

## Free-energy density functional for the inhomogeneous hard-sphere fluid: Application to interfacial adsorption

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We propose a simplified version of the free-energy density functional for the inhomogeneous hard-sphere fluid mixture recently derived by Rosenfeld [Phys. Rev. Lett. **63**, 980 (1989)]. This new functional, which requires four distinct weight functions, generates a triplet-direct-correlation function for the one-component fluid, which is in good agreement with Monte Carlo simulation results. It also performs well in describing the density profile of the hard-sphere fluid in contact with hard and soft walls. Yet, it is not suitable for studying the freezing transition.

### I. INTRODUCTION

In a recent article,<sup>1</sup> Rosenfeld introduced a free-energy density functional (DF) for the inhomogeneous hard-sphere fluid mixture which, in the uniform fluid limit, reproduces exactly the analytic description of the thermodynamics and the pair structure as given by the scaled-particle<sup>2</sup> and Percus-Yevick<sup>3</sup> (PY) theories. When compared to other DF's proposed in the recent literature,<sup>4</sup> which are used to study various phenomena involving nonuniform systems (adsorption and wetting at solid-liquid interfaces<sup>5</sup> or freezing transition<sup>6</sup>), Rosenfeld's DF offers two major advantages: first, it is by construction a functional for a multicomponent fluid, while other DF's cannot be easily generalized to mixtures without introducing some inconsistencies.<sup>7</sup> Second, it yields simple explicit expressions for the  $n$ -body direct correlation functions of the uniform fluid, and comparison with recent simulation results for the triplet function  $c^3(\mathbf{r}, \mathbf{r}')$  of the one-component fluid shows reasonably good agreement.<sup>8</sup> It is fair to acknowledge that, after several other attempts,<sup>9,10</sup> the results presented by Rosenfeld, Levesque, and Weis<sup>8</sup> represent the first significant step towards a comprehensive picture of the direct triplet correlations in a three-dimensional dense liquid. On the other hand, and contrary to other functionals,<sup>4</sup> Rosenfeld's DF is unable to predict the occurrence of the solid phase.

Then, what is the real theoretical status of this DF? In Refs. 1 and 8, it is argued that general constraints on the nature of the PY free-energy functional dictate its complete form and that, in this sense, it differs from all other existing theories, which are only "tailored" to reproduce the available properties of the homogeneous fluid. This statement is certainly excessive, as shown in the present work, where we propose a much simpler DF than Rosenfeld, which is also intimately connected to the PY solution and which achieves a comparable or even better success in predicting the triplet correlation function  $c^3(\mathbf{r}, \mathbf{r}')$ . More precisely, our functional, belonging to the same class of nonlocal DF's with linear, weighted (or coarse-grained) densities proposed by Percus,<sup>11</sup> employs the

minimal number of weight functions necessary for reproducing the PY  $c^2(r)$ . Then, as an application, we show that this functional works also very well for describing the density profile of a hard-sphere fluid adsorbed onto hard and Lennard-Jones planar walls. Yet, it is not adapted to the study of the freezing transition.

### II. DERIVATION

We start with the PY direct correlation function for the three-dimensional hard-sphere mixture, written as<sup>1,8,12</sup>

$$-c_{ij}^2(r) = \chi^{(3)} \Delta V_{ij}(r) + \chi^{(2)} \Delta S_{ij}(r) + \chi^{(1)} \Delta R_{ij}(r) + \chi^{(0)} \Theta(R_i + R_j - r). \quad (1)$$

For clarity we keep Rosenfeld's notations:  $R_i$  is the radius of the sphere of type  $i$ ;  $\Theta(r)$  is the Heaviside step function;  $\Delta V_{ij}$ ,  $\Delta S_{ij}$ , and  $\Delta R_{ij}$  are functions of the distance  $r$  which have simple geometrical definitions;<sup>12</sup>  $\chi^{(0)}$ ,  $\chi^{(1)}$ ,  $\chi^{(2)}$ , and  $\chi^{(3)}$  are functions of the radii  $R_i$  and concentrations  $\rho_i$ .

Equation (1) has a remarkable structure. First, as the  $\rho_i$  vary,  $c_{ij}^2(r)$  lies in the vector space spanned by the four functions of  $r$ ,  $\Theta_{ij}$ ,  $\Delta V_{ij}$ ,  $\Delta S_{ij}$ , and  $\Delta R_{ij}$ . Second, each  $\chi^{(k)}$  depends only on four reduced quantities, which are the basic variables of the scaled particle theory:<sup>2</sup>

$$\xi^{(k)} = \sum_{i=1}^n \rho_i R_i^{(k)}, \quad k = 0, 1, 2, 3 \quad (2)$$

where the  $R_i^{(k)}$  are the "fundamental measures" characterizing particle  $i$ :  $R_i^{(0)} = 1$ ,  $R_i^{(1)} = R_i$  (the radius),  $R_i^{(2)} = 4\pi R_i^2$  (the surface area), and  $R_i^{(3)} = 4/3\pi R_i^3$  (the volume); incidentally, we may note that four independent variables are not enough to describe an  $n$ -component mixture with  $n > 2$ . The success of Eq. (1) in this case is quite uncertain and as yet unchecked, as far as we know.

The purpose now is to build a density functional from which (1) can be derived. The structure of  $c_{ij}^2$  and the exact solution for the one-dimensional hard rod fluid<sup>13</sup> sug-

gest<sup>11</sup> that one considers a special family of DF's where the excess part of the free energy can be written as

$$\beta F_{\text{ex}}[\{\rho_i\}] = \int d\mathbf{r} \Phi(\{n_\alpha(\mathbf{r})\}), \quad (3)$$

where  $\Phi$  is a general function of *linear* averages (or weighted densities)

$$n_\alpha(\mathbf{r}) = \sum_{i=1}^n \int d\mathbf{r}' \rho_i(\mathbf{r}') \omega_i^{(\alpha)}(\mathbf{r}-\mathbf{r}') \quad (4)$$

and  $\omega_i^{(\alpha)}(\mathbf{r})$  ( $\alpha=1,2,\dots,m$ ) are some unknown density-independent weight functions ( $\beta=1/kT$  is the inverse temperature). As proposed by Percus,<sup>11</sup> the weight functions (and therefore the  $n_\alpha$ 's) can be either scalars or vectors. Since the direct correlation function is given by

$$-c_{ij}^2(\mathbf{r}_1, \mathbf{r}_2) = \beta \delta^2 F_{\text{ex}} / \delta \rho_i(\mathbf{r}_1) \delta \rho_j(\mathbf{r}_2), \quad (5)$$

it is clear that  $c_{ij}^2(r)$  has precisely the peculiar PY structure in the uniform limit

$$-c_{ij}^2(k) = \sum_{\alpha, \beta} \frac{\partial^2 \Phi}{\partial n_\alpha \partial n_\beta} \omega_i^{(\alpha)}(k) \omega_j^{(\beta)}(k), \quad (6)$$

where we have introduced Fourier transforms with respect to  $r$  with obvious notations (scalar product between vectorial quantities is implicit).

At this point, can the weight functions  $\omega_i^{(\alpha)}$  be uniquely derived from general geometric considerations? Certainly not. On the other hand, some restrictions on the multivariable function  $\Phi(\{n_\alpha\})$  can be found by considering the limit  $R_i \rightarrow \infty$ . In this way, Rosenfeld,<sup>1,8</sup> who makes an *a priori* choice for the  $\omega_i^{(\alpha)}$ , is able to derive a possible form of  $\Phi$ . (However, his argument is uncomplete or at least unclear: in order to get information on a possible vectorial part in  $\Phi$ , one must consider a *nonuniform* system in the absence of any external field. This system can only be the solid phase, and therefore one has to admit that, even in this case, the work needed for inserting a macroscopic particle at constant pressure is  $PV$ .) In any case, it is clear that an arbitrariness exists in the choice of the weight functions and in their normalization (i.e., their value for  $k=0$ ).

In fact, it is more reasonable (although less ambitious) to "tailor"  $\Phi(\{n_\alpha\})$  on its uniform PY (or scaled particle) limit, that is, the Helmholtz excess free-energy density (divided by  $kT$ ), as given in the PY theory by integration of the compressibility equation. Then one chooses the obvious normalization conditions

$$\omega_i^{(\alpha)}(k=0) = R_i^{(\alpha)}, \quad \alpha=0,1,2,3 \quad (7a)$$

for the first four scalar weight functions, and

$$\omega_i^{(\alpha)}(k=0) = 0 \quad (7b)$$

for the other scalar weights and for the vectorial ones. Then  $n_\alpha(\mathbf{r}) \rightarrow n_\alpha = \xi^{(\alpha)}$  ( $\alpha=0,1,2,3$ ) in this limit and

$$\begin{aligned} \Phi = \Phi^{\text{PY}} = & -n_0 \ln(1-n_3) + n_1 n_2 / (1-n_3) \\ & + (1/24\pi) n_2^3 / (1-n_3)^2. \end{aligned} \quad (8)$$

How many weight functions are then necessary for recov-

ering (1) from (6)? If we impose the natural scaling condition

$$\omega_i^{(\alpha)}(k) / \omega_i^{(\alpha)}(k=0) = \omega^{(\alpha)}(t_i = kR_i), \quad (9)$$

four independent scalar functions  $\omega^{(\alpha)}(t)$  should be sufficient. Indeed, one readily obtains from (1)–(8) the system of four equations,

$$\Delta V_{ij}(k) = \omega_i^{(3)}(k) \omega_j^{(3)}(k), \quad (10a)$$

$$\Delta S_{ij}(k) = \omega_i^{(2)}(k) \omega_j^{(3)}(k) + \omega_i^{(3)}(k) \omega_j^{(2)}(k), \quad (10b)$$

$$\begin{aligned} \Delta R_{ij}(k) = & \omega_i^{(1)}(k) \omega_j^{(3)}(k) + \omega_i^{(3)}(k) \omega_j^{(1)}(k) \\ & + 1/4\pi \omega_i^{(2)}(k) \omega_j^{(2)}(k), \end{aligned} \quad (10c)$$

$$\begin{aligned} \Theta_{ij}(k) = & \omega_i^{(0)}(k) \omega_j^{(3)}(k) + \omega_i^{(3)}(k) \omega_j^{(0)}(k) \\ & + \omega_i^{(1)}(k) \omega_j^{(2)}(k) + \omega_i^{(2)}(k) \omega_j^{(1)}(k), \end{aligned} \quad (10d)$$

which has the *unique* solution in  $k$  space,

$$\omega_i^{(3)}(k) = 4\pi [\sin(kR_i) - kR_i \cos(kR_i)] / k^3, \quad (11a)$$

$$\omega_i^{(2)}(k) = 4\pi R_i \sin(kR_i) / k, \quad (11b)$$

$$\omega_i^{(1)}(k) = [\sin(kR_i) + kR_i \cos(kR_i)] / 2k, \quad (11c)$$

$$\omega_i^{(0)}(k) = \cos(kR_i) + (kR_i/2) \sin(kR_i). \quad (11d)$$

$\omega_i^{(3)}$  and  $\omega_i^{(2)}$  are the same functions as those introduced by Rosenfeld,<sup>1</sup> but  $\omega_i^{(1)}$  and  $\omega_i^{(0)}$  differ, since we have not introduced unnecessary vector-type functions. In  $r$  space we have

$$\omega_i^{(3)}(r) = \Theta(R_i - r), \quad (12a)$$

$$\omega_i^{(2)}(r) = \delta(R_i - r), \quad (12b)$$

$$\omega_i^{(1)}(r) = (1/8\pi) \delta'(R_i - r), \quad (12c)$$

$$\omega_i^{(0)}(r) = -(1/8\pi) \delta''(R_i - r) + \delta'(R_i - r) / (2\pi r), \quad (12d)$$

so that in reality the weight functions are distributions [ $\delta'(r)$  and  $\delta''(r)$  are, respectively, the first and second derivative of  $\delta(r)$ .] We see no objection to this fact since these quantities are always integrated. We also note that there is no guarantee that the weighted densities  $n_\alpha(\mathbf{r})$  stay positive in all circumstances. *A priori* we have no objection again since the  $n_\alpha$ 's have no obvious physical meaning. However, this point deserves further discussion (see Sec. IV below).

The higher-order direct correlation functions are obtained by successive functional derivation of  $\beta F_{\text{ex}}[\{\rho_i\}]$  with respect to the one-particle densities. The complete expression of  $c_{ijk}^3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$  in the homogeneous fluid is given in the Appendix. Note that we have only 20 different terms, instead of 32 in Rosenfeld's DF.<sup>8</sup> However, we are not penalized for this simplification, as shown in Figs. 1(a)–1(e), where we compare the theoretical predictions to the simulation results for the one-component fluid.<sup>8</sup> In fact, the agreement is even better, in particular in the intermediate region  $k\sigma \approx 5-7$  (for  $k\sigma > 9$  the two functionals give indistinguishable results). However, it is clear from the figures that both theories are unable to reproduce the fine structure of  $c^3$ .

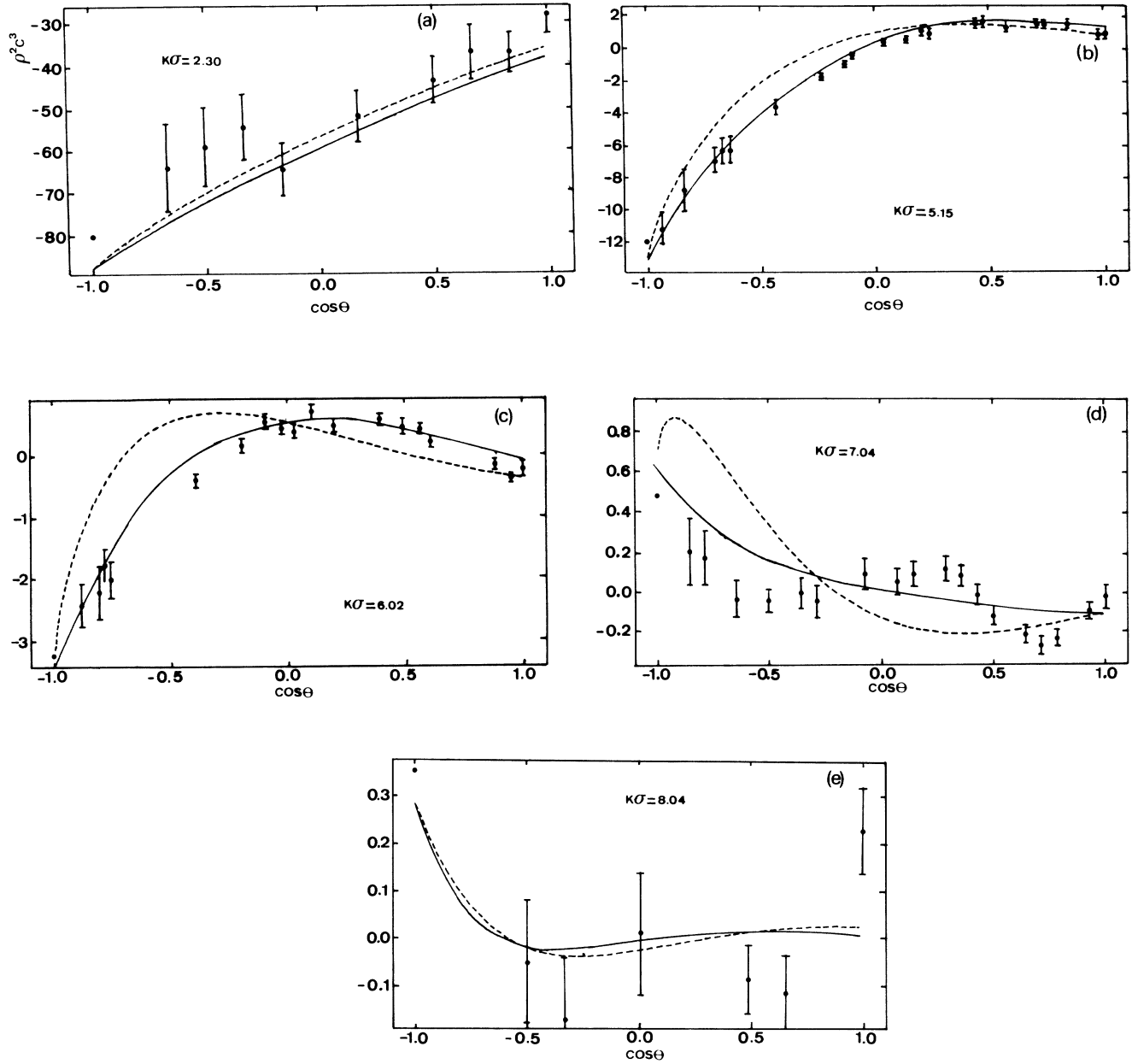


FIG. 1. (a) Triplet-direct-correlation function  $\rho^2 c^3(k\sigma=2.3045, \cos\Theta)$  vs  $\cos\Theta$  in the isosceles triangle geometry ( $k_1=k_2=k$ ,  $k_3=k\sqrt{2\sqrt{1+\cos\Theta}}$ ) for hard spheres at packing fraction  $\eta=0.45$ . The points represent the simulation results (Ref. 8), the dashed line represents the result of Rosenfeld's function (Ref. 8), and the solid line represents the result of the present theory. (b) Same as (a) but for  $k\sigma=5.153$ . (c) Same as (a) but for  $k\sigma=6.024$ . (d) Same as (a) but for  $k\sigma=7.0404$ . (e) Same as (a) but for  $k\sigma=8.0383$ .

### III. APPLICATIONS

#### A. Adsorption at a wall

We first consider the much studied case of a one-component hard-sphere fluid in contact with a hard wall. The external potential is defined by

$$v(z) = \begin{cases} \infty, & z < 0 \\ 0, & z > 0 \end{cases} \quad (13)$$

so that the density profile  $\rho(z)$  varies only in the direction normal to the wall. Then the weighted densities are

$$n_0(z) = \frac{1}{2}[\rho(z+R) + \rho(z-R)] - (R/4)[\rho'(z+R) - \rho'(z-R)], \quad (14a)$$

$$n_1(z) = \frac{1}{4} \int_{-R}^R dz' \rho(z+z') + (R/4)[\rho(z+R) + \rho(z-R)], \quad (14b)$$

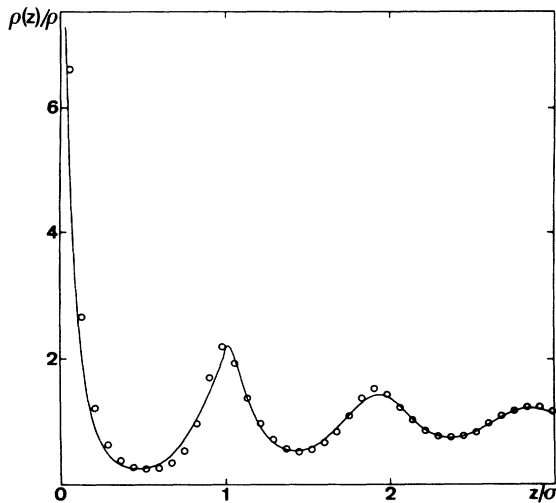


FIG. 2. Density profile of hard spheres near a hard wall at packing fraction  $\eta=0.46$ . The circles represent the simulation results (Ref. 15) and the solid line the prediction of the present theory.

$$n_2(z) = 2\pi R \int_{z-R}^{z+R} dz' \rho(z'), \quad (14c)$$

$$n_3(z) = \pi \int_{-R}^R dz' \rho(z+z') [R^2 - (z')^2]. \quad (14d)$$

The profile is obtained by solving the Euler-Lagrange equation which corresponds to the minimization of the grand potential<sup>14</sup>  $\Omega[\rho] = F[\rho] + \int dz \rho(z)[v(z) - \mu]$ . The result for the packing fraction  $\eta=0.46$  is shown in Fig. 2 and compared to a recent Monte Carlo simulation.<sup>15</sup> The agreement is really good, except of course at contact

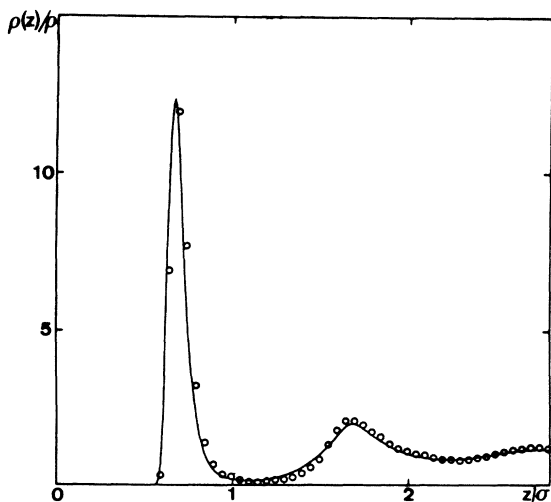


FIG. 3. Density profile of hard spheres near a Lennard-Jones 9-3 wall ( $\eta=0.244$ ,  $\epsilon/k=2876$  K,  $z_0=0.562\sigma$ ,  $T=150$  K). The circles represent the simulation results (Ref. 16) and the solid line the prediction of the present theory.

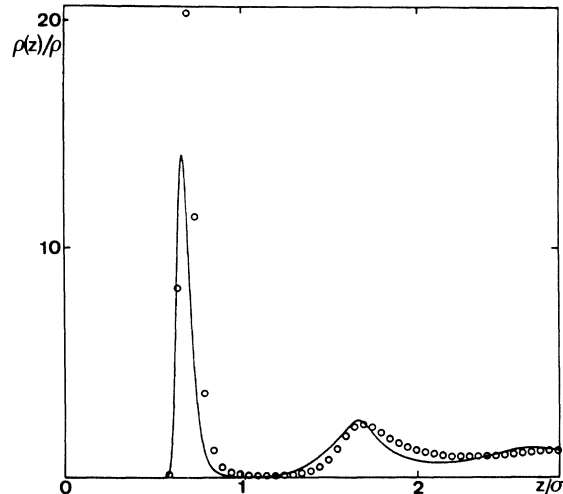


FIG. 4. Same as Fig. 3 for  $\eta=0.32$  and  $T=100$  K.

where  $\rho(0) = \beta P^{\text{PY}} \neq \beta P^{\text{exact}}$ . We stress in particular that the oscillations are almost perfectly in phase, a performance which is reached by no other density functional. We also have to note that the weighted density  $n_0(z)$  reaches negative values near  $z=R$ , as could be expected from the expression (14a).

We next consider adsorption onto a Lennard-Jones 9-3 wall

$$v(z) = \epsilon [(z_0/z)^9 - (z_0/z)^3]. \quad (15)$$

Monte Carlo simulations for this system have been performed recently.<sup>16</sup> Comparison with the theoretical predictions is shown in Fig. 3 for the case of a strongly adsorbing wall ( $\epsilon/k=2876$  K;  $z_0/\sigma=0.562$ ) at  $T=150$  K and  $\eta=0.244$ . Again good agreement is observed, even though it is a demanding situation [ $\rho(z)/\rho \approx 12$  at the maximum]. However, at lower temperature ( $T=100$  K) and higher bulk density ( $\eta=0.32$ ) the agreement is worsening significantly, as seen in Fig. 4.

### B. Freezing transition

Like Rosenfeld's DF,<sup>1,8</sup> the simplified version presented here is unable to predict a freezing transition for three-dimensional hard spheres, if one uses the full expression (3) for  $F_{\text{ex}}$  instead of a functional expansion, truncated at second order, about the excess free energy of the coexisting liquid, using the PY  $c^2(r)$  as input.<sup>6</sup> However, unlike Rosenfeld, we do not find that the liquid corresponds to the minimal free energy; if, as usual,<sup>6</sup> we represent the solid density by a superposition of isotropic Gaussian peaks of width  $\alpha$  centered on the lattice sites, and vary  $\alpha$  to minimize the free energy, we find that  $F_{\text{ex}}$  decreases so rapidly that it becomes negative for values of  $\alpha$  which are much too small (e.g., for  $\rho\sigma^3=1$ ,  $F_{\text{ex}} < 0$  for  $\alpha\sigma^2$  larger than  $\sim 42$ , we recall that the freezing transition occurs near  $\alpha\sigma^2 \approx 80$  in the simulation). The mathematical reason for this phenomenon is that  $n_0(r)$

and  $n_1(\mathbf{r})$  are negative in regions where  $n_3(\mathbf{r})$  is close to 1 and thus  $\ln(1-n_3)$  and  $1/(1-n_3)$  are large. The fact that  $n_3(\mathbf{r})$  (which is the only dimensionless quantity) may come close to 1 is by itself a serious problem, which originates from the short range (radius  $R$ ) of the weight function  $\omega^{(3)}$ . Indeed, in the low-temperature, high-pressure limit of a perfect solid, where  $\rho(\mathbf{r})$  becomes a sum of  $\delta$  functions

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R}), \quad (16)$$

one would find

$$n_3(\mathbf{r}) = \sum_{\mathbf{R}} \Theta(R - |\mathbf{r} - \mathbf{R}|), \quad (17)$$

i.e.,  $n_3(\mathbf{r}) = 1$  in a sphere of radius  $R$  around each site. This problem does not occur in the other functionals proposed in the literature,<sup>4</sup> where the range of the weight function is the hard-sphere diameter  $\sigma$ .

#### IV. DISCUSSION

As pointed out by Percus,<sup>11</sup> the task of building a functional for the free energy of a nonuniform system from the available properties of the uniform fluid requires a compromise between "underdetermination and overdetermination." When Tarazona<sup>4</sup> or Curtin and Ashcroft<sup>4</sup> build a DF for the *one-component* hard-sphere system and introduce only one weighted density  $n(\mathbf{r})$ , they do not take advantage of the existence of the PY solution for mixtures, which to be sure contains additional information on the physics of the system. It is then difficult to extend such a DF to the case of mixture because one does not know how to introduce and combine the needed additional weight functions.<sup>7</sup> This problem is automatically solved in Rosenfeld's approach or in the present one because one considers weight functions for each individual sphere and then simply adds the different contributions to build the  $n_\alpha(\mathbf{r})$ 's.

How can we then interpret these quantities? When there is only one weighted density  $n(\mathbf{r})$ , it may be regarded as an effective local density and this interpretation is very useful to understand the process of the freezing transition.<sup>4,6</sup> If some of the  $n_\alpha(\mathbf{r})$ 's are vectors, like in Rosenfeld's approach, there is no obvious interpretation available. In the simplified version presented here, there are only four scalar variables, whatever the number of fluid components, and it seems natural to regard them as the generalization of the four independent variables of the scaled particle theory to the case of the nonuniform fluid. From this point of view, the degeneracy present in the uniform one-component system (where  $\eta$  is the only relevant variable) is removed by the appearance of a nonuniformity due to an external field or to the spontaneous crystallization. If we adopt this interpretation, the

$n_\alpha(\mathbf{r})$ 's now have a physical meaning and we must forbid all negative values. Moreover,  $n_3(\mathbf{r})$ , which is the local packing fraction, must be bounded by 1. Actually, we must regard with caution situations where  $n_3(\mathbf{r})$  becomes locally larger than 0.45–0.5, since we cannot expect the PY theory for  $\Phi$  or  $c_{ij}(r)$  to be accurate in this case. More generally, we may expect that a bad performance of the functional will be related to the appearance locally of negative values of  $n_0$  (and possibly  $n_1$ ) and high values of  $n_3$ . This is the reason why it is not adapted to the study of the freezing transition. This is also why it becomes inaccurate in the adsorption problem studied at the end of Sec. III A: in the vicinity of the first peak we get  $n_3(z) \approx 0.65$ .

It is clear that improving the present functional requires us to go beyond the PY theory for the excess free energy  $\Phi$  and the direct correlation functions  $c_{ij}^d(r)$ . For  $\Phi$ , one can use the extension to mixtures<sup>17</sup> of the Carnahan-Starling expression, which can be still written in terms of the variables of the scaled-particle theory

$$\Phi = [(1/36\pi)n_2^3/n_3^2 - n_0] \ln(1 - n_3) + n_1 n_2 / (1 - n_3) + (1/36\pi)n_2^3 / (1 - n_3)^2 n_3. \quad (18)$$

The problem is more difficult for  $c_{ij}(r)$ , since it seems necessary, in order to fit accurately the simulation data,<sup>18</sup> to give up the structure of the PY expression, i.e., the nice separation between geometrical (density-independent) factors and density-dependent functions. On the other hand, keeping the same weight functions  $\omega_i^{(\alpha)}$  and using (18) instead of (8) would be incoherent. Clearly, one must take into account the fact that the direct correlation functions are nonzero outside the hard cores. We have not yet succeeded in overcoming this difficulty.

In summary, we have proposed a density functional for the inhomogeneous hard-sphere fluid mixture which is a simplified version of Rosenfeld's DF. It predicts a good triplet direct correlation function for the bulk one-component fluid but fails to give a freezing transition. When applied to nonfreezing problems such as liquid-solid interfaces it gives good results if the nonuniformity is not too large. Another advantage is that it can be readily used in the case of mixtures. Corresponding results will be presented in a forthcoming publication.<sup>19</sup>

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#### APPENDIX

In this appendix, we give the explicit expression of the triplet direct correlation function  $c_{ijk}^3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$ , which can be derived from our functional. We get

$$\begin{aligned}
-c_{ijk}^3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = & \chi^{(03)}[\omega_i^{(0)}(k_1)\omega_j^{(3)}(k_2)\omega_k^{(3)}(k_3) + \omega_i^{(3)}(k_1)\omega_j^{(0)}(k_2)\omega_k^{(3)}(k_3) \\
& + \omega_i^{(3)}(k_1)\omega_j^{(3)}(k_2)\omega_k^{(0)}(k_3) + \omega_i^{(1)}(k_1)\omega_j^{(2)}(k_2)\omega_k^{(3)}(k_3) \\
& + \omega_i^{(2)}(k_1)\omega_j^{(1)}(k_2)\omega_k^{(3)}(k_3) + \omega_i^{(1)}(k_1)\omega_j^{(3)}(k_2)\omega_k^{(2)}(k_3) \\
& + \omega_i^{(3)}(k_1)\omega_j^{(1)}(k_2)\omega_k^{(2)}(k_3) + \omega_i^{(2)}(k_1)\omega_j^{(3)}(k_2)\omega_k^{(1)}(k_3) \\
& + \omega_i^{(3)}(k_1)\omega_j^{(2)}(k_2)\omega_k^{(1)}(k_3) + 1/4\pi\omega_i^{(2)}(k_1)\omega_j^{(2)}(k_2)\omega_k^{(2)}(k_3)] \\
& + \chi^{(13)}\{\omega_i^{(1)}(k_1)\omega_j^{(3)}(k_2)\omega_k^{(3)}(k_3) + \omega_i^{(3)}(k_1)\omega_j^{(1)}(k_2)\omega_k^{(3)}(k_3) \\
& + \omega_i^{(3)}(k_1)\omega_j^{(3)}(k_2)\omega_k^{(1)}(k_3) + 1/4\pi[\omega_i^{(2)}(k_1)\omega_j^{(2)}(k_2)\omega_k^{(3)}(k_3) \\
& + \omega_i^{(2)}(k_1)\omega_j^{(3)}(k_2)\omega_k^{(2)}(k_3) + \omega_i^{(3)}(k_1)\omega_j^{(2)}(k_2)\omega_k^{(2)}(k_3)]\} \\
& + \chi^{(23)}[\omega_i^{(2)}(k_1)\omega_j^{(3)}(k_2)\omega_k^{(3)}(k_3) + \omega_i^{(3)}(k_1)\omega_j^{(2)}(k_2)\omega_k^{(3)}(k_3) \\
& + \omega_i^{(3)}(k_1)\omega_j^{(3)}(k_2)\omega_k^{(2)}(k_3)] + \chi^{(33)}\omega_i^{(3)}(k_1)\omega_j^{(3)}(k_2)\omega_k^{(3)}(k_3),
\end{aligned}$$

with  $k_3 = |\mathbf{k}_1 + \mathbf{k}_2|$  and

$$\chi^{(03)} = \frac{\partial \chi^{(0)}}{\partial n_3} = 1/(1-n_3)^2,$$

$$\chi^{(13)} = \frac{\partial \chi^{(1)}}{\partial n_3} = 2n_2/(1-n_3)^3,$$

$$\chi^{(23)} = \frac{\partial \chi^{(2)}}{\partial n_3} = 2n_1/(1-n_3)^3 + 3/4\pi n_2^2/(1-n_3)^4,$$

$$\chi^{(33)} = \frac{\partial \chi^{(3)}}{\partial n_3} = 2n_0/(1-n_3)^3 + 6n_1n_2/(1-n_3)^4 + 1/\pi n_2^3/(1-n_3)^5.$$

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