Fundamental measure density functional theory for nonadditive hard-core mixtures: The one-dimensional case

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We treat a one-dimensional binary mixture of hard-core particles that possess nonadditive diameters. For this model, a density functional theory is constructed following similar principles as an earlier extension of Rosenfeld's fundamental measure theory to three-dimensional nonadditive hard-sphere mixtures. The theory applies to arbitrary positive and moderate negative nonadditivity and reduces to Percus' exact functional in the additive case. Bulk direct correlation functions are obtained as functional derivatives of the excess free energy functional. Results for the partial pair correlation functions in bulk, as calculated via the Ornstein-Zernike route and using the direct correlation functions as input, show very good agreement with results from our Monte Carlo computer simulations of the mixture.

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I. INTRODUCTION

The theoretical study of one-dimensional fluids is motivated by experimental realizations of such systems, including dispersions of mesoscopic colloidal particles that are confined topographically inside narrow channels [1] or with the aid of one-dimensional laser traps [2]. Low spatial dimensionality simplifies theoretical treatment as compared to the three-dimensional case, as has been exploited, e.g., in investigations of depletion interactions [3,4], model colloid-polymer mixtures [5], transport phenomena [6,7], and adsorption in model porous media [8,9].

The one-dimensional hard-core model (or hard-rod model or Tonks gas [10]) is a basic model fluid with short-ranged repulsive interparticle forces and continuous position coordinates. Its exact free energy functional has been obtained by Percus both for the pure (one-component) system [11] and for additive mixtures [12]. In an additive mixture the distance at which particles of unlike species interact, σ_{ij}, where i and j label the species and $i \neq j$, is given by the mean of the individual particle sizes, $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$, where σ_{ii} (σ_{jj}) is the interaction distance between particles of the same species i (j). In a hard-core model the pair interaction potential is infinite if the center-to-center distance x between two particles is $x < \sigma_{ij}$, and zero otherwise. Nonadditive mixtures, however, violate the additive relationship between the length scales; they rather satisfy $\sigma_{ij} = (1 + \Delta)(\sigma_{ii} + \sigma_{jj})/2$, where the parameter Δ measures the degree of nonadditivity and the additive case is recovered for $\Delta = 0$.

For three-dimensional nonadditive hard spheres (NAHS) it is known from simulations and theory that small positive values of Δ are already sufficient to induce stable fluid-fluid demixing into phases with different chemical compositions (see, e.g., Refs. [13–15] for classic studies and Refs. [16–26] for more recent work). In contrast, for $\Delta < 0$ a single fluid phase is stable, but clustering phenomena can occur, as, e.g., recently observed experimentally in (two-dimensional) magnetic dispersions [27]. Besides colloids, the NAHS model has been used to model racemic molecular mixtures [28] and

dense fluid hydrogen [29]. Moreover, it constitutes the natural reference model for mixtures with soft interactions [30,31]. In colloids it is of relevance for modeling, e.g., colloid-microemulsion mixtures as well as for mixtures of charged and neutral colloids in nonaqueous solvents. From a fundamental point of view, binary NAHS form arguably the simplest (hard-core) model that displays liquid-liquid phase separation, i.e., phase separation into different *dense* fluid phases in which particle packing effects are of relevance. A variety of methods of study has been used including computer simulations and liquid integral equation theories, but also approaches such as scaled-particle theory [32–37] and the virial expansion [38]. Furthermore, a detailed investigation of depletion phenomena, based on density functional theory (DFT) [39–41], has been carried out [42,43].

Rosenfeld's fundamental measure theory (FMT) [41] is a DFT that is widely used in the study of inhomogeneous hard-sphere systems. Based on ideas of scaled-particle theory and Percus-Yevick theory, the DFT of Ref. [41] was formulated for additive hard-sphere mixtures. Subsequent refinements [44,45] were performed to account for phenomena such as freezing. Significant insight into the nature of FMT was gained from applying the approach to hard-core (and other) lattice gases [46,47]. For a recent continuum study, see Ref. [48], where a FMT for aligned hexagons is given (this paper contains also an in-depth discussion of some of the history and the current state of FMT). See Refs. [49,50] for a detailed simulation study and critical discussion of FMT predictions for depletion phenomena in very asymmetric additive hard-sphere mixtures. For several models that correspond to special cases of nonadditivity, FMTs have been constructed, including the Widom-Rowlinson model of a symmetric binary mixture [51] (where $\sigma_{11} = \sigma_{22} = 0$ such that $\sigma_{12} > 0$ is the only relevant length scale), and the Asakura-Oosawa model of colloid-polymer mixtures [where species 2 with $\sigma_{22} = 0$ models ideal polymers with radius of gyration $\sigma_{12} - (\sigma_{11}/2)$] [52,53].

In Ref. [54] a FMT for nonadditive hard-sphere mixtures was proposed. This DFT was shown to give very satisfactory

results for bulk pair correlation functions and for the location of the fluid-fluid demixing critical point (for $\Delta > 0$) as compared to computer simulation results from the literature. In the present contribution we apply the same construction principles to the binary one-dimensional nonadditive hard-core mixture and arrive at a DFT for this model. The theory applies to arbitrary positive and moderate negative nonadditivity such that $\sigma_{12} > \max(\sigma_{11}, \sigma_{22})/2$ is satisfied. In the additive case, $\Delta = 0$, it reduces to Percus's exact functional. The quality of the DFT is demonstrated by comparing results for the partial pair correlation functions as obtained from the Ornstein-Zernike route to results from our computer simulations. Excellent agreement is found, even at considerably high densities. Nevertheless, there are also shortcomings, such as the prediction of a spurious demixing phase transition at very high densities, which is clearly absent in reality. The explicit form of the excess free energy functional, as given in Eq. (19), is more compact than the somewhat formal derivation might suggest at first glance. Nevertheless, the derivation given is as explicit and self-contained as possible, both in order to exemplify its structural strength, as well as to highlight the analogy with the three-dimensional case.

The paper is organized as follows. In Sec. II the model is defined and the DFT is constructed. Results for pair correlation functions are presented in Sec. III, and we conclude in Sec. IV.

II. DENSITY FUNCTIONAL THEORY

A. The model

We consider a binary mixture with pair potentials $V_{ij}(x)$ that act between particles of species i and j, where $i, j = 1, 2$, given by

$$V_{ij}(x) = \begin{cases} \infty, & x < \sigma_{ij,} \\ 0 & \text{otherwise,} \end{cases} \quad (1)$$

where x is the center-center distance between the two particles; σ_{11}, σ_{12}, and σ_{22} are the distances of minimal approach between particles of species $ij = 11$, 12, and 22, respectively. We introduce particle radii as $R_1 = \sigma_{11}/2$ and $R_2 = \sigma_{22}/2$, as well as a further length R_{12} which satisfies $\sigma_{12} = R_1 + R_2 + R_{12}$, and hence $R_{12} = \sigma_{12} - (\sigma_{11} + \sigma_{22})/2$. The relationship of the nonadditivity parameter to the radii is $\Delta = R_{12}/(R_1 + R_2)$, and hence $R_{12} = (R_1 + R_2)\Delta$. Note that in the additive case $R_{12} = 0$ and $\Delta = 0$. For cases of negative nonadditivity we restrict ourselves in the following to $|R_{12}| < \min(R_1, R_2)$, which corresponds to $\sigma_{12} > \max(\sigma_{11}, \sigma_{22})/2$. See Fig. 1 for an illustration of the length scales involved and how nonadditivity arises naturally when two-dimensional (hard-core) shapes are confined on a line.

B. Excess free energy functional

The Helmholtz excess (over ideal gas) free energy as a functional of the one-body density distributions, $\rho_i(x)$, for species $i = 1, 2$, where x is the space coordinate, is assumed to be of the form
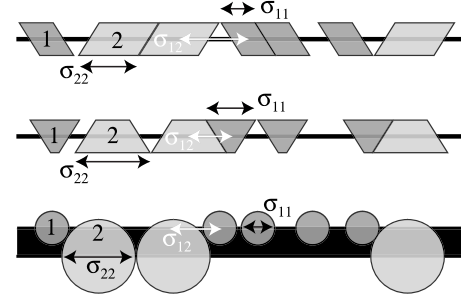

FIG. 1. Illustration of nonadditive hard-core mixtures in one dimension, where the hard-core interaction distance σ_{ij} between a pair of particles of species ij is $\sigma_{11} = 2R_1$, $\sigma_{12} = R_1 + R_{12} + R_2$, and $\sigma_{22} = 2R_2$. Top graph: A mixture of small left-tilted (species 1) and large right-tilted (species 2) rhombi exhibits positive nonadditivity. Middle graph: A mixture of small (species 1) and large inverted (species 2) wedges exhibits negative nonadditivity. Note how σ_{12} (white arrow) is larger (top) or smaller (middle) than the arithmetic mean of σ_{11} and σ_{22} (black arrows). Bottom: A similar situation of negative nonadditivity arises when disks are confined to either boundary of a strip of finite width.

$$\mathcal{F}_{\text{exc}}[\rho_1, \rho_2] = k_B T \int dx \int dx' \sum_{\alpha, \beta = 0, 1} K_{\alpha\beta}(x - x')$$
$$\times \Phi_{\alpha\beta}(\{n_\nu^{(1)}(x)\}, \{n_\tau^{(2)}(x')\}), \quad (2)$$

where k_B is the Boltzmann constant, T is absolute temperature, $K_{\alpha\beta}(\cdot)$ are (density-independent) convolution kernels, and $\Phi_{\alpha\beta}(\cdot)$ are explicit functions of sets of weighted densities for each species, $\{n_\nu^{(1)}(x)\}$ and $\{n_\tau^{(2)}(x')\}$, where the upper index (1,2) labels the species and the lower index (μ, τ) labels the type of weighted density. Note that in Eq. (2) the weighted densities for species 1 at position x are coupled to the weighted densities for species 2 at position x' via the kernels $K_{\alpha\beta}(x - x')$. Both $K_{\alpha\beta}(\cdot)$ and $\Phi_{\alpha\beta}(\cdot)$ can be viewed as the $\alpha\beta$ component of a corresponding a second-rank tensor (matrix).

The weighted densities are obtained from the bare density profiles via convolution,

$$n_\nu^{(i)}(x) = \int ds \, \rho_i(s) w_\nu^{(i)}(x - s), \quad i = 1, 2, \quad \nu = 0, 1, \quad (3)$$

where i labels the species, ν labels the type of weighted density, and $w_\nu^{(i)}(\cdot)$ are (density-independent) weight functions that are characteristic of the particle geometries. These are given by

$$w_1^{(i)}(x) = \text{sgn}(R_i)\Theta(|R_i| - |x|), \quad (4)$$

$$w_0^{(i)}(x) = \delta(|R_i| - |x|)/2, \quad (5)$$

$$w_{-1}^{(i)}(x) = \text{sgn}(R_i)\delta'(|R_i| - |x|)/4, \quad (6)$$

where $\text{sgn}(\cdot)$ is the sign function, $\Theta(\cdot)$ is the Heaviside step function, $\delta(\cdot)$ is the Dirac distribution, and $\delta'(\cdot)$ is the derivative of the Dirac distribution with respect to the argument. The weight functions $w_1^{(i)}(x)$ and $w_0^{(i)}(x)$ for both spe-

cies $i=1,2$ with $R_i>0$ are the familiar Rosenfeld weight functions in one dimension (see, e.g., [55]), which are used in the FMT re-formulation of Percus's functional for one-dimensional additive hard-core mixtures [11,12]; these are used in (3). Equation (6) introduces a further geometric function $w_{-1}^{(i)}(x)$, which will be used below as one component of the matrix of convolution kernels $K_{\alpha\beta}(\cdot)$, namely, $K_{10}(\cdot)$, but will *not* serve to build weighted densities according to (3). The generalization of (4) and (5) to $R_i<0$ serves the same purpose.

Before continuing with the construction of the functional, we make the relationship of the weight functions to the exact low-density limit of the free energy functional explicit. On the second virial level the exact functional is bilinear in densities, $\mathcal{F}_{\mathrm{exc}}[\rho_1,\rho_2]\simeq(-k_BT/2)\int dx\int dx'\Sigma_{i,j=1,2}\rho_i(x)\rho_j(x')f_{ij}(x-x')$, where the Mayer function $f_{ij}(x)$ is related to the pair potential as $f_{ij}(x)=\exp[-V_{ij}(x)/(k_BT)]-1$. For the hard-core mixture under consideration $f_{ij}(x)=-\Theta(\sigma_{ij}-|x|)$. Convolutions of weight functions are conveniently carried out as products in Fourier space, where the weight functions are obtained as $\tilde{w}_\nu^{(j)}(k)=\int_{-\infty}^{\infty}dx\,\exp(i\,kx)w_\nu^{(j)}(x)$, with i being the imaginary unit. Explicitly these are given as

$$\tilde{w}_1^{(i)}(k) = 2\,\sin(kR_i)/k, \tag{7}$$

$$\tilde{w}_0^{(i)}(k) = \cos(kR_i), \tag{8}$$

$$\tilde{w}_{-1}^{(i)}(k) = -k\,\sin(kR_i)/2. \tag{9}$$

The weight functions can be related to the Mayer bonds of the mixture via products in Fourier space (and hence convolutions in real space) as

$$-\tilde{f}_{12}(k) = 2\,\sin[k(R_1+R_2+R_{12})]/k = \tilde{w}_1^{(1)}(k)\tilde{w}_{-1}^{(12)}(k)\tilde{w}_1^{(2)}(k)$$
$$+ \tilde{w}_1^{(1)}(k)\tilde{w}_0^{(12)}(k)\tilde{w}_0^{(2)}(k) + \tilde{w}_0^{(1)}(k)\tilde{w}_0^{(12)}(k)\tilde{w}_1^{(2)}(k)$$
$$+ \tilde{w}_0^{(1)}(k)\tilde{w}_1^{(12)}(k)\tilde{w}_0^{(2)}(k), \tag{10}$$

$$-\tilde{f}_{ii}(k) = 2\,\sin(2kR_i)/k = 2\tilde{w}_1^{(i)}(k)\tilde{w}_0^{(i)}(k), \quad i=1,2. \tag{11}$$

It is instructive to rewrite Eq. (10) by grouping the weight functions that contain the same length scale R_i (i.e., those with the same upper index i) into vectors (for $i=1,2$) and into a matrix (for $i=12$). This yields

$$-\tilde{f}_{12}(k) = (\tilde{w}_0^{(1)},\tilde{w}_1^{(1)})\begin{pmatrix}\tilde{w}_1^{(12)} & \tilde{w}_0^{(12)} \\ \tilde{w}_0^{(12)} & \tilde{w}_{-1}^{(12)}\end{pmatrix}\begin{pmatrix}\tilde{w}_0^{(2)} \\ \tilde{w}_1^{(2)}\end{pmatrix}, \tag{12}$$

where the argument k has been omitted on the right-hand side in order to unclutter the notation.

We choose to use the matrix that appears in (12) as the convolution kernels $K_{\alpha\beta}(\cdot)$ that appear in the generic formulation of the free energy functional Eq. (2). Hence in Fourier space

$$\begin{pmatrix}\tilde{K}_{00}(k) & \tilde{K}_{01}(k) \\ \tilde{K}_{10}(k) & \tilde{K}_{11}(k)\end{pmatrix} = \begin{pmatrix}\tilde{w}_1^{(12)}(k) & \tilde{w}_0^{(12)}(k) \\ \tilde{w}_0^{(12)}(k) & \tilde{w}_{-1}^{(12)}(k)\end{pmatrix}$$
$$= \begin{pmatrix}2\,\sin(kR_{12})/k & \cos(kR_{12}) \\ \cos(kR_{12}) & -k\,\sin(kR_{12})/2\end{pmatrix}, \tag{13}$$

and in real space, as is relevant for the free energy functional (2),

$$\begin{pmatrix}K_{00}(x) & K_{01}(x) \\ K_{10}(x) & K_{11}(x)\end{pmatrix}$$
$$= \begin{pmatrix}w_0^{(12)}(x) & w_1^{(12)}(x) \\ w_{-1}^{(12)}(x) & w_0^{(12)}(x)\end{pmatrix}$$
$$= \begin{pmatrix}\mathrm{sgn}(R_{12})\Theta(|x|-|R_{12}|) & \delta(|x|-|R_{12}|)/2 \\ \delta(|x|-|R_{12}|)/2 & \mathrm{sgn}(R_{12})\delta'(|x|-|R_{12}|)/4\end{pmatrix}, \tag{14}$$

where we have used x as the space coordinate in (14); as noted above, in the free energy functional Eq. (2), the argument is $K_{\alpha\beta}(x-x')$ for all elements $\alpha,\beta=0,1$.

The remaining task is to prescribe the functional dependence of $\Phi_{\alpha\beta}$ on the weighted densities. In order to do so we impose a relationship with the zero-dimensional excess free energy $\phi_{0D}(\eta)$, here expressed as a function of the auxiliary variable η (which can be viewed as the average occupation number of the zero-dimensional system). Together with its first and second derivatives, this is given by [55]

$$\phi_{0D}(\eta) = (1-\eta)\ln(1-\eta) + \eta, \tag{15}$$

$$\phi_{0D}'(\eta) = -\ln(1-\eta), \tag{16}$$

$$\phi_{0D}''(\eta) = \frac{1}{1-\eta}. \tag{17}$$

Straightforward dimensional analysis yields constraints on the analytic form of $\Phi_{\alpha\beta}$. Note that the product $K_{\alpha\beta}\Phi_{\alpha\beta}$ must be of dimension (length)$^{-2}$ [cf. Eq. (2)]. The dimensionality of $K_{\alpha\beta}$ is (length)$^{-\alpha-\beta}$ [see Eq. (14)]. The only dimensional weighted density is $n_0^{(i)}$, which carries (length)$^{-1}$; recall that $n_1^{(i)}$ is dimensionless. Hence $\Phi_{\alpha\beta}$ must contain $2-\alpha-\beta$ factors of $n_0^{(i)}$. Furthermore, we assume that $\Phi_{\alpha\beta}$ depends on the sum $n_1^{(1)}+n_1^{(2)}$ via the $(\alpha+\beta)$th derivative of ϕ_{0D}. This leads to the following form:

$$\begin{pmatrix}\Phi_{00} & \Phi_{01} \\ \Phi_{10} & \Phi_{11}\end{pmatrix} = \begin{pmatrix}n_0^{(1)}(x)n_0^{(2)}(x')\phi_{0D}'' & n_0^{(1)}(x)\phi_{0D}' \\ n_0^{(2)}(x')\phi_{0D}' & \phi_{0D}\end{pmatrix}, \tag{18}$$

where the (omitted) argument of ϕ_{0D}, ϕ_{0D}', and ϕ_{0D}'' is $n_1^{(1)}(x)+n_2^{(2)}(x')$. Inserting Eqs. (14) and (18) into the generic form (2), we obtain the excess free energy functional explicitly as

$$\mathcal{F}_{\mathrm{exc}}[\rho_1,\rho_2] = k_B T \int dx \int dx' \bigg(w_{-1}^{(12)}(x-x')[(1-n_1^{(1)}-n_1^{(2)})$$

$$\times \ln(1-n_1^{(1)}-n_1^{(2)}) + (1-n_1^{(1)}-n_1^{(2)})]$$

$$- w_0^{(12)}(x-x')(n_0^{(1)}+n_0^{(2)})\ln(1-n_1^{(1)}-n_1^{(2)})$$

$$+ w_1^{(12)}(x-x')\frac{n_0^{(1)}n_0^{(2)}}{1-n_1^{(1)}-n_2^{(2)}} \bigg), \quad (19)$$

where the spatial arguments of the weighted densities $n_\nu^{(1)}(x)$ and $n_\nu^{(2)}(x')$ for $\nu=0,1$ have been omitted to unclutter the notation, and the convolution kernels $w_\nu^{(12)}(\cdot)$ with $\nu = 1,0,-1$ are defined in (4)–(6) with $R_i = R_{12}$.

In the additive case, $R_{12}=0$, the Percus functional is recovered by noting that $w_1^{(12)}(x)=0$, $w_{-1}^{(12)}(x)=0$, and $w_0^{(12)}(x) = \delta(x)$, which yields $\mathcal{F}_{\mathrm{exc}}[\rho_1,\rho_2]=k_B T\int dx(n_0^{(1)}+n_0^{(2)})\ln(1-n_1^{(1)}-n_1^{(2)})$, with all weighted densities being evaluated at x.

III. RESULTS

As a stringent test for the quality of the density functional theory obtained, we compute partial pair correlation functions in bulk, $g_{ij}(x)$, via the Ornstein-Zernike route. The starting point is set by the bulk direct correlation functions that follow from functional differentiation of the excess free energy functional, $c_2^{(ij)}(x-x')=-(k_B T)^{-1}\delta^2\mathcal{F}_{\mathrm{exc}}/\delta\rho_i(x)\delta\rho_j(x')$, where the density distributions are set to constant (bulk) values after the derivative has been taken. This yields analytic expressions for the direct correlation function in real space; those can be (analytically) transformed to Fourier space to obtain expressions for the $\tilde{c}_2^{(ij)}(k)$. Those are given by

$$\tilde{c}_{11}(k) = -\frac{2-2\eta+4R_{12}\rho_2}{(1-\eta)^2}\tilde{w}_0^{(1)}\tilde{w}_1^{(1)}$$

$$- \frac{(1-\eta)\rho_2+(1-\eta+4R_{12}\rho_2)\rho_1}{(1-\eta)^3}\tilde{w}_1^{(1)}\tilde{w}_1^{(1)}, \quad (20)$$

$$\tilde{c}_{22}(k) = -\frac{2-2\eta+4R_{12}\rho_1}{(1-\eta)^2}\tilde{w}_0^{(2)}\tilde{w}_1^{(2)}$$

$$- \frac{(1-\eta)\rho_1+(1-\eta+4R_{12}\rho_1)\rho_2}{(1-\eta)^3}\tilde{w}_1^{(2)}\tilde{w}_1^{(2)}, \quad (21)$$

$$\tilde{c}_{12}(k) = \frac{-1}{1-\eta}(\tilde{w}_0^{(1)}\tilde{w}_0^{(12)}\tilde{w}_1^{(2)} + \tilde{w}_0^{(1)}\tilde{w}_1^{(12)}\tilde{w}_0^{(2)} + \tilde{w}_1^{(1)}\tilde{w}_0^{(12)}\tilde{w}_0^{(2)}$$

$$+ \tilde{w}_1^{(1)}\tilde{w}_{-1}^{(12)}\tilde{w}_1^{(2)}) - \frac{1}{(1-\eta)^2}[\rho_1\tilde{w}_1^{(1)}\tilde{w}_1^{(12)}\tilde{w}_0^{(2)}$$

$$+ (\rho_1+\rho_2)\tilde{w}_1^{(1)}\tilde{w}_0^{(12)}\tilde{w}_1^{(2)} + \rho_2\tilde{w}_0^{(1)}\tilde{w}_1^{(12)}\tilde{w}_1^{(2)}]$$

$$- \frac{2\rho_1\rho_2}{(1-\eta)^3}\tilde{w}_1^{(1)}\tilde{w}_1^{(12)}\tilde{w}_1^{(2)}, \quad (22)$$

where $\eta=\sigma_{11}\rho_1+\sigma_{22}\rho_2$ and the $w_\nu^{(i)}(k)$ have been stripped off the argument k for the sake of notational clarity. Partial structure factors are calculated via solving the Ornstein-Zernike equation in Fourier space [56], and (numerically) Fourier

transforming back to real space, which yields results for the partial pair correlation functions $g_{ij}(x)$.

In order to obtain benchmark results we have carried out canonical Monte Carlo (MC) simulations with 40–80 hard-core particles on a line and 10^7 MC moves per particle. Histograms of relative particle coordinates yield the $g_{ij}(x)$. In the following we fix the size ratio as $\sigma_{22}=2\sigma_{11}$ and consider various different degrees of positive nonadditivity. In Fig. 2, results for $g_{ij}(x)$ at $\Delta=0,0.1666,0.25$ and two different state points characterized by the packing fractions $\eta_i=\sigma_i\rho_i$, $i =1,2$, are shown. For the additive case the $g_{ij}(x)$ possess identical shape, but are shifted along the x axis [57–59]. Finite values of Δ break this symmetry. Upon increasing Δ and keeping the overall densities of both components fixed a considerable increase in structuring is found. The DFT results model those from simulations very well; significant differences become apparent only at considerably high densities. The DFT violates the core condition, $g_{ij}(x<\sigma_{ij})=0$, but numerically the violation is not very strong. A test-particle calculation would circumvent this problem.

For completeness, the bulk excess free energy per volume V is

$$F_{\mathrm{exc}}/(k_B T V) = -(\rho_1+\rho_2)\ln(1-\eta) + \frac{2R_{12}}{1-\eta}\rho_1\rho_2. \quad (23)$$

Note that the so-called fundamental measures are obtained from Eqs. (7)–(9) as $\xi_\nu^{(i)}=\tilde{w}_\nu^{(i)}(k\to0)$ yielding the particle length $w_1^{(i)}=2R_1$, the Euler characteristic $w_0^{(i)}=1$, and a vanishing value $\xi_{-1}^{(j)}=0$.

It is worth pointing out that this DFT predicts a (superfluous) bulk demixing phase transition for $\Delta\neq0$. Such failure is not uncommon for approximations of this type, and is, e.g., also present in the FMT for the one-dimensional Asakura-Oosawa model [53]; see also Ref. [5] for a discussion of the free volume theory that is reproduced in bulk by this FMT (and by the present one in the Asakura-Oosawa limit). For given packing fractions η_1 and η_2, the spinodal value of the nonadditivity is $\Delta_{\mathrm{spin}}=\sqrt{2}(1-\eta_1-\eta_2)/(3\sqrt{\eta_1\eta_2})$. For the state points considered in Fig. 2 this occurs at $\Delta=1.22$ (for $\eta_1=0.15$, $\eta_2=0.3$), and $\Delta=0.33$ (for $\eta_1=0.25$, $\eta_2=0.5$). Note that, although close-packed bulk states for $\Delta>0$ consist of two macroscopically distinct parts of the system where in one part all particles of species 1 agglomerate and in the other part all particles of species 2 agglomerate, such order should be immediately lost for any density below close packing (i.e., at finite values of both chemical potentials). This is expected on the grounds of general arguments that apply to one-dimensional models with short-ranged forces (see, e.g., Ref. [60] for a recent discussion).

IV. CONCLUSIONS

In conclusion, we have obtained a fundamental measure density functional for a one-dimensional binary hard-core mixture with nonadditive diameters. The construction of the functional follows very similar lines as in the corresponding case of binary nonadditive hard-sphere mixtures in three dimensions. The quantities involved, in particular the weight
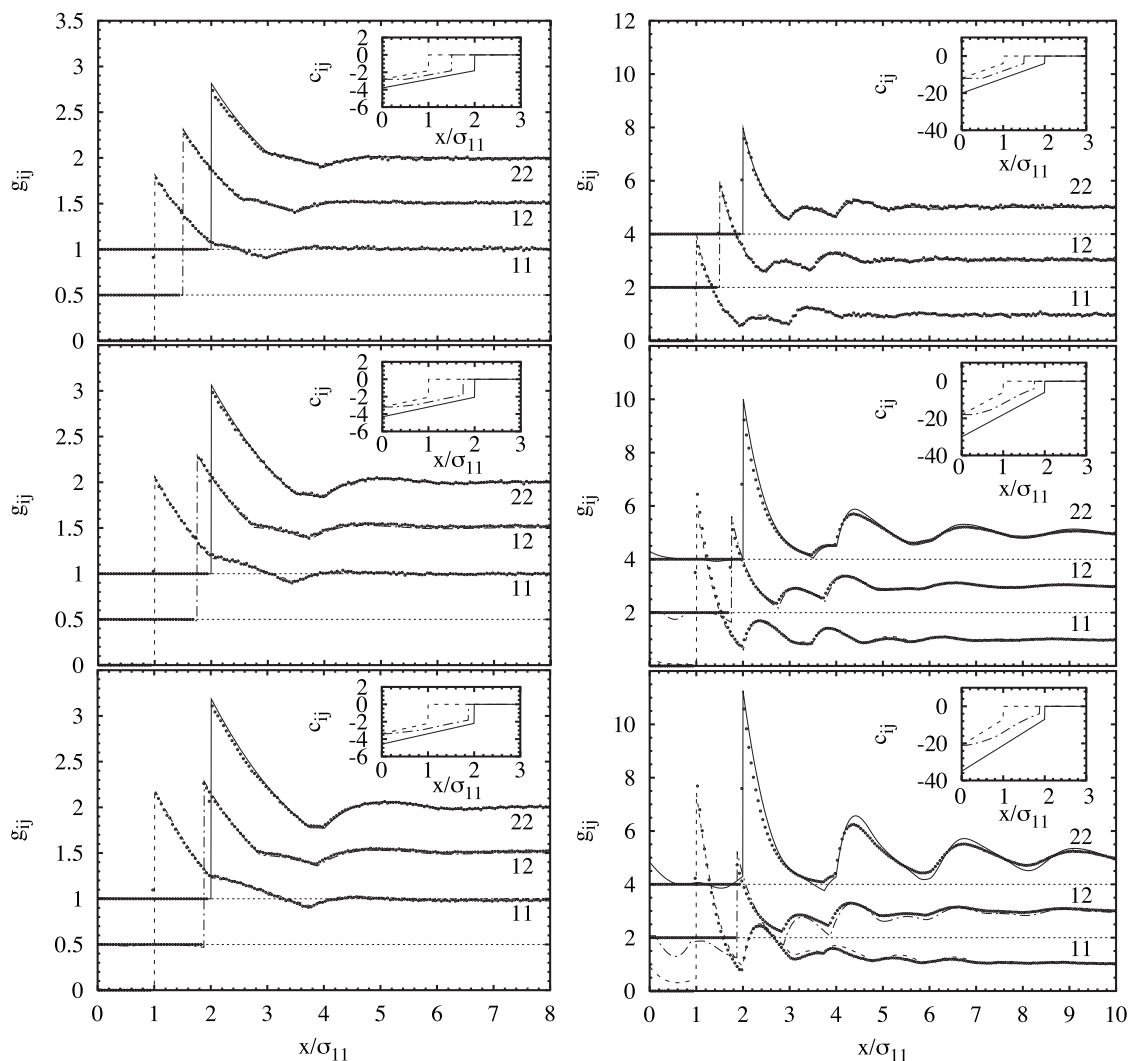
FIG. 2. Partial pair correlation functions $g_{ij}(x)$ for one-dimensional binary hard-core particles as a function of the scaled distance x/σ_{11} for species $ij = 11, 12, 22$ (as indicated) for size ratio $\sigma_{22}/\sigma_{11} = 2$ obtained from (i) DFT employing the Ornstein-Zernike route (lines) and (ii) MC simulation (symbols). The insets show the DFT result for the direct correlation functions $c_{ij}(x)$ for $ij = 11$ (dashed lines), 12 (dash-dotted lines), and 22 (solid lines). The size ratio is $\sigma_{22}/\sigma_{11} = 2$ and the nonadditivity increases, $\Delta = 0, 0.1666, 0.25$, from top to bottom (in both columns). Left column: Packing fractions are $\eta_1 = 0.15$, $\eta_2 = 0.3$; the results for g_{12} (g_{22}) are shifted upward by one (two) units for clarity. Right column: packing fractions are $\eta_1 = 0.25$, $\eta_2 = 0.5$; the results for g_{12} (g_{22}) are shifted upward by two (four) units for clarity.

functions and convolutions kernels that are used to express the Mayer bonds of the mixture via convolution, and hence the exact low-density limit of the functional, are considerably simpler than the corresponding quantities of the three-dimensional theory. As a test for the accuracy of the functional, results for the partial bulk pair correlation functions were shown to compare very favorably to results from computer simulations. Experimental realizations of the model might be obtained by confining mixtures of charged and neutral colloids in one-dimensional geometries. In such systems negative nonadditivity arises naturally. A different realization of mixtures with negative nonadditivity could be via hard-core particles that adsorb to the boundaries of an extended one-dimensional channel (see Fig. 1).

[1] Q.-H. Wei, C. Bechinger, and P. Leiderer, Science **287**, 625 (2000).

[2] H. Hansen-Goos, C. Lutz, C. Bechinger, and R. Roth, Europhys. Lett. **74**, 8 (2006).

[3] H. N. W. Lekkerkerker and B. Widom, Physica A **285**, 483 (2000).

[4] S. M. Oversteegen and H. N. W. Lekkerkerker, Physica A **310**, 181 (2002).

[5] J. M. Brader and R. Evans, Physica A **306**, 287 (2002).

[6] U. Marini Bettolo Marconi and P. Tarazona, J. Chem. Phys. **110**, 8032 (1999).

[7] F. Penna and P. Tarazona, J. Chem. Phys. **119**, 1766 (2003).

[8] R. D. Kaminsky and P. A. Monson, Langmuir **9**, 561 (1993).

[9] H. Reich and M. Schmidt, J. Stat. Phys. **116**, 1683 (2004).

[10] L. Tonks, Phys. Rev. **50**, 955 (1936).

[11] J. K. Percus, J. Stat. Phys. **15**, 505 (1976).

[12] J. K. Percus, J. Stat. Phys. **28**, 67 (1982).

[13] J. L. Lebowitz and D. Zomick, J. Chem. Phys. **54**, 3335 (1971).

[14] T. W. Melnyk and B. L. Sawford, Mol. Phys. **29**, 891 (1975).

[15] P. Ballone, G. Pastore, G. Galli, and D. Gazzillo, Mol. Phys. **59**, 275 (1986).

[16] M. Dijkstra, Phys. Rev. E **58**, 7523 (1998).

[17] A. A. Louis, R. Finken, and J. P. Hansen, Phys. Rev. E **61**, R1028 (2000).

[18] W. T. Góźdź, J. Chem. Phys. **119**, 3309 (2003).

[19] K. Jagannathan and A. Yethiraj, J. Chem. Phys. **118**, 7907 (2003).

[20] F. Saija and P. V. Giaquinta, J. Chem. Phys. **117**, 5780 (2002).

[21] F. Saija and P. V. Giaquinta, J. Phys. Chem. B **106**, 2035 (2002).

[22] K. Jagannathan, G. Reddy, and A. Yethiraj, J. Phys. Chem. B **109**, 6764 (2005).

[23] F. Lo Verso, D. Pini, and L. Reatto, J. Phys.: Condens. Matter **17**, 771 (2005).

[24] A. Santos, M. L. de Haro, and S. B. Yuste, J. Chem. Phys. **122**, 024514 (2005).

[25] A. Ayadim and S. Amokrane, Phys. Rev. E **74**, 021106 (2006).

[26] P. Sillrén and J. P. Hansen, Mol. Phys., doi: 10.1080/00268970701416605 (2007).

[27] N. Hoffmann, F. Ebert, C. N. Likos, H. Löwen, and G. Maret, Phys. Rev. Lett. **97**, 078301 (2006).

[28] A. Patrykiejew, S. Sokolowski, and O. Pizio, J. Phys. Chem. B **109**, 14227 (2005).

[29] H. Juranek, R. Redmer, and Y. Rosenfeld, J. Chem. Phys. **117**, 1768 (2002).

[30] G. Kahl, J. Chem. Phys. **93**, 5105 (1990).

[31] J. A. Anta and G. Kahl, Mol. Phys. **84**, 1273 (1995).

[32] E. Bergmann, Mol. Phys. **32**, 237 (1976).

[33] E. Bergmann, Chem. Phys. Lett. **38**, 285 (1976).

[34] E. Bergmann and R. Tenne, Chem. Phys. Lett. **38**, 285 (1976).

[35] R. M. Mazo and R. J. Bearman, J. Chem. Phys. **93**, 6694 (1990).

[36] H. M. Schaink, Z. Naturforsch., A: Phys. Sci. **48**, 899 (1993).

[37] H. M. Schaink, Physica A **210**, 113 (1994).

[38] F. Saija, G. Fiumara, and P. V. Giaquinta, J. Chem. Phys. **108**, 9098 (1998).

[39] R. Evans, Adv. Phys. **28**, 143 (1979).

[40] R. Evans, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992), Chap. 3, p. 85.

[41] Y. Rosenfeld, Phys. Rev. Lett. **63**, 980 (1989).

[42] R. Roth and R. Evans, Europhys. Lett. **53**, 271 (2001).

[43] R. Roth, R. Evans, and A. A. Louis, Phys. Rev. E **64**, 051202 (2001).

[44] P. Tarazona, Phys. Rev. Lett. **84**, 694 (2000).

[45] J. A. Cuesta, Y. Martinez-Raton, and P. Tarazona, J. Phys.: Condens. Matter **14**, 11965 (2002).

[46] L. Lafuente and J. A. Cuesta, Phys. Rev. Lett. **89**, 145701 (2002).

[47] L. Lafuente and J. A. Cuesta, Phys. Rev. Lett. **93**, 130603 (2004).

[48] J. A. Capitán and J. A. Cuesta, Phys. Rev. E **76**, 011403 (2007).

[49] A. R. Herring and J. R. Henderson, Phys. Rev. Lett. **97**, 148302 (2006).

[50] A. R. Herring and J. R. Henderson, Phys. Rev. E **75**, 011402 (2007).

[51] M. Schmidt, Phys. Rev. E **63**, 010101(R) (2000).

[52] M. Schmidt, H. Löwen, J. M. Brader, and R. Evans, Phys. Rev. Lett. **85**, 1934 (2000).

[53] M. Schmidt, H. Löwen, J. M. Brader, and R. Evans, J. Phys.: Condens. Matter **14**, 9353 (2002).

[54] M. Schmidt, J. Phys.: Condens. Matter **16**, L351 (2004).

[55] Y. Rosenfeld, M. Schmidt, H. Löwen, and P. Tarazona, Phys. Rev. E **55**, 4245 (1997).

[56] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 3rd ed. (Academic Press, London, 2006).

[57] R. Roth and R. Evans (private communication).

[58] C. Grodon, M. Dijkstra, R. Evans, and R. Roth, Mol. Phys. **103**, 3009 (2005).

[59] C. Grodon, M. Dijkstra, R. Evans, and R. Roth, J. Chem. Phys. **121**, 7869 (2004).

[60] J. A. Cuesta and A. Sánchez, J. Stat. Phys. **115**, 869 (2004).