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Density-functional theory for fluids in porous media

Matthias Schmidt
Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf, Universitatsstraße 1, 40225 Düsseldorf, Germany

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As models for substances adsorbed within amorphous solid matrices, we consider mixtures of spheres with either hard or ideal interactions where several (matrix) components are quenched and the remaining (adsorbate) components are equilibrated. We propose a density-functional theory, based on the exact zero-dimensional limit, which treats both matrix and adsorbate components on the level of the respective one-body density profiles. As a test, we calculate pair correlation functions for hard spheres adsorbed in either a hard sphere or an ideal sphere matrix, and find good agreement with our computer simulation results.

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I. INTRODUCTION

The behavior of atomic, molecular, and complex fluids, e.g., colloidal suspensions, adsorbed in porous media, is of considerable practical as well as fundamental interest. Disordered substrates that are permeable to a substance are encountered in environmental, biological, and industrial fields. From a fundamental point of view, one is interested how condensed matter phenomena (like phase transitions) are altered by confinement [1] and the presence of disorder [2]. The details of the porous medium are often disregarded and to model such amorphous substances one relies on equilibrium fluid configurations of model systems. The advantages are twofold: (i) The statistics of such model matrices are well studied and understood, e.g., in the case of the hard sphere (HS) systems. (ii) A direct link to the statistical mechanics of equilibrated fluids is provided. The primary tool in the description of adsorbates to such a matrix are quenched-annealed (QA) averages [3,4]. There the adsorbate free energy (rather than the partition sum) is averaged over (many) representations of disorder. Hence the matrix is quenched, while the adsorbate is annealed (allowed to equilibrate) in the presence of the disordered background. Typically, one assumes that there is no back feeding toward the matrix: The porous medium is unaffected by the presence of the adsorbate. Besides computer simulations, theoretical work is mainly based on the replica trick, which relates the QA system to a special limit of a corresponding fully equilibrated extended (replicated) system, which is tackled with integral equation theory and replica Ornstein-Zernike equations [3,4].

Density-functional theory (DFT) [5] is a powerful approach to equilibrium (fully annealed) fluids [6] and solids [7]. It models the influence of an external potential energy $V^{\rm ext}$ acting on the system. Commonly, DFT is applied to well defined, idealized pores (see e.g., Ref. [8]). In principle, a disordered matrix may be represented by an appropriate $V^{\rm ext}$ acting on the adsorbate. To treat amorphous pore structures within this approach requires solution (minimization of the grand potential) for a given $V^{\rm ext}$, and subsequent explicit averaging "by hand" over many realizations of $V^{\rm ext}$. This was recently carried out with a mean-field DFT for a lattice fluid model [9], and formidable insight into adsorption, metastability, and hysteresis was gained. However, the principle approach seems to be limited to simple models and is cumbersome, if not inapplicable, in the case of more sophisticated DFTs and continuum models.

In this work, we argue that a more general DFT is feasible, where the matrix is described on the level of the (one-body) density distribution of its constituent particles, and where the functional *is* the average free energy (averaged over matrix realizations), depending on matrix and adsorbate density profiles. We expect this to be very powerful, as matrix details (of single representations) are disregarded, and only relevant statistical properties enter. Here, we present explicit approximations for (a restricted set of) common adsorbate-matrix models. Our approach is an extension of a theory for fully annealed mixtures [6], which is considered to be "for multicomponent HS fluids, the most accurate and successful approximate functional" [8]. The theory captures local packing effects, and correlation functions are predicted in a nonperturbative fashion, without need of external input. We demonstrate the good accuracy of the approach by comparing calculated pair distribution functions to computer simulation data.

II. MODELS

To model adsorbates in porous media, we restrict ourselves to mixtures with spherical symmetric pair interactions, where each species i consists of spheres with radii R_i. Two kinds of pair interactions $V_{ij}(r)$ between species i and j as a function of the separation distance r are considered: (i) ideal interactions such that $V_{ij}(r)=0$ for all distances r; ii) hard core interactions such that $V_{ij}(r)=V_{\rm HC}(r)=\infty$, if $r<R_i+R_j$, and zero otherwise. This covers additive hard sphere mixtures, mixtures of hard and ideal spheres like realized in the Asakura-Oosawa (AO) colloid-ideal polymer model [10], as well as the Widom-Rowlison (WR) model [11], where only particles of unlike species experience hard core repulsion. We further discriminate between quenched ($i\equiv 0a$) and annealed ($i\equiv 1b$) species, where i is a composite index, such that the first digit 0,1 correspond to quenched and annealed species, respectively, and a,b are integers that label the different (sub)species.

Below we will consider two simple binary mixtures of one quenched (index 0) and one annealed (index 1) component. The first case is constituted by hard spheres in a hard sphere matrix, where all interactions are hard core, V_{ij}

$=V_{\mathrm{HC}}$, for $i,j=0,1$. In the second case we treat the hard sphere adsorbate in an ideal sphere matrix, where $V_{00}=0, V_{01}=V_{\mathrm{HC}}, V_{11}=V_{\mathrm{HC}}$. (This is formally equivalent to an AO model where the polymer species is quenched and colloids are annealed.) In both of these binary cases the interactions between matrix and adsorbate are hard core interactions.

III. THEORY

A. Zero-dimensional limit

Let us start by considering a situation of extreme confinement, where all particles are forced to sit on top of each other, a situation which allows for an exact solution of the many-body problem. Although the detailed shape of the confining external potential V^{ext} will not affect the excess free energy, for clarity we explicitly choose $V^{\mathrm{ext}}(r)=0$ if $r<\epsilon$, and ∞ otherwise. This corresponds to a hard cavity of (i dependent) radius $R_i+\epsilon$. Hence each particle's center is allowed to move inside a sphere of volume $4\pi\epsilon^3/3$. In the limit $\epsilon\to 0$, a zero-dimensional ($0d$) situation is encountered, and it is assured that all particles present in the cavity overlap.

In the following, we first give a detailed derivation of the $0d$ free energy for two simple QA models. Then, in Sec. III A 3, we proceed to the case of general mixtures, where an arbitrary number of components is treated. Readers primarily interested in the hard sphere examples (and subsequent results) may wish to skip Sec. III A 3.

1. Hard spheres in a hard sphere matrix

In order to illustrate the general procedure, we start with an example where both calculations and notation are simple. We consider a binary system of hard spheres, where species 0 is quenched (hence represents the matrix), and species 1 is annealed (hence represents the adsorbate). The first step is to calculate the grand partition sum Ξ_0 for the matrix particles in the $0d$ situation. This problem is equivalent to calculating the grand partition sum for pure hard spheres in $0d$ [12,13]. To obtain Ξ_0 we need to consider all states that are allowed (are compatible with the hard core exclusion). Those are (i) the empty state, and (ii) the state with exactly one hard sphere. Hence one obtains

$$\Xi_0=1+z_0, \tag{1}$$

where the (scaled) fugacity is $z_i=\exp(\beta\mu_i)(4\pi\epsilon^3/3)\Lambda_i^{-3}$, and $\beta=1/k_BT$, where k_B is the Boltzmann constant and T being the absolute temperature, and Λ_i is the (irrelevant) thermal wavelength of species $i=0,1$. The first (second) term on the right hand side of Eq. (1) corresponds to case i (ii) above. The grand potential is then given as $\Omega_0=-k_BT\ln\Xi_0$, and the mean particle number $\bar{\eta}_0$ can be obtained using the thermodynamic relation $\bar{\eta}_0=z_0\partial\ln\Xi_0/\partial z_0$. The Helmholtz free energy is obtained by Legendre transform as $\beta A_0^{\mathrm{tot}}(\bar{\eta}_0)=\beta\Omega_0+\bar{\eta}_0\ln(z_0)$. Its excess (over ideal gas) part is $\beta A_0=\beta A_0^{\mathrm{tot}}-\bar{\eta}_0[\ln(\bar{\eta}_0)-1]$. Carrying out the calculations yields

$$\beta A_0(\bar{\eta}_0)=(1-\bar{\eta}_0)\ln(1-\bar{\eta}_0)+\bar{\eta}_0, \tag{2}$$

the result for (fully annealed) hard spheres [12,13]

To obtain the $0d$ excess free energy of the annealed component A_1 we proceed in a similar fashion than above, but with the important distinction of using QA averages instead of fully annealed ones. We consider each matrix configuration as being fixed (in effect exerting an external potential on the adsorbate), and sum over all allowed adsorbate states with the correct statistical weight in the grand ensemble of the adsorbate. As in $0d$ the matrix has only two configurations (either the cavity is empty or a single matrix particle is present), this is an easy task and yields

$$\Xi_1=\begin{cases}1+z_1 & \text{no matrix particle}\\ 1 & \text{else.}\end{cases} \tag{3}$$

The case of no matrix particles is the sum of the contributions from the state empty of adsorbate particles and the state with a single adsorbate particle. [This is again similar to the structure of Ξ_0, Eq. (1).] In the case of one single matrix particle the matrix-adsorbate hard core repulsion prohibits all states except precisely that one where no adsorbate particles are present. Clearly, all terms proportional to higher than linear powers in z_1 vanish due to the hard core repulsion between adsorbate particles.

To obtain the QA free energy we need to average the logarithm of Ξ_1 over all matrix configurations. As $\ln 1=0$, only the first line in Eq. (3) contributes, and its statistical weight in the grand ensemble of matrix configurations is $1/\Xi_0$ (the factor unity stems from the fact that matrix particles are absent). Hence the $0d$ grand potential for the adsorbate Ω_1 is simply given by

$$-\beta\Omega_1=\frac{\ln(1+z_1)}{1+z_0}. \tag{4}$$

To obtain the corresponding $0d$ excess free energy A_1, essentially the same steps as those above in the case A_0 are required: The average particle number of adsorbates is given as $\eta_1=-\partial\beta\Omega_1/\partial z_1$, and the Helmholtz free energy is obtained as $\beta A_1^{\mathrm{tot}}=\beta\Omega_1+\bar{\eta}_1\ln(z_1)$. Its excess part is obtained by subtracting the (adsorbate) ideal gas contribution, $\beta A_1=\beta A_1^{\mathrm{tot}}-\bar{\eta}_1[\ln(\bar{\eta}_1)-1]$. As final result, we find

$$\beta A_1(\bar{\eta}_0,\bar{\eta}_1)=(1-\bar{\eta}_0-\bar{\eta}_1)\ln(1-\bar{\eta}_0-\bar{\eta}_1)+\bar{\eta}_1-(1-\bar{\eta}_0)\ln(1-\bar{\eta}_0). \tag{5}$$

As an aside it is interesting to note that in the present case the sum A_0+A_1 equals the $0d$ excess free energy of binary annealed hard spheres. However, this constitutes a special case. In general, we do not find a simple relation between the QA and the corresponding fully annealed free energies. (The relation to the *replicated* fully annealed system is discussed below in Sec. III A 4.)

2. Hard spheres in an ideal sphere matrix

If the matrix particles are noninteracting, their grand partition sum is that of an ideal gas

$$\Xi_0 = \exp(z_0), \tag{6}$$

where we use the same notation as in the preceding subsection. Carrying out the same steps as above yields the (expected) result that the $0d$ excess free energy vanishes,

$$A_0(\bar{\eta}_0) = 0. \tag{7}$$

The grand partition sum for the matrix is equal to the above result, Eq. (3), in the case of the hard sphere matrix. In order to obtain the $0d$ QA grand potential for the adsorbate, Ω_1, we again have to average the logarithm of the adsorbate partition sum over all matrix configurations. This yields

$$-\beta\Omega_1 = \frac{\ln(1+z_1)}{\exp(z_0)}, \tag{8}$$

from which the adsorbate free energy is obtained as

$$\beta A_1(\bar{\eta}_0, \bar{\eta}_1) = [\exp(-\bar{\eta}_0) - \bar{\eta}_1]\ln[\exp(-\bar{\eta}_0) - \bar{\eta}_1] + \bar{\eta}_1 + \bar{\eta}_0 \exp(-\bar{\eta}_0). \tag{9}$$

Note that in the fully annealed case, the present model is equal to the AO model where species 0 (1) is identified as polymer (colloid), where the (exact) $0d$ free energy is $\beta A_{\mathrm{AO}}(\bar{\eta}_0, \bar{\eta}_1) = (1-\bar{\eta}_1-\bar{\eta}_0)\ln(1-\bar{\eta}_1)+\bar{\eta}_1$ [14,15], clearly different from the above QA result.

3. Multicomponent mixtures

Here we give a formal derivation for general mixtures with more than two components. Let N_i particles of type i be in the cavity, and $\{N_i\}$ denote the set of occupation numbers. Irrespective of the precise particle coordinates, the (reduced) potential energy due to interactions between like particles of type i is $U(N_i) = (N_i/2)(N_i-1)\beta V_{ii}(r=0)$. The contribution from interactions between unlike particles (of types i and j) is $U(N_i, N_j) = N_i N_j \beta V_{ij}(r=0)$. The total potential energy may be expressed as $U(\{N_i\}) = \Sigma_i U(N_i) + \Sigma_{i<j} U(N_i, N_j)$, where the summations run over all species. Due to the nature of interactions, $U(\{N_i\})$ takes on values $0,\infty$. Let us further decompose the occupation numbers into (disjunct) subsets of quenched and annealed species, $\{N_{0a}\} \cup \{N_{1b}\} = \{N_i\}$. The potential energy may be arranged similarly, such that $U(\{N_i\}) = U_{00}(\{N_{0a}\}) + U_{01}(\{N_{0a}\},\{N_{1b}\}) + U_{11}(\{N_{1b}\})$, where U_{00} stems from matrix-matrix, interactions U_{01} from matrix-adsorbate interactions, and U_{11} from adsorbate-adsorbate interactions.

The grand partition sum for the matrix in the $0d$ situation is

$$\Xi_0 = \sum_{\{N_{0a}\}} \left[\prod_a \frac{(z_{0a})^{N_{0a}}}{N_{0a}!} \right] \mathrm{e}^{-U_{00}(\{N_{0a}\})}, \tag{10}$$

where (for $i=0a$) the reduced fugacity is $z_i = \exp(\beta\mu_i) 4\pi\epsilon^3/(3\Lambda_i^3)$, μ_i is the chemical potential, and Λ_i is the thermal wavelength of species i; notation is such (for $t=0$) that $\Sigma_{\{N_{ta}\}} \equiv \Sigma_{N_{t1}=0}^{\infty} \Sigma_{N_{t2}=0}^{\infty} \dots$, and the product runs over all quenched species a. The grand potential is $\Omega_0 = -k_B T \ln \Xi_0$. In the context of fully equilibrated systems, it was demonstrated that imposing the exact crossover on an approximate functional may be exploited to derive systematically DFTs for systems including hard spheres [7], the AO model [14], and the WR mixture [16]. Here we add adsorbate particles. For a given matrix realization $\{N_{0a}\}$, the matrix particles are inert, and act as an external potential on the adsorbate. Its grand partition sum is

$$\Xi_1(\{N_{0a}\}) = \sum_{\{N_{1b}\}} \left[\prod_b \frac{(z_{1b})^{N_{1b}}}{N_{1b}!} \right] \times \mathrm{e}^{-U_{11}(\{N_{1b}\})} \mathrm{e}^{-U_{01}(\{N_{0a}\},\{N_{1b}\})}. \tag{11}$$

To obtain the QA adsorbate grand potential Ω_1, we need to average over all matrix realizations as

$$-\beta\Omega_1 = \frac{1}{\Xi_0} \sum_{\{N_{0a}\}} \left[\prod_a \frac{(z_{0a})^{N_{0a}}}{N_{0a}!} \right] \times \mathrm{e}^{-U_{00}(\{N_{0a}\})} \ln \Xi_1(\{N_{0a}\}). \tag{12}$$

From Ω_0 and Ω_1, standard relations yield the mean numbers of particles $\bar{\eta}_{0a}$, $\bar{\eta}_{1b}$ through $\bar{\eta}_{tc} = -z_{tc}\partial\beta\Omega_t/\partial z_{tc}$ (for $tc = 0a, 1b$). The Helmholtz free energy is obtained via Legendre transform as $\beta A_t^{\mathrm{tot}} = \beta\Omega_t - \Sigma_c \mu_{tc} \partial\beta\Omega_t/\partial\mu_{tc} \equiv \beta\Omega_t + \Sigma_c \ln(z_{tc})\bar{\eta}_{tc}$. Its excess (over ideal gas) part is $\beta A_t = \beta A_t^{\mathrm{tot}} - \Sigma_c \bar{\eta}_{tc}[\ln(\bar{\eta}_{tc})-1]$. Explicit dependence on the natural variables is $A_0(\{\bar{\eta}_{0a}\})$, and $A_1(\{\bar{\eta}_{0a}\},\{\bar{\eta}_{1b}\})$.

4. Relation to the replica trick

Before proceeding with the construction of the DFT, let us elucidate the relation of the present analysis to the replica trick. Using the replica trick one starts from a fully equilibrated system, in which the adsorbate species are replicated s times. The replicas do not interact among each other (their interactions are ideal), but interact with the matrix particles in the same fashion. Such replicated models still fall into our class of models (provided the QA system aimed at does), hence the above formalism (for A_0) may be applied, and the $0d$ excess free energy, A_2, of the replicated system obtained. The $0d$ QA free energy is obtainable in the limit $\beta A_1 = \lim_{s\to 0}[\partial \exp(-\beta A_2)/\partial s]\exp(\beta A_2)$. One can show that $A_2 = A_0(\{\bar{\eta}_{0a}\}) + s A_1(\{\bar{\eta}_{0a}\},\{\bar{\eta}_{1b}\})$ for small s (where the absence of replica symmetry breaking is assumed).

B. Density-functional theory

1. Geometry-based free energy functional

Returning to three dimensions, we apply well-tried geometrical recipes to derive approximate DFTs [6,7,14,16]. The formalism requires as input the $0d$ excess free energy A of the model under consideration, and hence can be applied to either the pure matrix, where $A=A_0$, to the adsorbate, $A=A_1$, or even to the replicated system, $A=A_2$. Within the framework, the excess Helmholtz free energy is expressed as

$$F^{\mathrm{exc}}[\{\rho_i(\mathbf{r})\}]=k_{\mathrm{B}}T\int d^3x\,\Phi(\{n_\alpha^{(i)}(\mathbf{x})\}), \tag{13}$$

where $\{\rho_i(\mathbf{r})\}$ is the set of all density profiles. The reduced free energy density Φ is a function of a set of weighted densities $\{n_\alpha^{(i)}(\mathbf{x})\}$, where i labels the species and α the type of weighted density. The weighted densities are obtained by convolutions with the actual density profiles, $n_\alpha^{(i)}(\mathbf{x})=\int d^3r\rho_i(\mathbf{r})w_\alpha^{(i)}(\mathbf{x}-\mathbf{r})$. As all nonvanishing interactions are hard core, it is sufficient to take the usual fundamental measure weight functions [6,7], which recover (upon convolution) the Mayer bonds $\exp(-\beta V_{\mathrm{HC}}(r))-1$. They are defined as

$$w_3^{(i)}(\mathbf{r})=\theta(R_i-r),w_2^{(i)}(\mathbf{r})=\delta(R_i-r), \tag{14}$$

$$\mathbf{w}_{\mathrm{v}2}^{(i)}(\mathbf{r})=w_2^{(i)}(\mathbf{r})\mathbf{r}/r,\hat{\mathbf{w}}_{\mathrm{m}2}^{(i)}(\mathbf{r})=w_2^{(i)}(\mathbf{r})\left[\frac{\mathbf{r}\mathbf{r}}{r^2}-1/3\right], \tag{15}$$

where $r=|\mathbf{r}|$, $\theta(r)$ is the Heaviside step function, $\delta(r)$ is the Dirac distribution, and 1 is the identity matrix. Further, linearly dependent, weights are $w_1^{(i)}(\mathbf{r})=w_2^{(i)}(\mathbf{r})/(4\pi R_i)$, $\mathbf{w}_{\mathrm{v}1}^{(i)}(\mathbf{r})=\mathbf{w}_{\mathrm{v}2}^{(i)}(\mathbf{r})/(4\pi R_i),w_0^{(i)}(\mathbf{r})=w_1^{(i)}(\mathbf{r})/R_i$. The weight functions $w_\alpha^{(i)}$ have dimension of length$^{3-\alpha}$. They differ in their tensorial rank: $w_0^{(i)},w_1^{(i)},w_2^{(i)},w_3^{(i)}$ are scalars; $\mathbf{w}_{\mathrm{v}1}^{(i)},\mathbf{w}_{\mathrm{v}2}^{(i)}$ are vectors; $\hat{\mathbf{w}}_{\mathrm{m}2}^{(i)}$ is a matrix; the subscript letters identify the rank.

We determine the functional dependence of Φ on the weighted densities by imposing the exact crossover to $0d$, where $\rho_i(\mathbf{r})=\overline{\eta_i}\delta(\mathbf{r})$, and follow recent treatments of fundamental measure theory [7] by considering multi-cavity limits to obtain $\Phi=\Phi_1+\Phi_2+\Phi_3$, with contributions

$$\Phi_1=n_0^{(i)}\varphi_i(\{n_3^{(l)}\}), \tag{16}$$

$$\Phi_2=(n_1^{(i)}n_2^{(j)}-\mathbf{n}_{\mathrm{v}1}^{(i)}\cdot\mathbf{n}_{\mathrm{v}2}^{(j)})\varphi_{ij}(\{n_3^{(l)}\}), \tag{17}$$

$$\Phi_3=\frac{1}{8\pi}\Bigg(n_2^{(i)}n_2^{(j)}n_2^{(k)}/3-n_2^{(i)}\mathbf{n}_{\mathrm{v}2}^{(j)}\cdot\mathbf{n}_{\mathrm{v}2}^{(k)}+\frac{3}{2}[\mathbf{n}_{\mathrm{v}2}^{(i)}\hat{\mathbf{n}}_{\mathrm{m}2}^{(j)}\mathbf{n}_{\mathrm{v}2}^{(k)}-\mathrm{tr}(\hat{\mathbf{n}}_{\mathrm{m}2}^{(i)}\hat{\mathbf{n}}_{\mathrm{m}2}^{(j)}\hat{\mathbf{n}}_{\mathrm{m}2}^{(k)})]\Bigg)\varphi_{ijk}(\{n_3^{(l)}\}), \tag{18}$$

where repeated-index summation convention is used, and mth order derivatives of the $0d$ excess free energy are $\varphi_{i\,\ldots\,k}(\{\overline{\eta_l}\})\equiv\ \partial^m\beta A_t(\{\overline{\eta_l}\})/\partial\overline{\eta_i}\ldots\partial\overline{\eta_k}$. For $t=0,1,2$, functionals F_t^{exc} for matrix, adsorbate, and replicated system are obtained, respectively. Two routes to the QA free energy functional are possible: either directly through A_1, giving F_1^{exc}, or via application of the replica trick to F_2^{exc}. The results from the two routes can be shown to be equal, which is a sign of internal consistency of the current approach.

2. Minimization principle

In order to apply the theory to an actual problem, the principal way is as follows. We first need to obtain the matrix density profiles from minimization (with respect to all matrix density fields $\rho_{0a}(\mathbf{x})$) of the grand potential functional

$$\begin{aligned}\tilde{\Omega}_0[\{\rho_{0a}(\mathbf{x})\}]={}&F_0^{\mathrm{exc}}[\{\rho_{0a}(\mathbf{x})\}]+k_BT\int d^3x\sum_a\ \rho_{0a}(\mathbf{x})\\&\times[\ln(\rho_{0a}(\mathbf{x})\Lambda_{0a}^3)-1]\\&+\int d^3x\sum_a\ (V_{0a}^{\mathrm{ext}}(\mathbf{x})-\mu_{0a})\rho_{0a}(\mathbf{x}),\end{aligned} \tag{19}$$

where V_{0a}^{ext} is an external potential acting on $0a$, generating matrix inhomogeneities. At the minimum

$$\frac{\delta\tilde{\Omega}_0}{\delta\rho_{0a}(\mathbf{r})}=0. \tag{20}$$

Once the ρ_{0a} are known, the adsorbate densities are obtained from minimization [only with respect to the adsorbate density distributions $\rho_{1b}(\mathbf{x})$] of the grand potential

$$\begin{aligned}&\tilde{\Omega}_1[\{\rho_{0a}(\mathbf{x})\};\{\rho_{1b}(\mathbf{x})\}]\\&\quad=F_1^{\mathrm{exc}}[\{\rho_{0a}(\mathbf{x})\};\{\rho_{1b}(\mathbf{x})\}]+k_BT\int d^3x\sum_b\ \rho_{1b}(\mathbf{x})\\&\qquad\times[\ln(\rho_{1b}(\mathbf{x})\Lambda_{1b}^3)-1]+\int d^3x\sum_b\ (V_{1b}^{\mathrm{ext}}(\mathbf{x})\\&\qquad-\mu_{1b})\rho_{1b}(\mathbf{x}),\end{aligned} \tag{21}$$

where V_{1b}^{ext} acts on adsorbate $1b$, and the $\rho_{0a}(\mathbf{x})$ are treated as *fixed input quantities*. Again, at the minimum

$$\frac{\delta\Omega_1}{\delta\rho_{1b}(\mathbf{r})}=0. \tag{22}$$

Note that the (bulk) Gibbs adsorption equation is intrinsically fulfilled: $(\rho_{1b}-\rho_{1b}^{\mathrm{free}})\mathcal{V}=-\partial[\tilde{\Omega}_1-\tilde{\Omega}_1(\{\rho_{0a}\equiv0\})]/\partial\mu_{1b}$, where $\mathcal{V}$ is the system volume, and $\rho_{1b}^{\mathrm{free}}$ is the density in equilibrium without matrix.

IV. RESULTS

A. Structural correlations

As an application, we consider the structural correlations of hard spheres adsorbed in sphere matrices. We consider the two types of matrices summarized in Sec. II, where the matrix is either a hard sphere fluid, or a fluid of noninteracting (hence freely overlapping) spheres.

Madden and Glandt [3] derived a set of replica Ornstein-Zernike (ROZ) equations for one quenched (index 0) and one annealed (index 1) species, given as

$$h_{00}=c_{00}+c_{00}\otimes\rho_0h_{00}, \tag{23}$$

$$h_{01}=c_{01}+c_{01}\otimes\rho_0 h_{00}+c_{11}\otimes\rho_1 h_{01}, \tag{24}$$

$$h_{11}=c_{11}+c_{01}\otimes\rho_0 h_{01}+c_{11}\otimes\rho_1 h_{11}, \tag{25}$$

where $\otimes$ denotes the spatial convolution, $h_{ij}=g_{ij}-1$ are the total correlation functions, g_{ij} are the partial pair correlation functions, and c_{ij} are the direct correlation functions. Given and Stell [4] have shown that Eqs. (23)–(25) are approximations; the exact ROZ equations contain contributions from nonvanishing direct correlation functions between different replicas.

In liquid integral equation theories, Eqs. (23)–(25) are supplemented by (approximate) closures, and the resulting set of equations is solved numerically, see e.g., Ref. [17,18]. Here we proceed in a different fashion, and *derive* the direct correlation functions c_{ij} from our density functional. Then we use Eqs. (23)–(25) to obtain the h_{ij} and hence the $g_{ij}(r)$, which will be compared to computer simulation data below. This procedure constitutes a demanding test for the present theory, as the $c_{ij}(r)$ are obtained by second functional derivatives as

$$c_{00}(|\mathbf{r}-\mathbf{r}'|)=\left.\frac{\delta^2 F_0^{\mathrm{exc}}[\rho_0]}{\delta\rho_0(\mathbf{r})\,\delta\rho_0(\mathbf{r}')}\right|_{\rho_0=\mathrm{const}}, \tag{26}$$

$$c_{01}(|\mathbf{r}-\mathbf{r}'|)=\left.\frac{\delta^2 F_1^{\mathrm{exc}}[\rho_0;\rho_1]}{\delta\rho_0(\mathbf{r})\,\delta\rho_1(\mathbf{r}')}\right|_{\rho_0,\rho_1=\mathrm{const}}, \tag{27}$$

$$c_{11}(|\mathbf{r}-\mathbf{r}'|)=\left.\frac{\delta^2 F_1^{\mathrm{exc}}[\rho_0;\rho_1]}{\delta\rho_1(\mathbf{r})\,\delta\rho_1(\mathbf{r}')}\right|_{\rho_0,\rho_1=\mathrm{const}}. \tag{28}$$

Clearly, as the approximation is done on the level of F_t^{exc}, any inaccuracies will be enhanced by taking two derivatives to obtain the c_{ij}. We find that the approximate ROZ equations, Eqs. (23)–(25), are sufficient within the present approximations, i.e., the direct correlation functions between species from different replicas vanish identically.

In order to compare the DFT results, we have carried out Monte Carlo (MC) computer simulations with 1024 particles, and 2×10^6 MC moves per particles. Averages were taken over 20 different representations of the matrix, which we find to be sufficient to obtain reliable data.

We first turn to the case of hard spheres in a hard sphere matrix. For simplicity, we consider the case of equal sphere sizes $\sigma_0=\sigma_1(=\sigma)$, and equal packing fractions $\eta_0=\eta_1=0.15$. (The total packing fraction is hence $\eta_0+\eta_1=0.3$, a moderately large value.) To obtain the matrix pair correlation function $g_{00}(r)$, we need to solve Eq. (23), which is completely decoupled from Eqs. (24) and (25) containing also adsorbate distribution functions. Hence as input only c_{00} is required. We obtain it from Eq. (26), where F_0^{exc} is the density functional obtained from applying the procedure outlined in Sec. III B 1 to the HS $0d$ excess free energy for hard spheres, A_0, which is given in Eq. (2). F_0^{exc} derived in this way is equal to Rosenfeld's functional [6] in Tarazona's tensorial formulation [7]. This reproduces the direct correlation function for pure hard spheres in the Percus-Yevick approximation [6,7]. For $\eta_0=0.15$ this is known to be very accurate, as can be seen in Fig. 1(a), where we plot $g_{00}(r)$ along with the corresponding result from computer simulation. Both curves practically lie on top of each other.

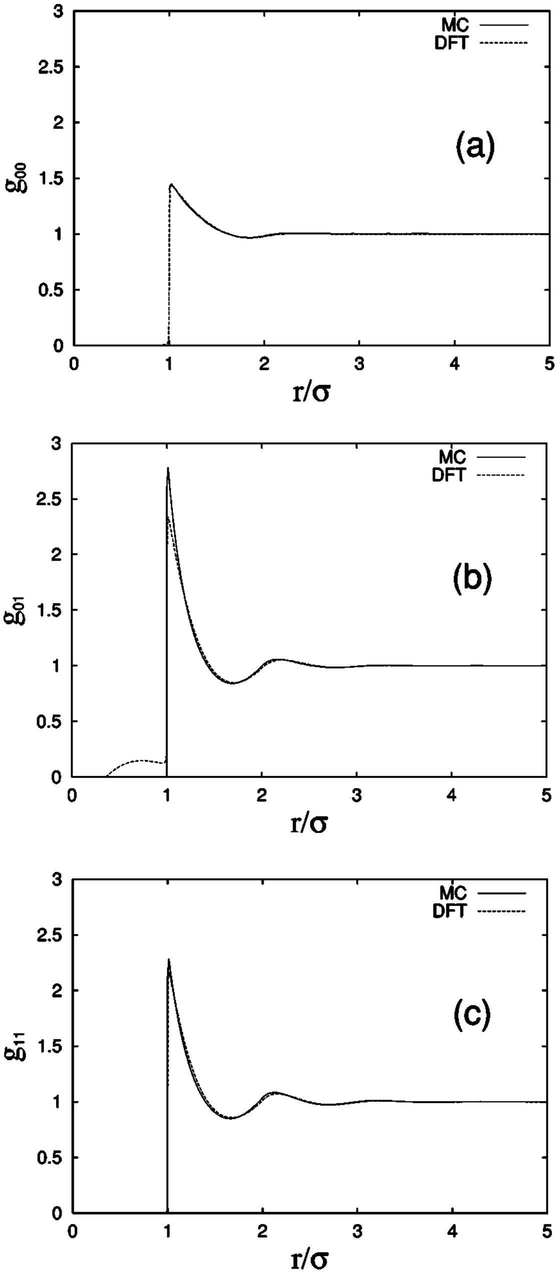

FIG. 1. Partial pair distribution functions $g_{ij}(r)$ as a function of the scaled distance r/σ for hard spheres of diameter σ and packing fraction $\eta_1=0.15$ adsorbed in a hard sphere matrix with the same diameter σ and packing fraction $\eta_0=0.15$. Solid lines denote Monte Carlo results, dashed lines denote DFT results. Different cases are shown: (a) g_{00} matrix-matrix pair correlations; (b) g_{01} matrix-adsorbate pair correlations; (c) g_{11} adsorbate-adsorbate pair correlations.

In order to obtain the partial pair correlation functions involving the adsorbate species, $g_{01}(r)$ and $g_{11}(r)$, we solve Eqs. (24) and (25), where the direct correlation functions c_{01} and c_{11} are obtained through Eqs. (27) and (28), with F_1^{exc} obtained from the prescription in Sec. III B 1 applied to the

$0d$ free energy of hard spheres in a hard sphere matrix, A_1, given in Eq. (5). We display $g_{01}(r)$ and $g_{11}(r)$ in Figs. 1(b), 1(c), respectively. Both functions display considerably stronger oscillations than g_{00}. For g_{01} the agreement with MC data is very good for $r/\sigma \gtrsim 1.1$. In the immediate vicinity of contact, $r/\sigma \lesssim 1.1$, and at contact, $r \rightarrow \sigma^+$, the DFT result underestimates the simulation result. Inside the core region, $r/\sigma < 1$, due to the overlap restriction, $g_{ij}(r)=0$ is an exact condition. Our theory fails to reproduce this and yields nonzero values [the extreme value being $g_{01}(r=0)=-0.46$]. This deficiency is known from other geometry-based density functionals for fully annealed systems [14,15], and could be remedied with a test-particle limit calculation, i.e., minimizing the density profiles (see Sec. III B 2) in the presence of an external potential V^{ext} that describes a particle fixed at the origin. We expect such results to also improve the behavior for $r/\sigma \lesssim 1.1$, albeit at the expense of more numerical work. Note further that the core condition is fulfilled in the low density (virial) expansion, i.e., we recover the correct limiting behavior $g_{ij} \rightarrow \exp[-\beta V_{ij}(r)]$. Finally, $g_{11}(r)$, displayed in Fig. 1(c), fares again better. The DFT result is very good even near contact, and the violation of the core condition is smaller $[g_{11}(r=0)=-0.09]$.

To exemplify that the good quality of the DFT result is not accidental, we change the matrix properties by switching off the interactions between matrix particles. Hence the matrix is constituted by freely overlapping spheres that are homogeneously distributed. Clearly, such configurations act differently on the adsorbate than in the previous case of the hard sphere matrix. Again we restrict ourselves to $\sigma_0=\sigma_1$ $(=\sigma)$, and consider slightly higher packing fractions $\eta_0 = \eta_1 = 0.2$. In order to calculate the $g_{ij}(r)$, we proceed as in the previous case, but instead of using Eqs. (2) and (5) for the $0d$ free energies A_0 and A_1, we take the appropriate expressions for the current model, given in Eqs. (7) and (9), respectively. DFT and simulation results are displayed in Fig. 2. As the matrix is an ideal gas, $g_{00}(r)=1$ for all distances, and the DFT trivially fulfills this relation, as $F_0^{\mathrm{exc}}=0$. The core condition is again violated [the extreme cases are $g_{01}(r=0)=-0.84, g_{11}(r=0)=-0.96$]. Apart from that, the accuracy of $g_{01}(r)$ and $g_{11}(r)$ is generally quite good and comparable to that found in the previous case. We conclude that the DFT correctly describes the structural correlations of bulk fluid states in homogeneously distributed random matrices.

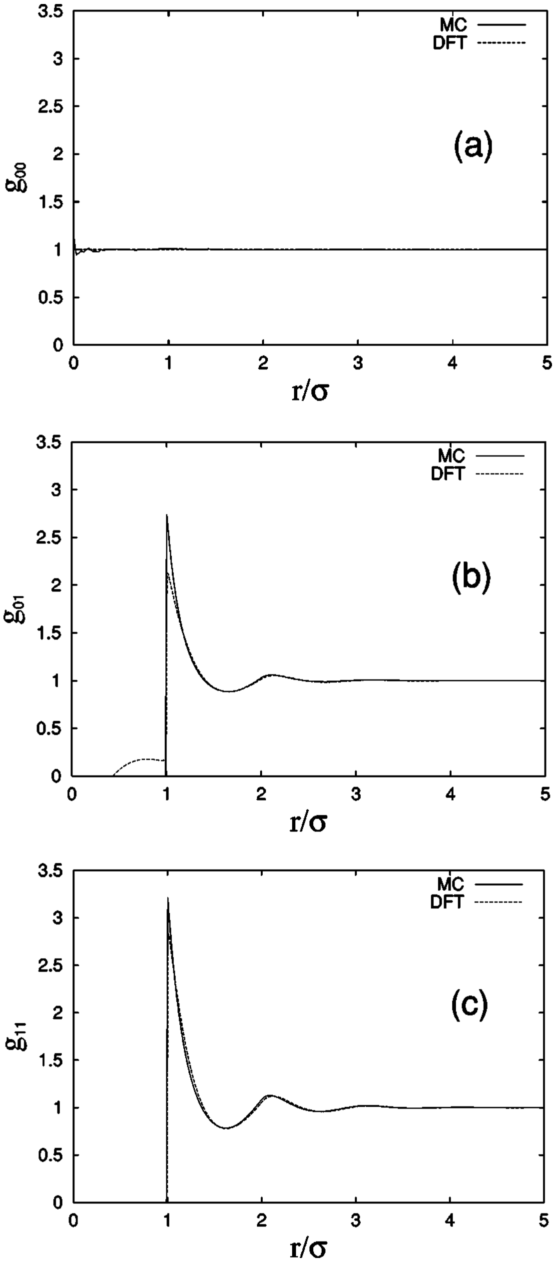

FIG. 2. Same as Fig. 1, but for a matrix of freely overlapping spheres of diameter σ and packing fractions $\eta_0 = \eta_1 = 0.2$.

V. CONCLUSIONS

In summary, we have presented the first DFT, to the best of our knowledge, for QA systems that treats the quenched species (which model a porous material) on the level of their one-body density profiles. This provides an enormous simplification over a treatment where the matrix particles are described by an external potential (which is a highly nontrivial three-dimensional field for a single matrix realization) and averaging over matrix realization has to be done explicitly. We have presented evidence for the potential of our approach, through the investigation of pair correlation functions of hard spheres adsorbed in two different types of matrices, where we find good agreement with computer simulation results. Possible future applications may focus on freezing in porous media; note that the bulk (no matrix) HS transition is described very accurately [7]. Furthermore, the effects caused by inhomogeneous matrices should be interesting. Wetting of (macroscopic) surfaces of the porous material, confinement within slits, pores, or cavities that are filled with porous material, as well as behavior near rough walls would be further interesting applications. Results for fluid demixing will be presented elsewhere [19].

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