

Density functional theory for sphere-needle mixtures: Toward finite rod thickness

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For mixtures of hard spheres and hard spherocylinders of large aspect ratio a recently proposed density functional theory is extended to incorporate effects due to nonvanishing rod thickness. This is accomplished by introducing several new geometric weight functions into the framework. We demonstrate explicitly how these weight functions recover the sphere-rod Mayer bond.

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Mixtures of colloidal spheres and mesoscopic rods, like colloidal rods or stiff polymer chains, suspended in a molecular solvent, are well-characterized model systems governed by steric (excluded volume) forces [1–6]. Interesting questions concern the bulk phase behavior and effective sphere–sphere and sphere–wall interactions mediated by the presence of the rods [3,6]. Based on Rosenfeld’s fundamental-measure theory for mixtures of nonconvex bodies [7,8], recently a density-functional theory (DFT) [9] for a minimal model of hard sphere colloids and infinitely thin needles [10] was proposed [11] and used to investigate the structure of the interface between sphere-rich and sphere-poor phases [12,13], and the wetting behavior of a hard wall [14]. This binary DFT proved to predict phase behavior accurately compared to the simulation results of [10], and to give high-quality results for (fluid) density profiles in inhomogeneous situations, when compared both to results from an effective one-component treatment [14] using the depletion potential between spheres [15,16], and to computer simulation results of the free fluid–fluid interface of the binary mixture [13]. By combining Yu and Wu’s functional for mixtures of polymeric fluids [17] and the theory of Ref. [11], Bryk arrived at a DFT for binary mixtures of hard rods and polymer chains [18].

In all these cases, the rods are assumed to have vanishing thickness. Due to the geometry, the statistical weight of configurations with overlapping rods vanishes, and hence the rods behave as though being ideal. (The rod–sphere interaction is unaffected by this argument and is governed by excluded volume.) Rosenfeld’s theory when applied to a mixture of hard spheres of finite (large) packing fraction and a second component of (thick) spherocylinders at vanishing density was shown to predict the entropic force and torque on the rod near a hard wall very accurately [19] and more general cases have also been considered [20].

In order to capture effects of finite rod thickness *and* finite rod density an extension to the theory for vanishingly thin

rods [11] was made in Ref. [12], incorporating the Onsager limit of the rods [21], hence recovering exactly the rod–rod Mayer bond in the limit of large aspect ratio. The Onsager model continues to be a valuable system to study the properties of anisometric particles, see, e.g., Refs. [22–24] for recent work. Cinacchi and Schmid proposed a DFT for general anisotropic particles interpolating between the Rosenfeld and the Onsager functional [25]. The theory of Ref. [12] is, however, restricted to the limit of $LD/\sigma^2 \ll 1$ where L and D are the rod length and thickness, respectively, and σ is the sphere diameter.

In the present contribution, we extend the framework, restricting ourselves still to the Onsager limit of $L/D \gg 1$. This is accomplished by introducing several new geometric weight functions. We demonstrate how these weight functions recover the leading order contribution (in D) to the rod–sphere Mayer bond. Our model is a binary mixture of hard spheres (species S) of diameter σ and hard needlelike spherocylinders (species N) with length L (of the cylindrical part) and diameter D . This is considered in the (Onsager) limit of large rod aspect ratio of length-to-thickness, $L/D \gg 1$. The one-body density distributions of spheres and needles are denoted by $\rho_S(\mathbf{r})$ and $\rho_N(\mathbf{r}, \mathbf{\Omega})$, respectively, where \mathbf{r} is the position coordinate (pointing to the center of the respective particle shape) and $\mathbf{\Omega}$ is a unit vector describing the needle orientation.

We start by defining the density functional. In order to not duplicate material, explicit expressions are given only for the new quantities. We refer the reader directly to Ref. [12] for a full account of the known terms. We do, however, discuss the relation to the sphere–rod Mayer bond in detail below. The Helmholtz excess (over ideal gas) free energy functional is expressed as

$$F_{\text{exc}}[\rho_S, \rho_N] = k_B T \int d^3r \int \frac{d^2\Omega}{4\pi} \Phi(\{n_i^\alpha\}), \quad (1)$$

where k_B is the Boltzmann constant and T is temperature, n_i^α are weighted densities that are obtained through convolutions of the bare density profiles with geometric weight functions w_i^α ; α refers to the particle species and i refers to the type of weighted density. The weight functions w_i^α are obtained by

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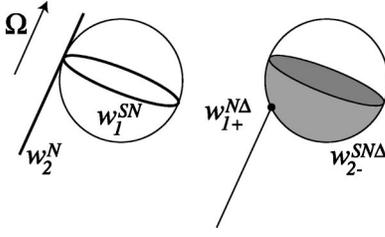


FIG. 1. Illustration of the geometry of the weight functions: w_2^N describes the residual rod surface (thick line), w_1^{SN} is nonvanishing on the equator of the sphere (bold circle), $w_1^{N\Delta+}$ corresponds to one rod endcap (dot), and $w_2^{SN\Delta-}$ describes a hemisphere (gray).

imposing the correct (second order) low-density behavior of (1); this is achieved by the so-called deconvolution of the Mayer bond, which we will turn to below. The functional form of Φ is obtained from consideration of the dimensional crossover [26,27] and scaled-particle ideas [28].

The weight functions necessary to recover the Mayer bond are found to be

$$w_1^{SN}(\mathbf{r}, \boldsymbol{\Omega}) = (2\pi)^{-1} \delta(\mathbf{r} \cdot \boldsymbol{\Omega}) \delta(R - r), \quad (2)$$

$$w_{2\pm}^{SN\Delta}(\mathbf{r}, \boldsymbol{\Omega}) = \delta(R - r) \Theta(\pm \boldsymbol{\Omega} \cdot \mathbf{r}), \quad (3)$$

$$w_{1\pm}^{N\Delta}(\mathbf{r}, \boldsymbol{\Omega}) = (D/2) \delta(\mathbf{r} \pm L\boldsymbol{\Omega}/2), \quad (4)$$

$$w_2^N(\mathbf{r}, \boldsymbol{\Omega}) = \pi D \int_{-L/2}^{L/2} dl \delta(\mathbf{r} + \boldsymbol{\Omega}l), \quad (5)$$

where $R = \sigma/2$ is the sphere radius, $\delta(\cdot)$ is the Dirac distribution, $\Theta(\cdot)$ is the stepfunction, and $r = |\mathbf{r}|$. We use “mixed” weight functions that depend on properties of both species (see Fig. 1 for illustrations). w_1^{SN} describes the “equator” of the sphere, where the polar axis is pointing into the direction given by the (needle) orientation $\boldsymbol{\Omega}$. $w_{2\pm}^{SN\Delta}$ describes the “northern” (subscript +) and “southern” (subscript -) hemisphere. Hence, $w_{2+}^{SN\Delta} + w_{2-}^{SN\Delta} = w_2^S$, where w_2^S is the usual sphere surface weight function [28]. The rod endcaps are described by $w_{1\pm}^{N\Delta}$, where $w_{1+}^{N\Delta} + w_{1-}^{N\Delta} = Dw_0^N$ (as defined in Ref. [11]). The weight function w_2^N makes the dimensional analysis consistent [7,8], and is proportional to a known weight, $w_2^N = 4\pi Dw_1^N$, where w_1^N is given in [11] and obtained directly through [7,8].

Weighted densities are built using spatial convolution, but retaining the angular dependence:

$$n_1^{SN}(\mathbf{x}, \boldsymbol{\Omega}) = \int d^3r \rho_S(\mathbf{r}) w_1^{SN}(\mathbf{x} - \mathbf{r}, \boldsymbol{\Omega}), \quad (6)$$

$$n_{2\pm}^{SN\Delta}(\mathbf{x}, \boldsymbol{\Omega}) = \int d^3r \rho_S(\mathbf{r}) w_{2\pm}^{SN\Delta}(\mathbf{x} - \mathbf{r}, \boldsymbol{\Omega}), \quad (7)$$

$$n_{1\pm}^{N\Delta}(\mathbf{x}, \boldsymbol{\Omega}) = \int d^3r \rho_N(\mathbf{r}) w_{1\pm}^{N\Delta}(\mathbf{x} - \mathbf{r}, \boldsymbol{\Omega}), \quad (8)$$

$$n_2^N(\mathbf{x}, \boldsymbol{\Omega}) = \int d^3r \rho_N(\mathbf{r}, \boldsymbol{\Omega}) w_2^N(\mathbf{x} - \mathbf{r}, \boldsymbol{\Omega}). \quad (9)$$

Note that orientation-dependent *sphere* densities are built via (6) and (7).

Following Rosenfeld’s dimensional analysis [7,8,28], and in accordance with the scaled-particle theory for mixtures of non-spherical particles [29], the (reduced) free energy density is found to be $\Phi = \Phi_S + \Phi_{SN} + \Phi_{SNN} + \Delta\Phi$, where Φ_S is the hard sphere term [28], Φ_{SN} is the contribution in the case of infinitely thin needles [11], and Φ_{SNN} is the correction in the Onsager limit [12] with $LD/\sigma^2 \ll 1$; these terms are given explicitly in Eqs. (11), (12), and (17) of Ref. [12], respectively. The new contribution is

$$\Delta\Phi = \frac{n_1^{SN} n_2^N + n_{1+}^{N\Delta} n_{2-}^{SN\Delta} + n_{1-}^{N\Delta} n_{2+}^{SN\Delta}}{1 - n_3^S}, \quad (10)$$

where $n_3(\mathbf{r}) = \Theta(R - |\mathbf{r}|) * \rho_S(\mathbf{r})$ is the usual local packing fraction for spheres. This completes the prescription of the functional.

The corresponding fundamental measures, $\xi_{\alpha}^i = \int d^3r \int d^2\Omega w_{\alpha}^i / (4\pi)$, are

$$\xi_1^{SN} = R, \quad \xi_{2\pm}^{SN\Delta} = 2\pi R^2, \quad \xi_{1\pm}^{N\Delta} = D/2, \quad \xi_2^N = \pi LD, \quad (11)$$

equal to the integral mean curvature of the sphere, surface of a hemisphere of radius R , radius of a hemispherical endcap of the rod, and residual (for small D/L) rod surface, respectively.

The exact second virial coefficient between sphere and rod is

$$B_2^{SN} = \pi R^2 \left(L + \frac{4R}{3} \right) + \pi DR(L + 2R) + \pi D^2 \left(\frac{L}{4} + R \right) + \frac{\pi D^3}{6}, \quad (12)$$

where the theory of Ref. [12] obtains the first term (independent of D), and the present contribution recovers also the next term, linear in D .

Expanding (10) for small density leads to second (leading) order $\Delta\phi = n_1^{SN} n_2^N + n_{1+}^{N\Delta} n_{2-}^{SN\Delta} + n_{1-}^{N\Delta} n_{2+}^{SN\Delta} = \rho_S \rho_N (\xi_1^{SN} \xi_2^N + \xi_{1+}^{N\Delta} \xi_{2-}^{SN\Delta} + \xi_{1-}^{N\Delta} \xi_{2+}^{SN\Delta}) = \rho_S \rho_N \pi (LDR + 2DR^2)$. Hence, the additional contribution to the second virial coefficient is $B_2^{SN\Delta} = \Delta\phi / (\rho_S \rho_N) = \pi (LDR + 2DR^2)$, indeed equal to the second term of the exact result, given in (12).

In the following we demonstrate the relation to the sphere-rod Mayer bond f_{SN} being -1 if both particles overlap and zero otherwise. We split $f_{SN} = f_{SN}^{(D=0)} + \Delta f_{SN}$, where $f_{SN}^{(D=0)}$ is the Mayer bond for vanishingly thin needles, which can be deconvolved into one-body weight functions, see appendix A 1 of [12] (where this contribution is denoted by f_{SN}). We express the correction, valid for small D/L , as

$$\begin{aligned} -\Delta f_{SN}(\mathbf{r}, \boldsymbol{\Omega}) &= \frac{D}{2} (\Theta(|\mathbf{r} \cdot \boldsymbol{\Omega}| - L/2) \delta(|\mathbf{r} - (\mathbf{r} \cdot \boldsymbol{\Omega})\boldsymbol{\Omega}| - R) \\ &\quad + \delta(|\mathbf{r} + L\boldsymbol{\Omega}/2| - R) \Theta(-\mathbf{r} \cdot \boldsymbol{\Omega} - L/2) \\ &\quad + \delta(|\mathbf{r} - L\boldsymbol{\Omega}/2| - R) \Theta(\mathbf{r} \cdot \boldsymbol{\Omega} - L/2)), \end{aligned} \quad (13)$$

where \mathbf{r} is the difference vector between particle centers and $\boldsymbol{\Omega}$ is the rod orientation. Note that $D\delta(x)/2 = \Theta(D/4 - |x - D/4|)$ for $D \rightarrow 0$. Using the weight functions, (2)–(5), this can be expressed as

$$-\Delta f_{SN} = w_1^{SN} * w_2^N + w_{1+}^{N\Delta} * w_{2-}^{SN\Delta} + w_{1-}^{N\Delta} * w_{2+}^{SN\Delta}, \quad (14)$$

where $*$ denotes the spatial convolution.

We next chose a specific coordinate system, and demonstrate the validity of Eq. (14). We first consider the first term on the right-hand side of Eq. (14) and take the needle orientation $\mathbf{\Omega}$ to be parallel to the z axis and both needle and sphere to lie within the y - z plane, i.e., $\mathbf{\Omega} = (0, \bar{\varphi})$, $\mathbf{r} = (r, \vartheta, 0)$. Then,

$$w_1^{SN} * w_2^N = \frac{D}{2} \int_0^\pi \int_0^{2\pi} \delta(R \cos \vartheta') \int_{-L/2}^{L/2} \delta \left(\begin{array}{c} -R \sin \vartheta' \sin \varphi' \\ r \sin \vartheta - R \sin \vartheta' \cos \varphi' \\ r \cos \vartheta - R \cos \vartheta' + l \end{array} \right) dl R^2 \sin \vartheta' d\varphi' d\vartheta' \quad (15)$$

$$= \frac{D}{2} \int_0^{2\pi} \int_{-L/2}^{L/2} \delta \left(\begin{array}{c} -R \sin \varphi' \\ r \sin \vartheta - R \cos \varphi' \\ r \cos \vartheta + l \end{array} \right) dl R d\varphi' \quad (16)$$

$$= \frac{D}{2} \Theta \left(\frac{L}{2} - |r \cos \vartheta| \right) \int_0^{2\pi} \delta(R \sin \varphi') \delta(r \sin \vartheta - R \cos \varphi') R d\varphi' \quad (17)$$

$$= \frac{D}{2} \Theta \left(\frac{L}{2} - |r \cos \vartheta| \right) \delta(r \sin \vartheta - R), \quad (18)$$

which recovers the first line of Eq. (13).

We next consider the term $w_{1+}^{N\Delta} * w_{2-}^{SN\Delta}$ in Eq. (14); the calculation of $w_{1-}^{N\Delta} * w_{2+}^{SN\Delta}$ can be performed analogously and is skipped here. We write the convolution in its most general form, i.e. using absolute coordinates,

$$\int w_{1+}^{N\Delta}(\mathbf{r} - \mathbf{r}', \mathbf{\Omega}) w_{2-}^{SN\Delta}(\mathbf{r}'' - \mathbf{r}') d^3 r' \quad (19)$$

$$= \int \frac{D}{2} \delta \left(\mathbf{r} - \mathbf{r}' + \frac{\mathbf{\Omega} L}{2} \right) \delta(R - |\mathbf{r}'' - \mathbf{r}'|) \Theta(-\mathbf{\Omega} \cdot (\mathbf{r}'' - \mathbf{r}')) d^3 r'. \quad (20)$$

Then we place everything in the x - y plane, $\vartheta = \bar{\vartheta} = \vartheta' = \pi/2$; the sphere shall sit on the negative x axis: $\varphi'' = -\pi/2$. Using the remaining translational symmetry, we put the tip of the needle in the origin: $r = L/2$, $\varphi = \pi + \bar{\varphi}$. To summarize, we have: $\mathbf{r} = (L/2, \pi/2, \pi + \bar{\varphi})$, $\mathbf{r}' = (r', \vartheta', \varphi')$, $\mathbf{r}'' = (r'', \pi/2, -\pi/2)$, $\mathbf{\Omega} = (\pi/2, \bar{\varphi})$. Using these coordinates, we can transform Eq. (20) and obtain:

$$w_{1+}^{N\Delta} * w_{2-}^{SN\Delta} = \frac{D}{2} \int_0^\infty \int_0^{2\pi} \int_0^\pi \delta(r' \sin \vartheta' \sin \varphi') \times \delta(r' \sin \vartheta' \cos \varphi') \delta(r' \cos \vartheta') \times \delta(R - \sqrt{r''^2 + r'^2 + 2r'r'' \sin \vartheta' \sin \varphi'}) \times \Theta(r'' \sin \bar{\varphi} + r' \sin \vartheta' \sin \varphi' \sin \bar{\varphi} + r' \sin \vartheta' \cos \varphi' \cos \bar{\varphi}) r'^2 \sin \vartheta' d\vartheta' d\varphi' dr' \quad (21)$$

$$= \frac{D}{2} \int_0^\infty \int_0^{2\pi} \delta(r' \sin \varphi') \delta(r' \cos \varphi') \times \delta(R - \sqrt{r''^2 + r'^2 + 2r'r'' \sin \varphi'}) \Theta(r'' \sin \bar{\varphi} + r' \sin \varphi' \sin \bar{\varphi} + r' \cos \varphi' \cos \bar{\varphi}) r' d\varphi' dr' \quad (22)$$

$$= \frac{D}{2} \sum_{\pm} \int_0^\infty \delta(r') \delta(R - \sqrt{r''^2 + r'^2}) \Theta(r'' \sin \bar{\varphi} \pm r' \cos \bar{\varphi}) dr' \quad (23)$$

$$= \frac{D}{2} \delta(R - r'') \Theta(r'' \sin \bar{\varphi}) \quad (24)$$

which recovers the second line of Eq. (13).

We turn to a brief investigation of the prediction of the DFT for the bulk free energy. There the contribution of (10) to the free energy per volume is obtained by setting $\rho_i = \text{constant}$, and hence $n_i^\alpha = \xi_i^\alpha \rho_i$. With the sphere packing fraction $\eta = \pi \rho_s \sigma^3 / 6$, the resulting excess free energy is

$$\frac{\beta F_{\text{exc}}}{V} = \phi_{\text{hs}}(\eta) - \rho_N \ln(1 - \eta) + \frac{\pi L^2 D}{4} \frac{\rho_N^2}{1 - \eta} + \frac{3}{2} \left(\frac{L}{2R} + \frac{LD}{2R^2} + \frac{D}{R} \right) \frac{\rho_N \eta}{1 - \eta}, \quad (25)$$

where ϕ_{hs} is equal to the Percus–Yevick compressibility (scaled-particle) result for pure hard spheres, V is the system volume, and the second and third term inside the parentheses is the contribution due to (10).

In conclusion, we have extended the DFT of Refs. [11] and [12] to include effects of nonvanishing rod thickness. To that end, we have introduced two qualitatively new weight functions into the geometric framework. Our theory accounts for excluded volume effects caused by finite rod aspect ratios, D/L . We emphasize, however, that although we treat the statistical weight associated with finite D , the present theory will not resolve features of density variation on length scales comparable to D . We also have only dealt with contributions of the order of $1/(1-n_3^S)$ to the excess free energy. Rosenfeld's prescription [7,8] also involves terms proportional to $1/(1-n_3^S)^2$, which we have not treated here. Whether the weight functions introduced in the present work can be used to modify these terms is an interesting problem, that we leave for future research.

The proposed theory should lead to rich bulk phase behavior as one has, besides demixing into fluid phases with different chemical composition of species, also the possibility of nematic ordering of rods. In turn this clearly leads to a rich variety of interesting interfacial situations. It would also be interesting to see how the present theory performs against other theoretical approaches or computer simulations. From the practical point of view, the present functional causes only

a moderate increase of computational complexity as the new weighted densities are built with spatial convolutions only (the angular convolution of Ref. [12] is more involved).

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