Supplemental Material for: Hyperdensity Functional Theory of Soft Matter

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I. NEURAL CLUSTER HYPERDENSITY FUNCTIONAL FOR HARD SPHERES

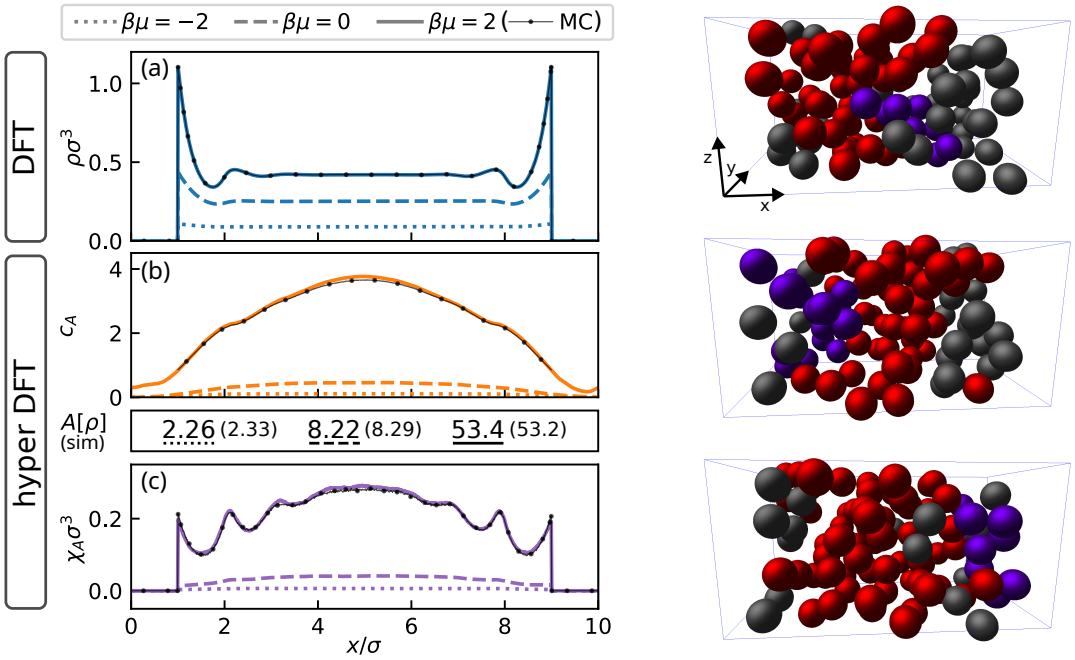

FIG. S1. Hyperdensity functional results for the cluster statistics of three-dimensional hard spheres. The order parameter $\hat{A}$ is chosen as the number of particles in the largest cluster. The system is under planar confinement between two hard walls with separation distance 8σ. Theoretical results are shown for three different values of the scaled chemical potential: $\beta\mu = -2$ (dotted), 0 (dashed), and 2 (solid lines); reference simulation data is given for the latter case $\beta\mu = 2$ (symbols). (a) Shown are neural density functional results for the scaled density profile $\rho(x)\sigma^3$ as a function of the scaled distance x/σ across the slit. The results are obtained from numerical solution of the Euler-Lagrange equation of classical density functional theory, using the neural hard sphere one-body correlation functional $c_1(x,[\rho])$ of Ref. [2] as input. (b) Corresponding hyperdirect correlation functions $c_A(x)$ are obtained from evaluating the trained neural hyperdirect correlation functional $c_A(x,[\rho])$ at the three respective density profiles. Functional integration according to $A[\rho] = \int \mathcal{D}[\rho] c_A(x,[\rho])$ [see Eq. (10) in the main text] gives theoretical predictions for the mean value A of the size of the largest cluster, as compared to the simulation reference $A = \langle \hat{A} \rangle$ (values in parenthesis). (c) Theoretical results for hyperfluctuation profiles $\chi_A(x)$ are obtained from solving the hyperdirect Ornstein-Zernike relation [Eq. (7) in the main text] for the three considered situations using as input $\rho(x)$ and the neural functionals $c_A(x,[\rho])$ and $c_2(x,x',[\rho]) = \delta c_1(x,[\rho])/\delta\rho(x')$. The simulation reference for $\chi_A(x)$ is obtained from sampling the covariance $\chi_A(x) = \mathrm{cov}(\hat{\rho}(x), \hat{A})$ [see Eq. (3) in the main text]. The three simulation snapshots (right column) depict typical confined hard sphere configurations for $\beta\mu = 2$. The highlighted particles belong to the largest cluster (bright red) or to the second-largest cluster (dark violet). The number $\hat{A}$ of particles in the largest cluster fluctuates considerably over microstates.

We demonstrate the applicability of the neural hyperdensity functional theory to more realistic fluid models than the one-dimensional systems considered in the main text. We address the mean cluster statistics of three-dimensional hard spheres based on neural functional methods. The observable $\hat{A}$ is the number of particles in the largest cluster, as described in the main text. We restrict ourselves to planar geometry and consider systems that are periodic in the two lateral directions with overall simulation box size $10\sigma \times 5\sigma \times 5\sigma$ [1]. This geometric reduction extends to all considered quantities and equations, including the hyper-Ornstein-Zernike equation [Eq. (7) in the main text]. The supervised training of $c_A(x,[\rho])$ is based on 428 simulation runs under randomized conditions both of the scaled

chemical potential $\beta\mu \in [-5, 10]$ and the form of the external potential $V_{\rm ext}(x)$ [1, 2]. As a representative test case not encountered during training, we consider confinement between two hard walls with separation distance 8σ. As shown in Fig. S1 the hyperdensity functional theory yields results with near-simulation precision.

II. ONE-BODY AND TWO-BODY OBSERVABLES

We address observables $\hat{A}(\mathbf{r}^N)$ of simple one- and two-body form that reduce the hyperdensity functional approach to standard density functional settings. We first consider cases where the observable $\hat{A}(\mathbf{r}^N)$ is of one-body form

$$\hat{A}(\mathbf{r}^N) = \sum_i a_1(\mathbf{r}_i), \tag{S1}$$

where $a_1(\mathbf{r})$ is a given function of position $\mathbf{r}$. Using the one-body density operator $\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$, we can rewrite Eq. (S1) as $\hat{A}(\mathbf{r}^N) = \int d\mathbf{r}\hat{\rho}(\mathbf{r})a_1(\mathbf{r})$. Building the equilibrium average thereof yields the thermal mean A as a density functional

$$A[\rho] = \int d\mathbf{r}\rho(\mathbf{r})a_1(\mathbf{r}). \tag{S2}$$

The corresponding hyperdirect correlation functional $c_A(\mathbf{r}, [\rho])$ follows from $c_A(\mathbf{r}, [\rho]) = \delta A[\rho]/\delta\rho(\mathbf{r})$ [Eq. (9) in the main text] as

$$c_A(\mathbf{r}, [\rho]) = a_1(\mathbf{r}). \tag{S3}$$

The associated hyperfluctuation profile $\chi_A(\mathbf{r})$ follows from the covariance form $\chi_A(\mathbf{r}) = \mathrm{cov}(\hat{\rho}(\mathbf{r}), \hat{A})$ [Eq. (3) in the main text] as

$$\chi_A(\mathbf{r}) = \int d\mathbf{r}' a_1(\mathbf{r}')\mathrm{cov}(\hat{\rho}(\mathbf{r}), \hat{\rho}(\mathbf{r}')) = \int d\mathbf{r}' a_1(\mathbf{r}')H_2(\mathbf{r}, \mathbf{r}'), \tag{S4}$$

where $H_2(\mathbf{r}, \mathbf{r}') = \mathrm{cov}(\hat{\rho}(\mathbf{r}), \hat{\rho}(\mathbf{r}'))$ is the standard density-density correlation function [3, 4]. Inserting Eqs. (S3) and (S4) into the hyper-Ornstein-Zernike equation $c_A(\mathbf{r}, [\rho]) = \chi_A(\mathbf{r})/\rho(\mathbf{r}) - \int d\mathbf{r}' c_2(\mathbf{r}, \mathbf{r}', [\rho])\chi_A(\mathbf{r}')$ [Eq. (7) in the main text] yields the specific one-body form of the hyper-Ornstein-Zernike equation

$$\int d\mathbf{r}'' a_1(\mathbf{r}'')\Big[\rho(\mathbf{r})\int d\mathbf{r}' c_2(\mathbf{r}, \mathbf{r}')H_2(\mathbf{r}', \mathbf{r}'') + \rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}'') - H_2(\mathbf{r}, \mathbf{r}'')\Big] = 0. \tag{S5}$$

The identity (S5) is straightforward to prove directly as the term in brackets already vanishes due to the standard inhomogeneous two-body Ornstein-Zernike equation [3, 5] $H_2(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + \rho(\mathbf{r})\int d\mathbf{r}'' c_2(\mathbf{r}, \mathbf{r}'')H_2(\mathbf{r}'', \mathbf{r}')$.

In alternative reasoning, Eq. (S5) holds for any permissible form of $a_1(\mathbf{r})$. Hence a valid identity is retained upon functionally differentiating Eq. (S5) with respect to $a_1(\mathbf{r})$ or, analogously, treating $a_1(\mathbf{r})$ as a mere test function. Both routes give the standard inhomogeneous two-body Ornstein-Zernike relation starting from the hyper-Ornstein-Zernike relation (S5), which serves as a consistency check.

For the specific choice $\hat{A} = N$, i.e. $a_1(\mathbf{r}) = 1$ in Eq. (S1), the hyperfunctional framework relates back to the local compressibility $\chi_\mu(\mathbf{r}) = \beta\chi_A(\mathbf{r})$, which is a prominently featured fluctuation profile [6, 7, 9–12]. Turning to the density functional dependence, the hyperdirect correlation functional becomes constant unity, $c_A(\mathbf{r}, [\rho]) = 1$, in accordance with Eq. (S3). As a consequence the hyper-Ornstein-Zernike equation [Eq. (7) in the main text] reduces upon multiplication by $\rho(\mathbf{r})$ to $\rho(\mathbf{r})\int d\mathbf{r}' c_2(\mathbf{r}, \mathbf{r}', [\rho])\chi_\mu(\mathbf{r}') + \beta\rho(\mathbf{r}) = \chi_\mu(\mathbf{r})$, which is the fluctuation Ornstein-Zernike relation [10, 11] for the local compressibility $\chi_\mu(\mathbf{r})$. The functional integral [Eq. (10) in the main text] reduces according to Eq. (S2) to the explicit result $A[\rho] = \int d\mathbf{r}\rho(\mathbf{r})$. Hence the mean number of particles, expressed as the density functional $\bar{N}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})$, is recovered, which certainly is correct due to $\int d\mathbf{r}\rho(\mathbf{r}) = \int d\mathbf{r}\langle\hat{\rho}(\mathbf{r})\rangle = \langle\int d\mathbf{r}\hat{\rho}(\mathbf{r})\rangle = \langle N\rangle = A$.

The reduction of the hyperdensity functional framework to spatial integration of the standard Ornstein-Zernike relation extends to two-body forms of $\hat{A}(\mathbf{r}^N)$ albeit with an increase in complexity. We sketch essentials of the two-body case, where the observable under consideration has the form

$$\hat{A}(\mathbf{r}^N) = \sum_{ij} a_2(\mathbf{r}_i, \mathbf{r}_j), \tag{S6}$$

with the sums over i and j running over all particles and the function $a_2(\mathbf{r}, \mathbf{r}')$ is a given two-body field that depends on positions $\mathbf{r}$ and $\mathbf{r}'$. Using two density operators $\hat{\rho}(\mathbf{r})$ and $\hat{\rho}(\mathbf{r}')$ we can re-write Eq. (S6) as $\hat{A}(\mathbf{r}^N) =$

$\int d\mathbf{r}d\mathbf{r}'\hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}')a_2(\mathbf{r},\mathbf{r}')$. In order to formulate the mean A, we build the thermal average on both sides. Observing that $\langle\hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}')\rangle = H_2(\mathbf{r},\mathbf{r}') + \rho(\mathbf{r})\rho(\mathbf{r}')$ the result is

$$A[\rho] = \int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')a_2(\mathbf{r},\mathbf{r}') + \int d\mathbf{r}d\mathbf{r}'H_2(\mathbf{r},\mathbf{r}')a_2(\mathbf{r},\mathbf{r}'), \tag{S7}$$

where the first term on the right hand side is already an explicit density functional. Expressing the second term also as a density functional requires to have access to $H_2(\mathbf{r},\mathbf{r}',[\rho])$ as a density functional, which is nontrivial. Conventionally one would base this functional dependence on solving the inhomogeneous two-body Ornstein-Zernike equation for the specific situation at hand and having access to $c_2(\mathbf{r},\mathbf{r}',[\rho]) = -\delta^2\beta F_{\mathrm{exc}}[\rho]/[\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')]$ as a density functional (see, e.g., Ref. [13] and references therein), thus providing a link to the standard theory of inhomogeneous liquids.

III. RELATIONSHIP TO HYPERFORCE CORRELATIONS

Besides its present role in the hyperdensity functional approach, the hyperfluctuation profile $\chi_A(\mathbf{r})$ features prominently in the recently formulated exact hyperforce sum rule [14]

$$-\nabla\chi_A(\mathbf{r}) - \chi_A(\mathbf{r})\nabla\beta V_{\mathrm{ext}}(\mathbf{r}) + \mathrm{cov}(\hat{A}(\mathbf{r}^N), \beta\hat{\mathbf{F}}_{\mathrm{int}}(\mathbf{r})) + \Big\langle\sum_i \delta(\mathbf{r}-\mathbf{r}_i)\nabla_i\hat{A}(\mathbf{r}^N)\Big\rangle = 0, \tag{S8}$$

where $\hat{\mathbf{F}}_{\mathrm{int}}(\mathbf{r}) = -\sum_i \delta(\mathbf{r}-\mathbf{r}_i)\nabla_i u(\mathbf{r}^N)$ is the one-body interparticle force density operator and $\hat{A}(\mathbf{r}^N)$ can have general many-body dependence on the coordinates $\mathbf{r}^N$. The form (S8) is straightforwardly obtained from starting with $\langle\hat{A}\beta\hat{\mathbf{F}}(\mathbf{r})\rangle + \langle\sum_i \delta(\mathbf{r}-\mathbf{r}_i)\nabla_i\hat{A}(\mathbf{r}^N)\rangle = 0$ [14] and substracting the vanishing contribution $\langle\beta\hat{\mathbf{F}}(\mathbf{r})\rangle\langle\hat{A}\rangle = 0$, which is zero due to $\langle\hat{\mathbf{F}}(\mathbf{r})\rangle = 0$, hence allowing to convert the correlation expression (mean of the product) into covariance form. Then expressing $\hat{\mathbf{F}}(\mathbf{r})$ via its three constituent kinetic, external, and interparticle contributions, $\hat{\mathbf{F}}(\mathbf{r}) = \nabla\cdot\hat{\boldsymbol{\tau}}(\mathbf{r}) - \hat{\rho}(\mathbf{r})\nabla V_{\mathrm{ext}}(\mathbf{r}) + \hat{\mathbf{F}}_{\mathrm{int}}(\mathbf{r})$, where the kinetic stress phase space function is $\hat{\boldsymbol{\tau}}(\mathbf{r}) = -\sum_i \delta(\mathbf{r}-\mathbf{r}_i)\mathbf{p}_i\mathbf{p}_i/m$, yields Eq. (S8). The sum rule (S8) is derived on the basis of the standard ensemble [14] and hence all averages correspond to the original Hamiltonian H. Nevertheless, the hyperfluctuation profile $\chi_A(\mathbf{r})$ emerges naturally in the derivation based on the thermal invariance against phase space shifting [14].

For one-body observables (S1) we can find a simple link to Eq. (S8). We address the last term on the right hand side thereof as $\langle\sum_i \delta(\mathbf{r}-\mathbf{r}_i)\nabla_i\hat{A}(\mathbf{r}^N)\rangle = \langle\sum_i \delta(\mathbf{r}-\mathbf{r}_i)\nabla_i a_1(\mathbf{r}_i)\rangle = \rho(\mathbf{r})\nabla a_1(\mathbf{r}) = \rho(\mathbf{r})\nabla c_A(\mathbf{r})$, where in the first step we have started from $\hat{A}(\mathbf{r}^N) = \sum_i a_1(\mathbf{r}_i)$, which gives $\nabla_i\hat{A}(\mathbf{r}^N) = \nabla_i a(\mathbf{r}_i)$, and then have identified the specific form $c_A(\mathbf{r}) = a_1(\mathbf{r})$ according to Eq. (S3). Hence for one-body forms (S1) we have shown that $\langle\sum_i \delta(\mathbf{r}-\mathbf{r}_i)\nabla_i\hat{A}(\mathbf{r}^N)\rangle = \rho(\mathbf{r})\nabla c_A(\mathbf{r},[\rho])$, which is a simple limiting case for the behaviour of $c_A(\mathbf{r},[\rho])$.

A specific example for a one-body observable $\hat{A}$ could be a simple model of a static countoscope [15], where $a_1(\mathbf{r}) = \Theta(l-|\mathbf{r}|)$ is an indicator function for the countoscope of diameter $2l$; here $\Theta(\cdot)$ indicates the Heaviside unit step function. Alternatively, one could use a version with planar symmetry, $a_1(\mathbf{r}) = \Theta(l-|x|)$, where x is a Cartesian coordinate of $\mathbf{r}$.

Two-body observables $\hat{A}$ of the form (S6) arise naturally in systems governed by pairwise interparticle interactions, where the interparticle potential energy can be written as $u(\mathbf{r}^N) = \sum_{ij,i\neq j}\phi(|\mathbf{r}_i-\mathbf{r}_j|)/2$; see Ref. [13] for the formulation of classical density functional theory from the force point of view, which is based on expressing the local force density $\langle\hat{\mathbf{F}}_{\mathrm{int}}(\mathbf{r})\rangle$ as a two-body observable when only pair interparticle interactions are present in the system.

In general, the hyperdensity functional theory allows the treatment of both many-body observables $\hat{A}$ and many-body interparticle interaction potentials $u(\mathbf{r}^N)$. The simple cases laid out here can act as a reference for making future analytical progress in these directions.

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