

Direct correlation function from the consistent fundamental-measure free energies for hard-sphere mixtures

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In a recent paper [Phys. Rev. E **86**, 040102(R) (2012)], Santos presented a self-consistency condition that can be used to limit the possible forms of fundamental measure theory. Here, the direct correlation function, resulting from the Santos functional, is derived, and it is found to be very close to the result of the White Bear density functional, except near the origin where it diverges.

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In a recent paper, Santos introduced a novel argument aimed at eliminating a source of ambiguity in the derivation of the fundamental measure theory (FMT) approach to density functional theory for hard spheres [1]. The result is a new ansatz for the improvement of FMT beyond the basic Rosenfeld functional [2]. The proposal is quite interesting as the most accurate density functionals currently in use (such as the “White Bear” functional [3,4]) are exactly of this type: heuristic improvements beyond functionals based on Rosenfeld’s original reasoning together with the additional requirement that the forms reproduce known exact results in low-dimensional systems. The introduction of a new element that eliminates some of the arbitrariness of these extensions is, therefore, welcome. The proposal of Santos is based on an exact scaling relation of the type successfully exploited by him and co-workers in the development of highly accurate approximations for the free energy and pair-distribution function of mixtures of hard spheres [5,6]. The purpose of this Brief Report is to examine one consequence of the proposed ansatz, namely, the implied direct correlation function (DCF).

The direct correlation function is a fundamental element in DFT as it provides a connection between model free energy functionals and liquid-state properties for which much is known [7]. Given a (grand-canonical) free energy functional $\Omega[\rho] = F_{\text{id}}[\rho] + F_{\text{ex}}[\rho] - \mu\rho$, where $\rho(\mathbf{r})$ is the ensemble-averaged local density, F_{id} is the ideal gas contribution, which is not relevant here, μ is the chemical potential, and $F_{\text{ex}}[\rho]$ is the excess term, the (two-body) direct correlation function is given by taking two functional derivatives with respect to the density,

$$c_2(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\delta^2 \beta F_{\text{ex}}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}, \quad (1)$$

where $\beta = 1/k_B T$, k_B is Boltzmann’s constant, and T is the temperature [7,8]. This relation between the free energy functional and the DCF has always provided an important connection between free energy models and liquid-state

properties: For example, one of the first indications of the utility of the White Bear functional was its improvement in the predicted DCF of hard spheres [3].

In DFT, the only unknown is the excess term, and FMT is based on an ansatz of the form

$$\beta F_{\text{ex}} = \int \Phi(\mathbf{n}(\mathbf{r};[\rho])) d\mathbf{r}, \quad (2)$$

where the weighted densities have the generic expressions,

$$n_i(\mathbf{r};[\rho]) = \int w_i(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r}'. \quad (3)$$

Different models involve different collections of density-independent weight functions w_i and of different forms for the function $\Phi(\mathbf{n})$. The proposal of Santos makes use of the weight functions as introduced by Rosenfeld [$w_s(\mathbf{r}_{12}) = \delta(\frac{\sigma}{2} - r_{12})$, $w_\eta(\mathbf{r}_{12}) = \Theta(\frac{\sigma}{2} - r_{12})$, and $w_{v_i}(\mathbf{r}_{12}) = \hat{r}_{12,i} \delta(\frac{\sigma}{2} - r_{12})$ where σ is the hard-sphere diameter] and the Φ function of Rosenfeld $\Phi_R = s\Phi_1(\eta) + \Phi_2(\eta)(s^2 - v^2) + \Phi_3(\eta)s(s^2 - 3v^2)$, where $\eta(\mathbf{r};[\rho]) = n_\eta(\mathbf{r};[\rho])$ is the weighted density formed from the weight function $w_\eta(\mathbf{r}_{12})$, etc. The other terms are

$$\begin{aligned} \Phi_1(\eta) &= -\frac{1}{\pi\sigma^2} \ln(1 - \eta), \\ \Phi_2(\eta) &= \frac{1}{2\pi\sigma} \frac{1}{(1 - \eta)}, \\ \Phi_3(\eta) &= \frac{1}{24\pi} \frac{1}{(1 - \eta)^2}. \end{aligned} \quad (4)$$

The Rosenfeld functional reproduces the Percus-Yevik equation of state (evaluated using the compressibility equation) for a uniform fluid [$\rho(\mathbf{r}) = \rho$ with ρ being a position-independent constant] [2,7] (see the Supplemental Material [9] for details). The idea of the extension discussed by Santos is that one would like to use the knowledge of more accurate equations of state than Percus-Yevik to construct potentially more accurate approximations for Φ . Note that, for a uniform system, Eq. (2) shows that the excess free energy of a uniform liquid is simply $\beta F_{\text{ex}} = V\Phi[\mathbf{n}(\rho)]$, where V is the total volume. Santos introduces a correction so that

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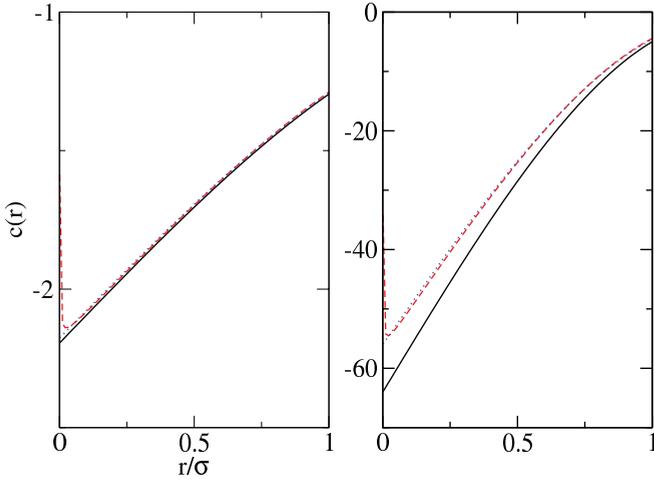


FIG. 1. (Color online) The direct correlation function as calculated using the full line: Percus-Yevik approximation; dotted line: the White Bear approximation; and dashed line: Eq. (6) with $\Lambda(y) = [1 - (y/2) - \ln(1 + y)]/3$ [1]. The left panel is for a low-density fluid with packing fraction $\eta = 0.1$, and the right panel is for a high-density fluid with $\eta = 0.5$. At low densities, the Percus-Yevik result is quite accurate, and at high densities, the White Bear result is in good agreement with the simulations [3].

$\Phi = \Phi_R + \Phi_S$, the form of which is fixed by the scaling relations to be

$$\Phi_S(\mathbf{n}) = (s^2 - v^2)\Phi_2(\eta)\Lambda\left(\frac{2s(s^2 - 3v^2)}{(s^2 - v^2)}\frac{\Phi_3(\eta)}{\Phi_2(\eta)}\right). \quad (5)$$

Here, the function $\Lambda(y)$ is chosen so that the free energy in the uniform limit agrees with some chosen form (such as Carnahan-Starling [10]). Calculation of the implied DCF in the uniform state based on Eq. (1) is straightforward (details are given in the Supplemental Material [9]). The result is that

$c(r; \rho) = 0$ for $r > \sigma$, whereas,

$$\begin{aligned} c(r < \sigma; \rho) &= c_{\text{PY}}(r < \sigma; \rho) - \frac{6\eta + x(1 - 8\eta - 2\eta^2) + 3\eta^2 x^3}{(1 - \eta)^3} \\ &\times \left[\Lambda\left(\frac{\eta}{1 - \eta}\right) + \frac{2\eta}{1 - \eta} \Lambda'\left(\frac{\eta}{1 - \eta}\right) \right. \\ &\left. + \frac{\eta^2}{2(1 - \eta)^3} \Lambda''\left(\frac{\eta}{1 - \eta}\right) \right] \\ &- \frac{\eta^2}{4(1 - \eta)^3} \left(\frac{1}{x} - 2x\right) \Lambda''\left(\frac{\eta}{1 - \eta}\right), \end{aligned} \quad (6)$$

where $x = r/\sigma$ and $\eta = \frac{\pi}{6}\rho\sigma^3$ and $c_{\text{PY}}(r; \rho)$ is the Percus-Yevik DCF that comes from Φ_R . One feature that stands out is that this function diverges for $x = 0$ unless $\Lambda''(\frac{\eta}{1-\eta}) = 0$. This divergence is unphysical and, as shown in the figure, spoils the otherwise reasonable agreement with the results of the White Bear functional. Hence, if this undesirable behavior is to be avoided, the only possibility is the relatively restricted set of corrections given by $\Lambda(y) = a + by$. However, Santos notes that, in general, one expects that $\Lambda(y) \sim O(y^2)$, so this eliminates the possibility of a correction. Santos also offers a modified version of his proposal that appears to avoid the divergence in the DCF but at the cost of violating his self-consistency condition [1]. It is interesting to note that similar terms arise in deriving the DCF from the Rosenfeld part of the free energy, but they cancel, thus, leaving the (finite) Percus-Yevik result (for a demonstration, see, e.g., the Supplemental Material [9]).

To summarize, the proposal of Santos produces a divergent DCF in the uniform liquid. Nevertheless, the reasoning behind it seems sound, and it is to be hoped that there might still be a way to exploit it so as to eliminate some of the ambiguities of the usual extensions of FMT while retaining their advantages, one of which is an excellent description of the DCF for hard spheres.

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