Radial distribution function for hard spheres

S. Bravo Yuste and A. Santos
Departamento de Física, Universidad de Extremadura, 06071 Badajoz, Spain
(Received 25 October 1990)

The radial distribution function $g(r)$ provided by the solution of the Percus-Yevick (PY) equation for hard spheres is rederived in terms of the simplest Padé approximant of a function defined in the Laplace space that is consistent with the following physical requirements: $g(r)$ is continuous for $r>1$, the isothermal compressibility is finite, and the zeroth- and first-order coefficients in the density expansion of $g(r)$ must be exact. An explicit expression for the solution of the generalized mean-spherical approximation (GMSA) is obtained as a simple extension involving two new parameters, which are determined by imposing two conditions: (i) the virial and the compressibility routes to the equation of state agree consistently, and (ii) this equation of state coincides with that of Carnahan and Starling [J. Chem. Phys. **51**, 635 (1969)]. The second- and third-order coefficients in the density expansion of $g(r)$ given by the GMSA are compared with the exact ones and with those given by the PY equation.

I. INTRODUCTION

Hard-sphere fluids are of interest as a model to test approximate theories and also as a useful reference system in perturbation schemes.[1] The well-known exact solution[2] of the Percus-Yevick (PY) integral equation provides a radial distribution function (RDF) $g(r)$ that has an overall good agreement with simulation data, although some discrepancies can be observed, especially at high densities.[1] To account for this, a number of parametrizations of simulation data have been proposed.[3] From a more fundamental point of view, Waisman[4] has solved the so-called generalized mean-spherical approximation (GMSA), where the direct correlation function $c(r)$ outside the core ($r>1$), which vanishes in the PY theory, is assumed to be given by a Yukawa form. Recent attempts are based on a functional ansatz for the tail function $d(r)$ that, by definition, is zero in the PY theory.[5]

The aim of this work is to get approximate expressions for the Laplace transform

$$G(t)=\int_0^{\infty} dr\, e^{-rt} r g(r) \tag{1.1}$$

by using simple heuristic arguments. In the simplest case, the Wertheim-Thiele solution of the PY equation is recovered. The next step gives an explicit expression for the function $G(t)$ of the GMSA. The method can be extended in a straightforward way to get more refined distribution functions.

The plan of the paper is as follows. The basic physical requirements for $G(t)$ are presented in Sec. II. Section III deals with the Padé approximant method to get an approximate expression for $G(t)$. The particular cases corresponding to the PY equation and the GMSA are considered explicitly. The first few terms of the series expansion of $g(r)$ in powers of density are obtained in Sec. IV. Finally, some concluding remarks are offered in Sec. V.

II. BASIC PHYSICAL REQUIREMENTS

The radial distribution function of a fluid, $g(r)$, gives us information about the structure and the correlations present in the fluid. It also provides the equation of state relating the pressure p, the temperature T, and the number density ρ:[1]

$$k_B T \left[\frac{\partial \rho}{\partial p}\right]_T = 1+\rho\int d\mathbf{r}\, h(r) , \tag{2.1}$$

$$\frac{p}{\rho k_B T} = 1+4\eta g(1^+) . \tag{2.2}$$

Equation (2.1) defines the compressibility route to the equation of state. In it, k_B is the Boltzmann constant and $h(r)\equiv g(r)-1$. The virial route, Eq. (2.2), has been particularized to hard spheres of unit diameter. In Eq. (2.2), $\eta=(\pi/6)\rho$ is the fraction of volume occupied by the spheres. At small densities, a useful representation of $g(r)$ is given in terms of a power-series expansion:

$$g(r)=\sum_{n=0}^{\infty} g_n(r)\eta^n . \tag{2.3}$$

The exact coefficients up to first order are

$$g_0(r)=\Theta(r-1) , \tag{2.4}$$

$$g_1(r)=\Theta(r-1)\Theta(2-r)(8-6r+\tfrac{1}{2}r^3) , \tag{2.5}$$

where Θ is the Heaviside step function.

The statistical-mechanical problem of determining $g(r)$ has not been solved. Thus one must resort to approximate theories. Any physically meaningful approximate RDF for hard spheres must accomplish the following two obvious conditions: (i) $g(r)$ is a continuous function for $r>1$ and vanishes for $r<1$, and (ii) $g(r)\to 1$ when $r\to\infty$

rapidly enough to guarantee that the integral of the right side of Eq. (2.1) converges at any fluid density. We shall also require that (iii) the zeroth- and first-order coefficients in the density expansion are given by Eqs. (2.4) and (2.5), respectively.

Let us translate the above conditions into Laplace space. Condition (iii) is equivalent to

$$G(t)=t[F_0(t)+F_1(t)\eta]e^{-t}-12\eta t[F_0(t)]^2e^{-2t}+O(\eta^2)\ , \tag{2.6}$$

where

$$F_0(t)=t^{-2}+t^{-3}\ , \tag{2.7}$$

$$F_1(t)=\tfrac{5}{2}t^{-2}-2t^{-3}-6t^{-4}+12t^{-5}+12t^{-6}\ . \tag{2.8}$$

The extrapolation of the structure of Eq. (2.6) to any order in η suggests the introduction of the auxiliary function $F(t)$ through

$$G(t)=\sum_{n=1}^{\infty}(-12\eta)^{n-1}t[F(t)]^n e^{-nt} \tag{2.9a}$$

$$=t\frac{F(t)e^{-t}}{1+12\eta F(t)e^{-t}}\ , \tag{2.9b}$$

or equivalently,

$$F(t)=e^t\frac{G(t)}{t-12\eta G(t)}\ . \tag{2.10}$$

Thus our condition (iii) means that the zeroth- and first-order terms in the density expansion of $F(t)$ are given by Eqs. (2.7) and (2.8), respectively.

Let us consider now condition (ii). Let $H(t)$ be the Laplace transform of $rh(r)$, defined similarly to Eq. (1.1). Both transforms are related by

$$G(t)=t^{-2}+H(t)\ . \tag{2.11}$$

Condition (ii) then implies that

$$H(t)=H^{(0)}+H^{(1)}t+o(t)\ , \tag{2.12}$$

where, according to Eq. (2.1),

$$H^{(1)}=\frac{1}{24\eta}\left[1-k_BT\left[\frac{\partial\rho}{\partial p}\right]_T\right]\ . \tag{2.13}$$

In the following, we shall generally use subscripts for the expansions in powers of density and superscripts for the expansions in powers of the Laplace variable t. Insertion of Eqs. (2.11) and (2.12) into Eq. (2.10) yields

$$F(t)=-\frac{1}{12\eta}\left[1+t+\tfrac{1}{2}t^2+\left[\frac{1}{6}+\frac{1}{12\eta}\right]t^3+\left[\frac{1}{24}+\frac{1}{12\eta}\right]t^4+O(t^5)\right]\ . \tag{2.14}$$

The next two terms not explicitly given in Eq. (2.14) are

$$F^{(5)}=-\frac{1}{12\eta}\left[\frac{1}{120}+\frac{1}{24\eta}-\frac{H^{(0)}}{12\eta}\right]\ , \tag{2.15}$$

$$F^{(6)}=F^{(5)}+\frac{1}{12\eta}\left[\frac{1}{144}+\frac{1}{36\eta}-\frac{1}{144\eta^2}+\frac{H^{(1)}}{12\eta}\right]\ . \tag{2.16}$$

In terms of the function $F(t)$, condition (ii) is given by Eq. (2.14).

Finally, we are going to consider condition (i). Laplace inversion of Eq. (2.9a) gives

$$rg(r)=\sum_{n=1}^{\infty}(-12\eta)^{n-1}f_{n-1}(r-n)\Theta(r-n)\ , \tag{2.17}$$

where $f_n(r)$ is such that its Laplace transform is $t[F(t)]^{n+1}$. Notice that, as an exception to our notation convention, the functions $f_n(r)$ are not directly related to the density expansion (2.3). In fact, $f_n(r)$ still depends on the density. According to condition (i), $f_0(0)=g(1^+)\neq 0$ and $f_n(0)=0$ for $n\geq 1$. This implies that, for large t, $tF(t)$ is of order t^{-1}, i.e.,

$$F(t)\sim t^{-2}\quad\text{when } t\to\infty\ . \tag{2.18}$$

The amplitude of this asymptotic behavior is precisely $g(1^+)$:

$$g(1^+)=\lim_{t\to\infty}t^2F(t)\ . \tag{2.19}$$

In summary, we define the function $F(t)$ through Eq. (2.10), and require that any physically meaningful approximate RDF be consistent with (i) Eq. (2.18), (ii) Eq. (2.14), and (iii) Eqs. (2.7) and (2.8).

III. PADÉ APPROXIMANT METHOD

The requirements (2.14) and (2.18) can be fulfilled if one proposes a Padé approximant of the form $F(t)=P(\nu;t)/P(\mu;t)$ with $\nu+\mu\geq 4$ and $\mu=\nu+2$, where $P(\nu;t)$ denotes a polynomial of degree ν. The simplest choice is $\nu=1$, $\mu=3$:

$$F(t)=F_{\rm PY}(t)$$

$$=-\frac{1}{12\eta}\frac{1+L^{(1)}_{\rm PY}t}{1+S^{(1)}_{\rm PY}t+S^{(2)}_{\rm PY}t^2+S^{(3)}_{\rm PY}t^3}\ . \tag{3.1}$$

By expanding $F_{\rm PY}(t)$ in powers of t and requiring agreement with Eq. (2.14), we get

$$L^{(1)}_{\rm PY}=\frac{1+\frac{1}{2}\eta}{1+2\eta}\ , \tag{3.2}$$

$$S^{(1)}_{\rm PY}=-\frac{3}{2}\frac{\eta}{1+2\eta}\ , \tag{3.3}$$

$$S^{(2)}_{\rm PY}=-\frac{1}{2}\frac{1-\eta}{1+2\eta}\ , \tag{3.4}$$

$$S^{(3)}_{\rm PY}=-\frac{(1-\eta)^2}{12\eta(1+2\eta)}\ . \tag{3.5}$$

This is precisely the form that adopts $F(t)$ in the case of the Wertheim-Thiele solution of the PY equation.[2,6] Our analysis shows that $F_{\rm PY}(t)$ allows the interpretation as the simplest Padé approximant for $F(t)$ that is consistent with the basic physical requirements described in Sec. II.

In fact, we have not explicitly imposed Eqs. (2.7) and (2.8) so far. From Eqs. (3.1)–(3.5) it is easy to check that those conditions are indeed satisfied. In this respect, we can say that the requirement (iii) about the low density behavior has already played a role by suggesting the introduction of $F(t)$, so that now Eqs. (2.7) and (2.8) are redundant. We shall come back to this point in Sec. IV.

For the sake of completeness, let us obtain the PY equations of state. The virial equation of state is given by Eq. (2.2) with $g_{\rm PY}(1^+)$ given by Eq. (2.19):

$$g_{\rm PY}(1^+)=-\frac{1}{12\eta}\frac{L_{\rm PY}^{(1)}}{S_{\rm PY}^{(3)}}=\frac{1+\frac{1}{2}\eta}{(1-\eta)^2}\ . \tag{3.6}$$

According to Eq. (2.16), the difference between $F_{\rm PY}^{(6)}(t)$ and $F_{\rm PY}^{(5)}(t)$ gives

$$H_{\rm PY}^{(1)}=\frac{8-2\eta+4\eta^2-\eta^3}{24(1+2\eta)^2}\ . \tag{3.7}$$

Insertion of Eq. (3.7) into Eq. (2.13) provides the compressibility equation of state.

The next obvious extension to the Padé approximant (3.1) consists of taking $\nu=2$, $\mu=4$:

$$F(t)=F_{\rm GMSA}(t)=-\frac{1}{12\eta}\frac{1+L^{(1)}t+L^{(2)}t^2}{1+S^{(1)}t+S^{(2)}t^2+S^{(3)}t^3+S^{(4)}t^4}\ . \tag{3.8}$$

Condition (2.14) implies that

$$L^{(1)}=L_{\rm PY}^{(1)}+\frac{12\eta}{1+2\eta}(\tfrac{1}{2}L^{(2)}-S^{(4)})\ , \tag{3.9}$$

$$S^{(1)}=S_{\rm PY}^{(1)}+\frac{12\eta}{1+2\eta}(\tfrac{1}{2}L^{(2)}-S^{(4)})\ , \tag{3.10}$$

$$S^{(2)}=S_{\rm PY}^{(2)}+\frac{12\eta}{1+2\eta}\left[\frac{1-4\eta}{12\eta}L^{(2)}+S^{(4)}\right]\ , \tag{3.11}$$

$$S^{(3)}=S_{\rm PY}^{(1)}-\frac{12\eta}{1+2\eta}\left[\frac{1-\eta}{12\eta}L^{(2)}+\tfrac{1}{2}S^{(4)}\right]\ . \tag{3.12}$$

In order to determine the parameters $L^{(2)}$ and $S^{(4)}$ we need two extra conditions. According to the philosophy of the Padé approximant method, those conditions would be given by Eqs. (2.15) and (2.16) with prescribed values for $H^{(0)}$ and $H^{(1)}$. Nevertheless, we are going to depart from that philosophy, since $H^{(0)}$ is not directly related to a thermodynamic quantity. Thus we choose to adjust the parameters $L^{(2)}$ and $S^{(4)}$ by requiring prescribed values for $g(1^+)$ and $H^{(1)}$. From Eq. (2.19), one has

$$g(1^+)=-\frac{1}{12\eta}\frac{L^{(2)}}{S^{(4)}}\ . \tag{3.13}$$

Expansion of Eq. (3.8) in powers of t and use of Eqs. (3.9)–(3.12) allow one to obtain $F^{(5)}$ and $F^{(6)}$ in terms of $L^{(2)}$ and $S^{(4)}$. According to Eq. (2.16), subtraction of $F^{(5)}$ from $F^{(6)}$ leads (after tedious algebra) to

$$H^{(1)}=H_{\rm PY}^{(1)}-6\eta\frac{(\eta-1)^2}{(1+2\eta)^2}[L^{(2)}+12\eta g_{\rm PY}(1^+)S^{(4)}]\times\left[L^{(2)}+12\eta g_{\rm PY}(1^+)S^{(4)}-\frac{\eta-1}{6\eta}\right]\ . \tag{3.14}$$

It is worth noticing that if one prescribes $g(1^+)=g_{\rm PY}(1^+)$, then one has $H^{(1)}=H_{\rm PY}^{(1)}$, and $S^{(4)}$, or $L^{(2)}$, is still undetermined. This would give a one-parameter family of RDF's, all of them consistent with the PY equations of state. Here, however, we impose that $g(1^+)$ and $H^{(1)}$ coincide with the values corresponding to the excellent Carnahan-Starling (CS) equation of state:[1,7]

$$\frac{p}{\rho k_B T}=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\ . \tag{3.15}$$

Using Eq. (3.15) in Eqs. (2.2) and (2.13), we get

$$g_{\rm CS}(1^+)=\frac{1-\frac{1}{2}\eta}{(1-\eta)^3}\ , \tag{3.16}$$

$$H_{\rm CS}^{(1)}=\frac{4-\eta}{12\eta(1+4\eta+4\eta^2-4\eta^3+\eta^4)}\ . \tag{3.17}$$

This assures the consistency between the virial and the compressibility routes to the equation of state. Substitution of Eqs. (3.16) and (3.17) into Eqs. (3.13) and (3.14) gives a quadratic equation for $S^{(4)}$ whose physical solution is

$$S^{(4)}=-\frac{(1-\eta)^4}{72\eta(\eta^3-3\eta-1)}\times\left[3+(1+2\eta)\times\left[\frac{3(\eta^2-5\eta+7)}{\eta^4-4\eta^3+4\eta^2+4\eta+1}\right]^{1/2}\right]\ . \tag{3.18}$$

The other solution is positive and must be discarded. Otherwise, as shown by Eq. (3.13), $L^{(2)}<0$ and there would exist a positive real value of t at which $F(t)=G(t)=0$, which is not compatible with a positive-definite RDF.

In 1973, Waisman[4] solved the Orstein-Zernike equation for a fluid of hard spheres under the ansatz that the direct correlation function $c(r)$ outside the core has a Yukawa form. The parameters of the Yukawa function are adjusted to give the Carnahan-Starling equation of state in a consistent way. This is known as the generalized mean-spherical approximation. Further analysis[8,9] showed that in the GMSA the Laplace transform $G(t)$ has the form given by Eqs. (2.9b) and (3.8). However, explicit expressions for the parameters appearing in Eq. (3.8) were not found and the RDF was obtained numerically.[4,8]

The method described here is a shortcut that allows one to get quite straightforwardly the function $G(t)$. In

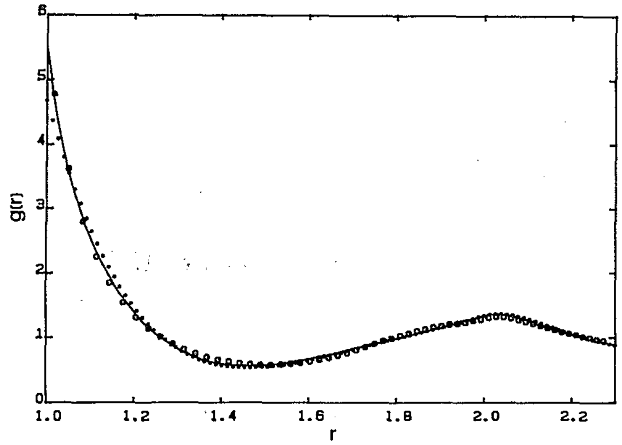

FIG. 1. Comparison between the radial distribution functions obtained from simulation (Ref. 10) (circles), the PY equation (dotted line), and the GMSA (solid line), at a density $\eta=0.484$.

the case of the GMSA, it is given by Eqs. (2.9b), (3.8)–(3.13), (3.16), and (3.18). Then, Eq. (2.17) can be used to easily get the RDF in a finite domain. Figure 1 compares the RDF obtained from simulation,[10] the PY equation, and the GMSA, at a density $\eta=0.484$, close to the liquid-solid transition. We can observe that the GMSA represents a significant improvement over the PY results in the range $1\le r\le 1.6$. For larger distances both theories are hardly distinguishable.

IV. DENSITY EXPANSION

So far, we have not checked that the function $F(t)$ given by Eqs. (3.8)–(3.13), (3.16), and (3.18) is consistent with Eqs. (2.7) and (2.8). From Eq. (3.18) one gets

$$S^{(4)}=-\frac{1}{\eta}(\alpha_0+\alpha_1\eta+\cdots)\,, \tag{4.1}$$

where $\alpha_0=(\sqrt{7/3}-1)/24$ and $\alpha_1=[7-103/(2\sqrt{21})]/24$. The two first terms in the density expansion of $L^{(2)}$ are obtained from Eq. (3.13) by taking into account the exact behavior $g(1^+)=1+\frac{5}{2}\eta+\cdots$. The result is

$$L^{(2)}=12[\alpha_0+(\tfrac{5}{2}\alpha_0+\alpha_1)\eta+\cdots]\,. \tag{4.2}$$

The density expansion of $L^{(1)}$, $S^{(1)}$, $S^{(2)}$, and $S^{(3)}$ can then be obtained from Eqs. (3.9)–(3.12). Finally, the expansion of $F(t)$ comes from Eq. (3.8).

Although the coefficients $\alpha_0,\alpha_1,\cdots$ have well-defined numerical values in the GMSA, it is convenient to consider them as free parameters for the time being. In principle, the coefficient F_0 should depend on the value of α_0, the coefficient F_1 should depend on the values of α_0 and α_1, and so on. However, it is a simple matter to verify that F_0 and F_1 are given by Eqs. (2.7) and (2.8), respectively, regardless of the values of α_0 and α_1. This shows again that condition (iii) is to some extent redundant once one chooses to impose conditions (i) and (ii) on a Padé approximant to the auxiliary function $F(t)$.

The first coefficient in Eq. (2.3) that is not exact in the PY equation and in the GMSA is $g_2(r)$. Here, we are going to obtain explicit expressions for $g_2(r)$ and $g_3(r)$ in both theories. From Eq. (2.9a), we have

$$G_2(t)=tF_2(t)e^{-t}-24tF_0(t)F_1(t)e^{-2t}+144t[F_0(t)]^3e^{-3t}\,, \tag{4.3}$$

$$G_3(t)=tF_3(t)e^{-t}-12\{[F_1(t)]^2+2F_0(t)F_2(t)\}e^{-2t}+432t[F_0(t)]^2F_1(t)e^{-3t}-1728[F_0(t)]^4e^{-4t}\,. \tag{4.4}$$

Thus, in order to get $g_2(r)$ and $g_3(r)$, we first need $F_2(t)$ and $F_3(t)$. In the case of the PY equation, they can be obtained from Eq. (3.1). The calculations are rather cumbersome and the final results are

$$F_{\mathrm{PY},2}(t)=4t^{-2}-14t^{-3}-12t^{-4}+96t^{-5}-48t^{-6}-144t^{-7}+144t^{-8}+144t^{-9}\,, \tag{4.5}$$

$$F_{\mathrm{PY},3}(t)=\tfrac{11}{2}t^{-2}-35t^{-3}+9t^{-4}+360t^{-5}-720t^{-6}-432t^{-7}+2376t^{-8}-864t^{-9}-2592t^{-10}+1728t^{-11}+1728t^{-12}\,. \tag{4.6}$$

In the case of the GMSA, Eq. (3.8) yields

$$F_{\mathrm{GMSA},2}(t)=F_{\mathrm{PY},2}(t)+\frac{6\alpha_0}{t(1-12\alpha_0t)}\,, \tag{4.7}$$

$$F_{\mathrm{GMSA},3}(t)=F_{\mathrm{PY},3}(t)+6\frac{36\alpha_0^2t^4+(7\alpha_0+\alpha_1-144\alpha_0^2)t^3-12\alpha_0t^2+288\alpha_0^2t+24\alpha_0}{t^4(1-12\alpha_0t)^2}\,. \tag{4.8}$$

Notice that $F_{\mathrm{GMSA},2}$ and $F_{\mathrm{GMSA},3}$ only depends on α_0 and α_1.

Laplace inversion of Eqs. (4.3) and (4.4) in the case of the PY equation gives

$$g_{\mathrm{PY},2}=\Theta(r-1)\Theta(2-r)(\tfrac{1}{35}r^6-\tfrac{9}{5}r^4+6r^3+9r^2-\tfrac{258}{5}r+47-\tfrac{162}{35}r^{-1})+\Theta(r-2)\Theta(3-r)(-\tfrac{1}{35}r^6+\tfrac{9}{5}r^4-6r^3-9r^2+\tfrac{324}{5}r-81+\tfrac{486}{35}r^{-1})\,, \tag{4.9}$$

$$g_{\mathrm{PY},3}=\Theta(r-1)\Theta(2-r)(\tfrac{1}{2100}r^9-\tfrac{3}{35}r^7+\tfrac{16}{35}r^6+\tfrac{12}{5}r^5-\tfrac{573}{25}r^4+\tfrac{77}{2}r^3+\tfrac{2658}{35}r^2-\tfrac{5367}{20}r+\tfrac{22\,843}{105}-\tfrac{13\,299}{350}r^{-1})+\Theta(r-2)\Theta(3-r)(-\tfrac{1}{1050}r^9+\tfrac{6}{35}r^7-\tfrac{32}{35}r^6-\tfrac{24}{5}r^5+\tfrac{249}{5}r^4-\tfrac{205}{2}r^3-\tfrac{1146}{7}r^2+\tfrac{3423}{4}r-\tfrac{20\,323}{21}+\tfrac{89\,049}{350}r^{-1})+\Theta(r-3)\Theta(4-r)(\tfrac{1}{2100}r-\tfrac{3}{35}r^7+\tfrac{16}{35}r^6+\tfrac{12}{5}r^5-\tfrac{672}{25}r^4+64r^3+\tfrac{3072}{35}r^2-\tfrac{3072}{5}r+\tfrac{90\,112}{105}-\tfrac{49\,152}{175}r^{-1})\,. \tag{4.10}$$

A similar calculation in the case of the GMSA gives rise to

$$g_{\mathrm{GMSA},2}(r)=g_{\mathrm{PY},2}(r)+\Theta(r-1)\frac{e^{-(r-1)/(12\alpha_0)}}{2r}, \tag{4.11}$$

$$g_{\mathrm{GMSA},3}(r)=g_{\mathrm{PY},3}(r)+\Theta(r-1)\left[\frac{4\alpha_0+\alpha_1}{24\alpha_0^2}(r-1)+\tfrac{3}{2}+72\alpha_0(1-288\alpha_0^2)\right]\frac{e^{-(r-1)/(12\alpha_0)}}{r}$$
$$+\Theta(r-2)1728(12\alpha_0-1)\alpha_0^2\frac{e^{-(r-2)/(12\alpha_0)}}{r}+\Theta(r-1)\Theta(2-r)72\alpha_0[r-2(12\alpha_0+1)+24\alpha_0(12\alpha_0+1)r^{-1}]. \tag{4.12}$$

The most remarkable point in Eqs. (4.11) and (4.12) is the existence of Yukawa tails. This contradicts the exact property, retained by the PY approximation, that $g_n(r)$ vanishes for $r\geq n+1$. The violation of this property is the price to be paid by the GMSA. On the other hand, the GMSA gives self-consistently the Carnahan-Starling equation of state. In any case, the fact that $g_{\mathrm{GMSA},n}(n+1)\neq 0$ is not very important in practice, since the range of the Yukawa tails is quite short: $12\alpha_0=0.264$.

The exact functions $g_{\mathrm{exact},2}(r)$ and $g_{\mathrm{exact},3}(r)$ were evaluated numerically by Ree *et al.*[11] The deviations $\Delta g_{\mathrm{PY},2}(r)=g_{\mathrm{PY},2}(r)-g_{\mathrm{exact},2}(r)$ and $\Delta g_{\mathrm{GMSA},2}(r)=g_{\mathrm{GMSA},2}(r)-g_{\mathrm{exact},2}(r)$ are plotted in Fig. 2. Similarly, Fig. 3 shows the deviations $\Delta g_{\mathrm{PY},3}(r)$ and $\Delta g_{\mathrm{GMSA},3}(r)$. From Fig. 2, we can observe that the GMSA predicts a much better function $g_2(r)$ than the PY equation only for short distances $(1\leq r<1.3)$. For $r>1.5$, $g_{\mathrm{PY},2}(r)$ coincides practically with the exact function. Similar conclusions can be drawn from Fig. 3. Here, the improvement of GMSA over PY extends up to $r\simeq 1.8$ and $g_{\mathrm{PY},3}(r)$ is practically correct for $r>2.2$. The good agreement between $g_{\mathrm{GMSA}}(r)$ and $g_{\mathrm{PY}}(r)$ for $r>1.6$ observed in Fig. 1 for a dense fluid indicates an effective cancellation of the discrepancies in the coefficients of the density expansion. This is consistent with the fact that, for intermediate and large distances, $g_{\mathrm{GMSA},2}(r)>g_{\mathrm{PY},2}(r)$, while $g_{\mathrm{GMSA},3}(r)<g_{\mathrm{PY},3}(r)$.

V. CONCLUDING REMARKS

The main objective of this paper has been to show that reliable approximate RDF's for a fluid of hard spheres can be obtained by imposing very weak requirements. In particular, we consider here (i) continuity of $g(r)$ for $r>1$ and (ii) rapid decay of $g(r)$ to its asymptotic value, so that the thermal compressibility is finite. It is evident that a RDF that does not fulfill one of the above conditions cannot qualify as a decent approximation. The problem arises of how to implement these conditions. Since they are of a global character, the use of the Laplace space seems appropriate. As a guide to choosing an auxiliary function on which to apply the approximations, we have additionally required that (iii) the density expansion of the approximate RDF must be exact up to first order. This condition prompts the introduction of $F(t)$ through Eq. (2.10). Then, conditions (i) and (ii) impose the behavior of $F(t)$ for large t, Eq. (2.18), and for small t, Eq. (2.14), respectively. It is evident that a simple way of reconciling both asymptotic behaviors is by means of Padé approximants.

The Padé approximant involving the least number of parameters turns out to be related to the solution of the PY equation. Similarly, the next step is related to the GMSA. Both theories predict quite good RDF's, the GMSA being significantly better for short distances at high densities. The solutions have been rederived here following very general principles and with great

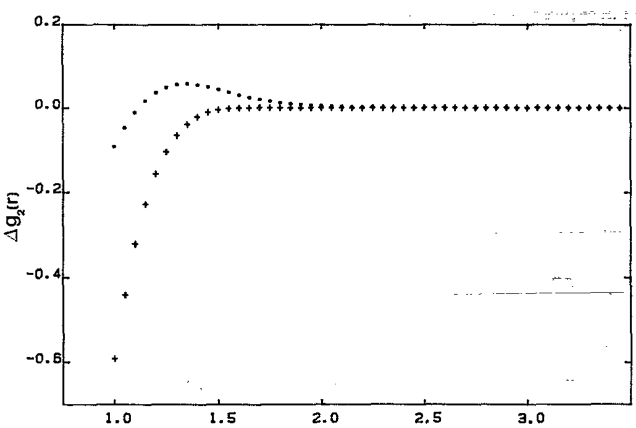

FIG. 2. Difference $\Delta g_2(r)$ between the approximate second-order coefficient $g_2(r)$ and the exact one (Ref. 11). The crosses correspond to the PY equation and the dots to the GMSA.

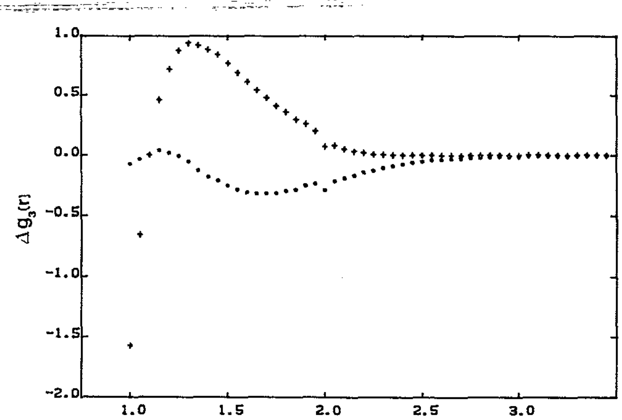

FIG. 3. The same as in Fig. 2, but for $\Delta g_3(r)$. The anomaly at $r=2$ is probably due to a small numerical error in the value tabulated in Ref. 11.

mathematical economy. In fact, the Laplace transform of $rg(r)$ in the GMSA had not been explicitly expressed previously, to the best of our knowledge. Furthermore, the second- and third-order coefficients in the density expansion of $g(r)$ corresponding to the GMSA have been obtained. They have contributions of Yukawa form, so that $g_2(r)\neq 0$ and $g_3(r)\neq 0$ for $r>3$ and $r>4$, respectively, in contrast to the exact property retained by the PY equation. This shortcoming of the GMSA might be related to the fact that it is constructed by assuming a Yukawa form for the direct correlation function outside the core, rather than by resumming a subset of diagrams in the exact density expansion (as is the case with the PY equation).

The method described in this paper can be extended along different lines. In the case of the hard spheres, one could go a step further and consider the next Padé approximant. This would imply imposition of two new conditions. The static structure of a lattice gas of hard particles can also be analyzed with the aid of the Z transform, the analog of the Laplace transform for functions of discrete, integer-valued argument. Finally, the method can also be adapted to a potential with an attractive part, such as the square-well interaction. In this latter case, no exact solution of the PY equation is known. Work is now in progress along these lines.

ACKNOWLEDGMENT

Partial support from the Dirección General de Investigación Científica y Técnica (Spain) through Grants No. PB87-0007 and No. PS89-0183 is gratefully acknowledged.

[1]J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).
[2]M. S. Wertheim, Phys. Rev. Lett. **10**, 321 (1963); E. Thiele, J. Chem. Phys. **39**, 474 (1963).
[3]L. Verlet and J. J. Weis, Phys. Rev. A **5**, 939 (1972); E. W. Grundke and D. Henderson, Mol. Phys. **24**, 269 (1972); D. Henderson and E. W. Grundke, J. Chem. Phys. **63**, 601 (1975).
[4]E. Waisman, Mol. Phys. **25**, 45 (1973).
[5]G. Giunta, C. Caccamo, and P. V. Giaquinta, Phys. Rev. A **31**, 2477 (1985).
[6]G. J. Throop and R. J. Bearman, J. Chem. Phys. **42**, 2048 (1965).
[7]N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).
[8]D. Henderson and L. Blum, Mol. Phys. **32**, 1627 (1976).
[9]J. S. Hoye and L. Blum, J. Stat. Phys. **16**, 399 (1977).
[10]J. A. Barker and D. Henderson, Annu. Rev. Phys. Chem. **23**, 439 (1972).
[11]F. H. Ree, R. N. Keeler, and S. L. McCarthy, J. Chem. Phys. **44**, 3407 (1966).