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Radial Distribution Function for Sticky Hard-Core Fluids

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Following heuristic arguments, analytic expressions for the radial distribution function $g(r)$ of one- and three-dimensional sticky hard-core fluids (i.e., square-well fluids in a scaled limit of infinite depth and vanishing width) are proposed. The expressions are derived in terms of the simplest Padé approximant of a function defined in the Laplace space that is consistent with the following physicaly requirements: $y(r) \equiv e^{\varphi(r)/k_B T} g(r)$ is finite at the contact point, and the isothermal compressibility is finite. In the case of sticky hard rods the expression obtained is exact, while in the case of sticky hard spheres it coincides with the solution of the Percus–Yevick equation.

KEY WORDS: Radial distribution function; square-well fluid; sticky hard-core limit.

1. INTRODUCTION

Recently, a method to get approximate explicit expressions for the radial distribution function (RDF) $g(r)$ of hard-sphere fluids has been proposed.[(1)] In the method, two very general conditions on $g(r)$, namely (i) continuity for distances greater than the sphere diameter and (ii) convergence of the moment related to the compressibility, are implemented in the Laplace space by the use of Padé approximants. The simplest approximant coincides precisely with the exact solution of the Percus–Yevick (PY) equation. The next step yields the solution of the generalized mean-spherical approximation.

The extension of the method to fluids whose particles may interact attractively (via the Lennard-Jones potential, for instance) is not straight-

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forward at all. In order to confront the problem, it is instructive to start with simple models. The sticky hard-sphere model introduced by Baxter[2] is perhaps the simplest one that incorporates attractive forces. It consists of a square-well fluid in a scaled limit of vanishing width and infinite depth. The exact solution of the PY equation for this model has been analyzed by several authors[2-5] and applied to the clustering in oil-continuous microemulsions.[6] The solution has also been compared with Monte Carlo simulations.[7]

In this paper we follow heuristic arguments similar to those of ref. 1 to propose analytic expressions for the RDFs of sticky hard rods and sticky hard spheres. The reasoning and ansatz are essentially common in both cases, the dimensionality playing a purely geometrical role. The method provides expressions that coincide with the exact solution in the case of sticky hard rods and with the PY solution in the case of sticky hard spheres. This illustrates the possibility of obtaining reliable RDFs by adequately implementing very weak requirements.

The paper is organized as follows. In Section 2 we present the basic definitions and equations that will be needed later on. In Section 3 the basic physical requirements used in our method are described and their consequences in the Laplace space are derived in parallel in the one- and three-dimensional cases. The ansatz of the method is worked out in Section 4: a function related to the Laplace transform of $g(r)$ is approximated by a rational function, or Padé approximant, satisfiying the requirements of Section 3. Finally, the results are summarized and discussed in Section 5.

2. BASIC EQUATIONS

The RDF $g(r)$ of a fluid informs us about the spatial correlations between a pair of particles a distance r apart.[8] It also provides the thermodynamic quantities of the fluid. In particular,

$$z \equiv \frac{p}{\rho k_B T} = 1 - \frac{1}{2d} \frac{\rho}{k_B T} \int d\mathbf{r}\, r \frac{d\varphi(r)}{dr} g(r) \tag{2.1}$$

$$\chi \equiv k_B T \left(\frac{\partial \rho}{\partial p} \right)_T = 1 + \rho \int d\mathbf{r}\, [g(r) - 1] \tag{2.2}$$

$$u_{ex} = \frac{1}{2} \rho \int d\mathbf{r}\, \varphi(r)\, g(r) \tag{2.3}$$

In these equations, p is the pressure, ρ is the number density, k_B is the Boltzmann constant, T is the absolute temperature, $\varphi(r)$ is the interaction potential, u_{ex} is the excess internal energy per particle, and d is the dimensionality. Thermodynamic consistency implies the following relationships:

$$\frac{1}{\chi}=\frac{\partial}{\partial\rho}(\rho z) \tag{2.4}$$

$$\rho\frac{\partial u_{ex}}{\partial\rho}=-k_B T^2\frac{\partial z}{\partial T} \tag{2.5}$$

At low densities, $g(r)$ can be conveniently expressed in terms of a power series expansion[8]

$$y(r)\equiv e^{\varphi(r)/k_B T}g(r)=1+\sum_{n=1}^{\infty} y_n(r)\,\rho^n \tag{2.6}$$

The first-order coefficient is

$$y_1(r)=\int d\mathbf{r}'\,f(\mathbf{r}')\,f(|\mathbf{r}-\mathbf{r}'|) \tag{2.7}$$

where $f(r)\equiv e^{-\varphi(r)/k_B T}-1$ is the Mayer function.

Let us consider now the square-well potential interaction:

$$\varphi(r)=\begin{cases}\infty, & r<1\\ -\varepsilon, & 1<r<\lambda\\ 0, & \lambda<r\end{cases} \tag{2.8}$$

where we have taken the diameter of the hard core as the length unit. For the square-well potential the virial equation of state, Eq. (2.1), and the energy equation of state, Eq. (2.3), become, respectively,

$$z=1+2^{d-1}\eta\{\lambda^d y(\lambda)-e^{\varepsilon/k_B T}[\lambda^d y(\lambda)-y(1)]\} \tag{2.9}$$

$$\frac{u_{ex}}{\varepsilon}=-d2^{d-1}\eta e^{\varepsilon/k_B T}\int_1^{\lambda} dr\, r^{d-1}y(r) \tag{2.10}$$

where $\eta\equiv\rho v_d$, $v_d=(\pi/4)^{d/2}\,\Gamma(1+d/2)$ being the volume of a d-dimensional sphere of unit diameter. The simplicity of the Mayer function for this potential allows one to evaluate explicitly the function $y_1(r)$ through Eq. (2.7). The result for one-dimensional systems with $\lambda\leqslant 3$ is

$$\begin{aligned} y_1(r)&=2x^2(\lambda-1)+2-(2x^2+2x+1)\,r, && 0\leqslant r\leqslant\lambda-1\\ &=-2x(\lambda-1)+2-r, && \lambda-1\leqslant r\leqslant 2\\ &=-2(x+\lambda+1)\,x+(x+2)\,xr, && 2\leqslant r\leqslant\lambda+1\\ &=2\lambda x^2-x^2 r, && \lambda+1\leqslant r\leqslant 2\lambda\\ &=0, && r\geqslant 2\lambda \end{aligned} \tag{2.11}$$

where $x \equiv e^{\varepsilon/k_B T} - 1$. The result for $d = 3$ can be found, for instance, in ref. 9 and will not be quoted here.[2]

The sticky hard model corresponds to the limits $\lambda \to 1^+$ and $\varepsilon \to \infty$ with $\alpha \equiv e^{\varepsilon/k_B T}(\lambda - 1)$ fixed, so that the second virial coefficient is finite. The parameter α is a monotonically decreasing function of T and measures the degree of "adhesiveness." The case of pure hard-core fluids is recovered if $\alpha = 0$. In the sticky hard-core limit the Mayer function becomes

$$f(r) = \alpha\delta_+(r-1) + \Theta(r-1) - 1 \tag{2.12}$$

where

$$\delta_+(x) \equiv \lim_{a \to 0^+} a^{-1}[\Theta(x) - \Theta(x-a)] \tag{2.13}$$

$\Theta(x)$ is the Heaviside step function. The relationship between $g(r)$ and $y(r)$ is then

$$g(r) = y(r)\,\Theta(r-1) + \alpha y(1)\,\delta_+(r-1) \tag{2.14}$$

In the limit $\lambda \to 1^+$ with α fixed, Eqs. (2.9) and (2.10) reduce to

$$z = 1 + 2^{d-1}\eta\{y(1) - \alpha[dy(1) + \bar{y}'(1^+)]\} \tag{2.15}$$

$$\frac{u_{\text{ex}}}{\varepsilon} = -d2^{d-1}\eta\alpha y(1) \tag{2.16}$$

In Eq. (2.15) we have denoted

$$\bar{y}'(1^+) \equiv \lim_{\lambda \to 1^+} \lim_{r \to 1^+} \frac{d}{dr}\, y(r) \tag{2.17}$$

which in general must be distinguished from

$$y'(1^+) \equiv \lim_{r \to 1^+} \frac{d}{dr} \lim_{\lambda \to 1^+} y(r) \tag{2.18}$$

The consistency conditions (2.4) and (2.5), expressed in terms of η and α, become

$$\frac{1}{\chi} = \frac{\partial}{\partial \eta}(\eta z) \tag{2.19}$$

$$\eta \frac{\partial}{\partial \eta}\left(\frac{u_{\text{ex}}}{\varepsilon}\right) = \alpha \frac{\partial z}{\partial \alpha} \tag{2.20}$$

[2] Note a misprint in the fourth line of Eq. (19) of ref. 9: the term $\lambda^3 r$ should read $\lambda^2 r$.

The density expansion coefficient $y_1(r)$ can be obtained either by taking the sticky hard-core limit on the square-well $y_1(r)$ or just by inserting (2.12) into (2.7). The results for $d=1$ and $d=3$ are, respectively,

$$y_1(r)=\alpha^2[\delta_+(r)+\delta_+(r-2)]+(2\alpha-2+r)\times[\Theta(r-2)-1], \qquad d=1 \tag{2.21}$$

$$\frac{6}{\pi}y_1(r)=18\alpha^2\delta_+(r)+\left[-\frac{12\alpha^2}{r}-8(1-3\alpha)+6(1-2\alpha)r-\frac{1}{2}r^3\right]\times[\Theta(r-2)-1], \qquad d=3 \tag{2.22}$$

3. PHYSICAL REQUIREMENTS

Two basic requirements that a physically meaningful approximation must fulfill are: (i) finiteness of $y(r)$ at $r=1$, and (ii) finiteness of the isothermal compressibility χ (as long as the system is in a disordered state). We also require: (iii) the approximation is exact up to first order in density. Following the same approach as in ref. 1, we will implement the above conditions in the Laplace space. Thus, we define

$$Y(t)=\int_1^\infty dr\, e^{-rt}r^m y(r) \tag{3.1}$$

$$G(t)=\int_0^\infty dr\, e^{-rt}r^m g(r)=Y(t)+\alpha y(1)\,e^{-t} \tag{3.2}$$

$$H(t)=\int_0^\infty dr\, e^{-rt}r^m[g(r)-1]=G(t)-m!\,t^{-(m+1)} \tag{3.3}$$

In the second step of (3.2) use has been made of (2.14). Equations such as Eq. (2.7) and the Ornstein–Zernike relation involve d-dimensional Fourier convolution integrals. This suggests that we choose the value of m in Eqs. (3.1)–(3.3) under the criterion that the Fourier transform $\tilde{\psi}(q)$ of a function $\psi(r)$ is related to the Laplace transform $\Psi(t)$ of $r^m\psi(r)$ in a simple way. These geometrical considerations lead to $m=0$ for $d=1$ and $m=d-2$ for $d=\text{odd}\geqslant 3$. For instance, $\tilde{\psi}(q)=-(2\pi/iq)[\Psi(iq)-\Psi(-iq)]$ in $d=3$. Here we will restrict ourselves to the cases $d=1$ and $d=3$.

Let us first consider condition (iii). Insertion of the expansion (2.6), with $y_1(r)$ given by (2.21), into (3.1) yields

$$Y(t)=\frac{e^{-t}}{t}+\eta\left[\left(\frac{1+\alpha t}{t}\right)^2 e^{-2t}-\frac{2\alpha t-t+1}{t^2}e^{-t}\right]+\mathcal{O}(\eta^2), \qquad d=1 \tag{3.4}$$

By substituting (3.4) into (3.2) we get

$$G(t) = [F_0(t) + F_1(t)\,\eta]\,e^{-t} + \eta[F_0(t)]^2\,e^{-2t} + \mathcal{O}(n^2), \qquad d=1 \tag{3.5}$$

where

$$F_0(t) = \frac{\alpha t + 1}{t}, \qquad d=1 \tag{3.6}$$

$$F_1(t) = -\frac{2\alpha^2 t^2 - \alpha t(t-2) - t + 1}{t^2}, \qquad d=1 \tag{3.7}$$

Similar steps in the case $d=3$ lead to

$$G(t) = t[F_0(t) + F_1(t)\,\eta]\,e^{-t} - 12\eta t[F_0(t)]^2\,e^{-2t} + \mathcal{O}(\eta^2), \qquad d=3 \tag{3.8}$$

with

$$F_0(t) = \alpha t^{-1} + t^{-2} + t^{-3}, \qquad d=3 \tag{3.9}$$

$$F_1(t) = (12\alpha^2 - 12\alpha + \tfrac{5}{2})(\alpha t^{-1} + t^{-2}) - 2t^{-3} - 6(1-4\alpha)\,t^{-4} + 12t^{-5} + 12t^{-6}, \qquad d=3 \tag{3.10}$$

Notice that the simplicity of Eq. (3.8) is a consequence of defining $G(t)$ with $m=1$ rather than $m=0$, since $y_1(r)$, Eq. (2.22), contains a term of the form r^{-1}.

The structure of Eqs. (3.5) and (3.8) suggests that we define an auxiliary function $F(t)$ through the relations

$$G(t) = \sum_{n=1}^{\infty} \eta^{n-1}[F(t)]^n\,e^{-nt} = \frac{F(t)\,e^{-t}}{1 - \eta F(t)\,e^{-t}}, \qquad d=1 \tag{3.11}$$

$$G(t) = t\sum_{n=1}^{\infty} (-12\eta)^{n-1}\,[F(t)]^n\,e^{-nt} = t\,\frac{F(t)\,e^{-t}}{1 + 12\eta F(t)\,e^{-t}}, \qquad d=3 \tag{3.12}$$

The requirement (iii) implies that

$$F(t) = F_0(t) + \eta F_1(t) + \mathcal{O}(\eta^2) \tag{3.13}$$

with F_0 and F_1 given by Eqs. (3.6) and (3.7) for $d=1$ and (3.9) and (3.10) for $d=3$.

Let us see now which constraints on $F(t)$ the condition $y(1) = \text{finite}$, requirement (i), imposes. Laplace inversion of (3.11) gives

$$y(r)\,\Theta(r-1) = \sum_{n=1}^{\infty} \eta^{n-1} \xi_n(r-n)\,\Theta(r-n), \quad d=1 \tag{3.14}$$

where the Laplace transform of $\xi_1(r)$ is $F(t) - \alpha y(1)$ and that of $\xi_n(r)$, $n \geqslant 2$, is $[F(t)]^n$. Analogously, Laplace inversion of (3.12) gives

$$y(r)\,\Theta(r-1) = \frac{1}{r} \sum_{n=1}^{\infty} (-12\eta)^{n-1}\, \xi_n(r-n)\,\Theta(r-n), \quad d=3 \tag{3.15}$$

where now $\xi_1(r)$ is the inverse Laplace transform of $tF(t) - \alpha y(1)$ and $\xi_n(r)$, $n \geqslant 2$, is that of $t[F(t)]^n$. According to Eqs. (3.14) and (3.15), $y(1) = \xi_1(0)$. Consequently, finiteness of $y(1)$ implies the following asymptotic behavior:

$$F(t) \sim \alpha + t^{-1} \quad \text{when} \quad t \to \infty, \qquad d=1 \tag{3.16}$$

$$tF(t) \sim \alpha + t^{-1} \quad \text{when} \quad t \to \infty, \qquad d=3 \tag{3.17}$$

the amplitude being precisely $y(1)$, i.e.,

$$y(1) = \lim_{t \to \infty} \frac{F(t)}{\alpha + t^{-1}}, \qquad d=1 \tag{3.18}$$

$$y(1) = \lim_{t \to \infty} \frac{tF(t)}{\alpha + t^{-1}}, \qquad d=3 \tag{3.19}$$

The slope of $y(r)$ at the contact point is given by the subleading term in the asymptotic behavior of $F(t)$:

$$y'(1^+) = \lim_{t \to \infty} t^2[F(t) - (\alpha + t^{-1})\, y(1)], \qquad d=1 \tag{3.20}$$

$$y'(1^+) = -y(1) + \lim_{t \to \infty} t^2[tF(t) - (\alpha + t^{-1})\, y(1)], \qquad d=3 \tag{3.21}$$

For sticky hard rods ($d=1$), $[F(t)]^n \sim t^0$ for large t, which implies $\xi_n(r) \sim \delta_+(r)$ for small r (and $n \geqslant 2$). Consequently, $y(r)$ possess a delta-comb contribution with peaks located at $r = 2, 3,\ldots$. On the other hand, for sticky hard spheres ($d=3$), $t[F(t)]^n \sim t^{-(n-1)}$ for large t, so that $\xi_n(r) \sim r^{n-2}$, $n \geqslant 2$, for small r. Thus, $y(r)$ has a jump discontinuity at $r=2$, but is continuous at $r = 3, 4,\ldots$.

Finally, let us consider the condition $\chi = \text{finite}$, requirement (ii). Notice that this condition implies, but is not implied by, the condition

$\lim_{r\to\infty} g(r)=1$. The compressibility equation of state (2.2) can be recast into the form

$$\chi = 1 + 2\eta \lim_{t\to 0} H(t), \qquad d=1 \tag{3.22}$$

$$\chi = 1 - 24\eta \lim_{t\to 0} \frac{d}{dt} H(t), \qquad d=3 \tag{3.23}$$

where $H(t)$ is defined in (3.3). Finiteness of χ then leads to the following behavior of $G(t)$ in the limit of small t:

$$G(t) = t^{-1}[1+\mathcal{O}(t)], \qquad d=1 \tag{3.24}$$

$$G(t) = t^{-2}[1+\mathcal{O}(t^2)], \qquad d=3 \tag{3.25}$$

Consequently, in this limit the auxiliary function $F(t)$ behaves as

$$\begin{aligned}\frac{1}{F(t)} &= e^{-t}\left[\eta + \frac{1}{G(t)}\right]\\ &= \eta(1-t) + t + \mathcal{O}(t^2), \qquad d=1\end{aligned} \tag{3.26}$$

$$\begin{aligned}\frac{1}{F(t)} &= e^{-t}\left[-12\eta + \frac{t}{G(t)}\right]\\ &= -12\eta\left(1 - t + \frac{1}{2}t^2 - \frac{1}{6}t^3 + \frac{1}{24}t^4\right)\\ &\quad + (1-t)\,t^3 + \mathcal{O}(t^5), \qquad d=3\end{aligned} \tag{3.27}$$

Before closing this section, we summarize the main points. First, we define the function $G(t)$ by (3.2). Its exact density expansion for sticky hard rods [sticky hard spheres] is given by Eqs. (3.5)–(3.7) [Eqs. (3.8)–(3.10)]. The form of this expansion suggests the introduction of the function $F(t)$ through Eq. (3.11) [Eq. (3.12)]. The behaviors of $F(t)$ at large t and at small t are exactly described by Eq. (3.16) [Eq. (3.17)] and Eq. (3.26) [Eq. (3.27)], respectively. The large-t behavior is a consequence of the exact property $y(r)=\text{finite}$ at $r=1$, while the small-t behavior comes from the requirement $\chi=\text{finite}$.

4. RATIONAL FUNCTION APPROXIMATION

4.1. Sticky Hard Rods

The knowledge of $F(t)$ at any density η allows one to get an explicit representation of the RDF for sticky hard rods [sticky hard spheres] through Eq. (3.14) [Eq. (3.15)]. In principle, the *exact* determination of $F(t)$ is a formidable task, especially in the case $d=3$. As seen in the previous section, any physically meaningful approximate method to get $F(t)$ must comply with conditions (i) (3.16) [(3.17)] and (ii) (3.26) [(3.27)]. The exact density expansion, Eq. (3.13), can also be used as a guide. A simple way of reconciling conditions (i) and (ii) is by means of a rational function, or Padé approximant, for $F(t)$:

$$F(t)=\frac{P_\nu(t)}{Q_\mu(t)} \tag{4.1}$$

where $P_\nu(t)$ and $Q_\mu(t)$ denote polynomials of degrees ν and μ, respectively. This rational form is indeed the one adopted by $F(t)$ in the low-density limit, as seen in Eqs. (3.6) [(3.9)] and (3.7) [(3.10)]. The number of unknown coefficients is $1+\nu+\mu$. In the case $d=1$, Eq. (3.26) imposes two constraints. Equation (3.16) implies that $\mu=\nu$ and imposes one extra constraint, namely that the ratio between the two first coefficients in the large-t expansion is precisely α. Similarly, in the case $d=3$, $\mu=\nu+1$ and the number of constraints is $5+1$. Consequently, $\nu\geqslant 1$ for $d=1$ and $\nu\geqslant 2$ for $d=3$. Obviously, the simplest choice corresponds to equal numbers of unknowns and constraints, i.e., $\nu=1$ for $d=1$ and $\nu=2$ for $d=3$. These will be the cases considered in this paper.

In the remainder of this subsection we will consider exclusively the case of sticky hard rods ($d=1$). Our Padé approximant for $F(t)$ is

$$F(t)=\frac{1}{\eta}\frac{1+L^{(1)}t}{1+S^{(1)}t} \tag{4.2}$$

with

$$S^{(1)}-L^{(1)}=\frac{1-\eta}{\eta} \tag{4.3}$$

on account of Eq. (3.26). The large-t behavior of Eq. (4.2) is

$$F(t)=\frac{1}{\eta}\left[\frac{L^{(1)}}{S^{(1)}}+\frac{S^{(1)}-L^{(1)}}{S^{(1)2}}t^{-1}-\frac{S^{(1)}-L^{(1)}}{S^{(1)3}}t^{-2}+\mathcal{O}(t^{-3})\right] \tag{4.4}$$

The condition (3.16) implies that

$$\frac{S^{(1)}L^{(1)}}{S^{(1)}-L^{(1)}}=\alpha \tag{4.5}$$

The set of equations (4.3) and (4.5) leads to a quadratic equation for $S^{(1)}$ or $L^{(1)}$. The criterion to choose the physical solution is that $L^{(1)}$ must vanish if $\alpha = 0$. Thus, one gets

$$S^{(1)} = \frac{1}{2\eta} \{[(1-\eta)(1-\eta+4\alpha\eta)]^{1/2} + 1 - \eta\} \tag{4.6}$$

$$L^{(1)} = \frac{1}{2\eta} \{[(1-\eta)(1-\eta+4\alpha\eta)]^{1/2} - 1 + \eta\} \tag{4.7}$$

Despite the little effort needed here to determine $F(t)$, it turns out that the corresponding Laplace transform $G(t)$, Eq. (3.11), coincides with the *exact* solution to the problem, as shown in the Appendix. Of course, if one takes $\alpha = 0$, the exact solution for a system of hard rods[10] is recovered.

The contact values $y(1)$ and $y'(1^+)$ are readily obtained from (3.18) and (3.20), respectively:

$$y(1) = \frac{1}{\alpha\eta} \frac{L^{(1)}}{S^{(1)}} \tag{4.8}$$

$$y'(1^+) = -\frac{1}{\eta} \frac{S^{(1)} - L^{(1)}}{S^{(1)^3}} \tag{4.9}$$

Also, one easily gets

$$\lim_{t \to 0} H(t) = -1 + \tfrac{1}{2}\eta + \eta L^{(1)}(S^{(1)} - L^{(1)}) \tag{4.10}$$

Substitution of (4.8) and (4.10) into (2.16) and (3.22), respectively, yields

$$\frac{u_{\mathrm{ex}}}{\varepsilon} = -\frac{\{[(1-\eta)(1-\eta+4\alpha\eta)]^{1/2} - 1 + \eta\}^2}{4\alpha\eta(1-\eta)} \tag{4.11}$$

$$\chi = (1-\eta)[(1-\eta)(1-\eta+4\alpha\eta)]^{1/2} \tag{4.12}$$

Since in the method followed here the sticky hard-core limit ($\lambda \to 1^+$) is taken from the beginning, we cannot use our knowledge of the RDF to get $\bar{y}'(1^+)$ [cf. Eq. (2.17)]. As a consequence, the virial equation of state, Eq. (2.15), cannot be completely determined in the framework of our method. A similar limitation was already recognized by Seaton and Glandt,[7] who performed Monte Carlo simulations working directly with sticky hard spheres. Since in the case of sticky hard rods we have obtained the exact RDF with our method, we can use the thermodynamic consistency conditions (2.19) and (2.20) to get z from (4.11) and (4.12). The result is

$$z = \frac{[(1-\eta)(1-\eta+4\alpha\eta)]^{1/2} - 1 + \eta}{2\alpha\eta(1-\eta)} \tag{4.13}$$

The value of $\bar{y}'(1^+)$ can now be obtained from Eq. (2.15) by making use of (4.8) and (4.13). It turns out that $\bar{y}'(1^+) = y'(1^+)$. This means that both limits in Eqs. (2.17) and (2.18) can be interchanged in the case of sticky hard rods.

In order to complete the thermodynamic description of the system, let us evaluate the excess free energy per particle a_{ex}. We start from the thermodynamic relation

$$\frac{1}{k_B T} \frac{\partial a_{\text{ex}}}{\partial \eta} = \frac{z-1}{\eta} \tag{4.14}$$

A straightforward integration yields

$$\frac{a_{\text{ex}}}{k_B T} = -\frac{[(1-\eta)(1-\eta+4\alpha\eta)]^{1/2} - 1 + \eta - 2\alpha\eta}{2\alpha\eta} + \ln \frac{[(1-\eta)(1-\eta+4\alpha\eta)]^{1/2} - 1 + \eta}{\alpha\eta\{[(1-\eta)(1-\eta+4\alpha\eta)]^{1/2} + 1 - \eta\}} \tag{4.15}$$

Let us go back to the correlation functions. Laplace inversion of $[F(t)]^n$ allows one to get $\zeta_n(r)$. The explicit expression for the RDF is then

$$g(r) = \frac{1}{\eta} \sum_{n=1}^{\infty} \left[\left(\frac{L^{(1)}}{S^{(1)}} \right)^n \delta_+(r-n) + \zeta_n(r-n)\, e^{-(r-n)/S^{(1)}} \Theta(r-n) \right] \tag{4.16}$$

where

$$\zeta_n(r) = \sum_{k=1}^{n} \frac{n!}{k!\,(n-k)!} \left(\frac{L^{(1)}}{S^{(1)}} \right)^{k-n} \left(1 - \frac{L^{(1)}}{S^{(1)}} \right)^k \frac{1}{S^{(1)k}} \frac{r^{k-1}}{(k-1)!} \tag{4.17}$$

is a polynomial of degree $n-1$. The exact RDF for sticky hard rods has already been derived by Seaton and Glandt.[11] For the sake of completeness, we are also going to obtain the direct correlation function $c(r)$, defined through the Ornstein–Zernike relation[8]:

$$\tilde{c}(q) = \frac{\tilde{h}(q)}{1 + \eta \tilde{h}(q)} \tag{4.18}$$

where

$$\tilde{c}(q) = 2 \int_0^{\infty} dr \cos(qr)\, c(r) \tag{4.19}$$

is the Fourier transform of $c(r)$, and $\tilde{h}(q)$ is that of $h(r) \equiv g(r) - 1$. The latter is known, since $\tilde{h}(q) = H(iq) + H(-iq)$. Thus, one gets

$$\tilde{c}(q) = \frac{2}{\eta(S^{(1)} + L^{(1)})} \left(-\frac{L^{(1)2}}{S^{(1)} - L^{(1)}} + \frac{L^{(1)} S^{(1)}}{S^{(1)} - L^{(1)}} \cos q + \frac{1}{S^{(1)} - L^{(1)}} \frac{\cos q - 1}{q^2} - \frac{\sin q}{q} \right) \tag{4.20}$$

Fourier inversion yields

$$c(r) = \frac{1}{\eta(S^{(1)} + L^{(1)})} \left[-\frac{L^{(1)2}}{S^{(1)} - L^{(1)}} \delta_+(r) + \frac{L^{(1)} S^{(1)}}{S^{(1)} - L^{(1)}} \delta_+(r-1) + \left(\frac{r-1}{S^{(1)} - L^{(1)}} - 1 \right) \Theta(1-r) \right] \tag{4.21}$$

As is well known, the PY approximation becomes exact for hard rods ($\alpha = 0$). Let us see that this is not true in the more general case of sticky hard rods ($\alpha > 0$). The PY closure is

$$c(r) = g(r) - y(r) \tag{4.22a}$$

$$= \alpha y(1)\, \delta_+(r-1) - y(r)\, \Theta(1-r) \tag{4.22b}$$

where Eq. (2.14) has been used in the last step. The exact $c(r)$, Eq. (4.21), is consistent with the PY $c(r)$, Eq. (4.22b), if

$$y(1) = \frac{1}{\alpha\eta} \frac{L^{(1)} S^{(1)}}{S^{(1)2} - L^{(1)2}} \tag{4.23}$$

$$y(1) = \frac{1}{\eta} \frac{1}{L^{(1)} + S^{(1)}} \tag{4.24}$$

In fact, both conditions are equivalent, as can be seen by using (4.5). Since $y(1)$ is exactly given by (4.8), Eq. (4.23) is clearly not verified, unless $L^{(1)} = 0$, i.e., $\alpha = 0$.

4.2. Sticky Hard Spheres

In this subsection we consider the case of sticky hard spheres ($d = 3$). The simplest Padé approximant ($\nu = 2$, $\mu = 3$) of the form (4.1) is

$$F(t) = -\frac{1}{12\eta} \frac{1 + L^{(1)} t + L^{(2)} t^2}{1 + S^{(1)} t + S^{(2)} t^2 + S^{(3)} t^3} \tag{4.25}$$

with

$$L^{(1)}=\frac{1+\frac{1}{2}\eta}{1+2\eta}+\frac{6\eta}{1+2\eta}L^{(2)} \tag{4.26}$$

$$S^{(1)}=-\frac{3}{2}\frac{\eta}{1+2\eta}+\frac{6\eta}{1+2\eta}L^{(2)} \tag{4.27}$$

$$S^{(2)}=-\frac{1}{2}\frac{1-\eta}{1+2\eta}+\frac{1-4\eta}{1+2\eta}L^{(2)} \tag{4.28}$$

$$S^{(3)}=-\frac{(1-\eta)^2}{12\eta(1+2\eta)}-\frac{1-\eta}{1+2\eta}L^{(2)} \tag{4.29}$$

by application of condition (3.27). For large t, Eq. (4.25) becomes

$$tF(t)=-\frac{1}{12\eta}\left[\frac{L^{(2)}}{S^{(3)}}+\frac{L^{(1)}S^{(3)}-L^{(2)}S^{(2)}}{S^{(3)^2}}t^{-1}\right.$$
$$\left.-\frac{L^{(1)}S^{(2)}S^{(3)}+L^{(2)}(S^{(1)}S^{(3)}-S^{(2)^2})-S^{(3)^2}}{S^{(3)^3}}t^{-2}+\mathcal{O}(t^{-3})\right] \tag{4.30}$$

Condition (3.17) leads to

$$\frac{L^{(2)}S^{(3)}}{L^{(1)}S^{(3)}-L^{(2)}S^{(2)}}=\alpha \tag{4.31}$$

Substitution of Eqs. (4.26)–(4.29) into Eq. (4.31) yields the following quadratic equation:

$$12\eta[(1-\eta)(1+2\eta)+\alpha(14\eta^2-4\eta-1)]\,L^{(2)^2}$$
$$+\,(1-\eta)^2\,(1+2\eta-12\alpha\eta)\,L^{(2)}-\alpha(1-\eta)^2\,(1+\tfrac{1}{2}\eta)=0 \tag{4.32}$$

The physical root is the one that vanishes when $\alpha\to 0$. Its expression is

$$L^{(2)}=\frac{(1-\eta)^2}{24\eta}$$
$$\times\frac{(1+2\eta)[24\alpha^2\eta(5\eta-2)/(1-\eta)^2+24\alpha\eta/(1-\eta)+1]^{1/2}-1-2\eta+12\alpha\eta}{(1-\eta)(1+2\eta)+\alpha(14\eta^2-4\eta-1)} \tag{4.33}$$

While the coefficients $L^{(1)}$ and $S^{(1)}$ in the case of sticky hard rods are real for any $\alpha>0$ and any $\eta<1$ [cf. Eqs. (4.6) and (4.7)], the coefficient $L^{(2)}$

in Eq. (4.33) is a complex number if $\alpha > \alpha_c \equiv (2+\sqrt{2})/4 = 0.8536$ and $\eta_- < \eta < \eta_+$, where

$$\eta_\pm = \frac{24\alpha^2 - 12\alpha + 1 \pm 6\alpha(16\alpha^2 - 16\alpha + 2)^{1/2}}{120\alpha^2 - 24\alpha + 1} \tag{4.34}$$

In the limit $\alpha \to \alpha_c$, one gets $\eta_\pm \to \eta_c \equiv (3\sqrt{2} - 4)/2 = 0.1213$. The Padé approximant (4.25) is meaningless if $\alpha > \alpha_c$ and $\eta_- < \eta < \eta_+$. As one approaches the critical point (η_c, α_c), the coefficient $L^{(2)}$ diverges to infinity.

The approximate RDF defined by Eqs. (4.25)–(4.29) and (4.33) coincides with the exact solution of the PY equation for sticky hard spheres derived by Baxter,[2] as can be easily seen by taking into account the relationships between Baxter's parameters τ and μ and our parameters α and $L^{(2)}$:

$$\alpha = \frac{1}{12\tau} \tag{4.35}$$

$$L^{(2)} = \frac{\mu}{12\eta} \frac{1-\eta}{1+2\eta-\mu} \tag{4.36}$$

The critical behavior of this solution has been analyzed in detail by Fishman and Fisher.[5]

Following our method, we now use Eq. (4.30) in Eqs. (3.19) and (3.21) to get

$$\alpha y(1) = -\frac{1}{12\eta} \frac{L^{(2)}}{S^{(3)}} \tag{4.37}$$

$$y'(1^+) = -y(1) + \frac{1}{12\eta} \frac{L^{(1)} S^{(2)} S^{(3)} + L^{(2)}(S^{(1)} S^{(3)} - S^{(2)^2}) - S^{(3)^2}}{S^{(3)^3}} \tag{4.38}$$

On the other hand, from the expansion of $F(t)$ in powers of t up to order t^6 one obtains

$$\lim_{t\to 0} \frac{d}{dt} H(t) = \frac{1}{(1+2\eta)^2} \times \left[\frac{1}{24}(4-\eta)(2+\eta^2) - (1-\eta)^3 L^{(2)} - 6\eta(1-\eta)^2 L^{(2)^2}\right] \tag{4.39}$$

Substitution of (4.37) and (4.39) into (2.16) and (3.23) gives the energy and compressibility equations of state, respectively. As discussed in the case of sticky hard rods, the quantity $\bar{y}'(1^+)$, which is needed in the virial equation of state, cannot be determined once the sticky hard-core limit has been taken. We cannot use now the thermodynamic consistency conditions to obtain the virial equation of state from the energy and compressibility equations of state, as the latter are not exact. Nevertheless, Baxter[2] was able to derive the virial equation of state by carefully taking the limit $\lambda \to 1^+$ in Eq. (2.9) and using the PY closure, Eq. (4.22a). From that result and Eq. (4.37) one can get $\bar{y}'(1^+)$:

$$\bar{y}'(1^+) = y'(1^+) - 72\eta^2\alpha^3[y(1)]^3 \tag{4.40}$$

Thus, in contrast to what happens in the case $d = 1$, the order of the limits in Eqs. (2.17) and (2.18) is relevant in the case $d = 3$. The difference between $\bar{y}'(1^+)$ and $y'(1^+)$ is of second order in η and of third order in α. While $\bar{y}'(1^+)$ is a remnant of the behavior of $y(r)$ in the shrinking interval $1 < r < \lambda$, $y'(1^+)$ is the limit value of $y'(\lambda^+)$.

5. DISCUSSION

In this paper we have been exploring the possibility of developing a method to get reliable analytic approximations for the radial distribution function (RDF) $g(r)$ of fluids whose particles interact via a hard-core potential $\varphi(r)$ with an attractive tail. In particular, we have taken the sticky hard-core potential in one and three dimensions as a simple and insightful test case. This potential is the limit of a square-well potential as its depth goes to infinity and its width goes to zero in a scaled way.[2]

The RDF is constructed by imposing the following exact conditions: (i) the auxiliary function $y(r) \equiv e^{\varphi(r)/k_B T} g(r)$ is finite at the contact point, (ii) the isothermal compressibility is finite in disordered states, and (iii) the exact zeroth-order and first-order coefficients in the density expansion of $g(r)$ are given. The two first conditions are rather qualitative, while the third condition is more explicit. The latter, however, is used only as a tool to suggest the introduction of a function $F(t)$ algebraically related to the Laplace transform of $g(r)$. The choice of $F(t)$ as a relevant function is supported by the fact that the explicit form of $g(r)$ for any density and temperature follows easily from that of $F(t)$. The interesting point is that conditions (i) and (ii) impose serious constraints on the behavior of $F(t)$ for large t and small t, respectively. This shows that the choices of conditions (i)–(iii) as the basic physical requirements strongly restrict the set of admissible approximations. The specific idea of the method consists of assuming for $F(t)$ the simplest Padé approximant satisfying the above constraints. This is, in fact, the only approximation made in this work.

In the one-dimensional case (sticky hard rods), the result obtained with our method coincides with the exact solution of the problem. In the three-dimensional case (sticky hard spheres), our approximation coincides with the Percus–Yevick (PY) solution. This confirms the adequacy of our choices and shows how a careful use of very weak requirements can lead to quite good analytic approximations. In this respect, it is worthwhile to point out that the PY equation is not exact for sticky hard rods.

Although the PY equation provides an excellent RDF for pure hard spheres, some discrepancies with simulation have been observed in the case of sticky hard spheres.[7] The method described here can easily be extended beyond the PY level by considering the next Padé approximant. The two new coefficients can be determined by imposing extra requirements, such as consistency between the different routes to the equation of state. Work is now in progress along this direction. In fact, the generalized mean spherical approximation for pure hard spheres was derived in ref. 1 following this idea.[3]

The generalization to any attractive hard-core potential of the method described in this paper is not an easy task. As a next step, we are now analyzing the case of the three-dimensional square-well fluid by proposing the following form for the function $F(t)$ introduced in Eq. (3.12):

$$F(t) = -\frac{1}{12\eta}\frac{1+\gamma t}{1+S^{(1)}t+S^{(2)}t^2+S^{(3)}t^3}\left[A+(1-A)\,e^{-(\lambda-1)t}\right] \tag{5.1}$$

where A is a bounded rational function. The exact condition (3.17) (with $\alpha = 0$) is automatically satisfied. On the other hand, the coefficients are determined by requiring the exact condition (3.27) and the continuity condition of $y(r)$ at $r = \lambda$. In the sticky hard-sphere limit, $A^{-1} \to (\alpha^{-1} - \gamma^{-1} + S^{(2)}/S^{(3)})(\lambda - 1)$, and the results derived in this paper are recovered. Equation (5.1) is suggested by the known low-density behavior of $g(r)$ and also by the exact form of $F(t)$ for the one-dimensional square-well system. This is justified by the fact that, despite the important physical differences between the RDF of sticky hard rods and that of sticky hard spheres, they exhibit, in the framework of our approximate method, a very close mathematical structure in the Laplace space, where the dimensionality essentially plays a merely geometrical role. Of course, this formal similarity is not expected to hold exactly.

[3] Note two misprints in ref. 1: the factor η in the denominator of Eq. (3.17) should be removed; in Eq. (3.18), the sign in front of $(1+2\eta)$ should be minus.

APPENDIX

In this appendix we show that the RDF obtained in Section 4 for sticky hard rods is exact.

In 1953, Salsburg *et al.*[12] were able to derive exact expressions for the distribution functions in a one-dimensional fluid whose particles interact with a nearest-neighbor pair potential. This includes the case of sticky hard rods. Taking the Laplace transform on the thermodynamic limit of Eq. (23b) of ref. 12, we easily get (3.11) with

$$F(t) = \frac{1}{\eta} e^{t} \frac{\Omega(t+c)}{\Omega(c)} \tag{A1}$$

where

$$\Omega(t) = \int_0^\infty dr\, e^{-rt}[f(r)+1] \tag{A2}$$

and the real constant c is determined by the condition

$$\frac{1}{\eta} + \frac{\Omega'(c)}{\Omega(c)} = 0 \tag{A3}$$

In the case of sticky hard rods the Mayer function is given by (2.12), so that

$$\Omega(t) = e^{-t}\left(\alpha + \frac{1}{t}\right) \tag{A4}$$

and (A1) becomes

$$F(t) = \frac{1}{\eta} \frac{1 + [\alpha/(1+\alpha c)]\, t}{1 + (1/c)\, t} \tag{A5}$$

The condition for c, Eq. (A3), takes the form

$$\frac{1}{\eta} = 1 + \frac{1}{c(1+\alpha c)} \tag{A6}$$

If we identify $L^{(1)} = \alpha/(1+\alpha c)$ and $S^{(1)} = 1/c$, Eq. (4.5) is automatically satisfied and Eq. (4.3) is equivalent to (A6). Consequently, the exact form of the function $F(t)$, Eq. (A5), coincides with the one obtained in this paper, Eq. (4.2).

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