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**Density functional theory of hard colloidal particles:
From bulk to interfaces**

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Abstract

In this work about *density functional theory of hard colloidal particles*, spheres, spherocylinders, and dumbbells are investigated in the bulk and at interfaces. Therefore, the theoretical framework of density functional theory (DFT) and fundamental measure theory (FMT) is introduced first. Then, FMT functionals are applied to hard-sphere systems to obtain free energies and density distributions for the (fcc) crystal and the fluid phase. The free energies are in good agreement with Monte Carlo (MC) simulation results, which is also reflected in the density distributions around single lattice sites. From the studied variants of FMT only the White Bear mark II (WBII) functional shows qualitatively correct behavior, which implies that only the WBII functional is a promising candidate for further studies of problems involving crystallization.

Accordingly, accurate values for the anisotropic hard-sphere crystal-fluid surface tensions and stiffnesses have been predicted by using the WBII approach in combination with MC simulations. Quantitative agreement between FMT and simulations is found, where FMT predicts a tension of $0.66 k_B T / \sigma^2$ with a small anisotropy of about $0.025 k_B T$. The corresponding stiffnesses are determined with e.g. $0.53 k_B T / \sigma^2$ for the (001) orientation and $1.03 k_B T / \sigma^2$ for the (111) orientation of the interface, where $k_B T$ is the thermal energy and σ is the diameter of the hard spheres. However, the anisotropy in the tension is crucial for the transformation to stiffnesses, which differ up to a factor of 4. Moreover, the results from theory and simulation are compared with existing experimental findings and classical nucleation theory is discussed in the context of analyzing experimental results.

In another sense, FMT has also been applied to non-spherical particles. For this purpose, the recently developed extended deconvolution FMT (edFMT) has been applied to systems of orientationally resolved spherocylinders and dumbbells. The spherocylinders are assumed to constitute a fluid phase with the possibility of orientational ordering and are subjected to an in-plane aligning field which rotates with a frequency ω_0 . Consequently, the system is investigated by using dynamical DFT, an extension of DFT to non-equilibrium, time-dependent situations. The setup causes a complex orientational response of the colloidal liquid crystal with five different dynamical states which are characterized by towing, breathing, splitting, overtaking, and unsplit overtaking, as ω_0 increases.

Applied to hard dumbbells, inhomogeneous fluids are analyzed in a slit and under gravity. The edFMT features a free parameter ζ , which has to be nonzero, to obtain a stable nematic phase even for very elongated particles. Adjusting it has been shown to lead to unrealistically large values for ζ , presumably because the theory is not valid for non-convex particles like dumbbells. However, the theory with $\zeta = 0$ gives excellent results when compared to MC simulations for not too large packing fractions.

Finally, the highly localized density peaks in a crystal cause critical numerical behavior where local packing fractions exceed meaningful values which leads to a divergence of the FMT functional. For this reason, numerical methods are outlined in the appendix of this work to avoid such problems and to ensure the convergence of solutions.