

# A fundamental-measure density functional for mixtures of parallel hard cylinders



Yuri Martínez-Ratón, José A. Capitán and José A. Cuesta

*Grupo Interdisciplinar de Sistemas Complejos (GISC), Departamento de Matemáticas,  
Escuela Politécnica Superior, Universidad Carlos III de Madrid,  
Avenida de la Universidad 30, E-28911 Leganés, Madrid, Spain.*

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## Abstract

We obtain a fundamental measure density functional for mixtures of parallel hard cylinders. To this purpose we first generalize to multicomponent mixtures the fundamental measure functional proposed by Tarazona and Rosenfeld for a one-component hard disk fluid, through a method alternative to the cavity formalism of these authors. We show the equivalence of both methods when applied to two-dimensional fluids. The density functional so obtained reduces to the exact density functional for one-dimensional mixtures of hard rods when applied to one-dimensional profiles. In a second step we apply an idea put forward some time ago by two of us, based again on a dimensional reduction of the system, and derive a density functional for mixtures of parallel hard cylinders. We explore some features of this functional by determining the fluid-fluid demixing spinodals for a binary mixture of cylinders with the same volume, and by calculating the direct correlation functions.

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## I. INTRODUCTION

The fundamental measure density functional originally derived by Rosenfeld for a fluid of hard spheres (HS) [1, 2, 3, 4, 5] can be considered as the most sophisticated density functional (DF) that has been successfully applied to the study of the highly confined HS fluid [6, 7] and to the HS freezing [8]. The theoretical formalism initially developed by Rosenfeld to obtain the HS fundamental measure functional (FMF) [1, 2, 3] was later complemented with the concept of dimensional crossover to zero dimension to obtain a DF that adequately describes the HS freezing [9, 10]. By dimensional crossover it is understood that when reducing the dimension of a  $D$ -dimensional system to that of a  $D'$ -dimensional one (e.g. by confining), the  $D$ -dimensional DF crosses over to the  $D'$ -dimensional one. This zero-dimensional (0D) crossover was later employed by Tarazona and Rosenfeld to introduce a new cavity formalism which showed how this unique property, together with the exact expressions for the zero- and one-dimensional (1D) HS functionals, are the only requirements needed to derive their final versions of the FMFs for the hard disk (HD) and the HS fluids [11]. These versions which, as it is standard in all FMFs, assume that the density profile dependence enters in the functional only through a finite set of weighted densities, leave little freedom for improvements without destroying the important dimensional crossover property. Recent efforts have been made to derive a HS functional with an imposed equation of state (EOS) as its uniform limit [12, 13]. This imposed EOS (for instance the Carnahan-Starling EOS) describes the fluid better than the scaled particle result [14] (the uniform limit of all the FMF derived from first principles) in the description of the HS liquid. However, all these modifications can be done at the expense of losing some, or all, of the dimensional crossovers—a crucial property if one wants to study highly confined fluids.

Thus, we can say that the fundamental measure theory (FMT) is close to its edge in the sense that it is questionable that any improvement can be achieved without rendering it intractable [15]. For instance, it has been argued that the inclusion of an infinite set of weighted densities can remove some defects of the HS FMF, because this is what happens—with the addition of a few more weighted densities—for the FMF for parallel hard hexagons [16] (which is constructed from the corresponding functional for parallel hard cubes [17, 18, 19]). After all, a circle is a polygon with infinitely many sides. Similar conclusions are reached when FMFs for lattice models are constructed [20, 21, 22]. In fact, the concept of cavity can be generalized in those models so as to account for higher orders of accuracy in the correlation functions [23, 24].

The first extension of the FMF to general anisotropic particles was carried out by Rosenfeld [25]. However this extension only works for isotropic fluids (with particle axes randomly oriented), because the Mayer function is not recovered from the low-density expansion of the proposed FMF when particles have a preferred alignment [26]. In recent works the definition of the one-particle weights necessary to calculate the weighted densities has been extended in such a way as to include an effective dependence on the orientations of both interacting particles [27, 28, 29, 30]. This way the Mayer function can be exactly decomposed as a sum of convolutions between those extended weights. Different FMFs for freely rotating particles: for a mixture of HS and hard needles [27, 28], and for a mixture of hard needles and infinitely thin hard plates [29, 30] have been proposed using these extended weights, and the resulting FMFs have some of the desired dimensional crossovers. However, the requirement of taking the breadth of the particles vanishing small seems to be indispensable to construct such functionals.

The parallel particle alignment (or the restricted orientation approximation) is a fundamental restriction that has to be taken if we want to derive a FMF from first principles, without any approximation about the particle characteristic lengths. The FMF for parallel hard cubes [17] and its later extension to hard parallelepipeds with orientation restricted to three perpendicular axes (Zwanzig model) [18, 19] were the first examples of FMFs for anisotropic particles derived from first principles using the original Rosenfeld's formalism and adding the dimensional cross-over constraint. The FMF for the Zwanzig model was applied to the calculation of phase diagrams of the one-component fluids made of hard rods and hard plates [31], and of phase diagrams of polydisperse rod-plate mixture [32, 33]. Also, it was applied to the study of interfacial phenomena in liquid crystals in three [34] and two [35] dimensions. Reference [36] summarizes most of the works done on the study of wall-liquid crystal fluid interfaces using the Zwanzig model.

In this article we want to derive a FMF for another particle geometry with the parallel alignment restriction. In this case the fluid is composed of a mixture of parallel hard cylinders (PHCL) with different radii  $R_i$  and lengths  $L_i$ . To achieve this we will first of all extend the FMF obtained by Tarazona and Rosenfeld [11] for a one-component HD fluid to a multicomponent mixture, using an alternative approach to the cavity formalism used by these authors. We prove that the resulting functional conforms all the dimensional crossovers and thus we show that both methods are completely equivalent. In a second step we derive a functional for a mixture of parallel hard cylinders starting from the already obtained HD functional by applying a differential operator, as explained in Ref. [18]. This procedure guarantees the dimensional crossover from 3D to 2D [18].

The parallel alignment restriction is, of course, a hard constraint that prevents the use of the derived functional in the study of those phenomena governed by changes in the orientational ordering of the constituent particles, as it often occurs in liquid-crystals. However, as the spatial correlations are accurately treated, those phases with a high degree of orientation, such as the smectic, columnar or crystalline phases at high pressures, should be well described by the present functional. Also, the study of non-uniform polydisperse liquid-crystalline phases, which are frequently present in experiments on colloidal mixtures [37, 38], is such a difficult task that the parallel alignment simplification seems to be the only way to take some steps forward in that direction.

The article is organized as follows. In Sec. II we derive the FMF for mixtures of HD. In Sec. III we use this result to construct a FMF for mixtures of PHCL. Section IV discusses the uniform mixture of PHCL and in Sec. V we derive the direct correlation functions for this mixture. After a section summarizing the results of the paper, we include two appendices. In Appendix A we prove that the FMF for a mixture of HD has an exact 2D→1D crossover. This is, of course, inherited by the FMF for PHCL. In Appendix B the expressions for the geometric terms defining the direct correlation functions are explicitly displayed.

## II. FUNDAMENTAL MEASURE DENSITY FUNCTIONAL FOR A MIXTURE OF HARD DISKS

In this section we will derive a density functional for mixtures of HD based upon Tarazona and Rosenfeld's proposal for a one-component HD fluid obtained by using the 0D cavity formalism of FMT [11]. We will maintain the functional structure of the excess part of the free energy density,  $\Phi^{(2D)}(\mathbf{r})$ , and extend it to a multicomponent mixture by calculating the kernel  $K_{ij}(r)$  ( $i$  and  $j$  label disk species) which enters the definition of the two-particle weighted density  $N(\mathbf{r})$  (see below). This functional structure is

$$\Phi^{(2D)}(\mathbf{r}) = -n_0(\mathbf{r}) \ln [1 - n_2(\mathbf{r})] + \frac{N(\mathbf{r})}{1 - n_2(\mathbf{r})}, \quad (1)$$

and its extension to mixtures amounts to writing

$$N(\mathbf{r}) = \sum_{i,j} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_i(\mathbf{r}_1) \rho_j(\mathbf{r}_2) \Omega_{ij}(\mathbf{r} - \mathbf{r}_1, \mathbf{r} - \mathbf{r}_2), \quad (2)$$

$$\Omega_{ij}(\mathbf{r}_1, \mathbf{r}_2) = \omega_i^{(0)}(\mathbf{r}_1) \omega_j^{(0)}(\mathbf{r}_2) K_{ij}(r_{12}). \quad (3)$$

The one-particle weighted densities  $n_0(\mathbf{r})$  and  $n_2(\mathbf{r})$  [ $n_2(\mathbf{r})$  being the local packing fraction] are those of Rosenfeld's for a FMF for HD mixtures [1, 2, 3], i.e.

$$n_0(\mathbf{r}) = \sum_i \int d\mathbf{r}' \rho_i(\mathbf{r}') \omega_i^{(0)}(\mathbf{r} - \mathbf{r}'), \quad (4)$$

$$n_2(\mathbf{r}) = \sum_i \int d\mathbf{r}' \rho_i(\mathbf{r}') \omega_i^{(2)}(\mathbf{r} - \mathbf{r}'), \quad (5)$$

with  $\rho_i(\mathbf{r})$  the density profile of species  $i$  and  $\omega_i^{(\alpha)}(\mathbf{r})$  the one-particle weights defined as

$$\omega_i^{(0)}(\mathbf{r}) = \frac{\delta(R_i - r)}{2\pi R_i}, \quad \omega_i^{(2)}(\mathbf{r}) = \Theta(R_i - r), \quad (6)$$

$R_i$  ( $i = 1, 2, \dots, c$ , with  $c$  the number of components of the mixture) being the particle radii, and  $\delta(x)$  and  $\Theta(x)$  the Dirac delta and Heaviside step functions respectively. Equation (2) is the natural extension to multicomponent mixtures of the two-particle weighted density  $N(\mathbf{r})$  initially introduced for a one-component fluid in Ref. [11]. The authors of this work found the expression for the kernel  $K(r_{12})$  through the requirement that inserting 0D density profiles in the excess part of free energy

$$\beta \mathcal{F}_{\text{ex}}^{(2D)}[\rho(\mathbf{r})] = \int d\mathbf{r} \Phi^{(2D)}(\mathbf{r}) \quad (7)$$

should recover the interaction part of the free energy of a 0D cavity  $\Phi^{(0D)} = \mathcal{N} + (1 - \mathcal{N}) \ln(1 - \mathcal{N})$ , with  $\mathcal{N} < 1$  the mean occupation of the cavity. As usual, the 0D cavity is understood as a cavity of arbitrary geometry which can accommodate one particle at the most.

To determine  $K_{ij}(r)$  we will follow another procedure: we will impose that the low density limit of the second functional derivative of (7) with respect to the density profiles  $\rho_i(\mathbf{r}_1)$  and  $\rho_j(\mathbf{r}_2)$  coincides with the overlap function of two HD of radii  $R_i$  and  $R_j$ , which turns out to be the exact low density limit of minus the direct correlation function, i.e.

$$\Theta(R_{ij}^{(+)} - r_{12}) = \int d\mathbf{r}' \langle \omega_i^{(0)}(\mathbf{r}') \omega_j^{(2)}(\mathbf{r}_{12} - \mathbf{r}') \rangle + 2K_{ij}(r_{12}) \int d\mathbf{r}' \omega_i^{(0)}(\mathbf{r}') \omega_j^{(0)}(\mathbf{r}_{12} - \mathbf{r}'), \quad (8)$$

where  $\langle f_{ij} \rangle = f_{ij} + f_{ji}$  has been introduced to denote symmetrization of  $f_{ij}$  with respect to its indices, and  $R_{ij}^{(+)} = R_i + R_j$ . The calculation of the integrals involved in Eq. (8) leads to

$$K_{ij}(r_{12}) = \pi r_{12} \langle \sin^{-1} t_{ij}(r_{12}) \rangle R_i \sqrt{1 - t_{ij}(r_{12})^2} \Theta(r_{12} - R_{ij}^{(-)}) \Theta(R_{ij}^{(+)} - r_{12}), \quad (9)$$

$$t_{ij}(r_{12}) = \frac{r_{12}^2 + R_i^2 - R_j^2}{2r_{12}R_i}, \quad (10)$$

where  $R_{ij}^{(-)} = |R_i - R_j|$ . The kernel (9) is symmetric with respect to the exchange of indices  $i$  and  $j$  due to the equality  $h_{ij} \equiv R_i \sqrt{1 - t_{ij}(r_{12})^2} = R_j \sqrt{1 - t_{ji}(r_{12})^2}$ , which is easily visualized

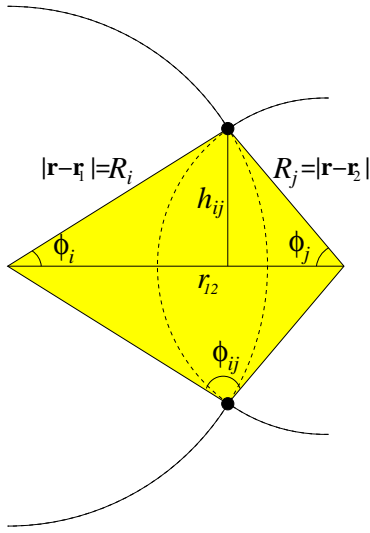


FIG. 1: Sketch of the triangular geometry defined by the lengths  $R_i$ ,  $R_j$  and  $r_{12}$ .

in Fig. 1: this figure shows a sketch of a typical configuration of two HD with different radii for which the  $K_{ij}(r_{12})$  is different from zero; in it the height  $h_{ij}$  of the triangle formed by the lengths  $r_{12}$ ,  $R_i$  and  $R_j$  can be calculated either as  $R_i \sin \phi_i$  or as  $R_j \sin \phi_j$ , thus proving the symmetry  $K_{ij}(r_{12}) = K_{ji}(r_{12})$ . Also, from Eq. (9) and the triangular geometry the kernel can be rewritten as  $K_{ij}(r_{12}) = \pi A_{ij}(r_{12}) \phi_{ij}(r_{12})$ , with  $A_{ij} = r_{12} h_{ij}$  the sum of the areas of both triangles (the shaded region of Fig. 1), and  $\phi_{ij} = \langle \sin^{-1} t_{ij} \rangle$ , the angle formed by the sides  $R_i$  and  $R_j$ .

For one component,  $K_{ij}(r)$  recovers the expression

$$K(r) = 4\pi R^2 \left( \frac{r}{2R} \right) \sin^{-1} \left( \frac{r}{2R} \right) \sqrt{1 - \left( \frac{r}{2R} \right)^2} \quad (11)$$

reported in Ref. [11]. It is interesting to note that, because of the presence of weights  $\omega_i^{(0)}(\mathbf{r})$  (proportional to Dirac delta functions) in the definition of  $N(\mathbf{r})$ , its expression can be greatly simplified. After insertion of  $K_{ij}(r)$  into Eq. (2) and integration over the radial variables  $r_1$  and  $r_2$  we find

$$N(\mathbf{r}) = \frac{1}{4\pi} \sum_{i,j} R_i R_j \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \rho_i(\mathbf{r} + R_i \mathbf{u}_1) \rho_j(\mathbf{r} + R_j \mathbf{u}_2) T(\phi_{12}), \quad (12)$$

where  $\phi_{12} = \phi_1 - \phi_2$ ,  $\mathbf{u}_i = (\cos \phi_i, \sin \phi_i)$ , and the function  $T(\phi)$  is defined as

$$T(\phi) = |\phi - 2\pi n| |\sin \phi|, \quad (13)$$

with  $n$  the integral part of the fraction  $(\phi + \pi)/(2\pi)$ . The first factor on the right hand side of (13) is the  $2\pi$ -periodic function shown in Fig. 2 with a dashed line. The function  $T(\phi)$  is plotted

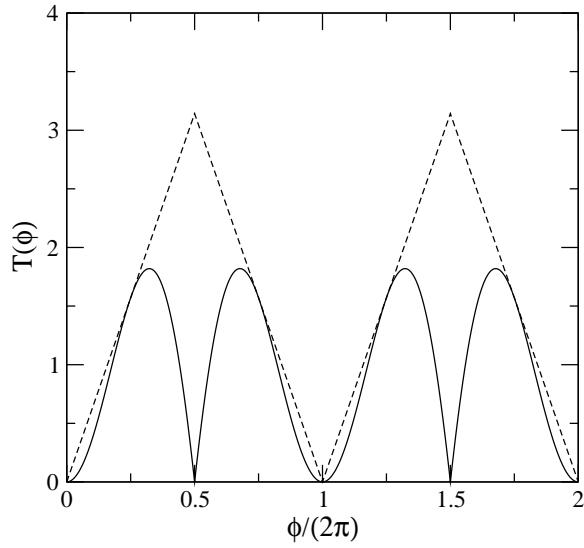


FIG. 2: The function  $T(\phi)$  in the interval  $[0, 4\pi]$  (solid line). Also is shown with dashed line the triangular wave function.

in the same figure. From the new form of  $N(\mathbf{r})$  given by Eq. (12) we can conclude that, despite the presence of a two-particle weight in its definition, the numerical cost required to evaluate it is the same as that required to calculate the local packing fraction  $n_2(\mathbf{r})$ , because both quantities are defined through a double integral.

Taking into account the result  $\int d\phi_1 \int d\phi_2 T(\phi_{12}) = 4\pi^2$  we find that the uniform limit of  $\Phi^{(2D)}$  [cf. Eq. (1)] coincides with the scaled particle theory (SPT) result for a mixture of HD [1, 2, 3, 14]

$$\Phi^{(2D)} = -\xi_0 \ln(1 - \xi_2) + \frac{1}{4\pi} \frac{\xi_1^2}{1 - \xi_2}, \quad (14)$$

where  $\xi_0 = \sum_i \rho_i$ ,  $\xi_1 = \sum_i \rho_i (2\pi R_i)$ , and  $\xi_2 = \sum_i \rho_i (\pi R_i^2)$ .

Because the derivation of  $K_{ij}(r)$  has not followed the requirement of exact reduction to 0D cavities, as in Ref. [11], the question arises as to whether this nice property holds for this new functional. In Appendix A we prove a stronger property: the functional (1) fulfills an exact 2D $\rightarrow$ 1D crossover; in other words, by inserting the profile  $\rho_i(\mathbf{r}) = \rho_i(x)\delta(y)$  into (1) and (7) we recover the exact functional for 1D hard rod mixtures [39], cf. Eqs. (A16) and (A18). With this we have also proven that the present method and the cavity formalism of Ref. [11] are two equivalent methods to obtain a FMF for mixtures of HD.

### III. DENSITY FUNCTIONAL FOR A MIXTURE OF PARALLEL HARD CYLINDERS

In this Section we will construct a FMF for a mixture of PHCL starting from two different density functionals for HD mixtures: the first one is calculated through Eq. (1), while the second one is Rosenfeld's proposal [3]

$$\Phi_R^{(2D)} = -n_0 \ln(1 - n_2) + \frac{1}{4\pi} \frac{v^2 - \mathbf{v}^2}{1 - n_2}, \quad (15)$$

where  $v = \sum_i \rho_i * w_i(\mathbf{r})$  and  $\mathbf{v} = \sum_i \rho_i * \mathbf{w}_i(\mathbf{r})$ , with the new weights

$$w_i(\mathbf{r}) = 2\pi R_i \omega_i^{(0)}(\mathbf{r}), \quad \mathbf{w}_i(\mathbf{r}) = w_i \frac{\mathbf{r}}{r}. \quad (16)$$

Note that the weighted density  $v(\mathbf{r})$  is not the absolute value of  $\mathbf{v}(\mathbf{r})$ . Rosenfeld obtained this expression by approximating the Mayer function of two HD by the sum of convolutions between single-particle weights  $f_{ij}(r) = \langle \omega_i^{(0)} * \omega_j^{(2)} \rangle(r) + (2\pi)^{-1} [w_i * w_j(r) - \mathbf{w}_i * \mathbf{w}_j(r)]$  and requiring also that the scaled particle result (14) was recovered in the uniform limit [3]. The expression (15), however, does not conform with any dimensional crossover to lower dimensions.

The FMF for PHCL is obtained by resorting to the dimensional crossover 3D $\rightarrow$ 2D which any functional  $\beta \mathcal{F}_{\text{ex}}^{(3D)}[\{\rho_i\}]$  fulfill. In Ref. [18] it was argued that having a FMF for a mixture of two-dimensional particles  $\mathcal{F}_{\text{ex}}^{(2D)}[\{\rho_i\}]$  one can construct an explicit expression for a FMF for a mixture of parallel anisotropic three-dimensional (3D) bodies whose constant section perpendicular to their main axes is that of the 2D particles. In the same reference it is shown that the resulting functional fulfills by construction the 3D $\rightarrow$ 2D dimensional crossover when the original fluid is confined such that the centers of mass of the particles are confined on a plane perpendicular to their axes. We will apply this method to obtain a FMF for a mixture of parallel cylinders as follows. First of all we need to redefine the functional in such a way as to include the  $z$ -coordinate dependence of the density profiles and correspondingly of the weighted densities. The new weights are obtained multiplying the old ones by the factors  $\Theta(L_i/2 - |z|)$ , i.e.

$$\omega_i^{(1)}(\mathbf{r}) = \omega_i^{(0)}(\mathbf{r}^\perp) \Theta(L_i/2 - |z|), \quad \omega_i^{(3)}(\mathbf{r}) = \omega_i^{(2)}(\mathbf{r}^\perp) \Theta(L_i/2 - |z|), \quad (17)$$

$$\Omega_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \Omega_{ij}(\mathbf{r}_1^\perp, \mathbf{r}_2^\perp) \Theta(L_i/2 - |z_1|) \Theta(L_j/2 - |z_2|). \quad (18)$$

The resulting free energy density, which we denote  $\tilde{\Phi}^{(2D)}$ , is the same as that given by Eq. (1), but with the substitutions  $n_0(\mathbf{r}) \rightarrow n_1(\mathbf{r})$ ,  $n_2(\mathbf{r}) \rightarrow n_3(\mathbf{r})$  and  $N(\mathbf{r}) \rightarrow N_2(\mathbf{r})$ . The new weighted densities are obtained through the same expressions given for the 2D case but using the new



weights (17), (18). Note that the vector position  $\mathbf{r}$  is now defined as  $\mathbf{r} = (\mathbf{r}^\perp, z)$ . The dimensional crossover 3D $\rightarrow$ 2D holds if the 3D excess free-energy density is obtained by the following formula [18, 19]

$$\Phi^{(3D)}(\mathbf{r}) = \sum_i \frac{\partial}{\partial L_i} \tilde{\Phi}^{(2D)}(\mathbf{r}). \quad (19)$$

In our case this leads to

$$\Phi^{(3D)} = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 + N_1}{1 - n_3} + \frac{n_2 N_2}{(1 - n_3)^2}, \quad (20)$$

where the one-particle weighted densities  $n_\alpha(\mathbf{r})$  are calculated as usual as  $n_\alpha(\mathbf{r}) = \sum_i \rho_i * \omega_i^{(\alpha)}(\mathbf{r})$  [\* stands for the convolution  $f * g(\mathbf{r}) \equiv \int d\mathbf{r}' f(\mathbf{r}') g(\mathbf{r} - \mathbf{r}')$ ]. The one-particle weights are defined jointly by Eq. (17) and

$$\omega_i^{(0)}(\mathbf{r}) = \frac{1}{2} \omega_i^{(0)}(\mathbf{r}_\perp) \delta(L_i/2 - |z|), \quad \omega_i^{(2)}(\mathbf{r}) = \frac{1}{2} \omega_i^{(2)}(\mathbf{r}_\perp) \delta(L_i/2 - |z|). \quad (21)$$

The two-particle weighted densities are calculated as

$$N_\alpha(\mathbf{r}) = \sum_{ij} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_i(\mathbf{r}_1) \rho_j(\mathbf{r}_2) \Omega_{ij}^{(\alpha)}(\mathbf{r} - \mathbf{r}_1, \mathbf{r} - \mathbf{r}_2), \quad (22)$$

with  $\Omega_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$  given by Eq. (18) while  $\Omega_{ij}^{(1)}(\mathbf{r}_1, \mathbf{r}_2)$  is

$$\Omega_{ij}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) = \Omega_{ij}(\mathbf{r}_1^\perp, \mathbf{r}_2^\perp) \left\langle \frac{1}{2} \Theta(L_i/2 - |z_1|) \delta(L_j/2 - |z_2|) \right\rangle. \quad (23)$$

As mentioned above, the free-energy functional  $\mathcal{F}^{(3D)}$  has a correct dimensional reduction to  $\mathcal{F}^{(2D)}$ , the free energy for a HD mixture, when the density profiles are taken as  $\rho_i(\mathbf{r}) = \rho_i^{(2D)}(\mathbf{r}^\perp) \delta(z)$  [ $\mathbf{r}^\perp = (x, y)$ ], i.e. projecting the cylinders on the plane perpendicular to their axes. It is easy to show that the dimensional cross-over 3D $\rightarrow$ 2D, where the projection is now in a plane parallel to the cylinder axes, also holds. To show this we take the density profiles as  $\rho_i(\mathbf{r}) = \rho_i(\mathbf{r}^\parallel) \delta(x)$  [ $\mathbf{r}^\parallel = (y, z)$ ], with  $\rho_i(\mathbf{r}^\parallel) = \rho_i^{(2D)}(y, z)$ . Inserting these  $\rho_i(\mathbf{r})$  into  $\tilde{\Phi}^{(2D)}(\mathbf{r})$  and using the already shown dimensional cross-over 2D $\rightarrow$ 1D of a FMF for a mixture of HD (see Appendix A), we obtain, from Eq. (19),

$$\Phi^{(3D)}(\mathbf{r}) \rightarrow \Phi_{\text{PHR}}^{(2D)}(\mathbf{r}) = -n_0(\mathbf{r}) \ln[1 - n_2(\mathbf{r})] + \frac{n_{1x}(\mathbf{r}) n_{1y}(\mathbf{r})}{1 - n_2(\mathbf{r})}, \quad (24)$$

the free-energy density of a mixture of parallel hard rectangles (the section of the cylinders along their axes) [18, 19]. The weighted densities for such particles are now defined as  $n_0(\mathbf{r}) =$

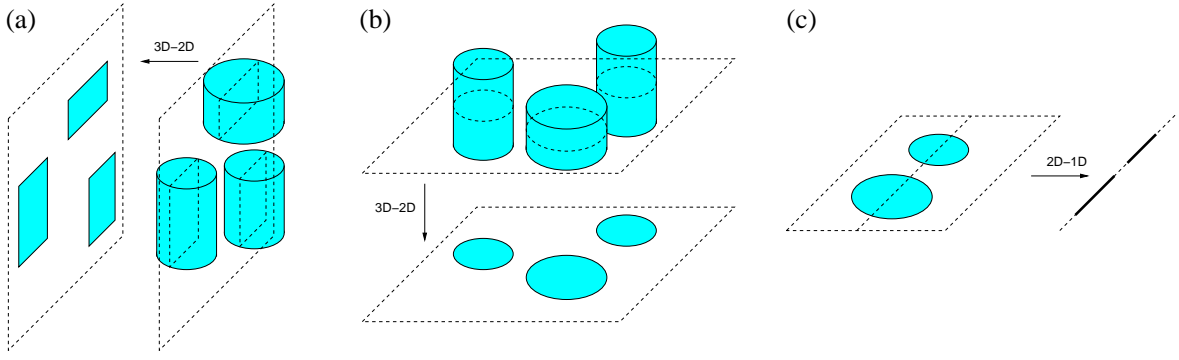


FIG. 3: Sketch of all dimensional crossovers fulfilled by the fundamental-measure functional for a mixture of parallel hard cylinders: (a) from cylinders (3D) to rectangles (2D), (b) from cylinders (3D) to disks (2D) and (c) from disks (2D) to rods (1D).

$\sum_i \rho_i^{(2D)} * [\delta_{\sigma_i}(y)\delta_{L_i}(z)]$ ,  $n_2(\mathbf{r}) = \sum_i \rho_i^{(2D)} * [\theta_{\sigma_i}(y)\theta_{L_i}(z)]$ ,  $n_{1x}(\mathbf{r}) = \sum_i \rho_i^{(2D)} * [\delta_{\sigma_i}(y)\theta_{L_i}(z)]$ , and  $n_{1y}(\mathbf{r}) = \sum_i \rho_i^{(2D)} * [\theta_{\sigma_i}(y)\theta_{L_i}(z)]$ , where the shorthand notations  $\delta_{u_i}(s) = \frac{1}{2}\delta(u_i/2 - |s|)$  and  $\theta_{u_i}(s) = \Theta(u_i/2 - |s|)$ , with  $s = y, z$  and  $\sigma_i = 2R_i$ , have been used.

Thus the FMF for PHCL that we have just obtained conforms with all dimensional crossovers to lower dimensions, which we have sketched in Fig. 3. Nevertheless, this functional is not perfect because it shares with that of HD the defect caused by the existence of “lost cases” [11, 15]. There are three-point 0D cavities such that particles sited at those points have pairwise overlap but no triple overlap. For those cavities the FMF of a HD mixture does not reduce adequately to  $\Phi^{(0D)}$  (the lost cases for the one-component fluid were already pointed out in Ref. [11]). As a consequence of that the FMF for a mixture of PHCL suffers from the same illness.

The excess free-energy density of PHCL obtained from its HD counterpart using (19) and Rosenfeld’ approximation  $\Phi_R^{(2D)}$  [cf. Eq. (15)] results in

$$\Phi_R^{(3D)} = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 + v_1 v_2 - \mathbf{v}_1 \mathbf{v}_2}{1 - n_3} + \frac{1}{4\pi} \frac{n_2 (v_2^2 - \mathbf{v}_2^2)}{(1 - n_3)^2}, \quad (25)$$

where  $v_\alpha(\mathbf{r}) = \sum_i \rho_i * w_i^{(\alpha)}(\mathbf{r})$ ,  $\mathbf{v}_\alpha(\mathbf{r}) = \sum_i \rho_i * \mathbf{w}_i^{(\alpha)}(\mathbf{r})$ , and

$$w_i^{(1)}(\mathbf{r}) = R_i \omega_i^{(0)}(\mathbf{r}), \quad \mathbf{w}_i^{(1)}(\mathbf{r}) = w_i^{(1)}(\mathbf{r}) \frac{\mathbf{r}^\perp}{R_i}, \quad (26)$$

$$w_i^{(2)}(\mathbf{r}) = 2\pi R_i \omega_i^{(1)}(\mathbf{r}), \quad \mathbf{w}_i^{(2)}(\mathbf{r}) = w_i^{(2)}(\mathbf{r}) \frac{\mathbf{r}^\perp}{R_i}, \quad (27)$$

where the  $\omega_i^{(\alpha)}(\mathbf{r})$  are those defined by Eqs. (17) and (21).

#### IV. UNIFORM MIXTURES

In this section we give the explicit expression for the uniform limit of the FMF for a mixture of PHCL, which coincides with the SPT result.

It is easy to show that  $\int d\mathbf{r}_1 \int d\mathbf{r}_2 \Omega_{ij}(\mathbf{r}_1, \mathbf{r}_2) = \pi R_i R_j$ . Taking into account this result, the uniform limit  $\rho_i(\mathbf{r}) = \rho_i$  of both free-energy densities,  $\Phi^{(3D)}$  from Eq. (20) and  $\Phi_R^{(3D)}$  from Eq. (25), yield the result

$$\Phi_u^{(3D)} = -\xi_0 \ln(1 - \xi_3) + \frac{\boldsymbol{\xi}_1 \cdot \boldsymbol{\xi}_2}{1 - \xi_3} + \frac{1}{8\pi} \frac{\xi_2^\parallel (\xi_2^\perp)^2}{(1 - \xi_3)^2}, \quad (28)$$

where we have defined the vectors  $\boldsymbol{\xi}_i \equiv (\xi_i^\perp, \xi_i^\parallel)$  ( $i = 1, 2$ ), with components

$$\xi_1^\perp = \sum_i \rho_i R_i, \quad \xi_1^\parallel = \sum_i \rho_i \frac{L_i}{2}, \quad (29)$$

$$\xi_2^\perp = \sum_i \rho_i 2\pi R_i L_i, \quad \xi_2^\parallel = \sum_i \rho_i 2\pi R_i^2, \quad (30)$$

while  $\xi_0 = \sum_i \rho_i$  and  $\xi_3 = \sum_i \rho_i \pi R_i^2 L_i$  are the total density and total packing fraction of the mixture, respectively. From Eqs. (28)–(30) we can see that the excess part of free-energy density is a function of certain weighted densities  $\xi_i^{(\alpha)}$ , which can be calculated as the sum of products between the particle densities  $\rho_i$  and their fundamental measures:  $\{R_i, L_i/2\}$ , the principal radii in the directions perpendicular and parallel to the cylinder axes,  $\{2\pi R_i L_i, 2\pi R_i^2\}$ , the areas of the surfaces oriented along the perpendicular and parallel directions, and  $\pi R_i^2 L_i$  the particle volume.

Within the SPT formalism, the excess part of the free-energy density of any mixture of convex particles should fulfill the following differential equation [3, 19]

$$-\Phi + \sum_i \xi_i \frac{\partial \Phi}{\partial \xi_i} + \xi_0 = \frac{\partial \Phi}{\partial \xi_3}. \quad (31)$$

This equation holds for (28), thus showing that of our functional gives the SPT result. Finally, the equation of state within SPT can be calculated as  $\beta P = \frac{\partial \Phi_u}{\partial \xi_3}$ , resulting in

$$\beta P = \frac{\xi_0}{1 - \xi_3} + \frac{\boldsymbol{\xi}_1 \cdot \boldsymbol{\xi}_2}{(1 - \xi_3)^2} + \frac{1}{4\pi} \frac{\xi_2^\parallel (\xi_2^\perp)^2}{(1 - \xi_3)^3}. \quad (32)$$

This equation of state can be used to study the possible demixing scenarios that a mixture of PHCL has.

In order to show the existence of demixing in a binary mixture of PHCL we first specialize the mixture to the case in which both particle volumes are unity, i.e.  $v_1 = v_2 = 1$ . This assumption

allows us to calculate the particle lengths and diameters as  $L_i = c\kappa_i^{2/3}$  and  $\sigma_i = c\kappa_i^{-1/3}$ , where  $\kappa_i = L_i/\sigma_i$  are the cylinders aspect ratios and  $c = (4/\pi)^{1/3}$ . It is easy to show that the expression (28) for this particular mixture gives us the following expression for the free-energy per particle  $\varphi = (\Phi_{\text{id}} + \Phi_u^{(3D)})/\rho$  (with  $\Phi_{\text{id}} = \sum_i \rho_i [\ln(v_i \rho_i) - 1]$ )

$$\varphi = \ln y - 1 + x \ln x + (1 - x) \ln(1 - x) + yS(x; r) + y^2T(x; r), \quad (33)$$

while the expression for the fluid pressure is

$$\beta P v_i = y + y^2S(x; r) + 2y^3T(x; r), \quad (34)$$

where  $y \equiv \eta/(1 - \eta)$ ,  $x \equiv x_2$  is the molar fraction of species 2 and  $r \equiv \kappa_2/\kappa_1$  is the ratio between the particles aspect ratios. Note that for this particular mixture we have  $\eta = \rho$ . Also,

$$S(x; r) = 3 + (r^{1/3} - 1)^2 (1 + 4r^{-1/3} + r^{-2/3}) x(1 - x), \quad (35)$$

$$T(x; r) = 1 + (r^{1/3} - 1)^2 [r^{-1/3} (2 + r^{-1/3}) + (1 - r^{-2/3}) x] x(1 - x). \quad (36)$$

Note that while the function  $S(x; r) = S(1 - x; r)$  is symmetric with respect to the value  $x = 1/2$ ,  $T(x; r)$  is not. Thus the spinodal instability curve with respect to the phase separation is not symmetric with respect to  $x = 1/2$ . Besides we have the obvious symmetry  $S(x; r) = S(1 - x; r^{-1})$  and  $T(x; r) = T(1 - x; r^{-1})$ .

The lost of mixture stability with respect to phase segregation can be calculated as usual as

$$\det \left( \rho_i^{-1} \delta_{ij} + \frac{\partial^2 \Phi_u^{(3D)}}{\partial \rho_i \partial \rho_j} \right) = 0, \quad (37)$$

which is equivalent to the following condition, expressed in the variables  $y$  and  $x$ ,

$$\frac{\partial}{\partial y} \left[ y^2 \frac{\partial \varphi}{\partial y} \right] \frac{\partial^2 \varphi}{\partial x^2} - \left( y \frac{\partial^2 \varphi}{\partial y \partial x} \right)^2 = 0. \quad (38)$$

Inserting (33) into (38) we calculate the demixing spinodals for different values of the asymmetry parameter  $r$  in the plane  $x - \eta$ . Figure 4 shows these demixing spinodals for values  $r = 20, 10, 5$  and 2.

Of course this analysis does not prove that a thermodynamically stable fluid-fluid demixing occurs, as inhomogeneous phases are not being accounted for.

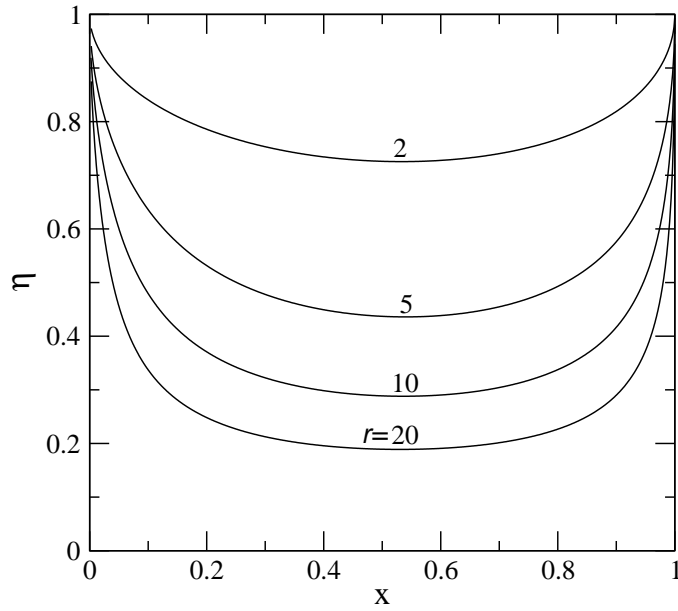


FIG. 4: Demixing spinodals for the phase separation between two nematic phases of different composition calculated for values of the asymmetry parameter  $r$  as labeled in the figure .

## V. DIRECT CORRELATION FUNCTION

The second functional derivative of  $\beta\mathcal{F}_{\text{ex}}^{(3\text{D})} = \int d\mathbf{r} \Phi^{(3\text{D})}(\mathbf{r})$  with respect to the density profiles  $\rho_i(\mathbf{r})$  and  $\rho_j(\mathbf{r})$  evaluated at the uniform densities  $\rho_i$  gives us, after a long and tedious calculation, the following expression for the direct correlation function

$$c_{ij}(\mathbf{r}_{12}) = [\chi_0 + \chi_1 \cdot \Delta\mathbf{R}_{ij}(\mathbf{r}_{12}) + \chi_2 \cdot \Delta\mathbf{S}_{ij}(\mathbf{r}_{12}) + \chi_3 \Delta V_{ij}(\mathbf{r}_{12})] f_{ij}(r_{12}), \quad (39)$$

where  $\chi_i = \frac{\partial(\beta P)}{\partial \xi_i}$  and

$$f_{ij}(r_{12}) = -\Theta\left(R_{ij}^{(+)} - r_{12}\right) \Theta\left(L_{ij}^{(+)} / 2 - |z_{12}|\right), \quad (40)$$

$$\Delta\mathbf{R}_{ij}(\mathbf{r}_{12}) = \left[ \Delta L_{ij}^{\perp}(r_{12}^{\perp}) / (2\pi), \Delta L_{ij}^{\parallel}(z_{12}) / 2 \right], \quad (41)$$

$$\Delta\mathbf{S}_{ij}(\mathbf{r}_{12}) = \left[ \Delta S_{ij}^{\perp}(\mathbf{r}_{12}), \Delta S_{ij}^{\parallel}(r_{12}^{\perp}) \right], \quad (42)$$

$$\Delta V_{ij}(\mathbf{r}_{12}) = \frac{1}{2} \Delta S_{ij}^{\parallel}(r_{12}^{\perp}) \Delta L_{ij}^{\parallel}(z_{12}), \quad (43)$$

with  $L_{ij}^{(\pm)} \equiv |L_i \pm L_j|$ , are the Mayer function (40) and the geometrical measures of the body defined by the overlap between two cylinders  $i$  and  $j$  whose centers of mass are separated by the vector  $\mathbf{r}_{12}$ . These measures are characteristic radii along the perpendicular and parallel directions (41), the oriented surfaces (42) and the total overlap volume (43). The radii in turn are defined

through the total length  $L_{ij}^{(\perp)}$  of the arches and the height  $L_{ij}^{(\parallel)}$  of the overlap body. The expressions for these quantities as well as for  $\Delta S_{ij}^{(\alpha)}$  ( $\alpha = \perp, \parallel$ ) are given in Appendix B.

The form of the direct correlation function (39) as a function of the geometric measures of the overlap body is exactly the same as that obtained from the Percus-Yevick approximation for a HS mixture, as it was first shown by Rosenfeld [2, 3]. The same formal expression is also obtained for a mixture of parallel hard cubes [18, 19].

## VI. CONCLUSIONS

We have derived a FMF for a mixture of HD, and further used it to construct another one for a mixture of PHCL. The resulting functional fulfills all dimensional crossovers, a feature that makes the obtained functional very useful in the study of fluid mixtures of perfectly aligned hard rods confined by external potentials. These external potentials may have planar or cylindrical geometry. Some interfacial phase transitions, such as wetting, layering and capillary ordering, can be studied as well using this functional.

Of course, the parallel alignment constraint limits the use of the PHCL functional to the study of highly oriented phases, such as nematic, smectic or crystal phases at very high pressures. A particularly interesting application of this functional is the determination of the phase behavior of polydisperse hard rod mixtures. The inclusion of smectic and columnar phases in the study makes the constraint of perfect particle alignment indispensable to achieve the numerical minimization of the functional. Some experimental works [37, 38] as well as simulations [40] predict that polydispersity enhances the columnar phase stability with respect to the smectic phase. It will be interesting to check these conclusions with the reported functional.

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We begin with the calculation of the one-dimensional limit for the two-particle weighted density  $N(\mathbf{r})$  defined in Eq. (2). Substituting the expressions  $\rho_i(\mathbf{r}) = \rho_i(x)\delta(y)$  (where  $\rho_i(x)$  is the one-dimensional density of species  $i$ ) and integrating over the coordinates  $y_i$  ( $i = 1, 2$ ) we obtain

$$\begin{aligned}
 N(x, y) &= \frac{1}{4\pi^2} \sum_{i,j} \frac{1}{R_i R_j} \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \rho_i(x_1) \rho_j(x_2) \delta \left( R_i - \sqrt{(x - x_1)^2 + y^2} \right) \\
 &\quad \times \delta \left( R_j - \sqrt{(x - x_2)^2 + y^2} \right) K_{ij}(|x_1 - x_2|) \\
 &= \frac{1}{4\pi^2} \sum_{i,j} \frac{\Theta(R_i - |y|)\Theta(R_j - |y|)}{u_i u_j} \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \rho_i(x_1) \rho_j(x_2) \\
 &\quad \times \delta(u_i - |x - x_1|) \delta(u_j - |x - x_2|) K_{ij}(|x_1 - x_2|),
 \end{aligned} \tag{A1}$$

where  $u_i \equiv \sqrt{R_i^2 - y^2}$  and we have used the identity

$$\delta \left( R_i - \sqrt{(x - x_1)^2 + y^2} \right) = \Theta(R_i - |y|) \frac{R_i}{u_i} \delta(u_i - |x - x_1|). \tag{A2}$$

Because of the deltas in the integral (A1), it can be readily performed and yields

$$\begin{aligned}
 N(x, y) &= \sum_{i,j} \frac{\Theta(R_i - |y|)\Theta(R_j - |y|)}{4\pi^2 u_i u_j} \{ [\rho_i(x + u_i) \rho_j(x + u_j) + \rho_i(x - u_i) \rho_j(x - u_j)] K_{ij}(|u_i - u_j|) \\
 &\quad + [\rho_i(x + u_i) \rho_j(x - u_j) + \rho_i(x - u_i) \rho_j(x + u_j)] K_{ij}(u_i + u_j) \}.
 \end{aligned} \tag{A3}$$

From Eqs. (9) and (10) for  $K_{ij}(r)$  we obtain

$$K_{ij}(|u_i \pm u_j|) = \pi |y| |u_i \pm u_j| |\lambda_i \pm \lambda_j|, \tag{A4}$$

where we have defined

$$\lambda_i \equiv \sin^{-1}(u_i/R_i) = \cos^{-1}(|y|/R_i). \tag{A5}$$

In order to proceed let us assume for a while that  $R_i \geq R_j$ . Then  $u_i \geq u_j$  and  $\lambda_i \geq \lambda_j$  and therefore

$$\begin{aligned}
 N(x, y) &= \sum_{i,j} \frac{\Theta(R_i - |y|)\Theta(R_j - |y|)|y|}{4\pi} \\
 &\quad \times \left\{ [\rho_i(x + u_i) + \rho_i(x - u_i)][\rho_j(x + u_j) + \rho_j(x - u_j)] \left( \frac{\lambda_i}{u_j} + \frac{\lambda_j}{u_i} \right) \right. \\
 &\quad \left. - [\rho_i(x + u_i) - \rho_i(x - u_i)][\rho_j(x + u_j) - \rho_j(x - u_j)] \left( \frac{\lambda_i}{u_i} + \frac{\lambda_j}{u_j} \right) \right\}.
 \end{aligned} \tag{A6}$$

In order to get the equivalent expression when  $R_i < R_j$  we should just exchange the indices  $i$  and  $j$  in the above expression. But this expression is invariant under this exchange of indices, therefore it holds for any  $R_i$  and  $R_j$ .

Let us now obtain the densities  $n_0(\mathbf{r})$  and  $n_2(\mathbf{r})$  given by Eqs. (4) and (5). When inserting the one-dimensional density profile one gets

$$n_2(x, y) = \sum_i n_{2i}(x, y), \quad n_{2i}(x, y) = \Theta(R_i - |y|) \int_{x-u_i}^{x+u_i} \rho_i(t) dt, \quad (\text{A7})$$

$$n_0(x, y) = \sum_i n_{0i}(x, y), \quad n_{0i}(x, y) = \frac{\Theta(R_i - |y|)}{2\pi u_i} [\rho_i(x + u_i) + \rho_i(x - u_i)]. \quad (\text{A8})$$

Notice that, as  $u_i = R_i$  when  $y = 0$ , then  $n_2(x, 0) = n_1(x)$  and  $n_{0i}(x, 0) = n_{0i}(x)/\pi R_i$ , with

$$n_1(x) = \sum_i \int_{x-R_i}^{x+R_i} \rho_i(t) dt, \quad n_0(x) = \sum_i n_{0i}(x) = \frac{1}{2} \sum_i [\rho_i(x + R_i) + \rho_i(x - R_i)], \quad (\text{A9})$$

the two weighted densities of the exact DF for a mixture of 1D hard rods [39].

For the sake of notational clarity, in what follows we will omit the arguments of  $n_0(x, y)$  and  $n_2(x, y)$ . Equations (A7) and (A8) help us to rewrite (A6) as

$$\begin{aligned} N(x, y) &= \sum_{i,j} \left\{ \pi |y| n_{0i} n_{0j} (u_i \lambda_i + u_j \lambda_j) - \frac{|y|}{4\pi} \frac{\partial n_{2i}}{\partial x} \frac{\partial n_{2j}}{\partial x} \left( \frac{\lambda_i}{u_i} + \frac{\lambda_j}{u_j} \right) \right\} \\ &= 2\pi |y| n_0 \sum_i u_i \lambda_i n_{0i} - \frac{|y|}{2\pi} \frac{\partial n_2}{\partial x} \sum_i \frac{\lambda_i}{u_i} \frac{\partial n_{2i}}{\partial x} \end{aligned} \quad (\text{A10})$$

(for notational simplicity we have omitted the  $x$  and  $y$  dependence of the weighted densities).

Now we can integrate  $\Phi^{(2D)}(x, y)$ , as given by Eq. (1), with respect to  $y$  to obtain

$$\begin{aligned} \tilde{\Phi}^{(1D)}(x) &= \int_{-\infty}^{\infty} \Phi^{(2D)}(x, y) dy = \int_{-\infty}^{\infty} dy \left\{ -n_0(x, y) \ln[1 - n_2(x, y)] + \frac{N(x, y)}{1 - n_2(x, y)} \right\} \\ &= 2 \int_0^{\infty} dy \left\{ -n_0(x, y) \ln[1 - n_2(x, y)] + \frac{N(x, y)}{1 - n_2(x, y)} \right\}, \end{aligned} \quad (\text{A11})$$

because the integrand is an even function of  $y$ . On the other hand, when  $y \geq 0$

$$\frac{\partial n_2}{\partial y} = -2\pi y n_0, \quad (\text{A12})$$

$$\frac{\partial}{\partial y} (u_i \lambda_i n_{0i}) = -n_{0i} - \frac{\lambda_i y}{2\pi u_i} \frac{\partial^2 n_{2i}}{\partial x^2}, \quad (\text{A13})$$

therefore

$$\tilde{\Phi}^{(1D)}(x) = 2 \int_0^{\infty} dy \sum_i \left\{ \frac{\partial}{\partial y} [u_i \lambda_i n_{0i} \ln(1 - n_2)] + \frac{\partial}{\partial x} \left[ \frac{\lambda_i y}{2\pi u_i} \ln(1 - n_2) \frac{\partial n_{2i}}{\partial x} \right] \right\}. \quad (\text{A14})$$



The first term in this equation can readily be integrated. Since for  $y = 0$  we have  $u_i(0) = R_i$  and  $\lambda_i(0) = \pi/2$  and for  $y = R_i$  we have  $u_i(R_i) = \lambda_i(R_i) = 0$ , it follows that

$$\tilde{\Phi}^{(1D)}(x) = \Phi^{(1D)}(x) + \frac{\partial \Psi}{\partial x}(x), \quad (\text{A15})$$

where

$$\Phi^{(1D)}(x) = -n_0(x) \ln[1 - n_1(x)] \quad (\text{A16})$$

is the exact DF for a 1D hard rod mixture [39] in terms of the weighted densities (A9), and

$$\Psi(x) = \int_0^\infty dy \sum_i \left[ \frac{\lambda_i y}{\pi u_i} \ln(1 - n_2) \frac{\partial n_{2i}}{\partial x} \right]. \quad (\text{A17})$$

Assuming proper boundary conditions for the density when  $x \rightarrow \pm\infty$ , the free-energy functional for the system is given by

$$\beta \mathcal{F}_{\text{ex}}^{(2D)}[\{\rho_i\}] = \int_{-\infty}^\infty \tilde{\Phi}^{(1D)}(x) dx = \int_{-\infty}^\infty \Phi^{(1D)}(x) dx. \quad (\text{A18})$$

This completes the proof of the exact 2D $\rightarrow$ 1D dimensional crossover of the DF for HD (1).

## APPENDIX B: GEOMETRIC MEASURES OF THE OVERLAP BETWEEN TWO CYLINDERS

In this appendix we provide explicit expressions for the geometrical measures of the body formed by overlapping two cylinders with radii  $R_i$  and lengths  $L_i$ . To begin with, the formal definition of all these measures is

$$f_{ij}(\mathbf{r}_{12}) = -\Theta_{R_{ij}^{(+)}}(r_{12}^\perp) \Theta_{L_{ij}^{(+)}}(z_{12}), \quad (\text{B1})$$

$$\Delta L_{ij}^\parallel(\mathbf{r}_{12}) = \Theta_{R_{ij}^{(+)}}(r_{12}^\perp) [\Theta_{L_i} * \Theta_{L_j}(z_{12})], \quad (\text{B2})$$

$$\Delta L_{ij}^\perp(\mathbf{r}_{12}) = \langle \Theta_{R_i} * \delta_{R_j}(r_{12}^\perp) \rangle \Theta_{L_{ij}^{(+)}}(z_{12}), \quad (\text{B3})$$

$$\Delta S_{ij}^\parallel(\mathbf{r}_{12}) = 2 [\Theta_{R_i} * \Theta_{R_j}(r_{12}^\perp)] \Theta_{L_{ij}^{(+)}}(z_{12}), \quad (\text{B4})$$

where  $\Theta_u(r^\perp) = \Theta(u - r^\perp)$ ,  $\Theta_u(z) = \Theta(u/2 - z)$ , and  $\delta_u(r^\perp) = \delta(u - r^\perp)$ . It is rather easy to evaluate these expressions appealing to their geometrical meaning. Hence, the total arch lengths of the cross-section of the overlap body is

$$\Delta L_{ij}^\perp(r_{12}^\perp) = 2 \left\{ \langle R_i \cos^{-1} t_{ij} \rangle \Theta \left( r_{12}^\perp - R_{ij}^{(-)} \right) + \frac{\pi}{2} \left( R_{ij}^{(+)} - R_{ij}^{(-)} \right) \Theta \left( R_{ij}^{(-)} - r_{12}^\perp \right) \right\}, \quad (\text{B5})$$

while its height is

$$\Delta L_{ij}^{\parallel}(z_{12}) = \frac{L_{ij}^{(+)}}{2} - |z_{12}| - \left( \frac{L_{ij}^{(-)}}{2} - |z_{12}| \right) \Theta \left( L_{ij}^{(-)}/2 - |z_{12}| \right). \quad (\text{B6})$$

Similarly, the expression for twice the area of the base of the overlap body is given by

$$\Delta S_{ij}^{\parallel}(r_{12}^{\perp}) = 2 \left\{ \left\langle R_i^2 \left[ \cos^{-1} t_{ij} - \frac{r_{12}^{\perp}}{2R_i} \sqrt{1 - t_{ij}^2} \right] \right\rangle \Theta \left( r_{12}^{\perp} - R_{ij}^{(-)} \right) + \frac{\pi}{4} \left( R_{ij}^{(+)} - R_{ij}^{(-)} \right)^2 \Theta \left( R_{ij}^{(-)} - r_{12}^{\perp} \right) \right\}, \quad (\text{B7})$$

while its lateral area is readily obtained as

$$\Delta S_{ij}^{\perp}(\mathbf{r}_{12}) = \Delta L_{ij}^{\perp}(r_{12}^{\perp}) \Delta L_{ij}^{\parallel}(z_{12}). \quad (\text{B8})$$

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