# Replica density functional theory: an overview

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## Abstract

An account is given of density functional theory (DFT) for quenched–annealed
fluid mixtures that are used to model fluids adsorbed in random porous
matrices. The theory is based on the replica trick and allows the treatment
of situations where the quenched random matrix as well as the annealed
fluid are inhomogeneous on average. Applications of the framework include
investigation of the adsorption properties of hard spheres and model colloid–
polymer mixtures in bulk matrices and at matrix surfaces, and the influence
of the quenched disorder on phase transitions like fluid demixing, isotropic–
nematic ordering, and freezing. Particularly rich wetting behaviour was found
for colloid–polymer mixtures adsorbed against a porous wall.

## 1. Introduction

The influence of random confinement on the behaviour of many-body systems is of strong
current interest [1, 2]. One strategy to study the behaviour of fluids adsorbed in random
porous matrices relies on modelling porous substances by quenched configurations of model
fluids. The advantage is that the model fluid that represents the matrix can be chosen such
that its properties are well understood and hence a direct link to the statistical mechanics of
equilibrium fluids is provided. The primary tool for the description of adsorbates in such
matrices are quenched–annealed (QA) averages [3, 4]: the annealed average is over all fluid
configurations, and the additional quenched average is over all realizations of the matrix.

The replica method allows for a convenient treatment of the quenched disorder, and a
common approach to studying QA mixtures is using liquid integral equation theory based
on the replica Ornstein–Zernike equations [3, 4] and appropriate closure relations. Although
generalizations to inhomogeneous situations exist [5, 6], this is primarily an approach for the
description of matrices with uniform density distribution and, as a consequence, for fluids that
are uniform upon averaging over the disorder.

A recent alternative theoretical approach is to directly work on the level of the free energy functional, averaged over the disorder. This replica DFT (or quenched–annealed DFT) [7, 8] is a practical and tractable way to treat both uniform systems, as well as a broad range of inhomogeneous situations, either caused by inhomogeneous matrix distributions (like surfaces or gradients in the matrix density) or by external fields (like gravity) acting on the annealed fluid.

Here we summarize the principles of replica DFT, including the structure of the grand potential functionals for matrix and adsorbate and the corresponding minimization principles (section 2). A discussion of previous applications of the framework to various ordering phenomena is presented in section 3. Some concluding remarks are given in section 4.

## 2. Replica density functional theory

We take the equilibrium behaviour of both matrix and adsorbate to be ruled by a respective grand potential functional, that for the matrix being a common equilibrium density functional, that for the adsorbate being the density functional in the external field that the matrix particles exert, averaged over all microscopic realization of the matrix. While the minimization condition for the matrix is the same as that for an equilibrium fluid, that for the adsorbate is different from that in DFT for a fully annealed binary mixture, representing the QA character of the situation. For simplicity, we will take in the following both matrix and adsorbate to be simple pure fluids. The formulation for mixtures as well as the treatment of rotational degrees of freedom involves notational, but no conceptual burdens. An explicit derivation of the replica DFT framework, relying on the replica trick of considering an extended (fully annealed) mixture in the limit of vanishing number of (replicated) components, can be found in [8]. For a way to construct explicit approximations for the excess free energy functional via fundamental measure theory, see [7].

In detail, we consider a matrix of quenched particles (species 0) and allow for inhomogeneous one-body density profiles $\rho_0(\mathbf{r})$, where $\mathbf{r}$ is the space coordinate. The inhomogeneity is generated in response to an external potential, $V_0^{\text{ext}}(\mathbf{r})$, that acts on the matrix particles before the quench. As the matrix configurations are drawn from an equilibrium distribution according to the Hamiltonian of the 0-particles, equilibrium DFT [9, 10] applies: the grand potential functional at chemical potential $\mu_0$, temperature $T$, and volume $V$ is decomposed as

$$\tilde{\Omega}_0([\rho_0], \mu_0, T, V) = F^{\text{id}}[\rho_0] + F_0^{\text{exc}}[\rho_0] + \int d\mathbf{r}\, \rho_0(\mathbf{r})(V_0^{\text{ext}}(\mathbf{r}) - \mu_0), \qquad (1)$$

where the (Helmholtz) free energy of the ideal gas is

$$F^{\text{id}}[\rho_i] = k_B T \int d\mathbf{r}\, \rho_i(\mathbf{r})[\ln(\rho_i(\mathbf{r})\Lambda_i^3) - 1], \qquad (2)$$

with $k_B$ being the Boltzmann constant, and $\Lambda_i$ being the (irrelevant) thermal de Broglie lengthscale of species $i = 0$ or 1 (the latter to be introduced below). The dependence of $F_0^{\text{exc}}[\rho_0]$ and $F^{\text{id}}[\rho_i]$ on $T$ and $V$ is suppressed in the notation. The equilibrium distribution of matrix particles, $\rho_0(\mathbf{r})$, is obtained from solution of

$$\frac{\delta \tilde{\Omega}_0([\rho_0], \mu_0, T, V)}{\delta \rho_0(\mathbf{r})} = 0, \qquad (3)$$

and the grand potential, $\Omega_0(T, V, \mu_0)$, can then be calculated by inserting the equilibrium density profile into the grand potential functional, $\Omega_0(T, V, \mu) = \tilde{\Omega}_0([\rho_0], \mu_0, T, V)$.

We now use $\rho_0(\mathbf{r})$ as obtained from solution of (3) as the (possibly inhomogeneous) density distribution of matrix particles that act as a quenched matrix for the annealed adsorbate fluid (species 1). Application of the replica trick reveals the following structure of the averaged (over all microscopic matrix configurations) grand potential functional for the adsorbate [8],

$$\tilde{\Omega}_1([\rho_0, \rho_1], \mu_1, T, V) = F^{\mathrm{id}}[\rho_1] + F_1^{\mathrm{exc}}[\rho_0, \rho_1] + \int \mathrm{d}\mathbf{r}\, \rho_1(\mathbf{r})(V_1^{\mathrm{ext}}(\mathbf{r}) - \mu_1), \tag{4}$$

where $\rho_1(\mathbf{r})$ is the one-body density distribution, $\mu_1$ is the chemical potential, and $V_1^{\mathrm{ext}}(\mathbf{r})$ is the external potential of species 1. The excess free energy functional $F_1^{\mathrm{exc}}[\rho_0, \rho_1]$ describes the interparticle interactions of adsorbate particles with adsorbate particles and with the matrix particles, and again depends parametrically on $T$ and $V$. The equilibrium distribution of matrix particles is then obtained from the minimization condition

$$\left. \frac{\delta \tilde{\Omega}_1([\rho_0, \rho_1], \mu_1, T, V)}{\delta \rho_1(\mathbf{r})} \right|_{\rho_0(\mathbf{r})} = 0, \tag{5}$$

where $\rho_0(\mathbf{r})$ is a fixed input field, obtained from solution of the minimization condition for the matrix, equation (3). This completes the prescription of the replica (or quenched–annealed) DFT. For practical applications, the excess free energy functionals, $F_0^{\mathrm{exc}}$ and $F_1^{\mathrm{exc}}$, need to be prescribed, usually in an approximate fashion.

It is instructive to compare to the formulation of DFT for a fully annealed binary mixture. In this case the grand potential functional is

$$\tilde{\Omega}_{\mathrm{bin}}([\rho_0, \rho_1], \mu_0, \mu_1, T, V) = F^{\mathrm{id}}[\rho_0] + F^{\mathrm{id}}[\rho_1] + F_{\mathrm{bin}}^{\mathrm{exc}}[\rho_0, \rho_1]$$
$$+ \sum_{i=0,1} \int \mathrm{d}\mathbf{r}\, \rho_i(\mathbf{r})(V_i^{\mathrm{ext}}(\mathbf{r}) - \mu_i), \tag{6}$$

with the minimization conditions

$$\frac{\delta \tilde{\Omega}_{\mathrm{bin}}([\rho_0, \rho_1], \mu_0, \mu_1, T, V)}{\delta \rho_0(\mathbf{r})} = 0 \qquad \text{and} \qquad \frac{\delta \tilde{\Omega}_{\mathrm{bin}}([\rho_0, \rho_1], \mu_0, \mu_1, T, V)}{\delta \rho_1(\mathbf{r})} = 0, \tag{7}$$

and the grand potential for the binary mixture is obtained by inserting the solution of (7) into the grand potential functional, $\Omega_{\mathrm{bin}}(\mu_0, \mu_1, T, V) = \tilde{\Omega}_{\mathrm{bin}}([\rho_0, \rho_1], \mu_0, \mu_1, T, V)$.

Equation (7) represents two *coupled* conditions for the two unknown fields $\rho_0(\mathbf{r})$ and $\rho_1(\mathbf{r})$. This is different from the quenched–annealed case, where the minimization condition for the matrix, equation (3), is decoupled from that for the adsorbate, equation (5). Such a decoupling might be expected on physical grounds as the behaviour of the matrix is not affected by the presence of the adsorbate. Note further that only an ideal gas contribution of species 1, but not species 2, appears in the quenched–annealed grand potential functional, equation (4), albeit including it erroneously does little harm in the light of equation (5).

## 3. Applications

A binary quenched–annealed hard core mixture was considered in one dimension as a model for a fluid adsorbate in narrow channels filled with a random matrix [8]. Two different density functional approaches could be employed to calculate adsorbate bulk properties and interface structure at matrix surfaces. The first approach uses Percus' exact functional [11] for the annealed component and an explicit averaging over matrix configurations; this yields numerically exact results for the bulk partition coefficient and for inhomogeneous density profiles. The second approach is based on the replica DFT whose results were found to approximate very well those of the former over the full range of possible densities.

In order to assess the accuracy of the replica DFT in three dimensions, an inhomogeneous test case was considered: an adsorbate fluid of hard spheres was brought into contact with a semi-infinite porous matrix modelled by immobilized configurations of freely overlapping spheres with a sharp-kink one-body density distribution [12]. Comparison of results from the DFT to those of computer simulations revealed good agreement for the adsorbate density profile across the matrix surface.

In the colloidal domain an excellent example of porous matrices is assemblies of thin rods that are immobilized due to coagulation or sedimentation [13]. The hard sphere fluid was considered in such a random fibre network modelled by quenched, vanishingly thin hard needles. The structure of the hard sphere fluid at the surface of an isotropic fibre network was considered and results from the replica DFT were found to agree well with computer simulation results.

In order to allow for the possibility of fluid–fluid demixing, colloid–polymer mixtures serve as an excellent model system [14]. Hence a model mixture was considered in [15] where colloids and matrix particles are represented by hard spheres and polymers by ideal spheres. Integrating out the degrees of freedom of the polymers leads to a binary colloid–matrix system with effective Asakura–Oosawa–Vrij pair potentials. These effective potentials were treated with an integral equation theory using the (exact) replica Ornstein–Zernike relations and the optimized random phase approximation as a closure relation. DFT results for the structure were obtained from the direct correlation functions obtained through differentiation of the excess free energy. Inverting the replica OZ relations then yields (partial) pair distribution functions. Results from both theories were found to be in good agreement with computer simulation results. The theoretical results for the demixing binodals compare well, provided the polymer-to-colloid size ratio, and hence the effect of many-body interactions neglected in the effective model, is not too large. Consistently, it was found that hard (ideal) matrix–polymer interactions induce capillary condensation (evaporation) of the colloidal liquid phase. The occurrence of capillary condensation was also found with grand ensemble Monte Carlo simulations [16].

Desorption phenomena are especially believed to be strongly influenced by the presence of a planar fluid–fluid (gas–liquid) interface *inside* the porous medium [17]. For the model colloid–polymer mixture density profiles normal to the interface and surface tensions were calculated and compared to the case without matrix [18]. Two kinds of matrix were considered: (i) colloid-sized matrix particles at low packing fractions and (ii) large matrix particles at high packing fractions, as can be experimentally realized [19]. These two cases were found to show fundamentally different behaviour. In case (ii), even at high packing fractions, the main effect of the matrix is to exclude volume and, to high accuracy, the results can be mapped onto those of a bulk system (without matrix) via a simple rescaling.

The influence of interface porosity on the wetting properties of colloid–polymer mixtures at the surface of a quenched hard sphere matrix was investigated [20]. While the porosity hardly changes the location of the transition from partial to complete wetting at colloidal bulk gas–liquid coexistence, the onset of wetting, as signalled by the first discontinuous layering transition, can be efficiently controlled by tailoring the porosity. Furthermore, it was found that the penetrability of the porous interface induces complete drying into the matrix upon approaching capillary coexistence.

The freezing transition presents a formidable challenge for a continuum treatment [21]. Progress has been made by employing a lattice model where the space coordinate is discretized. A two-dimensional lattice model of annealed hard squares that are subject to the influence of randomly placed quenched particles of the same size was considered in [22]. Hence the hard core interactions are such that nearest and next-nearest neighbours on the square lattice

are excluded. The randomly placed particles serve to model a random porous medium. By combining the replica DFT with the lattice fundamental measure theory [23, 24], a theory for quenched–annealed lattice fluids that treats the quenched particles on the level of their one-body density distribution was formulated. This approach was shown to yield thermodynamics that compare well with results from treating matrix realizations explicitly and performing subsequent averaging over the disorder. The freezing transition from a fluid to a columnar phase was found to be continuous and upon increasing matrix density to shift towards close packing, vanishing beyond a threshold matrix density.

A system of annealed hard spherocylinders adsorbed in a matrix of quenched hard spheres was considered in [25]. Theoretical predictions for the partition coefficient, defined as the ratio of density of rods in the matrix to that in a reservoir, were found to agree well with results from Monte Carlo simulations. Theory predicts the isotropic–nematic transition to remain first order upon increasing sphere packing fraction, and to shift towards lower rod densities. This scenario is consistent with the simulation results, that clearly show a jump in the nematic order parameter upon increasing the rod density at constant matrix packing fraction, corresponding to the isotropic–nematic transition, even for sphere matrix packing fractions up to about 0.3.

A further interesting example is that of a soft core fluid [26, 27] in a quenched matrix of soft core particles describing a mobile mixture in a model gel [28], where condensation in bulk and surface phenomena were studied.

## 4. Conclusions

Density functional theory provides a well-established route to investigate the properties of inhomogeneous fluids. Provided that one has access to a reasonable approximation to the excess free energy functional that describes the interparticle interactions, the effects that are caused by an external potential acting on the fluid can be investigated. Any practical application, however, faces significant (computational) problems in cases where the external potential does not possess any simplifying symmetries, like for example those that a smooth planar wall possess. Treating a random external potential (whether constituted by a quenched configurations of a model fluid or described otherwise) is hence already a formidable challenge for discrete lattice models [29, 30]. Answering delicate questions like hysteresis in sorption curves and out-of-equilibrium behaviour requires direct access to an explicit treatment of individual matrix configurations. The replica DFT overviewed in this contribution treats the matrix on the level of the one-body density distribution of the quenched matrix particles rather than directly as an external potential exerted on the fluid by the matrix particles. The benefit is that the density distribution of matrix particles might well possess a simple form, an extreme example being that of a distribution of matrix particles that averages to a constant. Consequently, inhomogeneities matrices, like the planar surfaces of a matrix, can be treated with reasonable effort, revealing rich wetting phenomena.

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