Sticky hard spheres beyond the Percus-Yevick approximation

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The radial distribution function $g(r)$ of a sticky-hard-sphere fluid is obtained by assuming a rational-function form for a function related to the Laplace transform of $rg(r)$, compatible with the conditions of finite $y(r) \equiv g(r)e^{\varphi(r)/k_B T}$ at contact point and finite isothermal compressibility. In a recent paper [S. Bravo Yuste and A. Santos, J. Stat. Phys. **72**, 703 (1993)] we have shown that the simplest rational-function approximation, namely, the Padé approximant (2,3), leads to Baxter's exact solution of the Percus-Yevick equation. Here we consider the next approximation, i.e., the Padé approximant (3,4), and determine the two new parameters by imposing the values of $y(r)$ at contact point and of the isothermal compressibility. Comparison with Monte Carlo simulation results shows a significant improvement over the Percus-Yevick approximation.

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I. INTRODUCTION

In 1968, Baxter [1] introduced the sticky-hard-sphere fluid. In it, the molecules interact through a square-well potential of infinite depth and vanishing width. This model is interesting not only because it is exactly solvable in the Percus-Yevick (PY) approximation [1], but also because it is appropiate for describing structural properties of colloids, micelles, and microemulsions [2].

In a recent paper [3], we derived analytic expressions for the radial distribution functions (RDF) of sticky hard rods and sticky hard spheres. In both cases, a function related to the Laplace transform of the RDF is given as the simplest Padé approximant compatible with some basic physical requirements. In the one-dimensional case the ansatz turns out to be exact, while in the three-dimensional case the result coincides with that of the PY approximation [1].

The aim of this paper is to extend the method of Ref. [3] by considering the next Padé approximant. Since two new coefficients appear, two extra requirements are needed. A similar situation is present in the case of pure hard spheres [4]. In that case, the two coefficients are fixed by requiring the virial and compressibility routes to the equation of state to agree self-consistently with the celebrated Carnahan-Starling (CS) equation of state [4]. Unfortunately, we are not aware of any semiempirical equation of state for sticky hard spheres playing a role similar to that as the CS equation does for pure hard spheres. Consequently, we have chosen to use simulation data [5] to get crude estimates of the energy and the compressibility. The RDF obtained in this way is compared with simulation results [5] and represents a significant improvement over the PY approximation.

The sticky-hard-sphere interaction and some basic definitions and equations are introduced in Sec. II. The method to get analytical expressions for the RDF is worked out in Sec. III. In Sec. IV our approximation is compared with simulation. The paper ends with a brief discussion in Sec. V.

II. STICKY HARD SPHERES

Let us consider a simple classic fluid at equilibrium at number density ρ and temperature T, whose molecules interact via the square-well potential

$$\varphi(r) = \begin{cases} \infty & , & r < 1 \\ -\varepsilon & , & 1 < r < \lambda \\ 0 & , & \lambda < r , \end{cases} \qquad (2.1)$$

where the hard-core diameter defines the length unit. Now we take the limits of infinite depth ($\varepsilon \to \infty$) and vanishing width ($\lambda - 1 \to 0$) with $\tau \equiv \frac{1}{12}(\lambda-1)^{-1}e^{-\varepsilon/k_B T}$ finite. Here k_B is the Boltzmann constant. The parameter τ is a monotonically increasing function of T and its inverse measures the degree of "adhesiveness" of the spheres. The case of pure hard spheres is recovered in the limit $\tau \to \infty$ (infinite temperature or, equivalently, zero adhesiveness).

For a general potential $\varphi(r)$, the structure of the fluid is described by the RDF $g(r)$ [6] or, equivalently, by the auxiliary function $y(r) \equiv g(r)e^{\varphi(r)/k_B T}$. The Fourier transform of $h(r) \equiv g(r) - 1$ is directly related to the structure factor $S(q)$:

$$S(q) = 1 + \rho \int d\mathbf{r}\, e^{-i\mathbf{q}\cdot\mathbf{r}}\, h(r) . \qquad (2.2)$$

The RDF also gives the thermodynamical quantities

$$z \equiv \frac{p}{\rho k_B T} = 1 - \frac{1}{6}\frac{\rho}{k_B T}\int d\mathbf{r}\, r\, \frac{d\varphi(r)}{dr}\, g(r) , \qquad (2.3)$$

$$\chi \equiv k_B T \left(\frac{\partial\rho}{\partial p}\right)_T = 1 + \rho \int d\mathbf{r}\, h(r) , \qquad (2.4)$$

$$u_{\text{ex}} = \frac{1}{2}\rho \int d\mathbf{r}\, \varphi(r)\, g(r) . \qquad (2.5)$$

In these equations, p is the pressure, χ is the isothermal susceptibility, and u_{ex} is the excess internal energy per particle. In the case of sticky hard spheres, Eqs. (2.3) and (2.5) become, respectively, [3]

$$z = 1 + 4\eta \left\{ y(1) - \frac{1}{12\tau} \left[3y(1) + \bar{y}'(1^+) \right] \right\} , \quad (2.6)$$

$$\frac{u_{ex}}{\epsilon} = -\eta\,\tau\,y(1) , \quad (2.7)$$

where $\eta \equiv \frac{\pi}{6}\rho$ and

$$\bar{y}'(1+) \equiv \lim_{\lambda \to 1+} \lim_{r \to 1+} \frac{d}{dr} y(r) . \quad (2.8)$$

Also, the relationship between $g(r)$ and $y(r)$ becomes

$$g(r) = y(r)\Theta(r-1) + \frac{1}{12\tau}y(1)\delta_+(r-1) , \quad (2.9)$$

where $\Theta(x)$ is the Heaviside step function. In all these equations we have taken into account the fact that $y(r)$ is finite and continuous at $r = 1$.

Equations (2.6), (2.4), and (2.7) are usually referred to as the virial, compressibility, and energy routes to the equation of state, respectively. Thermodynamical consistency implies that

$$\frac{1}{\chi} = \frac{\partial}{\partial\eta}(\eta z) , \quad (2.10)$$

$$\eta\frac{\partial}{\partial\eta}\left(\frac{u_{ex}}{\epsilon}\right) = -\tau\frac{\partial z}{\partial\tau} . \quad (2.11)$$

Of course, these equations do not necessarily hold when an approximate RDF is used to obtain z, χ, and u_{ex}.

Let us now introduce the Laplace transform $G(t)$ of $rg(r)$:

$$G(t) = \int_1^\infty dr\, e^{-rt}\, r\, g(r) . \quad (2.12)$$

The function $G(t)$ is related to the structure factor in a simple way:

$$S(q) = 1 - 24\eta\,\mathrm{Re}\lim_{t \to iq} t^{-1}\left[G(t) - t^{-2}\right] . \quad (2.13)$$

It is convenient to introduce a function $F(t)$ by [3,4]

$$G(t) = t\,\frac{F(t)e^{-t}}{1 + 12\eta F(t)e^{-t}} . \quad (2.14)$$

Inversion of this equation yields

$$rg(r) = \sum_{n=1}^\infty (-12\eta)^{n-1} f_n(r-n)\Theta(r-n) , \quad (2.15)$$

where $f_n(r)$ is the inverse Laplace transform of $t[F(t)]^n$. Thus, the knowledge of $F(t)$ is fully equivalent to that

of $g(r)$. In particular, $y(1)$ is simply obtained from the behavior of $F(t)$ for large t [3]:

$$F(t) = \frac{1}{12\tau}y(1)t^{-1} + y(1)t^{-2} + \mathcal{O}(t^{-3}) . \quad (2.16)$$

Since

$$t[F(t)]^n \approx \left[\frac{y(1)}{12\tau}\right]^n t^{-(n-1)} \quad (2.17)$$

for large t, we conclude that

$$f_n(r) \approx \frac{1}{(n-2)!}\left[\frac{y(1)}{12\tau}\right]^n r^{n-2} \quad (2.18)$$

for small r and $n \geq 2$. Consequently, $g(r)$ has a discontinuity at $r = n$ in its derivative of order $n - 2$, $n \geq 2$. In particular,

$$g(2-) - g(2+) = \frac{\eta}{24\tau^2}[y(1)]^2 . \quad (2.19)$$

On the other hand, the value of the susceptibility χ is determined by the behavior of $F(t)$ for small t [3,4]:

$$\frac{e^t}{F(t)} = -12\eta + t^3 - H_0 t^5 + \frac{\chi - 1}{24\eta}t^6 + \mathcal{O}(t^7), \quad (2.20)$$

where

$$H_0 \equiv \int_0^\infty dr\, r\, h(r) \quad (2.21)$$

is a quantity without a direct physical relevance.

Thus, the values of χ and $y(1)$ are straightforward related to the asymptotic behaviors of $F(t)$ for small and large t, respectively. Let us see that they are also related to the behavior of the structure factor for small and large wave numbers. First, comparison between Eqs. (2.2) and (2.4) yields

$$\chi = \lim_{q \to 0} S(q) . \quad (2.22)$$

If we assume that the leading behavior in Eq. (2.16) holds for t complex when $|t| \to \infty$, then $iqF(iq) \approx y(1)/12\tau$ for large q. Consequently, $G(iq) \approx G(iq) - (iq)^{-2} \approx e^{-iq}y(1)/12\tau$. Therefore, from (2.13),

$$S(q) \approx 1 + 2\frac{\eta}{\tau}y(1)\frac{\sin q}{q} , \quad (2.23)$$

or, equivalently,

$$y(1) = \frac{1}{2}\frac{\tau}{\eta}\lim_{q \to \infty}\frac{q}{\sin q}[S(q) - 1] . \quad (2.24)$$

Strictly speaking, the knowledge of $F(t)$ for sticky hard spheres is not sufficient to get the virial equation of state, since the value of $\bar{y}'(1^+)$ is not accessible from $y(r)$ once the sticky limit has been taken. This fact was already recognized by Seaton and Glandt [5]. On the other hand, the excess internal energy is directly related to $y(1)$ through Eq. (2.7).

III. RATIONAL-FUNCTION APPROXIMATIONS

Equations (2.16) and (2.20) give a large amount of information about $F(t)$. Since $y(1)$ must be finite, Eq. (2.16) tells us that $F(t) \sim t^{-1}$ for large t and that the coefficient of t^{-1} is 12τ times smaller than that of t^{-2}. Since χ (and, consequently, also H_0) must be finite in a disordered fluid, Eq. (2.20) gives the first five terms (i.e., up to t^4) of the expansion of $F(t)$ in powers of t.

These constraints of the behavior of $F(t)$ for large and small t are easily satisfied if one assumes a rational function form for $F(t)$. The rational function compatible with these constraints [3] containing the least number of parameters is the Padé approximant (2,3):

$$F(t) = -\frac{1}{12\eta} \frac{1 + L_{\mathrm{PY}}^{(1)}t + L_{\mathrm{PY}}^{(2)}t^2}{1 + S_{\mathrm{PY}}^{(1)}t + S_{\mathrm{PY}}^{(2)}t^2 + S_{\mathrm{PY}}^{(3)}t^3} . \qquad (3.1)$$

$$L_{\mathrm{PY}}^{(2)} = \frac{(1-\eta)^2}{24\eta} \frac{(1+2\eta)\sqrt{\eta\frac{5\eta-2}{6(1-\eta)^2} + 2\tau\frac{\eta}{1-\eta} + \tau^2} - \tau(1+2\eta) + \eta}{\tau(1-\eta)(1+2\eta) + \frac{1}{12}(14\eta^2 - 4\eta - 1)} . \qquad (3.6)$$

The approximation (3.1) turns out to be equivalent to Baxter's solution of the PY equation [1]. This is why we have labeled the coefficients in Eq. (3.1) with the initials PY. Once $F(t)$ is known, Eqs. (2.16) and (2.20) can be used to get $\tilde{y} \equiv y(1)$ and χ. The result is [3]

$$\tilde{y}_{\mathrm{PY}} = -\frac{\tau}{\eta} \frac{L_{\mathrm{PY}}^{(2)}}{S_{\mathrm{PY}}^{(3)}} , \qquad (3.7)$$

$$\chi_{\mathrm{PY}} = \frac{(1-\eta)^2}{(1+2\eta)^2}[1 - \eta + 12\eta L_{\mathrm{PY}}^{(2)}]^2$$

$$= (1-\eta)^4\tau^2 [\eta(1-\eta)\tilde{y}_{\mathrm{PY}} - (1+2\eta)\tau]^{-2} . \qquad (3.8)$$

In order to go beyond the above approximation, we consider the Padé approximant (3,4):

$$F(t) = -\frac{1}{12\eta} \frac{1 + L^{(1)}t + L^{(2)}t^2 + L^{(3)}t^3}{1 + S^{(1)}t + S^{(2)}t^2 + S^{(3)}t^3 + S^{(4)}t^4} . \qquad (3.9)$$

By imposing the same constraints as before, we can express all the parameters in terms of two of them, say $L^{(3)}$ and $S^{(4)}$. First, by expanding Eq. (2.20), we get

$$L^{(1)} = \frac{1 + \frac{1}{2}\eta}{1 + 2\eta} + \frac{6\eta}{1 + 2\eta}L^{(2)} - \frac{12\eta}{1 + 2\eta}(L^{(3)} + S^{(4)}) , \qquad (3.10)$$

$$S^{(1)} = -\frac{3}{2}\frac{\eta}{1 + 2\eta} + \frac{6\eta}{1 + 2\eta}L^{(2)} - \frac{12\eta}{1 + 2\eta}(L^{(3)} + S^{(4)}) , \qquad (3.11)$$

By imposing the constraints one gets [3]

$$L_{\mathrm{PY}}^{(1)} = \frac{1 + \frac{1}{2}\eta}{1 + 2\eta} + \frac{6\eta}{1 + 2\eta}L_{\mathrm{PY}}^{(2)} , \qquad (3.2)$$

$$S_{\mathrm{PY}}^{(1)} = -\frac{3}{2}\frac{\eta}{1 + 2\eta} + \frac{6\eta}{1 + 2\eta}L_{\mathrm{PY}}^{(2)} , \qquad (3.3)$$

$$S_{\mathrm{PY}}^{(2)} = -\frac{1}{2}\frac{1 - \eta}{1 + 2\eta} + \frac{1 - 4\eta}{1 + 2\eta}L_{\mathrm{PY}}^{(2)} , \qquad (3.4)$$

$$S_{\mathrm{PY}}^{(3)} = -\frac{(1-\eta)^2}{12\eta(1 + 2\eta)} - \frac{1 - \eta}{1 + 2\eta}L_{\mathrm{PY}}^{(2)} , \qquad (3.5)$$

$$S^{(2)} = -\frac{1}{2}\frac{1 - \eta}{1 + 2\eta} + \frac{1 - 4\eta}{1 + 2\eta}L^{(2)} + \frac{12\eta}{1 + 2\eta}(L^{(3)} + S^{(4)}) , \qquad (3.12)$$

$$S^{(3)} = -\frac{(1-\eta)^2}{12\eta(1 + 2\eta)} - \frac{1 - \eta}{1 + 2\eta}L^{(2)} + \frac{1 - 4\eta}{1 + 2\eta}L^{(3)}$$

$$-\frac{6\eta}{1 + 2\eta}S^{(4)} . \qquad (3.13)$$

Next, we expand Eq. (3.9) in powers of t^{-1}:

$$F(t) = -\frac{1}{12\eta} \left[\frac{L^{(3)}}{S^{(4)}}t^{-1} + \frac{L^{(2)}S^{(4)} - L^{(3)}S^{(3)}}{S^{(4)2}}t^{-2} \right]$$

$$+ \mathcal{O}(t^{-3}) . \qquad (3.14)$$

Then, Eq. (2.16) yields

$$\frac{L^{(2)}}{L^{(3)}} - \frac{S^{(3)}}{S^{(4)}} = 12\tau . \qquad (3.15)$$

Equations (3.10)–(3.13) and (3.15) are the five conditions that the physical requirements $y(1)$=finite and χ=finite impose on the seven parameters $L^{(i)}$ and $S^{(i)}$. While in the case of the approximant (3.1) the number of parameters equals the number of conditions, in the approximant (3.9) we have the freedom to fix two new conditions. A similar situation arises in the special case of pure hard spheres [4]. In this case, by requiring the virial and compressibility equations of state to agree with the

CS equation of state, we rederived the generalized mean spherical approximation (GMSA) [7]. In the same spirit, we require Eq. (3.9) to be consistent with prescribed values of $y(r)$ at contact point $\widetilde{y}$ and of the susceptibility χ. From Eqs. (2.16) and (3.14) one gets

$$\widetilde{y} = -\frac{\tau}{\eta} \frac{L^{(3)}}{S^{(4)}} . \qquad (3.16)$$

Next, inserting into Eq. (2.20) the expansion of Eq. (3.9) up to t^6, one arrives at

$$\chi = \tfrac{1}{(1+2\eta)^2}\{(1-\eta)^2[1-\eta+12\eta L^{(2)}]^2 - 288\eta^2 L^{(2)}[(1-\eta)(1-4\eta)L^{(3)} + (1-8\eta-2\eta^2)S^{(4)}]$$
$$- 24\eta(1-\eta)L^{(3)}[(1-\eta)(1-4\eta) + 72\eta^2 L^{(3)}]144\eta^2(2+\eta)S^{(4)}[1-\eta-12\eta S^{(4)}] - 5184\eta^3 L^{(3)} S^{(4)}\} , \qquad (3.17)$$

where use has been made of Eqs. (3.10)–(3.13). Equations (3.13), (3.15), and (3.16) can be used to express $L^{(2)}$, $S^{(3)}$, and $S^{(4)}$ in terms of $L^{(3)}$. Substitution into Eq. (3.17) gives then the following quadratic equation for $L^{(3)}$:

$$A(\eta,\tau,\widetilde{y})L^{(3)^2} + B(\eta,\tau,\widetilde{y})L^{(3)} + C(\eta,\tau,\widetilde{y},\chi) = 0 , \qquad (3.18)$$

with

$$A(\eta,\tau,\widetilde{y}) = 6\,\frac{\eta^2\widetilde{y}^2 + 4\eta\tau(3\tau-1)\widetilde{y} + 2\tau^2}{(1-\eta)\tau\widetilde{y}}\,B(\eta,\tau,\widetilde{y}) , \qquad (3.19)$$

$$B(\eta,\tau,\widetilde{y}) = 24\eta(1-\eta)\tau\widetilde{y}\left\{\eta(1-\eta)^2\widetilde{y}^2 - 12(1-\eta)\left[\eta + (1-\eta)\tau\right]\tau\widetilde{y} + 6(2+\eta)\tau^2\right\} , \qquad (3.20)$$

$$C(\eta,\tau,\widetilde{y},\chi) = \{\chi\left[\eta(1-\eta)\widetilde{y} - (1+2\eta)\tau\right]^2 - (1-\eta)^4\tau^2\}\widetilde{y}^2 . \qquad (3.21)$$

A necessary condition to have a physically meaningful approximation is that a positive real root of Eq. (3.18) exists. If $L^{(3)}$ were negative then there would exist a positive real value of t at which $F(t) = 0$ and, according to Eq. (2.14), $G(t) = 0$. But this is incompatible with a positive definite $g(r)$.

Let us see which restrictions the positivity condition of $L^{(3)}$ imposes on the admissible values of $\widetilde{y}$ and χ for a given state (η,τ). The coefficient A vanishes if $B = 0$. In fact, this is the only possibility unless $\tau \leq \tau_{\rm PY}^c$, where $\tau_{\rm PY}^c = (2-\sqrt{2})/6 \simeq 0.0976$ is the critical "temperature" predicted by the PY compressibility equation of state [1,3]. The coefficient B is zero if $\widetilde{y}$ is given by the value obtained from the approximant (3.1), i.e., if $\widetilde{y} = \widetilde{y}_{\rm PY}$. If, in addition, $\chi = \chi_{\rm PY}$, then $C = 0$. Figure 1 shows the loci $A = B = 0$, $C = 0$, and $\Delta \equiv B^2 - 4AC = 0$ in the plane $\widetilde{y}$-χ for the particular state $(\eta,\tau) = (0.1,0.1)$. The three curves cross at $\widetilde{y} = \widetilde{y}_{\rm PY}$, $\chi = \chi_{\rm PY}$, and split the plane into six regions. In Region (I) and (IV) Eq. (3.18) has a positive real root and a negative real root; both roots are negative in Regions (II) and (V), while they are complex conjugates in Regions (III) and (VI). The diagram of Fig. 1 is typical of $\tau > \tau_{\rm PY}^c$. In the hard sphere limit $(\tau \to \infty)$, the locus $C = 0$ becomes the line $\chi = \chi_{\rm PY} = (1-\eta)^4/(1+2\eta)^2$.

Therefore, the rational function approximation (3.9) for $F(t)$ requires that the prescribed values for $\widetilde{y}$ and χ define a point lying in region (I) or (IV). If we consider the PY values as a reference, Fig. 1 shows that an arbitrary correction to them might not be admissible. A necessary, although not sufficient, condition for a correction to be admissible is $\mathrm{sgn}(\widetilde{y}-\widetilde{y}_{\rm PY}) = \mathrm{sgn}(\chi-\chi_{\rm PY})$. Note that the

special prescription $\widetilde{y} = \widetilde{y}_{\rm PY}$, $\chi = \chi_{\rm PY}$ leads to $A = B = C = 0$, so that $L^{(3)}$ is arbitrary. This means that the value of $L^{(3)}$ is extremely sensitive to small deviations $\widetilde{y} - \widetilde{y}_{\rm PY}$ and $\chi - \chi_{\rm PY}$. The cross in Fig. 1 represents the location of the point $(\widetilde{y},\chi)$ estimated from computer simulation data [5] (see Section IV).
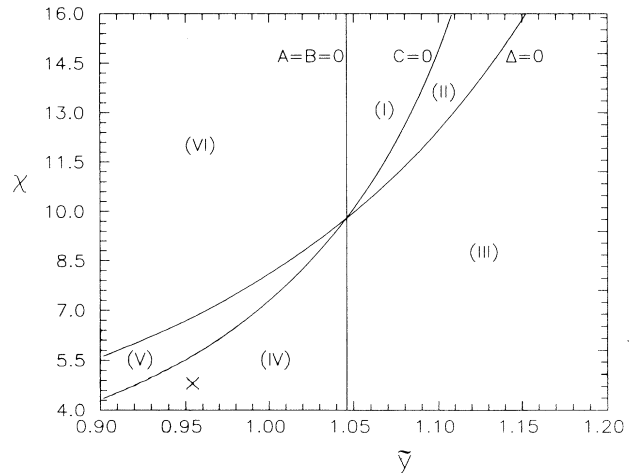

FIG. 1. Loci $A = B = 0$, $C = 0$, and $\Delta \equiv B^2 - 4AC = 0$ in the plane $\widetilde{y}$-χ at the state $(\eta,\tau) = (0.1,0.1)$, where A, B, and C are the coefficients of the quadratic equation for $L^{(3)}$. Its roots are the following: real, one positive and one negative [regions (I) and (IV)]; real, both negative [regions (II) and (V)]; and complex conjugates [regions (III) and (VI)]. The cross in region IV represents the values of $\widetilde{y}$ and χ estimated from simulation data of Ref. [5] .

Before closing this section, we summarize how to get the RDF from our approximation. At a given state (η, τ) one has to prescribe admissible values for $\widetilde{y}$ and χ. Then, the positive real root of Eq. (3.18) gives $L^{(3)}$, Eq. (3.16) gives $S^{(4)}$, and Eqs. (3.10)–(3.13) give $L^{(1)}$, $S^{(1)}$, $S^{(2)}$, and $S^{(3)}$. Once $F(t)$ is completely determined from Eq. (3.9) the RDF $g(r)$ is obtained via Eq. (2.15). All the steps, including the Laplace inversion [since the poles of $F(t)$ are the roots of a quartic equation], can be performed analytically. Furthemore, the structure factor of the fluid is easily obtained from Eqs. (2.13) and (2.14).

In the limit of hard spheres $(\tau \to \infty)$, $L^{(3)}$ tends to zero as τ^{-1} and Eq. (3.18) becomes a quadratic equation for $S^{(4)} = -(\tau/\eta\widetilde{y})L^{(3)}$, which remains finite. Equations (3.15) and (3.16) collapse to $L^{(2)} = -12\eta\widetilde{y}S^{(4)}$ and the results of Ref. [4] for the GMSA are recovered.

IV. COMPARISON WITH SIMULATION DATA

Despite the singular character of the sticky-hard-sphere interaction, Seaton and Glandt [5] have succeeded in adapting the Metropolis Monte Carlo method to deal directly with the sticky-hard-sphere Hamiltonian. In Ref. [5], the RDF obtained from simulation is compared with the PY results for the states $(\eta, \tau) = (0.2, 0.2)$ and $(\eta, \tau) = (0.1, 0.1)$. In the first case, which corresponds to a value of τ about twice the critical one, the agreement is good. Nevertheless, at $(\eta, \tau) = (0.1, 0.1)$, which is quite close to the PY critical state $(\eta_{PY}^c, \tau_{PY}^c) \simeq (0.1213, 0.0976)$, the PY result deviates significantly from the simulation data.

In order to compare our approximation (3.9) with simulation, we need to assign values to $\widetilde{y}$ and χ. In the case of pure hard spheres, the excellent CS equation of state provides a natural choice for $\widetilde{y}$ and χ. In that case, Eq. (3.9) leads to the GMSA, which represents a noticeable improvement over the PY approximation [4]. However, we do not know of any empirical equation of state for sticky hard spheres in the same spirit as the CS equation. We have tried "naive" extensions of the CS equation (such as interpolating between the virial, compressibility, and energy versions of the PY equation of state), but they fail at low temperature, i.e., at high "adhesiveness." The same happens with Padé approximants obtained from the first few terms in the virial expansion of the equation of state [8].

Thus we have chosen to take estimates for $\widetilde{y}$ and χ directly from the simulation data. The value of $\widetilde{y}$ is given, using Eq. (2.9), by the value of the δ-function coefficient of $g(r)$ at $r = 1$, which is reported in Ref. [5]. In this way, we get $\widetilde{y} \simeq 0.912$ at $(\eta, \tau) = (0.2, 0.2)$ and $\widetilde{y} \simeq 0.954$ at $(\eta, \tau) = (0.1, 0.1)$. The respective PY values are $\widetilde{y}_{PY} = \left(54 - \sqrt{1266}\right)/20 \simeq 0.921$ and $\widetilde{y}_{PY} = \left(19 - \sqrt{11}\right)/15 \simeq 1.046$. The determination of the susceptibility χ is much less direct, as it is not measured in the Monte Carlo simulation. Instead, Seaton and Glandt use the virial equation of state, which follows from Baxter's solution of the PY equation [1], to obtain (approximate) values of the pressure from the ("exact") simulation results for $\widetilde{y}$. This equation of state reads

$$z = 1 + 4\eta\left\{\widetilde{y} - \frac{1}{12\tau}\left[3(1+\eta)\frac{(1+2\eta-\mu)^2}{(1-\eta)^4} + 2\frac{-3\eta(2+\eta)^2 + 2(1+7\eta+\eta^2)\mu - (2+\eta)\mu^2}{(1+\eta)^4} + \frac{\mu^2}{6\eta(1-\eta)^2}\right.\right.$$
$$\left.\left. + \frac{\mu^3}{24\eta(1-\eta)^3}\right]\right\}, \tag{4.1}$$

with $\mu \equiv \eta(1 - \eta)\widetilde{y}/\tau$. From the values of the pressure reported in Ref. [5] and by using Eq. (2.10), we have estimated $\chi \simeq 0.87$ and $\chi \simeq 4.8$ at the states $(\eta, \tau) = (0.2, 0.2)$ and $(\eta, \tau) = (0.1, 0.1)$, respectively. The corresponding PY values are $\chi_{PY} \simeq 0.931$ and $\chi_{PY} \simeq 9.781$. In both states, the empirical point $(\widetilde{y}, \chi)$ lies on region IV (see Fig. 1).

At the state $(\eta, \tau) = (0.2, 0.2)$ the PY $g(r)$ agrees well with the simulation results [5], although the PY value of $g(2^-)$ is slightly higher than that of simulation. The approximation that we propose here gives a much better agreement.

On the other hand, the state $(\eta, \tau) = (0.1, 0.1)$ is much more interesting, since it is rather close to the critical point. Figure 2 shows the regular part of $g(r)$ as given by the PY approximation, Eq. (3.1), by our approximation, Eq. (3.9), and by the Monte Carlo simulation [5]. We observe that the PY curve differs significantly from the simulation results. In fact, the PY overestimates the values of $\widetilde{y}$ and χ by a 14% and a 204%, respectively. This can be qualitatively noted in Fig. 2, since $\widetilde{y}$ is the
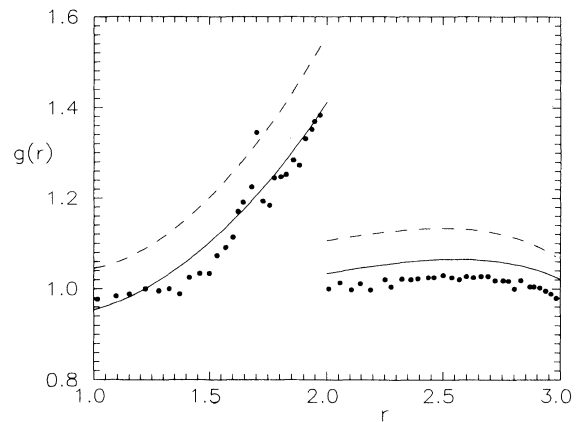

FIG. 2. Regular part of $g(r)$ at the state $(\eta, \tau) = (0.1, 0.1)$. The dashed line corresponds to the Padé approximant $(2,3)$ for $F(t)$ (Percus-Yevick approximation), the solid line corresponds to the Padé approximant $(3,4)$ for $F(t)$, and the bullets correspond to simulation results of Ref. [5].

limit of the regular part of $g(r)$ as $r \to 1+$ and $\chi - 1$ is proportional to the net area of $r^2 [g(r) - 1]$. When the empirical estimates of $\widetilde{y}$ and χ are used in our approximation (3.9) the agreement improves notably. Nevertheless, some discrepancies are still apparent for $r \geq 2$. This could be due to limitations of our analytical approximation and/or to inaccuracies in the empirical values of $\widetilde{y}$ and, especially, χ. Three sources of errors are present in our estimate of χ: (i) the uncertainty in the simulation values of $\widetilde{y}$, (ii) the use of Eq. (4.1), which is correct only in the PY approximation, and (iii) the numerical differentiation needed in Eq. (2.10). In fact, Fig. 2 suggests that the net area of $r^2 [g(r) - 1]$ obtained from simulation is *smaller* than the one corresponding to the solid line and, therefore, the value ($\chi \simeq 4.8$) we have taken in our approximation might be a poor *upper* estimate of the exact susceptibility at $(\eta, \tau) = (0.1, 0.1)$. If that is the case, a better estimate of χ would lead to a better approximate RDF, since we have observed that the agreement of our approximation with simulation increases as one is allowed to decrease the estimated value of χ.

V. DISCUSSION

In this paper, we have proposed an approximation that yields analytic expressions for the radial distribution function $g(r)$ and the structure factor $S(q)$ of a fluid of sticky hard spheres. The approximation consists of assuming a rational function form for a function $F(t)$ related to the Laplace transform of $rg(r)$. The conditions of finite susceptibility χ and finite $\widetilde{y} \equiv \lim_{r \to 1+} g(r)e^{\varphi(r)/k_B T}$ dictate the behaviors of $F(t)$ for small and large t, respectively. The simplest rational function compatible with those conditions is a Padé approximant (2,3) and the resulting approximation [3] coincides with the exact solution of the Percus-Yevick equation for sticky hard spheres [1]. Here we have been concerned with the next rational function approximation for $F(t)$, namely a Padé approximant (3,4). There are two new parameters, which need to be fixed. We have chosen to do that by imposing prescribed values of $\widetilde{y}$ and χ. Nevertheless, not all the pairs $(\widetilde{y}, \chi)$ are admissible

in our approximation at a given thermodynamic state. A necessary admissibility condition is $\mathrm{sgn}(\widetilde{y} - \widetilde{y}_{\mathrm{PY}}) = \mathrm{sgn}(\chi - \chi_{\mathrm{PY}})$, where $\widetilde{y}_{\mathrm{PY}}$ and χ_{PY} are the values obtained from the Padé approximant (2,3). This condition is satisfied by the simulation results for sticky hard spheres [5], as well as by the Carnahan-Starling values in the particular case of pure hard spheres.

Our approximation is subordinated to the knowledge of $\widetilde{y}$ and χ or, equivalently, to the knowledge of the equation of state. In the case of hard spheres, the CS equation of state provides an excellent route to obtain $\widetilde{y}$ and χ. The resulting approximation, which coincides with the generalized mean spherical approximation, improves the agreement of the PY results with simulation [4]. Since we are not aware of any good semiempirical equation of state for sticky hard spheres, we have chosen to make estimates of $\widetilde{y}$ and χ based on simulation data [5]. The estimate is much less reliable in the case of χ than in the case of $\widetilde{y}$.

In general, given the values of $\widetilde{y}$ and χ for a particular thermodynamic state, there is an infinite number of positive definite functions $g(r)$ compatible with those values. Out of that infinite number, our method selects a particular function, namely the one which is a "natural" extension of the PY approximation, when the latter is reinterpreted as a Padé approximant for the auxiliary function $F(t)$. Comparison with simulation shows that this extension represents a significant improvement over the PY results. We speculate that the agreement might even increase if more reliable values for χ were available.

It must also be pointed out that neither of the approximations (3.1) and (3.9) reflects the presence of δ-function singularities in $g(r)$ for $r > 1$, which are associated with the appearance of rigid structures in the fluid [5,8]. However, the amplitudes of those singularities are of the order of or smaller than 10^{-4} for the cases considered here [5].

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nator of Eq. (3.17) should be removed; in Eq. (3.18), the sign in front of $(1 + 2\eta)$ should be minus.

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