Fundamental Measure Theory for Inhomogeneous Fluids of Nonspherical Hard Particles

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Using the Gauss-Bonnet theorem we deconvolute exactly the Mayer f-function for arbitrarily shaped convex hard bodies in a series of *tensorial* weight functions, each depending only on the shape of a single particle. This geometric result allows the derivation of a free energy density functional for inhomogeneous hard-body fluids which reduces to Rosenfeld's fundamental measure theory [Phys. Rev. Lett. **63**, 980 (1989)] when applied to hard spheres. The functional captures the isotropic-nematic transition for the hard-spherocylinder fluid in contrast with previous attempts. Comparing with data from Monte Carlo simulations for hard spherocylinders in contact with a planar hard wall, we show that the new functional also improves upon previous functionals in the description of inhomogeneous isotropic fluids.

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With the advance in particle synthesis nonspherical colloids of various shapes can be designed giving rise, e.g., to dispersions of gibbsite platelets [1] or mixtures of silica spheres and silica-coated boehmite rods [2]. These colloidal suspensions display rich phase behavior including isotropic, nematic, and different crystalline phases. A powerful tool for the characterization of such systems in the presence of inhomogeneities is density functional theory (DFT) [3], which, in contrast to other approaches such as integral equation methods, is susceptible to comply with exact statistical mechanical sum rules [4] and possesses comparatively transparent derivations. In a seminal work [5] Rosenfeld constructed a DFT for spherical hard particles on the basis of a careful inspection of the second order virial expansion from which he identified an appropriate set of one-center weighted densities. This fundamental measure theory (FMT) was successfully used to describe the inhomogeneous hard-sphere fluid, including mixtures, and it was generalized for arbitrarily shaped hard bodies [6]. However, the original nonspherical FMT has the drawback that it does not reproduce the correct second virial coefficient for the nonisotropic fluid. Even worse, it does *not* yield a stable nematic phase for a rod fluid. This failure has understandably triggered some effort during the last years which was devoted to the construction of modified FMTs being compatible with the Onsager limit while providing the virtues inherent to FMT for spheres. However, in order to recover the exact second virial coefficient, specific assumptions had to be made for the shape of the particle, e.g., parallel hard cubes [7] or mixtures of colloidal spheres with thin needles or platelets [8].

While in the above work generically new weight functions depending on the properties of *several* species (e.g., sphere and needle) are constructed from geometric arguments which apply only in certain limiting cases (e.g., vanishing thickness), in the present work we devise an approach which sets out from the *exact* expression for the Mayer f-function of arbitrary convex hard bodies in terms of (geodesic) curvatures and a deconvolution in (tensorial) one-center weight functions, depending each on the properties of only one species of the fluid components. In its simplest form with only two additional tensorial densities, our theory reduces to the former FMTs for spheres [5,9], while it leads to a stable nematic phase.

As a starting point we use the excess (over ideal gas) free energy functional $\mathcal{F}_{\rm ex}[\{\rho_i\}]$ for an inhomogeneous ν-component hard-body mixture behaving as

$$\mathcal{F}_{\rm ex} \to -\frac{k_B T}{2}\sum_{i,j=1}^{\nu}\int d\mathcal{R}_i d\mathcal{R}_j \rho_i(\mathcal{R}_i)\rho_j(\mathcal{R}_j) f_{ij}(\mathcal{R}_i,\mathcal{R}_j) \tag{1}$$

in the dilute limit $\rho_i \to 0$. Here we have introduced the average particle number density $\rho_i(\mathcal{R}_i)$ of component i depending on the position $\mathbf{r}_i$ and orientation ϖ_i of the particles; i.e., $\mathcal{R}_i = (\mathbf{r}_i, \varpi_i)$. The interaction between two hard bodies $\mathcal{B}_i$ and $\mathcal{B}_j$ enters via the Mayer f-function

$$f_{ij}(\mathcal{R}_i,\mathcal{R}_j) = \begin{cases} 0 & \text{if } \mathcal{B}_i \cap \mathcal{B}_j = \emptyset \\ -1 & \text{if } \mathcal{B}_i \cap \mathcal{B}_j \neq \emptyset. \end{cases} \tag{2}$$

For the moment we fix the particle orientation ϖ_i. Convex $\mathcal{B}_i$ can then be parametrized by the vector $\mathbf{R}_i(\hat{\mathbf{r}})$ pointing from some reference point, e.g., the center of mass, to the point on the surface of $\mathcal{B}_i$ which lies in the direction of the unit vector $\hat{\mathbf{r}} = \mathbf{r}/|\mathbf{r}|$. Using the outward normal $\mathbf{n}_i(\hat{\mathbf{r}})$ to the surface of $\mathcal{B}_i$ at $\mathbf{R}_i(\hat{\mathbf{r}})$ we can define the weight functions of $\mathcal{B}_i$ by $\omega_i^{(3)}(\mathbf{r}) = \Theta(|\mathbf{R}_i(\hat{\mathbf{r}})| - |\mathbf{r}|)$, $\omega_i^{(2)}(\mathbf{r}) = \delta(|\mathbf{R}_i(\hat{\mathbf{r}})| - |\mathbf{r}|)/(\mathbf{n}_i(\hat{\mathbf{r}})\hat{\mathbf{r}})$, $\omega_i^{(1)}(\mathbf{r}) = \frac{H_i(\hat{\mathbf{r}})}{4\pi}\omega_i^{(2)}(\mathbf{r})$, $\omega_i^{(0)}(\mathbf{r}) = \frac{K_i(\hat{\mathbf{r}})}{4\pi}\omega_i^{(2)}(\mathbf{r})$, $\vec{\omega}_i^{(2)}(\mathbf{r}) = \mathbf{n}_i(\hat{\mathbf{r}})\omega_i^{(2)}(\mathbf{r})$, $\vec{\omega}_i^{(1)}(\mathbf{r}) = \frac{H_i(\hat{\mathbf{r}})}{4\pi}\vec{\omega}_i^{(2)}(\mathbf{r})$ (see Ref. [6]). The factor $(\mathbf{n}_i(\hat{\mathbf{r}})\hat{\mathbf{r}})^{-1}$, which does not appear in Rosenfeld's original proposal [6], follows from parametrizing $\mathcal{B}_i$ through $\mathbf{R}_i(\hat{\mathbf{r}})$. It guarantees a correct weighting according to the surface area of $\mathcal{B}_i$. The mean and

Gaussian curvature at that surface point are denoted by $H_i(\hat{\mathbf{r}})$ and $K_i(\hat{\mathbf{r}})$, respectively. They are obtained from the local principal curvatures κ_i^I and κ_i^{II} according to $H_i = \frac{1}{2}(\kappa_i^I + \kappa_i^{II})$ and $K_i = \kappa_i^I \kappa_i^{II}$. Then the Mayer function f_{ij} can be written as a deconvolution,

$$f_{ij} = I_{ij}^{\Delta\kappa} - \omega_i^{(0)} \otimes \omega_j^{(3)} - \omega_i^{(1)} \otimes \omega_j^{(2)} + \vec{\omega}_i^{(1)} \otimes \vec{\omega}_j^{(2)} + (i \leftrightarrow j), \quad (3)$$

except for the term $I_{ij}^{\Delta\kappa}$ which is derived exactly below. Here $(i \leftrightarrow j)$ stands for the previous terms with exchanged indices i and j. With the standard scalar product $\cdot$ for vectors, the convolution product $\otimes$ is defined by $\omega_i^{(\alpha)} \otimes \omega_j^{(\gamma)} = \int d\mathbf{r}\omega_i^{(\alpha)}(\mathbf{r} - \mathbf{r}_i) \cdot \omega_j^{(\gamma)}(\mathbf{r} - \mathbf{r}_j)$ for fixed particle orientation ϖ. The deconvolution Eq. (3) is remarkable as it shows that the excess free energy density Φ, defined through $\mathcal{F}_{\rm ex} = k_B T \int d\mathbf{r}\Phi(\mathbf{r})$, can be constructed as a function of the weighted densities

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

such that the exact low-density limit Eq. (1) is recovered (given that $I_{ij}^{\Delta\kappa} = 0$, which holds for spherical particles). It follows with an exact relation from scaled-particle theory that [5,6,10]

$$\Phi = \Phi^{\Delta\kappa} - n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \vec{n}_1 \vec{n}_2}{1 - n_3} + \frac{\phi}{(1 - n_3)^2} \quad (5)$$

with $\phi = \frac{1}{24\pi}(n_2^3 - 3n_2\vec{n}_2\vec{n}_2)$ and $\Phi^{\Delta\kappa}$ set to zero. In this Letter we derive for the first time the contribution $\Phi^{\Delta\kappa}$ based on an explicit exact expression for $I_{ij}^{\Delta\kappa}$ in Eq. (3). In the past $I_{ij}^{\Delta\kappa}$ and hence $\Phi^{\Delta\kappa}$ were not known and neglected with severe consequences for nonspherical particles such as a wrong low-density limit. Even worse, a simple calculation shows that the weighted densities defined above are independent of a given orientational distribution in a bulk fluid. As a consequence, Φ from Eq. (5) with $\Phi^{\Delta\kappa} = 0$ is independent of the fluid anisotropy. Hence the FMT does not capture the tendency of nonspherical particles to adopt a phase other than the isotropic one, while a nematic phase is observed in a fluid of extended rods. We now remediate this failure by deriving $I_{ij}^{\Delta\kappa}$ exactly such that $\Phi^{\Delta\kappa}$, which arises from curvature asymmetry, can be taken into account.

As has been observed by Rosenfeld [6], the Gauss-Bonnet theorem from differential geometry [11] can be used to rewrite f_{ij} in terms of integrals of the Gaussian curvature K. For convex $\mathcal{B}_i$ and $\mathcal{B}_j$ the surface of the intersection $\mathcal{B}_i \cap \mathcal{B}_j$ consists of two surfaces, $\partial\mathcal{B}_i \cap \mathcal{B}_j$ and $\mathcal{B}_i \cap \partial\mathcal{B}_j$, which are bounded by the same closed curve $\mathcal{C} = \partial\mathcal{B}_i \cap \partial\mathcal{B}_j$. Thus, with the arclength s and the geodesic curvature κ_i^g of $\mathcal{C}$ on $\partial\mathcal{B}_i$, one finds

$$\int_{\partial\mathcal{B}_i\cap\mathcal{B}_j} K_i dA_i + \int_{\mathcal{B}_i\cap\partial\mathcal{B}_j} K_j dA_j + \int_{\mathcal{C}} (\kappa_i^g + \kappa_j^g) ds = -4\pi f_{ij}. \quad (6)$$

From differential geometry we find the explicit expression

$$\kappa_i^g + \kappa_j^g = H_i \frac{1 - \mathbf{n}_i\mathbf{n}_j}{|\mathbf{n}_i \times \mathbf{n}_j|} - \Delta\kappa_i \frac{(\mathbf{v}_i^I\mathbf{n}_j)^2 - (\mathbf{v}_i^{II}\mathbf{n}_j)^2}{(1 + \mathbf{n}_i\mathbf{n}_j)|\mathbf{n}_i \times \mathbf{n}_j|} + (i \leftrightarrow j) \quad (7)$$

involving the deviatoric curvature $\Delta\kappa_i = \frac{1}{2}(\kappa_i^I - \kappa_i^{II})$ which is a measure of the deviation from sphericity. The unit vectors $\mathbf{v}_i^I$ and $\mathbf{v}_i^{II}$ lie in the tangent plane (perpendicular to $\mathbf{n}_i$) and point into the directions of the principal curvatures κ_i^I and κ_i^{II}; thus, $\mathbf{v}_i^I$, $\mathbf{v}_i^{II}$, and $\mathbf{n}_i$ constitute an orthonormal basis of $\mathbb{R}^3$. Using the relations $\int \frac{K_i}{4\pi} dA_i = \omega_i^{(0)} \otimes \omega_j^{(3)}$, $\int_{\mathcal{C}} \frac{H_i}{4\pi} \frac{ds}{|\mathbf{n}_i\times\mathbf{n}_j|} = \omega_i^{(1)} \otimes \omega_j^{(2)}$, and $\int_{\mathcal{C}} \frac{H_i\mathbf{n}_i\mathbf{n}_j}{4\pi} \times \frac{ds}{|\mathbf{n}_i\times\mathbf{n}_j|} = \vec{\omega}_i^{(1)} \otimes \vec{\omega}_j^{(2)}$, one obtains Eq. (3) with

$$I_{ij}^{\Delta\kappa} = \int_{\partial\mathcal{B}_i\cap\partial\mathcal{B}_j} \frac{\Delta\kappa_i}{4\pi} \frac{(\mathbf{v}_i^I\mathbf{n}_j)^2 - (\mathbf{v}_i^{II}\mathbf{n}_j)^2}{(1 + \mathbf{n}_i\mathbf{n}_j)} \frac{ds}{|\mathbf{n}_i \times \mathbf{n}_j|} \quad (8)$$

which cannot be written as a simple convolution of weight functions depending only on the properties of one species each. One can, however, expand the integrand in a Taylor series in powers of the components of unit vectors; i.e., $(1 + \mathbf{n}_i\mathbf{n}_j)^{-1} = 1 - \mathbf{n}_i\mathbf{n}_j + (\mathbf{n}_i\mathbf{n}_j)^2 - \ldots$. Pursuing the expansion up to order n allows for a deconvolution of $I_{ij}^{\Delta\kappa}$ in terms of *tensorial* weight functions of rank up to $n + 2$. In the simplest possible scenario we take $n = 0$, meaning that we use the approximation $(1 + \mathbf{n}_i\mathbf{n}_j)^{-1} \approx \zeta$, where we have introduced the constant $0 \leq \zeta \leq 2$ which can be different from 1 in order to compensate for the error arising from the omission of higher order terms in the expansion. In principle, the deconvolution can be performed exactly such that the Onsager limit is reproduced for long rods. However, in order to guarantee that the theory can be treated efficiently numerically, we truncate the series of convolution products.

The deconvolution of $I_{ij}^{\Delta\kappa}$ to the order $n = 0$ reads $I_{ij}^{\Delta\kappa} \approx \zeta \overleftrightarrow{\omega}_i^{(1)} \otimes \overleftrightarrow{\omega}_j^{(2)}$, where

$$\overleftrightarrow{\omega}_i^{(1)} = \omega_i^{(2)} \frac{\Delta\kappa_i(\hat{\mathbf{r}})}{4\pi} (\mathbf{v}_i^I(\hat{\mathbf{r}})\mathbf{v}_i^I(\hat{\mathbf{r}})^{\rm T} - \mathbf{v}_i^{II}(\hat{\mathbf{r}})\mathbf{v}_i^{II}(\hat{\mathbf{r}})^{\rm T}) \quad (9)$$

and $\overleftrightarrow{\omega}_i^{(2)} = \mathbf{n}_i(\hat{\mathbf{r}})\mathbf{n}_i(\hat{\mathbf{r}})^{\rm T}\omega_i^{(2)}$. These tensorial weight functions can be represented as 3×3 matrices with the dyadic product $(\mathbf{a}\mathbf{b}^{\rm T})_{ij} = a_i b_j$ and the scalar product $\overleftrightarrow{A} \cdot \overleftrightarrow{B} = \sum_{i,j} A_{ij} B_{ji}$ needed for the convolution.

Analogous to the derivation of Rosenfeld's excess free energy density [5,6,10], we obtain the additional term

$$\Phi^{\Delta\kappa} = -\zeta \frac{{\rm Tr}[\overleftrightarrow{n}_1\overleftrightarrow{n}_2]}{1 - n_3} \quad (10)$$

in the excess free energy density Φ, Eq. (5). Interestingly, deficiencies of ϕ for hard spheres, e.g., overstabilized crystals and wrong dimensional crossovers [12], had led Tarazona [9] to introducing the weighted density $\overleftrightarrow{n}_2$ for spheres and constructing ϕ as

$$\phi = \frac{3}{16\pi}(\vec{n}_2^{\mathrm{T}}\overleftrightarrow{n}_2\vec{n}_2 - n_2\vec{n}_2\vec{n}_2 - \mathrm{Tr}[\overleftrightarrow{n}_2^3] + n_2\,\mathrm{Tr}[\overleftrightarrow{n}_2^2]). \tag{11}$$

This ϕ yields the exact result in one dimension for the monocomponent system, describes the hard-sphere crystal very well, and provides also the presently best FMT for hard-sphere *mixtures* [13]. Here we provide for the first time $\overleftrightarrow{n}_2$ as a building block for ϕ in the spirit of Rosenfeld, i.e., from an inspection of the low-density limit rather than the crystal phase. In the following, we use ϕ from Eq. (11), but we have checked that the differences arising from the different expressions for ϕ are overruled by the influence of the different values of ζ in Eq. (10).

Concerning the choice of ζ we note that Rosenfeld's FMT for nonspherical particles [6] is recovered for $\zeta = 0$. In the case of spheres the deviatoric curvature $\Delta\kappa$ vanishes and therefore $\overleftrightarrow{\omega}^{(1)} \equiv 0$ and our FMT reduces to Rosenfeld's [5] when applied to the hard-sphere fluid. The term $\Phi^{\Delta\kappa}$ also vanishes in the isotropic bulk fluid so that we obtain the exact second virial coefficient B_2 for the *isotropic* bulk fluid from our theory. Deriving from our theory B_2 for fixed particle orientations ϖ and ϖ' yields an approximation to the mutual excluded volume $v(\varpi, \varpi')$. We find that for the isotropic (sphero)cylinder fluid the value $\zeta = \frac{5}{4}$ minimizes the average deviation (least squares) of $v(\varpi, \varpi')$ from the exact result. Including higher order terms in the Taylor expansion of $(1 + \mathbf{n}_i\mathbf{n}_j)^{-1}$ in Eq. (8) shows the convergence of the series to the exact $v(\varpi, \varpi')$. In particular, the inclusion of the next higher relevant order ($n = 2$) yields an improvement which is very similar to that due to the ζ-correction.

For the calculation of the isotropic-nematic transition we consider a bulk fluid of spherocylinders (length L, diameter D) with particle density ρ and packing fraction $\eta = n_3$. The spherocylinders are assumed to be distributed as a function of their azimuthal angle ϑ according to the normalized distribution function $g(\cos\vartheta)$. The orientation dependent density distribution is thus given by $\rho(\varpi) = \rho g(\cos\vartheta) \equiv \rho g(x)$. It follows that the tensorial weighted densities depend on $g(x)$ via the second moment $I_2 \doteq \int_0^1 dx x^2 g(x)$. The vectorial densities vanish as well as the nondiagonal elements of the tensorial weighted densities. One can check that $\mathrm{Tr}\overleftrightarrow{n}_1 = 0$ and $\mathrm{Tr}\overleftrightarrow{n}_2 = n_2$, which hold for arbitrary $\rho(\mathbf{r}, \varpi)$. For given fixed volume V, chemical potential μ, and particle number density $\rho = \frac{N}{V}$, the equilibrium orientational distribution $g(x)$ must minimize the grand potential density Ω/V which leads to $g(x) = \mathrm{const} \times \exp(\alpha^2 x^2)$ with $\alpha^2 = -\frac{1}{\rho}\frac{\partial\Phi}{\partial I_2}$ and a normalization constant. This derived distribution has been used as an empirical input for the description of the nematic phase in previous work [14].

In Fig. 1 we show the resulting isotropic-nematic transition for $\zeta = \frac{5}{4}$ and $\zeta = 1.6$. The latter value was determined empirically in order to obtain the best fit to the simulation data by Bolhuis and Frenkel [15] at small L/D. The value $\zeta = 1.6$ agrees with the observation that $\zeta > \frac{5}{4}$ improves the accuracy of the FMT on the level of B_2 for small angles between the spherocylinders which occur more frequently in the nematic phase than in the isotropic phase. When L/D grows large, $|\rho_{\mathrm{iso}} - \rho_{\mathrm{nem}}|$ at coexistence is underestimated. However, our theory provides a good description of the location of the isotropic-nematic transition of the hard-spherocylinder fluid. This has to be viewed in contrast with the previous FMTs for nonspherical particles: Rosenfeld's FMT [6] ($\zeta = 0$) does not yield a stable nematic phase at all, and the DFT by Cinacchi and Schmid [16], which yields an isotropic-nematic transition, is no longer based on one-center convolutions, which makes it computationally difficult.

Furthermore, our new functional yields without any empirical fitting accurate results for inhomogeneous fluids. In Fig. 2 we show the results of canonical Monte Carlo simulations of a hard-spherocylinder fluid close to a hard wall. We explore densities below the nematic wetting transition, so that the density $\rho_\vartheta(z)$ is a function only of the distance z between the center of the spherocylinder and the wall and of the orientational angle $\vartheta \in [0, \pi/2]$ between the cylinder axis and the wall normal. We tested that finite-size effects can be neglected and that statistical errors are less than $\lesssim 1\%$.

The comparison with our FMT for four different orientations ϑ with length-to-diameter ratio $L/D = 2.5$ [Fig. 2(a)] reveals a very good agreement with $\zeta = \frac{5}{4}$ and $\zeta = 1.6$, while the former FMT with $\zeta = 0$ performs somewhat worse. In particular, the wavelength of the os-

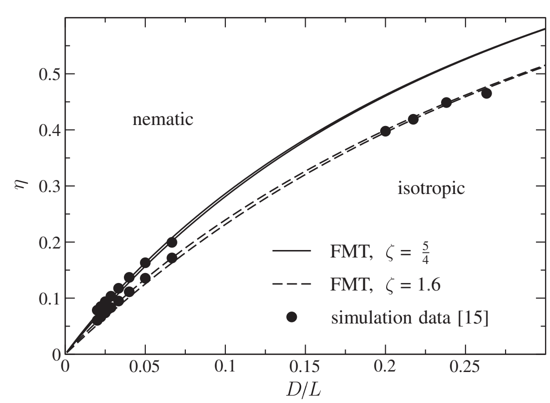

FIG. 1. The isotropic-nematic transition of hard spherocylinders (length L, diameter D, packing fraction η) as obtained from the FMT excess free energy density Φ, Eqs. (5) and (10), with $\zeta = \frac{5}{4}$ and $\zeta = 1.6$. For comparison we show simulation data obtained by Bolhuis and Frenkel [15]. The lower (upper) line or symbol indicates the density of the isotropic (nematic) phase at coexistence. At moderate aspect ratios the density gap is too small to be resolved in the simulations. For elongated rods the FMT underestimates the difference between coexisting densities.

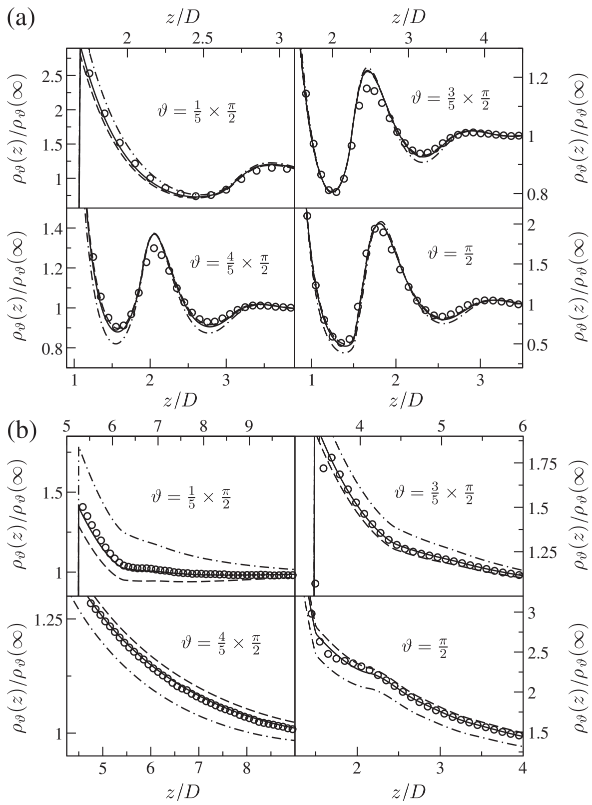

FIG. 2. Density profiles $\rho_\vartheta(z)$ from Monte Carlo simulations (open circles) and from minimization of the density functionals ($\zeta = 0$, dashed-dotted lines; $\zeta = 1.6$, dashed lines; $\zeta = \frac{5}{4}$, solid lines) for a fluid of hard spherocylinders at a hard planar wall located at $z = 0$. The length-to-diameter ratio and bulk packing fraction are (a) $L/D = 2.5$, $\eta \simeq 0.346$ and (b) $L/D = 10.0$, $\eta \simeq 0.127$.

cillations is very well captured. At $L/D = 5.0$ (not shown) the deviations for $\zeta = 0$ become more pronounced, and a slightly better description with $\zeta = \frac{5}{4}$ is provided compared to $\zeta = 1.6$. The data with $L/D = 10.0$ [Fig. 2(b)] clearly reveal the failure of $\zeta = 0$, which grossly overestimates the density profiles with low ϑ while it systematically underestimates the density of the spherocylinders with large ϑ. While $\zeta = 1.6$ also over- and underestimates the data for the orientations, the value $\zeta = \frac{5}{4}$ always gives a very accurate description of the data over the whole range of distances from the wall and for all spherocylinder orientations. This agreement is particularly encouraging as $\zeta = \frac{5}{4}$ is precisely the value which was obtained from the requirement that the *isotropic* low-density bulk fluid is optimally described. Apparently the suitability of the value $\zeta = \frac{5}{4}$ for the isotropic fluid survives beyond the low-density limit and in the inhomogeneous fluid. Note that underestimating the contact density in a certain range of ϑ must go in hand with overestimating it in another range of ϑ. This is a consequence of the contact theorem for fluids at hard walls [4] which states that the pressure is obtained as $p = k_B T \sum_{j=1}^{\nu} \rho_j^c$, where ρ_j^c is the density of orientation ϑ_j at contact with the hard wall. As the bulk pressure p does not depend on ζ, the sum $\sum_{j=1}^{\nu} \rho_j^c$ always yields the same result.

Based on a deconvolution of the Mayer f-function for nonspherical convex bodies, we derived a FMT free energy functional for general inhomogeneous hard-particle fluids by the introduction of two tensorial weight functions. The virtues of the new theory are apparent: it yields a stable nematic phase for the hard-spherocylinder fluid—an essential feature of fluids of nonspherical particles which was completely missed by the previous FMT [6]. Our theory is open for systematic extensions by the use of tensorial weighted densities with higher rank, which lead to better agreement with the Onsager limit. Obviously, it would be interesting to apply the present FMT to other phases, e.g., smectic and crystalline phases such as the gyroid cubic phase of hard pear-shaped particles [17] or the simple monoclinic phase of hard ellipsoids of revolution [18] which have been discovered recently in numerical simulations. Nonspherical particle fluids also provide an important testing ground for morphological thermodynamics, which is based on Hadwiger's theorem from integral geometry, allowing for an efficient calculation of free energies of fluids in contact with complexly shaped walls [19].

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