method[14-17] followed by Lebowitz and Percus[16] to obtain the PY equation which allows, as well, to obtain other, either old or new ones, integral equations for the relevant correlation functions[2]: While the functional method does not allow, in principle, a better justification of the PY equation than the one in preceding deductions, it certainly provides an interesting framework which might finally lead to a systematic study of some fundamental questions (justification and existence, range of validity, generalizations and extensions, etc.) concerning this and other nonlinear integral equations.

This is indeed the general purpose of the present article. We describe here our efforts to find better integral equations

for dense fluids by using functional methods. In particui we describe a (functional) method to find conditions on "generating functional" producing integral equations wh are exact up to any desired order in the system density $n$ the sense that the radial pair distribution function whicl the solution of that equation retains, at least, all the the c grams up to that order) and find explicitly those conditi for orders $n^2$ and $n^3$ (Sec. II). It may be mentioned that PY equation and other familiar equations, such as the hyp netted chains (HNC) equation, are only exact in genera. that sense up to first order in $n$. The method in Sec. II a allows to compare *a priori* the expected accuracy of any t integral equations. Section III contains further applicati of the method and, in particular, it describes some sim ways to obtain successively better integral equations. In S IV, we devise a different method, intimately related to one in Sec. II, however, to find systematically correction. the radial and direct correlation functions given by sin integral equations such as the PY and HNC equations: illustrate this case by correcting the latter two approxi: tions up to order $n^2$. Finally, Sec. V contains an explicit luation of the corrections to the PY equation up to orde in the case of a one-dimensional system of hard-core pa cles: we thus show how these corrections are zero in particular case.

## II. CONDITIONS ON THE GENERATING FUNCTIONA

This section describes the basics of the functional me od and applies the formalism to reach explicit condition the involved generating functional producing systematic better integral equations for dense fluids. This may achieved here, in practice, by following different proaches, e.g., by comparing with existing integral ec tions, or from a knowledge of the first few exact virial co cients.

Consider a classical system of $N$ interacting point p cles enclosed in a volume $V$ and described, in the absenc an external field, by the Hamiltonian $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1$,

$$\mathscr{H}_0 = \sum_{i=1}^{N} P_i^2/2m, \quad \mathscr{H}_1 = \sum_{i<j=1}^{N} \varphi_{ij}, \qquad ($$

where $\varphi_{ij} \equiv \varphi(r_i - r_j)$ represents the interaction poter between two particles at positions $r_i$ and $r_j$ respectivel. system, however is acted on by an external potential $\Psi$ m fying the Hamiltonian; it will be assumed this is due to

interaction between a "test particle" at position $r_0$ and the rest of the particles, i.e., one has now $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1 + \Psi$,

$$\Psi = \sum_{i=1}^{N} \varphi_{i0}, \quad \mathscr{H}_1 + \Psi = \sum_{i<j=0}^{N} \varphi_{ij}. \quad (2.2)$$

Let $n_1(r;\Psi)$ represent a functional of $\Psi(r)$, such that $n_1(r;0) \equiv n_1(r)$ is the one-particle distribution function of the unperturbed system, and denote by $\mathscr{Y}(r;\Psi)$ another functional of $\Psi(r)$ which is arbitrary except for the requirement that[2,16]

$$\mathscr{Y}(r_1;\Psi) = \mathscr{Y}(r_1) + \int dr_2 [n_1(r_2;\Psi) - n_1(r_2)]$$

$$\times \left( \frac{\delta\mathscr{Y}(r_1;\Psi)}{\delta n_1(r_2;\Psi)} \right)_{\Psi=0}. \quad (2.3)$$

This may be viewed as an expansion, where $\mathscr{Y}$ plays the role of a generating functional, which is truncated *ad hoc* in order to get closed equations for the pair distribution function. We shall choose here

$$\mathscr{Y}(r;\Psi) = h\,[v(r;\Psi)], \quad (2.4a)$$

where the function remains unspecified and

$$v(r;\Psi) = \omega \cdot n_1(r;\Psi) \exp\,[\beta\varphi(r-r_0)], \quad (2.4b)$$

where $\omega \equiv \omega(n,r-r_0)$ is also unknown, $n$ is the mean system density, and $\beta$ represents the inverse temperature.

The Ornstein–Zernike equation[18] reads

$$G(r_1-r_2) = C(r_1-r_2) + n \int dr_3 G(r_1-r_3)C(r_2-r_3), \quad (2.5)$$

where $G(r) = g(r) - 1, g(r) = n_2(r)/n_2$ is the radial distribution function, $C(r)$ represents the direct correlation function, and one has the functional relation[16]

$$-\beta \frac{\delta\Psi(r_2)}{\delta n_1(r_1;\Psi)} = \frac{\delta(r_1-r_2)}{n_1(r_1;\Psi)} - C(r_1-r_2;\Psi), \quad (2.6)$$

where $\delta(r)$ represents the Dirac delta function; one also has[16]

$$n_1(r;\Psi) = n_2(r_1,r_0)/n_1(r_0). \quad (2.7)$$

By combining Eqs. (2.3)–(2.7) it follows in the case of uniform fluids after some algebra that

$$C(x) = g(x) - 1 + \frac{h\,[v(n,x;0)] - h\,[v(n,x;\Psi)]}{n\omega(n,x)h\,[v(n,x;\Psi)]}, \quad (2.8)$$

where $x \equiv |x| \equiv |r - r_0|, v(n,x;\Psi) = n\omega(n,x)g(x)$ $\times \exp[\beta\varphi(x)]$ and $v(n,x;0) = n\omega(n,x)$ [this notation will be simplified sometimes as $v(x;\Psi)$ and $v(x;0)$, respectively, and the latter also as $v(n,x)$], $h \equiv dh(v)/dv$, and

$$h\,[v(x;\Psi)] = h\,[v(x;0)] + n^2\omega(n,x)x$$

$$/h\,[v(x;0)] \int ds[g(|s-x|)-1]C(s). \quad (2.9)$$

The last two equations, relating the relevant functions $C(r)$ and $g(r)$ to our arbitrary functions $h$ and $\omega$, allow us to recover most familiar results. For instance, it follows by us-

ing $h(v) = v$ and any function $\omega$ that

$$C(x) = g(x)[1 - e^{\beta\varphi(x)}] \quad (2.10a)$$

and

$$g(x)e^{\beta\varphi(x)} = 1 + n \int ds[g(|s-x|) - 1]g(s)[1 - e^{\beta\varphi(s)}] \quad (2.10b)$$

which is the Percus–Yevick result[8] combined with the Ornstein–Zernike equation (2.5), i.e., Eq. (2.10b) is the so-called PY equation for uniform fluids. Similarly, the choice $h(v) = \ln v$ leads immediately to the HNC equation in the case of any function $\omega$. Both, the PY and the HNC approximations can also be obtained by summing up certain diagrams chosen among those that contribute to the density expansion of $g(r)$,

$$g(r) = e^{-\beta\varphi(r)} \left[ 1 + \sum_{i=1}^{\infty} a_i(r)n^i \right]. \quad (2.11)$$

One may show in this way[2] that the term of order $n$ is the same in all the three cases (implying that the second and third virial coefficients in the expansion of the pressure based on the PY and the HNC equations are exact), while only a part of the diagrams in the upper terms are retained in both approximations. Our purpose here is to find conditions on the functions $h$ and $\omega$ leading to integral equations which are exact up to order $n^i$, $i > 2$, in the sense that the corresponding solution $g(r)$ retains (at least) all the diagrams up to order $n^i$.

To that end we shall perform a formal density expansion of Eq. (2.8).

$$C(x) = e^{-\beta\varphi(x)} - 1 + n\alpha(x) + n^2\beta(x) + n^3\gamma(x) + \cdots, \quad (2.12)$$

where the coefficients are definite functions of $\omega_i$, $n\omega$, $h$, and $x$, and substitute this in Eq. (2.9). After identifying the terms with the same power of $n$ in the resulting expansion, one obtains explicit expressions for the coefficients in Eq. (2.11). In order to shorten the expressions below, we first introduce the notation

$$H_1(0) \equiv \tfrac{1}{2}\ddot{h}(0)\dot{h}^{-1}(0) \quad (2.13)$$

and

$$H_2(0) \equiv \tfrac{1}{2}\dddot{h}(0)\dot{h}^{-1}(0)v(0), \quad (2.14)$$

where $v = n\omega(n,x);$ $v(0) \equiv v(n=0,x),$ and $h(0) \equiv h(v(0));$ one has, for instance,

$$a_1(x) = \int dr f_m(r) f_m(|r-x|), \quad (2.15a)$$

$$a_2(x) = \int dr f_m(r) a_1(r)[f_m(|r-x|) + f_m(|r+x|)]$$

$$+ \int dr f_m(r) a_1(|r-x|) - H_1(0)v(0)a_1^2(x), \quad (2.15b)$$

etc., where $f_m(r) = \exp[-\beta\varphi(r)] - 1$ is the Mayer function. Now, the PY case corresponds, as it was noticed previously, to the choice $h(v) = v$. That is, $\dot{h}(v) = 1, \ddot{h}(v) = 0,$

and $H_1(0) = 0$, so that one may write

$$\bar{a}_1(x) = 0, \quad \bar{a}_2(x) = -H_1(0)v(0)a_1^2(x), \qquad (2.16a)$$

$$\bar{a}_3(x) = -\int dr\, f_m(r)H_1(0)v(0)\{f_m(s)a_1^2(r)$$

$$- [f_m(s) + 1]a_1^2(s)\}$$

$$- \int dr\, f_m(s)H_1(0)v(0)a_1^2(r)$$

$$- H_2(0)[v'(0) + \tfrac{1}{3}v(0)]$$

$$+ H_1(0)[2H_1(0)v(0)v'(0) - v'(0) - 2v(0)], \qquad (2.16b)$$

where $v'(0) \equiv (dv/dn)_{n=0}$, $s = |s| = |r - x|$, and we have also introduced the notation $\bar{a}_i(x) = a_i(x) - a_i^{PY}(x)$, the latter representing the value of $a_i(x)$ in the PY approximation.

The preceding formalism may be used for different purposes. For instance, one may know *a priori*, from Eqs. (2.16), the kind of approximation (e.g., the diagrams which will be retained), as compared to the PY one, involved by an integral equation obtained from Eqs. (2.8) and (2.9) after using some convenient choices for the functions $h$ and $\omega$; of course, the comparison can be made also in relation to the HNC equation or to any other integral equation by making minor changes in Eqs. (2.16). Even more interesting, one may interpret the functions $a_i(x)$, $i > 1$, as the exact density expansion coefficients; these may be assumed to be associated to a certain integral equation which would follow in our formalism by using certain (unfortunately unknown) functions $h$ and $\omega$. Then, we may obtain conditions on $h$ and $\omega$ so that the corresponding integral equation is exact (contains all the diagrams) up to order $n^i$ for an arbitrary value of $i$. For instance, the condition

$$H_i(0)v(0,x) = -\bar{a}_2(x)a_1^{-2}(x), \qquad (2.17)$$

where $\bar{a}_i = a_i^{exact} - a_i(h,\omega)$ with the latter given by Eqs. (2.15), is necessary and sufficient to have an exact integral equation up to order $n^2$, while one would need, in addition, that

$$\bar{a}_3(x) = \int dr\, f_m(r)\{f_m(s)\bar{a}_2(r) + [f_m(s) + 1]\bar{a}_2(s)\}$$

$$+ \int dr\, f_m(s)\bar{a}_2(r) - H_2(0)a_1^2(x)$$

$$\times [v'(0) + \tfrac{1}{3}v(0)a_1(x)]$$

$$+ H_1(0)a_1(x)[2H_1(0)v(0)v'(0)a_1(x)$$

$$- v'(0)a_1(x) - 2v(0)a_2(x)] \qquad (2.18)$$

in order to be exact up to order $n^3$, etc. Given that these expressions, as well as the first few exact coefficients, can be evaluated in practice with not much effort for the most interesting interparticle potentials, the method is also valuable to that purpose. Moreover, one may expect, in principle, that an integral equation which is exact up to, say order $n^3$ (as compared to the most familiar ones which are only exact up to order $n$; see Sec. III will also increase its accuracy for higher orders.

## III. SOME PRACTICAL APPLICATIONS

This section is devoted to further discussing practica applications of the method in Sec. II; in particular, we devis two simple ways to approximate the functions $h$ and $\omega$ pro ducing the exact integral equation.

As a simple illustration we first show that, as it wa argued before, the PY equation and the HNC equation can not be exact up to order $n^3$ nor even up to order $n^2$. In fac the PY case follows from the formalism for $h(v) = v$ an any function $\omega$, so that one has from Eqs. (2.17) and (2.18) respectively, that $\bar{a}_2(x) = 0$ and $\bar{a}_3(x) = 0$ which are obv ously false. On the other hand, the generating function $h(v) = \ln v$ for the HNC equation reduces the conditio (2.17), for instance, to the relation $2\bar{a}_2(x) = a_1^2(x)$ whic cannot be true, in general.

In order to look for convenient explicit expressions fc the functions $h$ and $\omega$, one may proceed as follows. L $k(x) \equiv -2\bar{a}_2(x)/a_1^{-2}(x)$; the condition (2.17) and the d finition (2.13) then leads t $k(x) = \ddot{h}[v(0,x)]h^{-1}[v(0,x)]v(0,x)$. Assuming th: $v(0,x)$ can be inverted, i.e., $x = x(v)$, one h: $k(x) = \bar{k}(v) = \ddot{h}(v)h^{-1}(v)v$ whose solution is

$$h(v) = \text{const} \int dv \exp\left[\int \bar{k}(v)v^{-1}\, dv\right] + \text{const}, \qquad (3.1$$

where the integration constants turn irrelevant when this used in Eq. (2.9) Equation (3.1) thus states a relatic between the functions $h$ and $\omega$ which would produce an int gral equation exact up to order $n^2$. The procedure may i followed systematically to higher orders; i.e., one would u now Eq. (3.1) in condition (2.18) to obtain further relatio between $h$ and $\omega$, etc.

In order to follow that procedure in practice, it is mc convenient to fix intuitively a function $h$ and to adjust th the function $\omega$ (or $v$) satisfying the required conditions [i conditions such as the one in Eq. (2.1), etc.]. For instan. the choice $h(v) = v + v^2$ and $v(n,x) = v_0(x) + nv_1($ may be seen to lead, after not much effort, to a nonlin integral equation for the radial distribution function g( which is exact up to order $n^3$. The resulting equation in t case, which we avoid writing explicitly here because we or mention that case for illustrative purposes, is more comp: than the PY equation, for instance. However, the eff needed to treat numerically the new integral equation comparable to the one in the case of the PY equation fo realistic potential, so that the method may be useful in pr tice.

The above procedure to obtain "good" functions $h$ an may also be implemented, or complemented, in the follc ing way, for instance. Let us denote $h$ and $v$ the (unknov functions producing any desired accuracy, e.g., the ones p duced in Eq. (2.9), *the* exact integral equation. Let $\tilde{h}$ an denote some trial functions (obtained, for instance, means of the procedure in the previous paragraph) such t $h = \tilde{h} + \delta h$, $v = \tilde{v} + \delta v$, with small deviations $\delta h$ and The condition $\ddot{h}(v)h^{-1}(v)v = \ddot{h}(\tilde{v})\tilde{h}^{-1}(\tilde{v})\tilde{v}$ gives a r tion between $\delta v$ and $\delta h$ which, combined with Eq. (3.1), instance, will lead to a condition to be used iteratively order to approach $h$ and $v$. Summing up, the formalisn

Sec. II has a great versatility allowing specific aproaches to deal with different situations and different needs for accuracy.

## IV. CORRECTIONS OF THE PY AND HNC EQUATIONS

Our method may also be applied to obtain corrections for the expressions of the correlation functions $g(r)$ and $C(r)$ following from familiar approximations such as the PY and HNC equations. The basic idea now is that the desired pair distribution function, e.g., the one which is exact up to order $n'$, $i > 1$, may be written as

$$g(r) = g_0(r) + \lambda g_1(r), \tag{4.1}$$

where $g_0$ is the solution of a given integral equation, $g_1$ contains the missing diagrams, and $\lambda$ is a formal parameter ($\lambda \equiv 1$) used to identify the corrections. It will be assumed that

$$h(v) = h_0(v) + \lambda h_1(v), \tag{4.2}$$

where $h_0$ is the generating functional for the given integral equation and $h_1$ has to be adjusted to produce $g_1(r)$. In addition, the version of the method in the present section is characterized by the definition of the direct correlation function as the linear part following from Eq. (2.8) when one substitutes their Eqs. (4.1) and (4.2), i.e.,

$$C(r) = C_0(r) + \lambda C_1(r), \tag{4.3}$$

where $C_0$ is given by Eq. (2.8) with $h$ replaced by $h_0$, so that it represents the direct correlation function in the starting approximation. Our definition of $C(r)$ should not be considered as an actual approximation, given that Eq. (2.3), and Eq. (4.2) to some extent, are already arbitraries, but a rule generating a new type of integral equations.

The comparison of Eq. (4.3) with the expansion following from Eq. (2.8) with the substitutions (4.1) and (4.2) produces after some straightforward algebra:

$$C_1(r) = g_1(r)\left[1 - \dot{h}_0(\bar{v})\dot{h}_0^{-1}(v)e^{\beta\varphi}\right]$$

$$+ \left[v\dot{h}_0(v)\right]^{-1}[h_1(v) - h_1(\bar{v})]$$

$$- \left[v\dot{h}_0^2(v)\right]^{-1}\dot{h}_1(v)[h_0(v) - h_0(\bar{v})] \tag{4.4}$$

with $\bar{v} \equiv vg_0 \exp(\beta\varphi)$. Now, we require that $C(r)$ and $g(r)$ satisfy the Ornstein–Zernike equation, i.e., we substitute Eqs. (4.1) and (4.3) in Eq. (2.5); the resulting expression may be separated into two parts:

$$g_0(r) = C_0(r) + n \int ds[g_0(|s - r|) - 1]C_0(s) \tag{4.5}$$

and

$$g_1(r) = C_1(r) + n \int ds[g_0(|s - r|) - 1]C_1(s)$$

$$+ n \int ds g_1(|r - s|)[C_0(s) + \lambda C_1(s)]. \tag{4.6}$$

That is, the starting approximations $C_0$ and $g_0$ also satisfy the Ornstein–Zernike equation, while $C_1$ and $g_1$ do not. The present scheme also requires expansions,

$$g_{0,1} e^{-\beta\varphi} = a_0^{0,1} + a_1^{0,1}n + a_2^{0,1}n^2 + \cdots, \quad a_0^0 \equiv 1, \tag{4.7}$$

whose comparison with the one in Eq. (2.11) reveals

$$a_0^1 = 0, \quad a_i^0 + \lambda a_i^1 = a_i, \quad i > 1, \tag{4.8a}$$

as a consequence of Eq. (4.1). Moreover, when $g_0$ represents either the PY approximation or the HNC approximation, one has

$$a_1^1 = 0 \tag{4.8b}$$

because they are known to be exact up to order $n$ (cf. Sec. III).

The rest of this section will be devoted to the application of the above method to obtain the correction required by the PY and HNC results in order to produce correlation functions exact up to order $n^2$.

### A. The Percus–Yevick case

Let $h_0(v) = v$. It follows from Eq. (4.4) after performing a density expansion that

$$C_1(r) = [a_2^1(r)\{e^{-\beta\varphi(r)} - 1\}$$

$$- \tfrac{1}{2}\ddot{h}_1(0)v(0)a_1^2(r)]n^2 + \theta(n^3); \tag{4.9}$$

the use of Eqs. (4.9), (4.7), and (2.11) in Eq. (4.6) then shows that $g_1 \sim C_1$ up to order $n^2$ and, as a consequence, that

$$a_2^1(r) = -\tfrac{1}{2}\ddot{h}_1(0)v(0)a_1^2(r). \tag{4.10}$$

Now, as $g_1$ should include the diagrams lacking in $g_0$ up to order $n^2$, and $a_2 = a_2^{PY} + \lambda a_2^1$, so that $a_2^1 = \bar{a}_2\lambda^{-1}$, one has

$$\ddot{h}_1(0)v(0) = -2\bar{a}_2/\lambda a_1^2 \tag{4.11}$$

as the condition on $h_1$, and $v$ to obtain an integral equation which is exact up to order $n^2$.

This has a similar structure to condition (2.17), and it may in fact be exploited formally as before. For completeness, we shall, however, follow here a different approach: we shall choose $h_1$ and $v$ satisfying condition (4.11). For instance,

$$h_1(v) = v^2 \tag{4.12}$$

and, from Eq. (4.11), $v(0) = -\bar{a}_2/\lambda a_1$. Let then $v(n,r) = v(0,r)$: we have from Eq. (4.4) that

$$C_1(r) = g_1(r)[1 - e^{\beta\varphi(r)}] + (\bar{a}_2/\lambda a_1^2)[g_0 e^{\beta\varphi} - 1]^2, \tag{4.13}$$

and it follows from Eq. (4.6) an integral equation for $\lambda g_1$:

$$g_1 e^{\beta\varphi} = (\bar{a}_2/\lambda a_1^2)(g_0 e^{\beta\varphi} - 1)^2 + n$$

$$\times \int ds g_1(|r - s|)C_0(s) + n$$

$$\int ds C_1(s)[g_0(|r - s|) - 1 + \lambda g_1(|r - s|)]. \tag{4.14}$$

This method thus allows to use the already known results in the PY approximation to correct them up to order $n^2$ or higher.

## B. The HNC case

Let $h_0(v) = \ln v$. Equations (4.9)–(4.11) read now, respectively,

$$C_1(r) = \left\{ a_2^1 (e^{-\beta\varphi} - 1) - \tfrac{1}{4} a_1^2 v(0) \right.$$
$$\left. \times [\ddot{h}_1(0)v(0) + \dot{h}_1(0)] \right\} n^2 + \theta(n^3), \quad (4.15)$$

$$a_2^1 = - \tfrac{1}{4} a_1^2 v(0) [\ddot{h}_1(0)v(0) + \dot{h}_1(0)], \quad (4.16)$$

ane

$$v(0)[\ddot{h}_1(0)v(0) + \dot{h}_1(0)] = - 2\bar{a}_1/\lambda a_1^2. \quad (4.17)$$

A simple illustrative choice is

$$h_1(v) = v \quad (4.18)$$

implying $v(0,r) = - 2\bar{a}_2/\lambda a_1$ where $\bar{a}_2 \equiv a_2^{\prime,\text{xact}} - a_2^{\text{HNC}}$, and one has

$$C_1(r) = - \ln g_0(r) - \beta\varphi(r) - 1 + g_1(r)[1 - g_0(r)^{-1}]$$
$$- 2\bar{a}_2 a_1^{-2}[1 - g_0 e^{\beta\varphi} + \ln(g_0 e^{\beta\varphi})] \quad (4.19)$$

and

$$g_1(r) = C_1(r) + n \int ds[g_0(|\mathbf{r} - \mathbf{s}|) - 1]C_1(s)$$
$$+ n \int ds\, g_1(|\mathbf{r} - \mathbf{s}|)[C_0(s) + C_1(s)] \quad (4.20)$$

for the corrections up to order $n^2$.

## V. A SIMPLE EXPLICIT EXAMPLE

Finally, as a further illustration of the method, we shall compute explicitly the correction found in the preceding section to the PY equation in the case of a one-dimensional system of hard-core particles. Let us define

$$\tau_0(x) \equiv g_0(x)\exp[\beta\varphi(x)]; \quad (5.1)$$

the PY equation reads

$$\tau_0(x) = n \int_{\mathbb{R}} dr[\tau_0(r - x)e^{-\beta\varphi(r-x)} - 1]$$
$$\times \tau_0(r)[e^{-\beta\varphi(r)} - 1] + 1 \quad (5.2)$$

or

$$\tau_0(x) = n\theta(2 - x) \int_{x-1}^{1} dr\, \tau_0(r - x)\tau_0(r) + 1$$
$$+ n \int_{-1}^{1} dr\, \tau_0(r)[1 - \tau_0(r - x)], \quad (5.3)$$

where use was made of the expression

$$\exp[-\beta\varphi(x)] = \theta(x - 1) - \theta(x + 1) + 1,$$

where $\theta(y)$ represents the step function. It also follows that

$$a_1 = (2 - x)\theta(2 - x), \quad (5.4)$$

$$\bar{a}_2 = \tfrac{1}{4}\theta(2 - x)\{(x - 2)^2[1 - \theta(x - 1)]$$
$$+ (2x - 3)\theta(1 - x)\} \quad (5.5)$$

and, thus

$$\bar{a}_2 a_1^{-2} = \begin{cases} 0 & \text{when } |x| \geqslant 1 \\ \tfrac{1}{2}\dfrac{(1 - |x|)^2}{(2 - |x|)^2} & \text{when } |x| < 1 \end{cases}. \quad (5.6)$$

The correction up to order $n^2$ satisfies

$$\tau_1(x) = A(x)\theta(1 - x) + n\left[ \theta(2 - x) \int_{x-1}^{1} dx'\, f(x,x') \right.$$
$$\left. - \int_{-1}^{1} dx' f(x,x') \right], \quad (5.7)$$

where

$$f(x,x') = \tau_0(x' - x)[\tau_1(x') - A(x')]$$
$$+ \tau_1(x' - x)[\tau_0(x') + \tau_1(x') - A(x')] \quad (5.8)$$

and

$$A(x) = \tfrac{1}{2}(1 - |x|)^2(2 - |x|)^{-2}[\tau_0(x) - 1]^2. \quad (5.9)$$

Our corrected direct correlation function and radial distribution function are then given, respectively, by

$$C(x) = \begin{cases} 0 & \text{when } x > 1 \\ -\tau_0 - \tau_1 + \tfrac{1}{2}\dfrac{(1 - x)^2}{(2 - x)^2}(\tau_0 - 1)^2 & \text{when } x < 1 \end{cases} \quad (5.10)$$

and

$$g(x) = \begin{cases} \tau_0 + \tau_1 & \text{when } x > 1 \\ 0 & \text{when } x < 1 \end{cases}, \quad (5.11)$$

where $\tau_0$ and $\tau_1$ are the solutions of Eqs. (5.3) and (5.7), respectively. One may prove here rather simply, both from the expression in the present section and from those in Sec. IV, that $g_0 \to 1$ and $g_1 \to 0$, $g \to 1$ for any of the three limits $|x| \to \infty, \beta \to 0$, and $\varphi \to 0$. We also notice the following: Our method guarantees that functions (5.10) and (5.11) can only have corrections of order $n^3$ or higher. In the present particular case, however, the solution of Eq. (5.7) is

$$\tau_1(x) = \begin{cases} A(x), & |x| < 1 \\ 0, & |x| > 1 \end{cases} \quad (5.12)$$

and, when this is used in Eqs. (5.10) and (5.11), it readily follows that our corrected $C$ and $g$ are precisely equal to the ones in the PY approximation. This is in agreement with the theorem[19] that the PY approximation gives exact results in the case of a one-dimensional system of hard-core particles; even more, each correction in a density expansion is zero in this particular case. We are presently carrying a numerical analysis of some of the integral equations in this paper.

## ACKNOWLEDGMENTS

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