On the radial distribution function of a hard-sphere fluid

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The fluid of hard spheres (HSs) is a key model in the use and application of statistical mechanics to the study of the thermodynamic and structural properties of real fluids. This is due not only to the relative simplicity of the intermolecular potential but also to the availability of rather accurate (albeit semiempirical) expressions for the corresponding equation of state[1] (EOS) as well as the exact solution of the Ornstein-Zernike equation with the Percus-Yevick (PY) closure,[2] that provides an approximate analytical expression for the radial distribution function (rdf). Yet, interest in this system is very much alive since exact analytical expressions both for its thermodynamic and structural properties have defied derivation. A recent example of this interest of particular relevance to our purpose here is the analytical expression for the rdf proposed by Trokhymchuk *et al.* (TNJH).[3]

Fifteen years ago, two of us[4] developed an analytical method to determine reliable expressions for the rdf $g(r)$ of a HS fluid. Such method provides a reasonable extension of the solution to the PY equation by imposing weak physical requirements. Apart from being relatively simple, requiring as the only input the EOS of the HS fluid, it has the further asset of including by construction the full thermodynamic consistency between the virial and compressibility routes to the EOS. The method uses a rational function ansatz for a function related to the Laplace transform of $rg(r)$, and so it is referred to as the rational function approximation (RFA) method. It has subsequently been used to study the metastable region past the liquid-solid transition,[5] successfully adapted and generalized to deal with other systems (such as HS mixtures,[6] sticky hard spheres,[7] and square-well fluids[8]), used to derive other structural properties (such as the contact values of the derivatives of the rdf, the direct correlation function, and the bridge function[9]), and also used in connection with the perturbation theory of liquids.[10]

Interestingly enough, there are several common features in the RFA method and in the TNJH approach[3] to derive an approximate analytical form for $g(r)$. For instance, the underlying philosophy is the same as evidenced through the following text that we quote from Ref. 3: "A third possibility towards obtaining a nonempirical analytic representation of $g(r)$ is to assume a certain theoretically justified functional form for $g(r)$ (e.g., a result of the solution of the OZ equation) with adjustable parameters and impose then certain constraints (e.g., thermodynamic consistency) to determine these parameters." Such a statement is totally applicable to the RFA method. Furthermore, both use the asymptotic be-

havior of the rdf for $r \to \infty$, they enforce thermodynamic consistency, and both also require as input only a prescribed compressibility factor $Z \equiv p/\rho k_B T$ and its associated isothermal susceptibility $\chi = [\partial(\rho Z)/\partial\rho]^{-1}$. Therefore it seems natural to compare the outcomes of both approaches in order to assess their merits and limitations. The purpose of this Note is to carry out such a comparison.

In the TNJH approach,[3] the rdf is written as

$$g(r) = \begin{cases} g_d(r), & 1 < r < r_m \\ g_s(r), & r > r_m, \end{cases} \tag{1}$$

where r_m ($1 < r_m < 2$) denotes the first minimum of $g(r)$ and the "depletion" (d) and "structural" (s) parts have the following forms:

$$g_d(r) = \frac{A}{r}e^{\mu(r-1)} + \frac{B}{r}\cos(\beta(r-1)+\gamma)e^{\alpha(r-1)}, \tag{2}$$

$$g_s(r) = 1 + \frac{C}{r}\cos(\omega r + \delta)e^{-\kappa r}, \tag{3}$$

respectively. In Eqs. (1)–(3) and henceforth units are taken in which the diameter σ has a value of 1. The depletion and structural parts have the same functional dependence on r as the exact solution of the PY equation in the first shell, $1 < r < 2$, and in the limit $r \to \infty$, respectively. The approximation in (1) contains 11 parameters to be determined as functions of the density ρ (or, equivalently, of the packing fraction $\eta \equiv \pi\rho\sigma^3/6$). Trokhymchuk *et al.* impose five natural conditions: consistency with prescribed Z and χ, continuity of $g(r)$ and its first derivative at $r = r_m$, and the minimum condition at $r = r_m$. More explicitly,

$$g(1^+) = \frac{Z-1}{4\eta}, \quad \int_0^\infty dr\, r^2[g(r)-1] = \frac{\chi-1}{24\eta}, \tag{4}$$

$$g_d(r_m) = g_s(r_m), \quad \left.\frac{\partial g_d(r)}{\partial r}\right|_{r_m} = 0, \quad \left.\frac{\partial g_s(r)}{\partial r}\right|_{r_m} = 0. \tag{5}$$

In Ref. 3 the Carnahan-Starling-Kolafa[11] (CSK) EOS is used for Z and χ. Furthermore, the parameters γ and μ are fixed at their PY expressions,[2] κ and ω being given by parametrizations obtained by Roth *et al.*[12] This still leaves seven parameters to be determined under the five constraints in (4) and (5). By using the first equation of (4) and the first and third equations of (5), A, B, C, and δ are expressed in terms of

α, β, and r_m, as well as of $g_m \equiv g(r_m)$. These remaining four unknowns are determined by applying two conditions, namely, the second equation of (4) and the second equation of (5), and "by minimizing an appropriate functional," the form of which is not given in Ref. 3. In any case, due to the highly nonlinear character of the problem, the numerical solutions for α, β, r_m, and g_m are parametrized as functions of η in the range $0.2 \leq \rho\sigma^3 \leq 0.9$.

On a different vein, in the RFA method the Laplace transform of $rg(r)$ is taken to be given by

$$G(t) = \mathcal{L}\{rg(r)\} = \frac{t}{12\eta}\frac{1}{1-e^t\Phi(t)}, \qquad (6)$$

where $\Phi(t) = (1+S_1 t + S_2 t^2 + S_3 t^3 + S_4 t^4)/(1+L_1 t + L_2 t^2)$, the six coefficients S_1, S_2, S_3, S_4, L_1, and L_2 (which depend on the packing fraction) being evaluated in an algebraic form by imposing the following requirements:[4,5] (i) χ must be finite and hence the first two integral moments of the total correlation function $h(r) \equiv g(r)-1$, i.e., $\int_0^\infty dr\, r^n h(r)$ with $n=1,2$, must be well defined; (ii) the approximation must be thermodynamically consistent with a prescribed EOS, i.e., Eq. (4) must be verified. Using the first requirement one finds that L_1, S_1, S_2, and S_3 are linear functions of L_2 and S_4. The choice $L_2 = S_4 = 0$ yields the PY solution.[2] On the other hand, imposing requirement (ii) leads[4,5] to explicit expressions for L_2 and S_4 in terms of χ and Z. In turn, the rdf is given by

$$g(r) = \frac{1}{12\eta r}\sum_{n=1}^{\infty}\varphi_n(r-n)\Theta(r-n), \qquad (7)$$

with $\Theta(r)$ the Heaviside step function and $\varphi_n(r) = -\mathcal{L}^{-1}\{t[\Phi(t)]^{-n}\}$, which can be explicitly expressed by using the residue theorem.[5] To close the problem one has to give an EOS to fix Z and χ, so the whole procedure is a function of this choice. Here, we take the same choice as in Ref. 3, namely, the CSK EOS.[11]

The form of the TNJH approximation, Eqs. (1)–(3), is particularly simple, while the RFA method, as happens with the PY solution, gives an explicit expression [Eq. (7)] for each separate shell $n < r < n+1$. On the other hand, the formal simplicity of the TNJH is at the expense of introducing a number of unknowns exceeding the number of constraints, so that minimization of a certain empirical functional is needed. As a consequence, the problem becomes highly nonlinear and the numerical solutions are fitted to given expressions; a change in the desired EOS would then require to start all over again the fitting procedure. In contrast, the RFA only requires six coefficients which are explicitly expressed in terms of an arbitrary EOS. From a less practical but more fundamental point of view, it can be added that the TNJH $g(r)$ introduces an artificial second-order discontinuity at the minimum $r=r_m$, while it forces $g(r)$ to be analytic at $r = 2, 3, \ldots$.

We are now in a position to carry out the aforementioned comparison. Since both methods lead to reasonably accurate values for the rdf, in Fig. 1 we present the results of the relative deviations of such values with respect to the very recent simulation data[13] for three characteristic densities. It is quite clear that only in the case $\rho\sigma^3 = 0.9$ and for small dis-
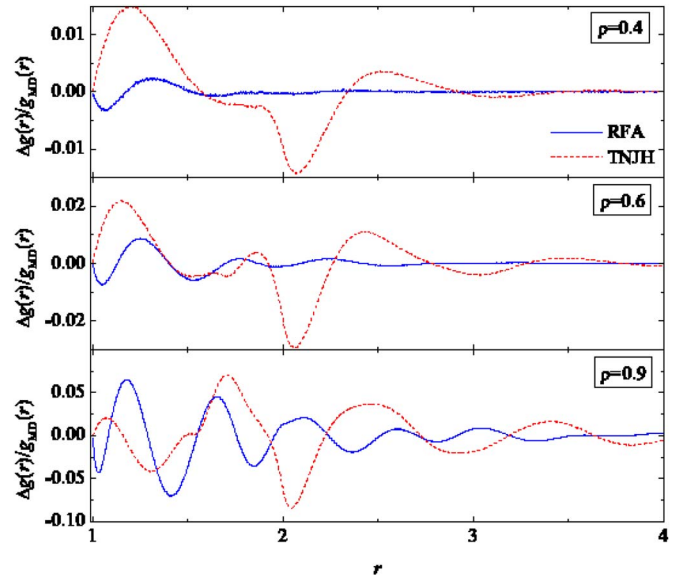

FIG. 1. (Color online) Relative deviation $\Delta g(r)/g_{\mathrm{MD}}(r) \equiv [g(r)-g_{\mathrm{MD}}(r)]/g_{\mathrm{MD}}(r)$ of the values of the rdf of a HS fluid with respect to the molecular dynamics simulation data (Ref. 13), $g_{\mathrm{MD}}(r)$, as a function of r for $\rho\sigma^3 = 0.4$ (top panel), $\rho\sigma^3 = 0.6$ (middle panel), and $\rho\sigma^3 = 0.9$ (bottom panel). The dashed lines represent the results of the approach of Ref. 3, while the solid lines refer to those of the RFA method (Ref. 4).

tances do the RFA values give a somewhat poorer agreement with the simulation results. In any case, and recognizing the value of the TNJH approach,[3] it is fair to say that the RFA method provides a rather accurate and simple alternative to compute the structural properties of the HS fluid. Certainly, there are fewer parameters in the RFA method and they have a clear physical link. Moreover, as the authors of Ref. 3 point out, the availability of analytical results in instances where simulations may fail (such as HS mixtures of a large size ratio) is crucial. In this context, the fact that we already have a simple extension of our approach to deal successfully with these and related systems[6–8] indicates that the RFA method is a valuable tool for the theoretical investigation of the structural properties of hard-core systems.

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