

Fundamental measure theory for mixtures of parallel hard cubes.

I. General formalism

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(Received 14 May 1997; accepted 16 July 1997)

This article, the first of a series of two, describes the formulation of Rosenfeld's fundamental measure theory for a mixture of parallel hard cubes, a model recently introduced to study the demixing transition for additive hard core potentials. Special emphasis is put on the good performance of the functional when reducing the dimensionality of the system, a necessary feature to give reasonable results in highly inhomogeneous situations. This property allows for an extremely simple formulation of the theory in arbitrary dimensions. In a subsequent article we will describe the properties of the mixture as they are predicted by the theory, in particular the demixing in presence of the freezing transition. © 1997 American Institute of Physics. [S0021-9606(97)50240-6]

I. INTRODUCTION

During the past decade the major aim of density functional theory (DFT) was producing a reasonable functional to describe inhomogeneous phases of fluids out of the available knowledge of the bulk fluid phase (mainly the equation of state and the direct correlation function, henceforth DCF). The theories elaborated in this spirit became very successful in the description of the freezing of the hard spheres (HS) fluid^{1,2} (by then the favorite test to settle the merits of density functional theories) and they also provided accurate density profiles in rather inhomogeneous situations, such as those created by the presence of a hard wall.³ Armed with such good descriptions of the HS fluid, the liquid theory community began to use them as a reference to deal perturbatively with more realistic potentials, mainly those arising in the theory of charge-stabilized colloidal suspensions,⁴ as well as to extend the formalism to nonspherical bodies in order to study mesophases in liquid crystals.⁵ These studies were rewarded with the accurate description of phase diagrams of these fluids and even with the uncovering of weird phase transitions (such as the recently found dense-expanded solid transition,^{6,7} arising from the interplay between the attractive and repulsive parts of the potential, much as in the vapor-liquid phase transition).

In spite of this unquestionable success, these theories are not free from severe criticism, their major defect being their empirical character. All of them are built upon the evaluation of the free energy of the bulk fluid at an either local (weighted density approximations^{8,9}) or averaged (effective liquid approximations^{1,2}) weighted density. The weight is chosen, by different procedures, in such a way that the functional yields the bulk fluid DCF,³ which thus becomes a fundamental ingredient of these theories. There is no reason to proceed in this way other than the intuitive idea that very inhomogeneous density profiles need to be smoothed out by the convolution with a function with nonzero values within a region of about the size of the interaction potential range, before they enter the calculations.³ The situation is even worse in the case of nonspherical bodies because the lack of

knowledge of the DCF of any such system makes it necessary to make further empirical hypothesis about its shape⁵ or else make use of truncated expansions into spherical harmonics.¹⁰ As a consequence of this one cannot trust that the resulting structure of the functional be in any way related to that of the unknown exact one, and furthermore, systematic refinements of the functional are out of question. On the other hand, the very philosophy of using only limited bulk fluid data to construct a functional able to describe the HS freezing has been questioned¹¹ by showing that the location of the solid-fluid coexistence line in this system is rather insensitive to the details of the theory. This argument is supported by the fact that these theories are unable to accurately locate the coexistence line for soft repulsive potentials,¹² for which the details become more relevant. As a matter of fact, the solid phase resulting from these theories has unphysical properties: to mention only two,^{13,14} (1) if vacancies are incorporated to the theory they are predicted to have a negative density, and (2) the free energy of the solid phase does not diverge at the closest packing density—and therefore denser solids are allowed!

Parallel to the development of these “classical” functionals another approach to this problem was maturing—the so-called *fundamental measure theory*¹⁵ (FMT); but this early version of the theory, despite its notable success for bulk and confined fluids, could not address the freezing problem because of its absurd prediction of an infinitely stable perfect solid at any density. As a result, this first FMT could not compete at the time with the classical functionals, since freezing was then considered the standard reference test for any DFT. Nevertheless, the theory was appealing for several reasons. First of all, its philosophy was closer to a “first principles” theory than any of the classical functionals, because this theory aimed to build a density functional out of the geometry of the particles, supplemented with some general assumptions; second, it yielded the Percus-Yevick (PY) DCF as a *result*, rather than incorporating it as an input of the theory, as any classical theory does; and third, its predictions for the bulk phase coincide with those of the scaled

particle theory,^{16,17} of which FMT is a kind of refined version devised to deal with inhomogeneous phases.

The origin of FMT can be traced back to a remarkable paper by Percus¹⁸ in which he tries to extrapolate from the knowledge of the exact 1D functional.¹⁹ This functional is in fact a weighted density functional, but with two important differences with respect to the classical ones: (i) it depends on *two* independent weighted densities, instead of one, and (ii) the weights are related to geometric characteristics (“volume” and “surface”) of *one* single particle, rather than to those of the pair potential. But Percus’ work is “classical” in spirit because he then speculates how to supplement a functional built upon an arbitrary number of weighted densities with the available knowledge of the bulk fluid. Thus the first actual formulation of FMT is due to Rosenfeld,¹⁵ who by means of the low density limit of the functional identified a set of such geometric “measures” with which to define the weighted densities, and then he determined the final shape of the functional by resorting to scaled particle theory. It turned out that the choice of those measures was not unique,²⁰ although the alternative formulation led to an equivalent functional.²¹

Even though a fundamental measure functional can also be formally constructed from an *approximate* decomposition of the Mayer function as a linear combination of one-particle measures,²² the accomplishment of this decomposition is an important physical ingredient of the theory, with specially marked effects for nonisotropic liquid crystals. However, the exact decomposition of the Mayer function, by using the Gauss–Bonnet theorem,^{22,23} is not always possible, and this is one of the limitations of the theory in its present formulation. Apart from HS, another system to which FMT can be applied is the fluid of parallel hard cubes (PHC).²⁴ One of the advantages of FMT is that it can be readily formulated for mixtures as easily as for single-component fluids, and this has permitted, for instance, study of the demixing of a binary mixture of PHC²⁴ which was reported to occur in Monte Carlo simulations on a lattice.²⁵ But the most serious limitation of the original formulation of FMT for HS was its being unable to account for the solid phase, and it was especially serious because the main aim of the theory was to describe inhomogeneous phases. This defect has recently been “repaired” and its detection has hit on a subtle point which has led to the concept of *dimensional crossover*,^{26,13} which is the property any system has of reducing its dimensionality when particles are constrained to move in a lower dimensional space. This imposes strong restrictions on the functionals which they must fulfill if they are to describe highly inhomogeneous situations (namely, narrow layers, slits, or even pores). In fact, the ability of the functional to reduce to the exact OD limit¹³—i.e., a cavity holding one particle at the most—is strongly related to its ability to describe a sensible solid phase.^{13,14} It turned out that the classical functionals had a well-defined OD limit—although not the exact one—while the original FMT diverged to minus infinity; hence its prediction of the perfect solid being always stable. Further considerations of this dimensional crossover property have

led to a reformulation of the DFT for HS in which the OD limit plays a crucial role.²⁷

For the system of PHC the study of the various dimensional crossovers has yielded a similar improvement of the functional²⁸ (although, as we will show here, it was already implicit in the original formulation of the functional). It turns out that this system performs in this respect much better than the HS, and in fact, as we will show, the generating character of the OD limit in the formulation of the theory prompts here in its clearest way. Thus in some sense, formulation of the FMT for PHC seems to be simpler than for any other conceivable model.

This is the first article of a series of two, in which we will give a detailed description of the formulation of FMT for PHC, including considerations on the various dimensional crossovers, which eventually lead to a very simple general formulation of the theory in *D* dimensions. In the second article we will describe part of the phenomenology of this system as it comes out of the present FMT, in particular the behavior of a binary mixture of PHC in the presence of freezing. The present article is organized as follows. In Sec. II the general formulation of FMT is outlined, and then applied in Sec. III to obtain a functional for a mixture of PHC in 1, 2, and 3 dimensions. In Sec. IV we discuss the predictions of the theory for the uniform fluid. In Sec. V we study the dimensional crossovers of the functional and see how they lead to the general *D*-dimensional formulation; finally we draw some conclusions in Sec. VI.

II. OUTLINE OF ROSENFELD’S FUNDAMENTAL MEASURE THEORY

The basic assumption of the FMT is to postulate the following form for the excess (over ideal gas contribution) Helmholtz free-energy functional:¹⁵

$$\beta F^{\text{ex}}[\{\rho_i(\mathbf{r})\}] = \int d\mathbf{r} \Phi(\{n_\alpha(\mathbf{r})\}), \quad (1)$$

($\beta^{-1} = k_B T$, Boltzmann’s constant times the temperature) where the free-energy density Φ is a function of a certain set of weighted densities

$$n_\alpha(\mathbf{r}) = \sum_i \int \rho_i(\mathbf{r}') \omega_i^{(\alpha)}(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \quad (2)$$

[$\rho_i(\mathbf{r})$ denotes the density function of species *i*, and *D* is the spatial dimension]. The weighted densities n_α are labeled so that their dimensions are $[n_\alpha] = (\text{volume})^{(\alpha-D)/D}$, and they may have any tensor character (scalar, vector,...). Furthermore, in the original FMT the weights are assigned a geometric meaning as “fundamental measures” of the hard bodies, and they are required to fulfill, in the uniform fluid limit,

$$n_\alpha = \kappa_\alpha \sum_i \rho_i R_i^{(\alpha)}, \quad (3)$$

where the $R_i^{(\alpha)}$ ’s are geometric invariants of the body (in *D* = 3, for instance, $R_i^{(0)} = 1$, $R_i^{(1)}$ = mean radius, $R_i^{(2)}$ = surface, and $R_i^{(3)}$ = volume of body *i*; the normalizing constants κ_α

are usually chosen so that $\kappa_0 = \kappa_D = 1$). Therefore α must be in the range $0, 1, \dots, D$, and consequently there is a finite set of weighted densities.

Now, to determine the function Φ , we can realize that its dimensions are $(\text{volume})^{-1}$, so it must consist of a linear combination of (scalar) terms, all of them with this same dimensions. On the other hand, the existence of the virial expansion for the free energy implies that Φ must be an analytic function of the $n_{\alpha s}$; therefore, these terms can only be made out of products of $n_{\alpha s}$ with a total dimension of $(\text{volume})^{-1}$, and the coefficients of their linear combination will thus be analytical functions of the only dimensionless density, n_D . In summary, Φ will have the following expression:

$$\Phi = \sum_{k=1}^D \sum_{\substack{\alpha_1 + \dots + \alpha_k = (k-1)D \\ 0 \leq \alpha_1, \dots, \alpha_k \leq D-1}} A_{\alpha_1 \dots \alpha_k}(n_D) n_{\alpha_1} \dots n_{\alpha_k}, \quad (4)$$

where it is implicitly assumed that vector or tensor densities can only appear within the product in a scalar combination.

Now we have to determine the weight functions $\omega_i^{(\alpha)}$. For that we can make use of the definition of the direct correlation functional,

$$c_{ij}(\mathbf{r}, \mathbf{r}') = -\beta \frac{\delta^2 F^{\text{ex}}[\{\rho_i(\mathbf{r})\}]}{\delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}')}, \quad (5)$$

and apply it to the excess free-energy functional (1) to find

$$c_{ij}(\mathbf{r}, \mathbf{r}') = -\sum_{\alpha, \gamma} \int d\mathbf{r}'' \frac{\partial^2 \Phi}{\partial n_\alpha \partial n_\gamma}(\mathbf{r}'') \omega_i^{(\alpha)}(\mathbf{r} - \mathbf{r}'') \times \omega_j^{(\gamma)}(\mathbf{r}' - \mathbf{r}''). \quad (6)$$

In the uniform fluid limit this functional reduces to the DCF of the mixture; thus

$$c_{ij}(\mathbf{r}) = -\sum_{\alpha, \gamma} \frac{\partial^2 \Phi}{\partial n_\alpha \partial n_\gamma} \omega_i^{(\alpha)} \otimes \omega_j^{(\gamma)}(\mathbf{r}), \quad (7)$$

where \otimes denotes the convolution

$$\omega_i^{(\alpha)} \otimes \omega_j^{(\gamma)}(\mathbf{r}) \equiv \int d\mathbf{r}' \omega_i^{(\alpha)}(\mathbf{r}') \otimes \omega_j^{(\gamma)}(\mathbf{r} - \mathbf{r}'). \quad (8)$$

Being the DCF a scalar function, an inner product must appear in the right-hand side of the above equation whenever the weights are not scalar (and this will be implicitly assumed). Now, in the low density limit, the DCF reduces to $f_{ij}(\mathbf{r})$, the Mayer function of the system. Thus according to Eq. (7) we will have

$$f_{ij}(\mathbf{r}) = \sum_{\alpha + \gamma = D} \phi_{\alpha\gamma} \omega_i^{(\alpha)} \otimes \omega_j^{(\gamma)}(\mathbf{r}), \quad (9)$$

$\phi_{\alpha\gamma}$ being some constants which allow us to freely choose the normalization of the weights. The constraint $\alpha + \gamma = D$ in Eq. (9) arises from our assumption on the dimensions of the n_α : $\omega_i^{(\alpha)} \otimes \omega_j^{(D-\alpha)}(\mathbf{r})$ are the only dimensionless combinations of two weights, and thus the only ones that can appear in the expression of f_{ij} .

Equation (9) is the key for the feasibility of the FMT as applied to a given hard-body fluid. If one is able to determine a decomposition like that in terms of one-particle weights, then, as we will see, the rest of the construction goes straightforward. However, such a decomposition (with a finite number of terms) does not exist for any molecular shape or even any spatial dimension.^{22,23} For instance, in spite that it can be found for HS,¹⁵ amazingly for hard disks (two-dimensional HS) an infinity of terms is needed [Eq. (9) must then be replaced by an approximate finite decomposition in order to circumvent the difficulty²⁹].

Equations (7) and (9) already show a limitation of hypothesis (1), namely that the DCF (7) has exactly the range of the Mayer function, something which is definitely wrong, although it is a good approximation.³⁰

There remains to be determined the shape of the functions $A_{\alpha_1 \dots \alpha_k}(n_D)$ in expression (4). This can be achieved in the following way. First of all, for the uniform fluid, the excess grand potential can be expressed in terms of the excess pressure, $P^{\text{ex}} = P - \beta^{-1} n_0$, as

$$\Omega^{\text{ex}} = -P^{\text{ex}} V = (\beta^{-1} n_0 - P) V,$$

where V is the volume; but this potential can also be expressed in terms of the excess free energy and the chemical potentials (μ_i^{ex}) as (N_i denotes the number of particles of species i)

$$\begin{aligned} \Omega^{\text{ex}} &= F^{\text{ex}} - \sum_i N_i \mu_i^{\text{ex}} \\ &= F^{\text{ex}} - \sum_i \rho_i \frac{\partial F^{\text{ex}}}{\partial \rho_i} = F^{\text{ex}} - \sum_\alpha n_\alpha \frac{\partial F^{\text{ex}}}{\partial n_\alpha}. \end{aligned}$$

From these two equations follows an expression for P :

$$\beta P = n_0 - \Phi + \sum_\alpha n_\alpha \frac{\partial \Phi}{\partial n_\alpha}. \quad (10)$$

Second, we can impose the scaled particle condition^{16,17}

$$\mu_i^{\text{ex}} \sim P V_i \quad \text{when} \quad V_i \rightarrow \infty, \quad (11)$$

V_i being the volume of the particle and P the pressure. This relation arises from the fact that μ_i^{ex} expresses the work needed to insert a particle of species i into the system. Now, since the excess chemical potential is given by [see Eq. (3)]

$$\beta \mu_i^{\text{ex}} = \frac{\partial \Phi}{\partial \rho_i} = \sum_\alpha \frac{\partial \Phi}{\partial n_\alpha} \kappa_\alpha R_i^{(\alpha)} \quad (12)$$

the leading term in the $V_i \rightarrow \infty$ limit will be [see Eq. (3)]

$$\beta \mu_i^{\text{ex}} \sim \frac{\partial \Phi}{\partial n_D} V_i. \quad (13)$$

A comparison with Eq. (11) immediately yields the following equation:

$$\beta P = \frac{\partial \Phi}{\partial n_D} \quad (14)$$

(notice that $\beta^{-1} n_0$ reduces to the ideal gas pressure for the uniform fluid). Let us remark that this is only an approximate

relationship which has been derived within the scaled particle approximation. Its introduction justifies *a posteriori* the seemingly arbitrary choice of a finite set of weighted densities: Since the scale particle approximation is being used, we should expect to recover the expression for the free energy these approximate theory yields, and this expression only involves the combinations of densities given in Eq. (3).^{16,17}


Equations (10) and (14) imply

$$-\Phi + \sum_{\alpha} n_{\alpha} \frac{\partial \Phi}{\partial n_{\alpha}} + n_0 = \frac{\partial \Phi}{\partial n_D}. \quad (15)$$

A simple substitution of Eq. (4) into (15) leads to a system of ordinary differential equations for the functions $A_{\alpha_1 \dots \alpha_k}(n_D)$, which can be solved up to some integration constants.

The last step, i.e., the determination of the integration constants, is achieved by requiring the DCF derived from the free-energy functional to have the right low density expansion, namely,

$$c_{ij} = \text{---} \text{---} + \sum_k \rho_k \text{---} \text{---} + \dots, \quad (16)$$

where, as usual,³⁰  denotes a Mayer function for particles i and j , and a black dot means integration over the corresponding spatial variable.

When this scheme is applied to one-dimensional HS, i.e., hard rods,²⁹ it reproduces the exact result,¹⁹ which is in fact what motivates assumption (1),¹⁸ and similar ones underlying different density functional theories.³ Its application to three-dimensional HS yields the PY DCF,¹⁵ but expressed in a geometrically meaningful way:

$$c_{ij}(\mathbf{r}) = [\chi^{(0)} + \chi^{(1)} R_{ij}(\mathbf{r}) + \chi^{(2)} S_{ij}(\mathbf{r}) + \chi^{(3)} V_{ij}(\mathbf{r})] f_{ij}(\mathbf{r}), \quad (17)$$

where $V_{ij}(\mathbf{r})$, $S_{ij}(\mathbf{r})$, $R_{ij}(\mathbf{r})$, and $f_{ij}(\mathbf{r})$ are, respectively, the volume, surface, mean radius, and minus the indicator (Mayer function) of the overlap region of two HS of radii σ_i and σ_j . Notice that the DCF is an outcome of the theory and that, since we actually have the density functional itself, higher order DCFs can be computed as well.³¹

The application of FMT to hard disks,²⁹ as commented above, is only approximate, but it nevertheless produces an expression for the DCF similar to that for HS:

$$c_{ij}(\mathbf{r}) = [\chi^{(0)} + \chi^{(1)} S_{ij}(\mathbf{r}) + \chi^{(2)} V_{ij}(\mathbf{r})] f_{ij}(\mathbf{r}), \quad (18)$$

where the symbols are the two-dimensional counterparts of those in Eq. (17). This expression compares reasonably well with the available numerical results.²⁹

The simplest functional of the form (4), as explicitly derived in Ref. 15, was not regular when applied to a delta function density profile¹³ (i.e., in the 0D limit; see Sec. V), and thus, as commented in Sec. I, had serious limitations, especially when applied to freezing. This problem can be circumvented by requiring the functional to have the exact 0D expression (see Sec. V) when applied to a delta function density profile. Indeed it was found¹³ that the general form of

Eq. (4) also contains functionals which are regular in the 0D limit. Moreover, consideration of this limit has eventually led to an alternative formulation of the HS functional, under completely different assumptions.²⁷ In the next section we apply the original simplest scheme to a mixture of PHC.

III. FREE-ENERGY FUNCTIONAL OF A MIXTURE OF PARALLEL HARD CUBES IN ONE, TWO, AND THREE DIMENSIONS

In this section we are going to apply the FMT formalism to obtain a functional for PHC in $D=2$ and 3. As to the $D=1$ case, PHC on a line are simply hard rods. In this case the system is thus indistinguishable from the 1D HS fluid, and therefore, as we have already discussed, the FMT yields the exact result. No further comments are then needed.

A. $D=2$

The Mayer function of two parallel hard squares is given by

$$f_{ij}(\mathbf{r}) = -\Theta(\sigma_{ij} - |x|)\Theta(\sigma_{ij} - |y|), \quad (19)$$

$\Theta(u)$ being Heaviside's step function [$\Theta(u \geq 0) = 1$, and $\Theta(u < 0) = 0$], and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, with σ_i the edge length of a square of species i . The Fourier transform of one of the step functions entering Eq. (19) can be written as

$$\int_{-\infty}^{\infty} dx e^{ikx} \Theta(\sigma_{ij} - |x|) = \frac{2}{k} \sin \sigma_{ij} k = \hat{\tau}_i(k) \hat{\zeta}_j(k) + \hat{\tau}_j(k) \hat{\zeta}_i(k), \quad (20)$$

where

$$\hat{\tau}_i(k) \equiv \frac{2}{k} \sin \frac{\sigma_i}{2} k, \quad \hat{\zeta}_i(k) \equiv \cos \frac{\sigma_i}{2} k, \quad (21)$$

which are the Fourier transforms of the two measures

$$\tau_i(x) = \Theta\left(\frac{\sigma_i}{2} - |x|\right), \quad \zeta_i(x) = \frac{1}{2} \delta\left(\frac{\sigma_i}{2} - |x|\right). \quad (22)$$

According to this, the Mayer function (19) can be written as

$$-f_{ij}(\mathbf{r}) = \omega_i^{(2)} \otimes \omega_j^{(0)}(\mathbf{r}) + \omega_i^{(0)} \otimes \omega_j^{(2)}(\mathbf{r}) + \omega_i^{(1)} \otimes \omega_j^{(1)}(\mathbf{r}) - \mathbf{w}_i^{(1)} \otimes \mathbf{w}_j^{(1)}(\mathbf{r}), \quad (23)$$

where

$$\omega_i^{(0)}(\mathbf{r}) \equiv \zeta_i(x) \zeta_i(y), \quad (24a)$$

$$\mathbf{w}_i^{(1)}(\mathbf{r}) \equiv (\zeta_i(x) \tau_i(y), \tau_i(x) \zeta_i(y)), \quad (24b)$$

$$\omega_i^{(1)}(\mathbf{r}) \equiv \mathbf{u} \cdot \mathbf{w}_i^{(1)}(\mathbf{r}), \quad \text{with } \mathbf{u} \equiv (1, 1), \quad (24c)$$

$$\omega_i^{(2)}(\mathbf{r}) \equiv \tau_i(x) \tau_i(y). \quad (24d)$$

With these weights we can now define the weighted densities according to Eq. (2). The uniform fluid limit of these densities is

$$(n_0(\mathbf{r}), \mathbf{n}_1(\mathbf{r}), n_1(\mathbf{r}), n_2(\mathbf{r})) \rightarrow (\xi_0, \xi_1 \mathbf{u}, 2\xi_1, \xi_2), \quad (25)$$

where

$$(\xi_0, \xi_1, \xi_2) \equiv \sum_i (1, \sigma_i, \sigma_i^2) \rho_i, \quad (26)$$

in agreement with Eq. (3). Notice that the dimensions of n_α are as discussed in Sec. II. For this set of weighted densities, Eq. (4) becomes

$$\Phi = a_0 n_0 + a_1 n_1^2 + b_1 \mathbf{n}_1 \cdot \mathbf{n}_1, \quad (27)$$

and substitution into Eq. (15) leads to

$$a'_0 = \frac{1}{1-n_2}, \quad a'_1 = \frac{a_1}{1-n_2}, \quad b'_1 = \frac{b_1}{1-n_2} \quad (28)$$

(the prime denotes derivative with respect to n_2), whose solution is given by

$$a_0 = d_0 - \ln(1-n_2), \quad a_1 = \frac{d_1}{1-n_2}, \quad b_1 = \frac{e_1}{1-n_2}, \quad (29)$$

d_0 , d_1 , and e_1 being integration constants. The value of d_0 is easily determined by the requirement for the excess free energy per particle of the uniform fluid that

$$0 = \lim_{\rho \rightarrow 0} \beta \frac{F^{\text{ex}}}{N} = \lim_{\rho \rightarrow 0} \frac{\Phi}{n_0} = d_0. \quad (30)$$

Now, as stated in Sec. II, determining the remaining constants needs the derivation of the DCF of the uniform fluid through Eq. (7), which, because of the form (27) for the free-energy density, will be given by

$$\begin{aligned} -c_{ij}(\mathbf{r}) = & \frac{1}{1-\xi_2} \{ \omega_i^{(2)} \otimes \omega_j^{(0)}(\mathbf{r}) + \omega_i^{(0)} \otimes \omega_j^{(2)}(\mathbf{r}) \\ & + 2d_1 \omega_i^{(1)} \otimes \omega_j^{(1)}(\mathbf{r}) + 2e_1 \mathbf{w}_i^{(1)} \otimes \mathbf{w}_j^{(1)}(\mathbf{r}) \} \\ & + (2d_1 + e_1) \frac{2\xi_1}{(1-\xi_2)^2} \{ \omega_i^{(2)} \otimes \omega_j^{(1)}(\mathbf{r}) \\ & + \omega_i^{(1)} \otimes \omega_j^{(2)}(\mathbf{r}) \} \\ & + \left[\frac{\xi_0}{(1-\xi_2)^2} + (2d_1 + e_1) \frac{4\xi_1^2}{(1-\xi_2)^3} \right] \\ & \times \omega_i^{(2)} \otimes \omega_j^{(2)}(\mathbf{r}). \end{aligned} \quad (31)$$

The low density limit of this equation is

$$\begin{aligned} -c_{ij}(\mathbf{r}) \sim & \omega_i^{(2)} \otimes \omega_j^{(0)}(\mathbf{r}) + \omega_i^{(0)} \otimes \omega_j^{(2)}(\mathbf{r}) \\ & + 2d_1 \omega_i^{(1)} \otimes \omega_j^{(1)}(\mathbf{r}) + 2e_1 \mathbf{w}_i^{(1)} \otimes \mathbf{w}_j^{(1)}(\mathbf{r}), \end{aligned}$$

thus $d_1 = 1/2$ and $e_1 = -1/2$ for it to match Eq. (23). This fully determines the functional Φ as

$$\Phi = -n_0 \ln(1-n_2) + \frac{n_1^2 - \mathbf{n}_1 \cdot \mathbf{n}_1}{2(1-n_2)}. \quad (32)$$

Let us now replace the values obtained for the constants back into Eq. (31) and perform the convolutions. For that we have to make use of Eq. (20) and

$$\tau_i \otimes \tau_j(u) = L_{ij}(u) \Theta(\sigma_{ij} - |u|), \quad (33)$$

with

$$L_{ij}(u) = \begin{cases} \sigma_{ij} - \lambda_{ij} & \text{if } |u| \leq \lambda_{ij} \\ \sigma_{ij} - |u| & \text{if } |u| > \lambda_{ij}, \end{cases} \quad (34)$$

$$\lambda_{ij} \equiv |\sigma_i - \sigma_j|/2. \quad (35)$$

As a result we get the following expression for the DCF of the uniform fluid:

$$c_{ij}(\mathbf{r}) = [\chi^{(0)} + \chi^{(1)} S_{ij}(\mathbf{r}) + \chi^{(2)} V_{ij}(\mathbf{r})] f_{ij}(\mathbf{r}), \quad (36)$$

where

$$\chi^{(0)} = \frac{1}{1-\xi_2}, \quad (37a)$$

$$\chi^{(1)} = \frac{2\xi_1}{(1-\xi_2)^2}, \quad (37b)$$

$$\chi^{(2)} = \frac{\xi_0}{(1-\xi_2)^2} + \frac{2\xi_1^2}{(1-\xi_2)^3}, \quad (37c)$$

and

$$S_{ij}(\mathbf{r}) = -\frac{1}{2} [L_{ij}(x) + L_{ij}(y)] f_{ij}(\mathbf{r}), \quad (38a)$$

$$V_{ij}(\mathbf{r}) = -L_{ij}(x) L_{ij}(y) f_{ij}(\mathbf{r}). \quad (38b)$$

Notice the similarity between Eqs. (36) and (18); in fact, $V_{ij}(\mathbf{r})$ and $S_{ij}(\mathbf{r})$ are the area and mean length (proportional to the perimeter) of the overlap region (a rectangle) of squares i and j when the center-to-center vector is \mathbf{r} . These geometric measures are the same as those used to define ξ_1 and ξ_2 , respectively [see Eq. (26)].

B. $D=3$

The Mayer function of two parallel hard cubes is given by

$$f_{ij}(\mathbf{r}) = -\Theta(\sigma_{ij} - |x|) \Theta(\sigma_{ij} - |y|) \Theta(\sigma_{ij} - |z|); \quad (39)$$

thus according to Eqs. (20) and (21), it can be decomposed as

$$\begin{aligned} -f_{ij}(\mathbf{r}) = & \omega_i^{(3)} \otimes \omega_j^{(0)}(\mathbf{r}) + \omega_i^{(0)} \otimes \omega_j^{(3)}(\mathbf{r}) + \mathbf{w}_i^{(2)} \otimes \mathbf{w}_j^{(1)}(\mathbf{r}) \\ & + \mathbf{w}_i^{(1)} \otimes \mathbf{w}_j^{(2)}(\mathbf{r}), \end{aligned} \quad (40)$$

where now

$$\omega_i^{(0)}(\mathbf{r}) \equiv \zeta_i(x) \zeta_i(y) \zeta_i(z), \quad (41a)$$

$$\begin{aligned} \mathbf{w}_i^{(1)}(\mathbf{r}) \equiv & (\tau_i(x) \zeta_i(y) \zeta_i(z), \zeta_i(x) \tau_i(y) \zeta_i(z), \\ & \zeta_i(x) \zeta_i(y) \tau_i(z)), \end{aligned} \quad (41b)$$

$$\begin{aligned} \mathbf{w}_i^{(2)}(\mathbf{r}) \equiv & (\zeta_i(x) \tau_i(y) \tau_i(z), \tau_i(x) \zeta_i(y) \tau_i(z), \\ & \tau_i(x) \tau_i(y) \zeta_i(z)), \end{aligned} \quad (41c)$$

$$\omega_i^{(3)}(\mathbf{r}) \equiv \tau_i(x) \tau_i(y) \tau_i(z), \quad (41d)$$

and we will introduce two more weights,

$$\omega_i^{(1)}(\mathbf{r}) \equiv \mathbf{u} \cdot \mathbf{w}_i^{(1)}(\mathbf{r}), \quad \omega_i^{(2)}(\mathbf{r}) \equiv \mathbf{u} \cdot \mathbf{w}_i^{(2)}(\mathbf{r}), \quad (42)$$

with $\mathbf{u} \equiv (1, 1, 1)$, since they will be needed later on. We again define weighted densities as in (2), whose uniform fluid limit is

$$(n_0(\mathbf{r}), \mathbf{n}_1(\mathbf{r}), \mathbf{n}_2(\mathbf{r}), n_3(\mathbf{r})) \rightarrow (\xi_0, \xi_1 \mathbf{u}, \xi_2 \mathbf{u}, \xi_3) \quad (43)$$

[and therefore $n_1(\mathbf{r}), n_2(\mathbf{r}) \rightarrow 3\xi_1, 3\xi_2$], with

$$(\xi_0, \xi_1, \xi_2, \xi_3) \equiv \sum_i (1, \sigma_i, \sigma_i^2, \sigma_i^3) \rho_i. \quad (44)$$

According to these definitions, Eq. (4) becomes

$$\begin{aligned} \Phi = & a_0 n_0 + a_1 n_1 n_2 + b_1 \mathbf{n}_1 \cdot \mathbf{n}_2 + a_2 n_2^3 + b_2 n_2 \mathbf{n}_2 \cdot \mathbf{n}_2 \\ & + c \mathbf{n}_2 \cdot \mathbf{n}_2 \cdot \mathbf{n}_2, \end{aligned} \quad (45)$$

where $\mathbf{v} \cdot \mathbf{v} \cdot \mathbf{v} \equiv v_x^3 + v_y^3 + v_z^3$. Notice that the c term did not appear in Ref. 24 — although, as we will see, it does not affect the results obtained there for the uniform fluid. The presence of the a 's and b 's terms simply resembles the functional form introduced for HS.¹⁵ Such terms can easily be justified for HS since the symmetry of the system imposes rotational invariance. However, this does not hold anymore for PHC and, in fact, none of those terms is rotationally invariant in this case, because they involve dot products with the fixed vector $\mathbf{u} = (1, 1, 1)$. Since the vector densities always have positive components, the symmetry which must be preserved in this case is axes exchange. Both the a 's and the b 's terms keep the functional symmetric under this op-

eration, but also the c term does. It cannot appear in a rotationally invariant functional, and therefore it has no counterpart for HS. The three terms, $a_2, b_2,$ and c , appearing in Eq. (45), are the only independent third-order, axes-exchange symmetric terms; it is straightforward to check that any other term of this kind must be a linear combination of these three. (Notice that this discussion is irrelevant for $D = 2$.)

If we now substitute Φ into Eq. (15) we obtain

$$\begin{aligned} a'_0 &= \frac{1}{1-n_3}, & a'_1 &= \frac{a_1}{1-n_3}, & b'_1 &= \frac{b_1}{1-n_3}, \\ a'_2 &= \frac{2a_2}{1-n_3}, & b'_2 &= \frac{2b_2}{1-n_3}, & c' &= \frac{2c}{1-n_3}, \end{aligned} \quad (46)$$

whose solution is

$$\begin{aligned} a_0 &= d_0 - \ln(1-n_3), & a_1 &= \frac{d_1}{1-n_3}, & b_1 &= \frac{e_1}{1-n_3}, \\ a_2 &= \frac{d_2}{(1-n_3)^2}, & b_2 &= \frac{e_2}{(1-n_3)^2}, & c &= \frac{\delta}{(1-n_3)^2}, \end{aligned} \quad (47)$$

$d_0, d_1, e_1, d_2, e_2,$ and δ being integration constants. The same requirement (30) implies $d_0 = 0$, as in the two-dimensional case. To determine the remaining constants, let us compute the DCF of the uniform fluid by inserting Eq. (45) into (7). According to expressions (47), it becomes

$$\begin{aligned} -c_{ij} = & \frac{1}{1-\xi_3} \{ \omega_i^{(3)} \otimes \omega_j^{(0)} + \omega_i^{(0)} \otimes \omega_j^{(3)} + d_1 (\omega_i^{(1)} \otimes \omega_j^{(2)} + \omega_i^{(2)} \otimes \omega_j^{(1)}) + e_1 (\mathbf{w}_i^{(1)} \otimes \mathbf{w}_j^{(2)} + \mathbf{w}_i^{(2)} \otimes \mathbf{w}_j^{(1)}) \} \\ & + \frac{\xi_2}{(1-\xi_3)^2} \{ 2(9d_2 + 2e_2) \omega_i^{(2)} \otimes \omega_j^{(2)} + 6(e_2 + \delta) \mathbf{w}_i^{(2)} \otimes \mathbf{w}_j^{(2)} + (3d_1 + e_1) (\omega_i^{(1)} \otimes \omega_j^{(3)} + \omega_i^{(3)} \otimes \omega_j^{(1)}) \} \\ & + \left[(3d_1 + e_1) \frac{\xi_1}{(1-\xi_3)^2} + (9d_2 + 3e_2 + \delta) \frac{6\xi_2^2}{(1-\xi_3)^3} \right] (\omega_i^{(2)} \otimes \omega_j^{(3)} + \omega_i^{(3)} \otimes \omega_j^{(2)}) \\ & + \left[\frac{\xi_0}{(1-\xi_3)^2} + (3d_1 + e_1) \frac{6\xi_1\xi_2}{(1-\xi_3)^3} + (3d_2 + e_2) \frac{54\xi_2^3}{(1-\xi_3)^4} \right] \omega_i^{(3)} \otimes \omega_j^{(3)} \end{aligned} \quad (48)$$

(we have omitted the dependence on \mathbf{r} in order to shorten the expression). By comparing with Eq. (40) the low density limit of this equation,

$$\begin{aligned} -c_{ij}(\mathbf{r}) \sim & \omega_i^{(3)} \otimes \omega_j^{(0)}(\mathbf{r}) + \omega_i^{(0)} \otimes \omega_j^{(3)}(\mathbf{r}) \\ & + d_1 (\omega_i^{(1)} \otimes \omega_j^{(2)}(\mathbf{r}) + \omega_i^{(2)} \otimes \omega_j^{(1)}(\mathbf{r})) \\ & + e_1 (\mathbf{w}_i^{(1)} \otimes \mathbf{w}_j^{(2)}(\mathbf{r}) + \mathbf{w}_i^{(2)} \otimes \mathbf{w}_j^{(1)}(\mathbf{r})), \end{aligned}$$

it can be inferred that $d_1 = 0$ and $e_1 = 1$.

In contrast to what happens in two dimensions, Φ is not fully determined yet. There are three coefficients left to be fixed. Thus we have to make use of the next order in the density expansion of the DCF [Eq. (16)], and this leads us to compute the diagram

$$\begin{array}{c} \text{k} \\ \triangle \\ \text{i} \quad \text{j} \end{array} = f_{ij}(\mathbf{r}) f_{ik} \otimes f_{kj}(\mathbf{r}). \quad (49)$$

The convolution of the right-hand side factorizes into three integrals, each of the form

$$\int \Theta(\sigma_{ik} - |t|) \Theta(\sigma_{kj} - |u-t|) dt \quad (u = x, y, z).$$

This integral can be readily computed, as it has the same form of Eq. (33) with $\sigma_i/2$ and $\sigma_j/2$ replaced by σ_{ik} and σ_{kj} respectively. Thus

$$\begin{matrix} & k \\ & \bullet \\ / & & \backslash \\ \circ & & \circ \\ | & & | \\ i & & j \end{matrix} = f_{ij}(\mathbf{r})[\sigma_k + L_{ij}(x)][\sigma_k + L_{ij}(y)][\sigma_k + L_{ij}(z)], \quad (50)$$

which inserted in Eq. (16) yields

$$-c_{ij}(\mathbf{r}) = -f_{ij}(\mathbf{r}) - \xi_3 f_{ij}(\mathbf{r}) + 3\xi_2 R_{ij}(\mathbf{r}) + 3\xi_1 S_{ij}(\mathbf{r}) + \xi_0 V_{ij}(\mathbf{r}) + \mathcal{O}(\rho^2), \quad (51)$$

with

$$R_{ij}(\mathbf{r}) = -\frac{1}{3}[L_{ij}(x) + L_{ij}(y) + L_{ij}(z)]f_{ij}(\mathbf{r}), \quad (52a)$$

$$S_{ij}(\mathbf{r}) = -\frac{1}{3}[L_{ij}(x)L_{ij}(y) + L_{ij}(x)L_{ij}(z) + L_{ij}(y)L_{ij}(z)]f_{ij}(\mathbf{r}), \quad (52b)$$

$$V_{ij}(\mathbf{r}) = -L_{ij}(x)L_{ij}(y)L_{ij}(z)f_{ij}(\mathbf{r}), \quad (52c)$$

By Fourier transforming functions (52), it is straightforward to see that

$$R_{ij} = \frac{1}{3}\{\omega_i^{(3)} \otimes \omega_j^{(1)} + \omega_i^{(1)} \otimes \omega_j^{(3)} + \omega_i^{(2)} \otimes \omega_j^{(2)} - \mathbf{w}_i^{(2)} \otimes \mathbf{w}_j^{(2)}\}, \quad (53a)$$

$$S_{ij} = \frac{1}{3}\{\omega_i^{(3)} \otimes \omega_j^{(2)} + \omega_i^{(2)} \otimes \omega_j^{(3)}\}, \quad (53b)$$

$$V_{ij} = \omega_i^{(3)} \otimes \omega_j^{(3)}. \quad (53c)$$

On the other hand, Eq. (48) has the following expansion up to first order in the densities:

$$-c_{ij} = -f_{ij} - \xi_3 f_{ij} + \xi_2 \{\omega_i^{(3)} \otimes \omega_j^{(1)} + \omega_i^{(1)} \otimes \omega_j^{(3)} + 2(9d_2 + 2e_2)\omega_i^{(2)} \otimes \omega_j^{(2)} + 6(e_2 + \delta)\mathbf{w}_i^{(2)} \otimes \mathbf{w}_j^{(2)}\} + 3\xi_1 S_{ij} + \xi_0 V_{ij}. \quad (54)$$

A comparison of this equation with Eqs. (51) and (53) immediately leads to $2(9d_2 + 2e_2) = 1$ and $6(e_2 + \delta) = -1$, whose solutions are $d_2 = 5/54 + 2\delta/9$ and $e_2 = -1/6 - \delta$. We cannot fix δ yet, and thus the expression obtained so far for the functional Φ has a free parameter, which will be fixed in Sec. V by the dimensional crossover requirement. Nevertheless, for the uniform fluid the δ dependence cancels out and we recover—except for the different normalization—the expression for the free energy per unit volume of the uniform mixture reported in Ref. 24, namely,

$$\Phi = -\xi_0 \ln(1 - \xi_3) + \frac{3\xi_1 \xi_2}{1 - \xi_3} + \frac{\xi_2^3}{(1 - \xi_3)^2}, \quad (55)$$

as well as that for the DCF,

$$c_{ij}(\mathbf{r}) = [\chi^{(0)} + \chi^{(1)} R_{ij}(\mathbf{r}) + \chi^{(2)} S_{ij}(\mathbf{r}) + \chi^{(3)} V_{ij}(\mathbf{r})]f_{ij}(\mathbf{r}), \quad (56)$$

with

$$\chi^{(0)} = \frac{1}{1 - \xi_3}, \quad (57a)$$

$$\chi^{(1)} = \frac{3\xi_2}{(1 - \xi_3)^2}, \quad (57b)$$

$$\chi^{(2)} = \frac{3\xi_1}{(1 - \xi_3)^2} + \frac{6\xi_2^2}{(1 - \xi_3)^3}, \quad (57c)$$

$$\chi^{(3)} = \frac{\xi_0}{(1 - \xi_3)^2} + \frac{6\xi_1 \xi_2}{(1 - \xi_3)^3} + \frac{6\xi_2^3}{(1 - \xi_3)^4}. \quad (57d)$$

IV. THERMODYNAMICS OF THE UNIFORM FLUID

Let us derive here the equation of state of a mixture of hard particles from the FMT introduced in Sec. II. We can readily see that, in the uniform fluid limit, Eq. (14) already provides a simple equation for the pressure of the mixture once we know that of the free-energy density, Φ , in terms of the weighted densities. The pressure thus obtained fulfills the compressibility equation for a mixture,³²

$$\beta \frac{\partial P}{\partial \rho_i} = 1 - \sum_j \rho_j \hat{c}_{ij}(\mathbf{0}) \quad (58)$$

(the hat denotes the Fourier transform). To see it we have to notice that, given the way in which Φ was derived, P is also given by Eq. (10); so, if we take the derivative of that equation with respect to ρ_i , we get

$$\begin{aligned} \beta \frac{\partial P}{\partial \rho_i} &= 1 + \sum_{\alpha, \gamma} n_\alpha \frac{\partial^2 \Phi}{\partial n_\alpha \partial n_\gamma} \hat{\omega}_i^{(\gamma)}(\mathbf{0}) \\ &= 1 + \sum_j \rho_j \sum_{\alpha, \gamma} \frac{\partial^2 \Phi}{\partial n_\alpha \partial n_\gamma} \hat{\omega}_i^{(\gamma)}(\mathbf{0}) \hat{\omega}_j^{(\alpha)}(\mathbf{0}), \end{aligned} \quad (59)$$

where we have used that in the uniform fluid limit, $n_\alpha = \sum_i \rho_i \hat{\omega}_i^{(\alpha)}(\mathbf{0})$, according to the definition [Eq. (2)]. The equivalence of Eqs. (58) and (59) follows from (7).

When applied to the expressions of Φ obtained in Sec. III for PHC in two and three dimensions, we obtain, respectively,

$$\beta P = \frac{\xi_0}{1 - \xi_2} + \frac{\xi_1^2}{(1 - \xi_2)^2} \quad (D=2), \quad (60)$$

$$\beta P = \frac{\xi_0}{1 - \xi_3} + \frac{3\xi_1 \xi_2}{(1 - \xi_3)^2} + \frac{2\xi_2^3}{(1 - \xi_3)^3} \quad (D=3). \quad (61)$$

Notice that, as a consequence of using the scaled particle approximation [Eq. (14)], the resulting equation of state is but a y -expansion of the D th order,³³ by construction exact up to the third virial coefficient (see below, Sec. V, and the Appendix).

Another interesting property of the equation for the pressure (14) is that

$$\beta \frac{\partial P}{\partial \xi_\alpha} = \left(\frac{D}{\alpha} \right) \frac{\partial^2 \Phi}{\partial n_\alpha \partial n_D} = \chi^{(\alpha)}, \quad (62)$$

since this is the coefficient of the term $\omega^{(D)} \otimes \omega^{(\alpha)}$ in the expression for $-c_{ij}$.³⁴ And this has a further unexpected consequence, because

$$-c_{ij}(\mathbf{0}) = \sum_\alpha \chi^{(\alpha)} (\sigma_{ij} - \lambda_{ij})^\alpha, \quad (63)$$

from which, if for instance $\sigma_j \geq \sigma_i$, we obtain

$$-c_{ij}(\mathbf{0}) = \sum_\alpha \chi^{(\alpha)} \sigma_i^\alpha = \beta \frac{\partial P}{\partial \rho_i}, \quad (64)$$

a ‘‘zero separation theorem’’ which is known³² to hold for the PY DCF.³⁵

The pressure of a uniform fluid can also be derived from the virial equation,³²

$$\beta P^v = \rho + \frac{1}{2D} \sum_{ij} \rho_i \rho_j \int \mathbf{r} \cdot \nabla f_{ij}(\mathbf{r}) g_{ij}(\mathbf{r}) d\mathbf{r}, \quad (65)$$

where $g_{ij}(\mathbf{r})$ is the pair correlation function of the mixture. It is a well-known result that for HS the PY equations of state obtained from the compressibility and the virial expressions are different,³⁰ a thermodynamic inconsistency arising from the approximation. Let us see what comes out of the virial equation when applied to a mixture of D -dimensional PHC. Since the Mayer function is $f_{ij}(\mathbf{r}) = -\omega_{ij}^{(D)}(\mathbf{r})$ (we will henceforth use $\omega_{ij}^{(\alpha)}$ to denote the weight $\omega_i^{(\alpha)}$ but with $\sigma_i/2$ replaced by σ_{ij}), then

$$\mathbf{r} \cdot \nabla f_{ij}(\mathbf{r}) = 2\sigma_{ij} \omega_{ij}^{(D-1)}(\mathbf{r}).$$

This is actually, up to a factor σ_{ij} , a delta distribution on the surface of the cube $i \cup j$, thus

$$\int d\mathbf{r} 2\omega_{ij}^{(D-1)}(\mathbf{r}) = \int_{\partial(i \cup j)} dS$$

and, given that g_{ij} is discontinuous at the surface of that cube, Eq. (65) becomes

$$\beta P^v = \rho + \frac{1}{2D} \sum_{ij} \rho_i \rho_j \sigma_{ij} \int_{\Delta \partial(i \cup j)} g_{ij}(\mathbf{r}) dS \quad (66)$$

$[\Delta \partial(i \cup j) \equiv \partial(i \cup j)^+ - \partial(i \cup j)^-]$ denotes the outer surface minus the inner surface; actually it is an integral of the jump of g_{ij} at the surface of the core. If we now use the continuity of the function $y_{ij} \equiv g_{ij} - c_{ij}$ across the surface of the interaction core and the fact that c_{ij} vanishes outside, we can simply write Eq. (66) as

$$\beta P^v = \rho - \frac{1}{2D} \sum_{ij} \rho_i \rho_j \sigma_{ij} \int_{\partial(i \cup j)^-} c_{ij}(\mathbf{r}) dS. \quad (67)$$

If we now apply this expression to the DCFs obtained in Sec. III for PHC in $D=2,3$, we obtain the remarkable result that $P^v = P$, and so the theory is thermodynamically consistent. Although this seems to be a general property of the FMT for PHC, we have not been able to prove it with such a generality, without resorting to the actual expressions for the DCF.

We can compare the virial expansions of Eqs. (60) and (61) with the exact expressions for the second and third virial coefficients,

$$\rho^2 B_2 = \frac{1}{2} \sum_{i,j} \rho_i \rho_j (\sigma_i + \sigma_j)^D, \quad (68)$$

$$\rho^3 B_3 = \frac{1}{3} \sum_{i,j,k} \rho_i \rho_j \rho_k (\sigma_i \sigma_j + \sigma_j \sigma_k + \sigma_k \sigma_i)^D, \quad (69)$$

to conclude that they are exact up to the third term. This is not surprising for $D=3$ because exactness up to the third-order diagram was imposed as a requirement to fully determine the DCF of the mixture (see Sec. III); however, such a condition was unnecessary for $D=2$, and yet it is automatically fulfilled (for a deeper insight on this fact see Sec. V as well as the Appendix).

As concerns the remaining virial coefficients, we can compare what comes out of the equations for the pressure with the exact results for the one-component fluid³⁶ and realize that they are all different. So it turns out that the theory begins to be approximate at the level of the fourth virial coefficient. Furthermore, in Ref. 36 the virial coefficients for the PY equations of state are also computed; as they do not match those given by this theory, we can conclude that, contrary to what happens for HS,¹⁵ the DCF coming out of this theory is not the PY one. This has an unfortunate consequence, namely that the pair correlation function cannot fulfill the ‘‘core condition,’’ i.e., it takes nonzero values inside the core.

V. HIGHLY INHOMOGENEOUS FLUIDS: DIMENSIONAL CROSSOVER

By construction, density functional theories are the appropriate tool to study fluids exhibiting all kinds of inhomogeneities. As discussed in Sec. I, a typical inhomogeneous situation in which classical functionals tested their validity is the solid phase, but this is neither the only one nor the most extreme among all of them. In recent years confined fluid have received a great deal of attention, due to the strong effects that spatial confinement has on the structural and dynamical properties of fluids, as well as on the location and character of phase transitions. But it is precisely for highly inhomogeneous phases appearing under confinement that density functionals show their limitations. Such strong inhomogeneities may also reduce the dimensionality of the system. Thus a fluid between two close plates would be a quasi-2D system, a fluid in a narrow cylindrical pore a quasi-1D system, and a solid phase, in which every particle can be considered as being inside a cavity holding no more than one single particle, can be considered a ‘‘quasi-0D’’ system. Now, it is clear that if we imposed those constraints on the exact 3D functional we would obtain the corresponding 2D, 1D, or 0D functional. But this property may not be satisfied for an approximate functional. As a matter of fact, none of the ‘‘classical’’ functionals³—built upon bulk 3D data—do it, because such a requirement needs to be imposed at the construction of the functional. This is an important

requirement if one wishes to use the 3D functional to describe fluids under extreme confinements. Furthermore, contrary to the accumulated evidence,³ it is also an important requirement for the functional to provide a sensible solid phase; otherwise, despite that a freezing transition is predicted, it may have unphysical properties, such as the already mentioned negative density of vacancies or the regular behavior of the free energy at closest packing.^{13,14}

The simplest FMT functional for HS, in either of its two forms,^{15,20} has proven to be suitable for describing the bulk phase, the density profiles near walls,²⁰ as well as those inside a slitlike pore,³⁷ but it dramatically fails to describe the solid, predicting a stable perfect solid for any density. The reason for this became clear when the *dimensional crossovers* of the functional were considered. To be precise, we will say that a given D -dimensional functional has a right D to $d (< D)$ dimensional crossover if

$$F^D[\{\rho_i\}] = F^d[\{\rho'_i\}], \quad \text{for} \\ \rho_i(x_1, \dots, x_D) = \rho'_i(x_1, \dots, x_d) \delta(x_{d+1}) \dots \delta(x_D), \quad (70)$$

where F^d stands for some good approximation of the d -dimensional free-energy functional. When constraint (70) is imposed on the HS FMT functional, it turns out that it has reasonable dimensional crossovers from 3D to 2D or 1D, but it develops a singularity when it is reduced to 0D.^{38,13} The 0D functional can be easily derived¹³ and it provides the following expression for the excess free energy:

$$\Phi^{(0)} = \eta + (1 - \eta) \ln(1 - \eta), \quad (71)$$

where $\eta (< 1)$ here is simply the average number of particles.

For a given density functional to predict a solid phase, it is sufficient that the 3D to 0D dimensional crossover yields a finite value, be it Eq. (71) or not; but for the solid not to have the abovementioned unphysical properties the crossover should produce Eq. (71).^{13,14} It turns out that there is a way to regularize the HS FMT functional that yields the exact 3D to 1D and 0D dimensional crossovers¹³ and does not change the results for the bulk phase. With this regularized functional it is possible to obtain a solid phase with the correct density of vacancies and a divergent free energy at the closest packing density.¹⁴

The same considerations can be made on the PHC model to realize that it already behaves well in this respect. It turns out²⁸ that the 2D functional has exact dimensional crossovers to 1D and 0D, and that the 3D functional can be tuned to fulfill all the three-dimensional crossovers (to 2D, 1D, and 0D) by properly setting the constant $\delta = 1/3$ in Eqs. (47), which remained free in the derivation of the 3D functional—although its value was irrelevant for the bulk results. The 3D functional for PHC is therefore fully determined to be

$$\Phi = -n_0 \ln(1 - n_3) + \frac{\mathbf{n}_1 \cdot \mathbf{n}_2}{1 - n_3} + \frac{n_2^3 - 3n_2 \mathbf{n}_2 \cdot \mathbf{n}_2 + 2\mathbf{n}_2 \cdot \mathbf{n}_2 \cdot \mathbf{n}_2}{6(1 - n_3)^2}.$$

To see why this is so, let us first consider the 3D to 2D dimensional crossover. Let us define a quasi-2D set of density functions as that made of densities $\rho_i(x, y, z)$ vanishing for $|z| > \sigma_i/2$. It is clear that a set of densities like those of Eq. (70) belong to this class. Because of the definition of the weighted densities, it is easy to check that for this type of densities [see Eq. (41)]

$$n_{2,z}^{(3)} = -\frac{1}{2} \text{sign } z \frac{\partial n_3^{(3)}}{\partial z}, \quad n_{1,x}^{(3)} = -\frac{1}{2} \text{sign } z \frac{\partial n_{2,y}^{(3)}}{\partial z}, \\ n_{1,y}^{(3)} = -\frac{1}{2} \text{sign } z \frac{\partial n_{2,x}^{(3)}}{\partial z}, \quad n_0^{(3)} = -\frac{1}{2} \text{sign } z \frac{\partial n_{1,z}^{(3)}}{\partial z}$$

[along this section, a superscript (D) will be used to specify the dimension], and therefore, Eq. (72) can be written [notice that, in terms of the vector components, the numerator of the last term in Eq. (72) is simply $6n_{2,x}^{(3)}n_{2,y}^{(3)}n_{2,z}^{(3)}$]

$$\Phi^{(3)} = -\frac{1}{2} \text{sign } z \frac{\partial}{\partial z} \left[-n_{1,z}^{(3)} \ln(1 - n_3^{(3)}) + \frac{n_{2,x}^{(3)}n_{2,y}^{(3)}}{1 - n_3^{(3)}} \right], \quad (72)$$

and thus

$$\beta F^{\text{ex}} = \int \int \int dx \, dy \, dz \, \Phi^{(3)} \\ = \int \int dx \, dy \left[-n_{1,z}^{(3)}(x, y, 0) \ln[1 - n_3^{(3)}(x, y, 0)] + \frac{n_{2,x}^{(3)}(x, y, 0)n_{2,y}^{(3)}(x, y, 0)}{1 - n_3^{(3)}(x, y, 0)} \right]. \quad (73)$$

If we now make the specific choice $\rho_i(x, y, z) = \rho_i(x, y) \delta(z)$, then it is straightforward to see that, according to definitions (24), $n_3^{(3)}(x, y, 0) = n_2^{(2)}(x, y)$, $n_{2,x}^{(3)}(x, y, 0) = n_{1,y}^{(2)}(x, y)$, $n_{2,y}^{(3)}(x, y, 0) = n_{1,x}^{(2)}(x, y)$, and $n_{1,z}^{(3)}(x, y, 0) = n_0^{(2)}(x, y)$, and so the integrand in Eq. (73) is simply $\Phi^{(2)}$ as given by Eq. (32).

If we consider quasi-1D density functions instead, i.e., functions $\rho_i(x, y, z)$ which vanish if $|z| > \sigma_i/2$ or if $|y| > \sigma_i/2$, then two more relations between the weighted densities arise, namely,

$$n_{2,y}^{(3)} = -\frac{1}{2} \text{sign } y \frac{\partial n_3^{(3)}}{\partial y}, \quad n_{1,z}^{(3)} = -\frac{1}{2} \text{sign } y \frac{\partial n_{2,x}^{(3)}}{\partial y}.$$

With them we can write

$$\Phi^{(3)} = \left(-\frac{1}{2} \right)^2 \text{sign}(yz) \frac{\partial^2}{\partial z \partial y} \left[-n_{2,x}^{(3)} \ln(1 - n_3^{(3)}) \right], \quad (74)$$

and so Eq. (73) can be further transformed into

$$\beta F^{\text{ex}} = \int dx \{ -n_{2,x}^{(3)}(x, 0, 0) \ln[1 - n_3^{(3)}(x, 0, 0)] \}. \quad (75)$$

This result is in perfect agreement with the exact solution of a 2D model of PHC in a narrow band.³⁹ When the bandwidth is smaller than twice the edge of a square, the system is essentially one dimensional and Eq. (75) is the

exact expression for the excess free energy. When the bandwidth permit two squares (but no more than two) to be on top of each other, two-dimensional corrections come into play;³⁹ but this is precisely the point at which Eq. (75) stops being true.

Again, if $\rho_i(x, y, z) = \rho_i(x) \delta(y) \delta(z)$, then the integrand of Eq. (75) turns out to be¹⁹ $\Phi^{(1)}$. This proves both the 3D to 1D as well as the 2D to 1D dimensional crossovers.

Finally, a further relation between the weighted densities which holds for quasi-0D densities (those vanishing if any coordinate is outside the interval $[-\sigma_i/2, \sigma_i/2]$),

$$n_{2,x}^{(3)} = -\frac{1}{2} \text{sign } x \frac{\partial n_3^{(3)}}{\partial x},$$

makes it possible to express

$$\Phi^{(3)} = \left(-\frac{1}{2}\right)^3 \text{sign}(xyz) \frac{\partial^3}{\partial z \partial y \partial x} \Phi^{(0)}(n_3^{(3)}), \quad (76)$$

with $\Phi^{(0)}$ defined by Eq. (71), and then to transform Eq. (75) into

$$\beta F^{\text{ex}} = \Phi^{(0)}(n_3^{(3)}(0,0,0)). \quad (77)$$

For $\rho_i(x, y, z) = \eta \delta(x) \delta(y) \delta(z)$, $n_3(0,0,0) = \eta$, and Eq. (77) is the 0D excess free energy given by Eq. (71). The 3D to 0D (and the obvious 1D to 0D) dimensional crossover is then proven.

We can take further advantage of Eq. (76), but first we have to distinguish between the three edge lengths of the cube, i.e., we need to consider general parallelepipeds. Thus $n^{(3)}$ has to be redefined with the weight $\omega_i^{(3)} \equiv \tau_i^x(x) \tau_i^y(y) \tau_i^z(z)$, where

$$\tau_i^\mu(x_\mu) \equiv \Theta\left(\frac{\sigma_i^{(\mu)}}{2} - |x_\mu|\right).$$

The transformation makes use of the identity

$$-\frac{1}{2} \text{sign } x_\mu \frac{\partial}{\partial x_\mu} \tau_i^\mu(x_\mu) = \frac{\partial}{\partial \sigma_i^{(\mu)}} \tau_i^\mu(x_\mu),$$

which implies that Eq. (76) can be rewritten as

$$\Phi^{(3)} = \frac{\partial^3}{\partial \sigma^{(z)} \partial \sigma^{(y)} \partial \sigma^{(x)}} \Phi^{(0)}(n_3^{(3)}), \quad (78)$$

where we have introduced the short-hand notation

$$\frac{\partial}{\partial \sigma^{(\mu)}} \equiv \sum_i \frac{\partial}{\partial \sigma_i^{(\mu)}}.$$

Formula (78) yields the same functional as Eqs. (72), (74), or (76) for quasi-2D, quasi-1D, or quasi-0D density functions, respectively, and so it has the right dimensional crossovers; furthermore, Eq. (78) is also valid for arbitrary density functions, so it actually allows to build the functional out of the 0D one, whichever the density functions, and even more, it provides a simple way to generalize the functional to arbitrary dimensions, namely,

$$\Phi^{(D)} = \frac{\partial^D}{\partial \sigma^{(D)} \dots \partial \sigma^{(1)}} \Phi^{(0)}(n_D^{(D)}), \quad (79)$$

where $n_D^{(D)}$ has the obvious meaning. In the Appendix it is shown that this generalization of the functional provides a DCF which is exact up to the third virial diagram [i.e., satisfying Eq. (16)].

The result that the D -dimensional functional can be obtained out of the 0D one by requiring it to fulfill the dimensional crossovers has also been reported for HS,²⁷ although derived in a completely different way. It seems, however, that attempts to find a derivation similar to Eq. (79) for HS are bound to fail.⁴⁰ The reasons why PHC behave so well in this respect as opposed to HS are yet unknown. The connection between the derivations of the HS and PHC functionals from the 0D ones are also not well understood. We are currently trying to make some progress along these lines.

VI. CONCLUSIONS

FMT seems to be a powerful and attractive framework to derive the functional for hard convex bodies from very fundamental assumptions. But it has important limitations. For instance, the impossibility of finding a decomposition (9) for the Mayer function^{22,23} limits its extension to arbitrary molecular shapes. Attempts to overcome this limitation should probably follow the new scheme of the theory for HS,²⁷ in which this decomposition is avoided. Nevertheless, with the present formulation the theory can still be extended to other molecular shapes (such as, for instance, mixtures of parallel cylinders²⁸) by using the ideas of this work.

Another aspect of the theory which deserves further study is its correct place within the context of liquid theory. Its connections to scaled particle theory are obvious here and there and, as we have shown, they are even at the heart of its original derivation; however, the formulation yields a functional valid for inhomogeneous phases as well as for the homogeneous ones, and when it is tested against dimensionality reduction, it not only seems to behave well, but it appears that this strong requirements can replace the resort to scaled particle theory.

Apart from these fundamental questions the theory has many potential applications, some of which will be the subject of the sequel to this article. The great advantage of FMT as opposed to alternative approaches is that it deals with homogeneous and inhomogeneous phases at the same foot, without having to incorporate the inhomogeneity by means of heuristic extensions of the theory. For the case of PHC its application is even simpler because of the simplicity of Eq. (79), which essentially tells us that the construction of the 0D free energy (depending of only one single weighted density) is all we need to compute that of the D -dimensional system, whichever D .

ACKNOWLEDGMENT

It is a pleasure to acknowledge Y. Rosenfeld for illuminating discussions, unvaluable suggestions, and continuous encouragement.

APPENDIX: LOW DENSITY EXPANSION OF THE D-DIMENSIONAL DCF

We are going to show in this Appendix that the functional given by Eq. (79) yields a DCF, $c_{ij}^{(D)}$, with the right low density expansion (16).

Toward this purpose we first take the second functional derivative of the excess free energy and then take the uniform limit; thus according to Eq. (79)

$$c_{ij}^{(D)}(\mathbf{r}) = \mathcal{D} C_{ij}^{(0)}(\mathbf{r}), \quad \mathcal{D} \equiv \frac{\partial^D}{\partial \sigma^{(D)} \dots \partial \sigma^{(1)}}, \quad (\text{A1})$$

$$c_{ij}^{(0)}(\mathbf{r}) = -\frac{1}{1-\eta} \omega_i^{(D)} \otimes \omega_j^{(D)}(\mathbf{r}), \quad (\text{A2})$$

where $\eta = \sum_k \rho_k \sigma_k^{(1)} \dots \sigma_k^{(D)}$, and

$$\omega_i^{(D)}(\mathbf{r}) = \prod_{\mu=1}^D \Theta\left(\frac{\sigma_i^{(\mu)}}{2} - |x_\mu|\right).$$

The convolution in Eq. (A2) factorizes and can be written [see Eq. (33)]

$$\omega_i^{(D)} \otimes \omega_j^{(D)}(\mathbf{r}) = \prod_{\mu=1}^D L_{ij}^{(\mu)}(x_\mu) \Theta(\sigma_{ij}^{(\mu)} - |x_\mu|), \quad (\text{A3})$$

where the superscripts in $L_{ij}^{(\mu)}$ and $\sigma_{ij}^{(\mu)}$ have been added as a reminder that the σ 's are those corresponding to the x_μ coordinate.

Now, the low density expansion of Eq. (A2) is

$$c_{ij}^{(0)}(\mathbf{r}) \sim -(1 + \eta + \dots) \omega_i^{(D)} \otimes \omega_j^{(D)}(\mathbf{r}); \quad (\text{A4})$$

let us see that when inserted in Eq. (A1) the resulting expansion is [see Eq. (50)]

$$\begin{aligned} c_{ij}^{(D)}(\mathbf{r}) &\sim f_{ij}(\mathbf{r}) \left(1 + \sum_k \rho_k \prod_{\mu=1}^D [\sigma_k^{(\mu)} + L_{ij}^{(D)}(x_\mu)] + \dots \right) \\ &= \text{---} + \sum_k \rho_k \text{---} + \dots \end{aligned}$$

From Eq. (A3), the first term in the $c_{ij}^{(D)}$ expansion will be

$$\begin{aligned} &-\mathcal{D} \omega_i^{(D)} \otimes \omega_j^{(D)}(\mathbf{r}) \\ &= -\prod_{\mu=1}^D \frac{\partial}{\partial \sigma^{(\mu)}} \{L_{ij}^{(\mu)}(x_\mu) \Theta(\sigma_{ij}^{(\mu)} - |x_\mu|)\}, \end{aligned}$$

which, by making use of the relations

$$\frac{\partial}{\partial \sigma^{(\mu)}} L_{ij}^{(\mu)}(x_\mu) = 1 \quad \text{and} \quad L_{ij}^{(\mu)}(\sigma_{ij}^{(\mu)}) = 0,$$

simply transforms into $f_{ij}(\mathbf{r})$. As concerns the second term,

$$\begin{aligned} -\eta \mathcal{D} \omega_i^{(D)} \otimes \omega_j^{(D)}(\mathbf{r}) &= -\sum_k \rho_k \prod_{\mu=1}^D \frac{\partial}{\partial \sigma^{(\mu)}} \{ \sigma_k^{(\mu)} \\ &\quad \times L_{ij}^{(\mu)}(x_\mu) \Theta(\sigma_{ij}^{(\mu)} - |x_\mu|) \}; \end{aligned}$$

since $\partial \sigma_k^{(\mu)} / \partial \sigma^{(\mu)} = 1$, this expression immediately yields the desired result.

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