

First-principles derivation of density functional formalism for quenched-annealed systems



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Abstract

We derive from first principles (without resorting to the replica trick) a density functional theory for fluids in quenched disordered matrices (QA-DFT). We show that the disorder-averaged free energy of the fluid is a functional of the average density profile of the fluid as well as the pair correlation of the fluid and matrix particles. For practical reasons it is preferable to use another functional: the disorder-averaged free energy plus the fluid-matrix interaction energy, which, for fixed fluid-matrix interaction potential, is a functional only of the average density profile of the fluid. When the matrix is created as a quenched configuration of another fluid, the functional can be regarded as depending on the density profile of the matrix fluid as well. In this situation, the replica-Ornstein-Zernike equations which do not contain the blocking parts of the correlations can be obtained as functional identities in this formalism, provided the second derivative of this functional is interpreted as the *connected* part of the direct correlation function. The blocking correlations are totally absent from QA-DFT, but nevertheless the thermodynamics can be entirely obtained from the functional. We apply the formalism to obtain the exact functional for an ideal fluid in an arbitrary matrix, and discuss possible approximations for non-ideal fluids.

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I. INTRODUCTION

The phase behaviour of fluids in quenched disordered matrices has been of prior interest in the last decade. The classical theoretical approach to these systems amounts to consider two different sets of state variables: the *annealed* variables (usually the position of the fluid particles), which are allowed to equilibrate, and the *quenched* variables (usually the position of the matrix particles), which have their values fixed. The reason for this distinction is that our system is not in thermal equilibrium with respect to the quenched variables, but it is in equilibrium with respect to the annealed variables for each fixed configuration of the quenched ones. Accordingly, two different statistical averages must be considered: the annealed average, which is the typical ensemble average of equilibrium systems, and the quenched average or average over disorder, which is performed over the quenched variables. For each configuration of the disorder, we can compute the equilibrium thermodynamic magnitudes of the system by means of the corresponding annealed averages. These averages will, of course, depend on the configuration of the quenched variables. However, if the matrix is statistically homogeneous (its statistical features are similar everywhere) and the system is large, we expect little variation between annealed averages corresponding to different matrix configurations. Thus, quenched averages of the annealed averages are meaningful to characterize thermodynamic magnitudes of these systems. Because of this double average, the problem becomes intractable within the classical equilibrium statistical-mechanics tools and new theoretical methods are called for.

Madden and Glandt [1] made an extension of the conventional diagrammatic treatment of liquid-state theory to obtain cluster expansions for the thermodynamics and structure of a fluid in a quenched matrix. They also derived a set of Ornstein-Zernike (OZ) equations relating the total and direct interparticle correlation functions, which can be solved with the appropriate closure relations [2]. Alternatively, Given and Stell [3] used the continuum version of the replica trick [4] to rederive this set of OZ equations and they noted that, although Madden and Glandt's cluster expansions were correct, there were some missing terms in the OZ equations. The corrected set of OZ equations was called the *replica* Ornstein-Zernike (ROZ) equations and, for fluids with quenched-averaged density profile

$\rho_1(\mathbf{x})$ and matrices with one-particle distribution $\rho_0(\mathbf{x})$, is given by

$$h_{00}(\mathbf{x}_1, \mathbf{x}_2) = c_{00}(\mathbf{x}_1, \mathbf{x}_2) + (c_{00}\rho_0 \otimes h_{00})(\mathbf{x}_1, \mathbf{x}_2), \quad (1)$$

$$h_{10}(\mathbf{x}_1, \mathbf{x}_2) = c_{10}(\mathbf{x}_1, \mathbf{x}_2) + (c_{10}\rho_0 \otimes h_{00})(\mathbf{x}_1, \mathbf{x}_2) + (c_c\rho_1 \otimes h_{10})(\mathbf{x}_1, \mathbf{x}_2), \quad (2)$$

$$h_{01}(\mathbf{x}_1, \mathbf{x}_2) = c_{01}(\mathbf{x}_1, \mathbf{x}_2) + (c_{00}\rho_0 \otimes h_{01})(\mathbf{x}_1, \mathbf{x}_2) + (c_{01}\rho_1 \otimes h_c)(\mathbf{x}_1, \mathbf{x}_2), \quad (3)$$

$$h_{11}(\mathbf{x}_1, \mathbf{x}_2) = c_{11}(\mathbf{x}_1, \mathbf{x}_2) + (c_{10}\rho_0 \otimes h_{01})(\mathbf{x}_1, \mathbf{x}_2) + (c_c\rho_1 \otimes h_{11})(\mathbf{x}_1, \mathbf{x}_2) \\ + (c_b\rho_1 \otimes h_c)(\mathbf{x}_1, \mathbf{x}_2), \quad (4)$$

$$h_c(\mathbf{x}_1, \mathbf{x}_2) = c_c(\mathbf{x}_1, \mathbf{x}_2) + (c_c\rho_1 \otimes h_c)(\mathbf{x}_1, \mathbf{x}_2), \quad (5)$$

where $(c\rho \otimes h)(\mathbf{x}_1, \mathbf{x}_2) \equiv \int d\mathbf{x}_3 c(\mathbf{x}_1, \mathbf{x}_3)\rho(\mathbf{x}_3)h(\mathbf{x}_3, \mathbf{x}_2)$, the subscripts 0 and 1 refer to the matrix and fluid, respectively, and

$$h_{11}(\mathbf{x}_1, \mathbf{x}_2) = h_c(\mathbf{x}_1, \mathbf{x}_2) + h_b(\mathbf{x}_1, \mathbf{x}_2), \quad (6)$$

$$c_{11}(\mathbf{x}_1, \mathbf{x}_2) = c_c(\mathbf{x}_1, \mathbf{x}_2) + c_b(\mathbf{x}_1, \mathbf{x}_2), \quad (7)$$

where the subscripts c and b denote the *connected* and *blocking* parts, respectively, of the correlation functions. In terms of the replicated system, the blocking parts, h_b and c_b , are the zero-replica limit of the corresponding correlation functions between two different replicas of the fluid [3]. Clearly $h_{10}(\mathbf{x}_1, \mathbf{x}_2) = h_{01}(\mathbf{x}_2, \mathbf{x}_1)$ and $c_{10}(\mathbf{x}_1, \mathbf{x}_2) = c_{01}(\mathbf{x}_2, \mathbf{x}_1)$ and then it can be shown that Eqs. (2) and (3) are equivalent, so that Eqs. (1), (2), (4) and (5) form an independent set.

Rosinberg et al. [5] used the same replica trick to derive the thermodynamics of these quenched-annealed (QA) systems. There are two important results drawn from this work that concern the present paper: (i) the thermodynamics is completely determined by the connected parts of the correlation functions, and (ii) the connected and blocking parts of h_{11} can be written without any reference to replicas as

$$\rho_1(\mathbf{x}_1)\rho_1(\mathbf{x}_2)h_c(\mathbf{x}_1, \mathbf{x}_2) = \rho_{11}(\mathbf{x}_1, \mathbf{x}_2) - \overline{\rho(\mathbf{x}_1|\{\mathbf{q}_i\})\rho(\mathbf{x}_2|\{\mathbf{q}_i\})}, \quad (8)$$

$$\rho_1(\mathbf{x}_1)\rho_1(\mathbf{x}_2)h_b(\mathbf{x}_1, \mathbf{x}_2) = \overline{\rho(\mathbf{x}_1|\{\mathbf{q}_i\})\rho(\mathbf{x}_2|\{\mathbf{q}_i\})} - \rho_1(\mathbf{x}_1)\rho_1(\mathbf{x}_2), \quad (9)$$

where $\overline{\dots}$ denotes the quenched average, $\rho(\mathbf{x}|\{\mathbf{q}_i\})$ is the equilibrium density profile of the fluid for a particular configuration $\{\mathbf{q}_i\}$ of the disorder, $\rho_1(\mathbf{x}) = \overline{\rho(\mathbf{x}|\{\mathbf{q}_i\})}$, and $\rho_{11}(\mathbf{x}_1, \mathbf{x}_2)$ is the disorder-averaged pair correlation function of the fluid.

The works of Madden and Glandt [1], Given and Stell [3] and Rosinberg et al. [5] established the extension of the classical integral equation theory to fluids in quenched

disordered matrices. Since then, this has been the main method to study QA systems and with its help much insight on the phase behaviour of these systems have been gained. But the replica trick is closely linked to the ROZ equations and so it has the typical limitations of any integral equation theory: it is virtually impossible to apply the theory to non-uniform phases. In the case of fluids without disorder this problem was solved by density functional theories (DFTs), so it seems natural to ask for an extension of DFT to QA systems.

There have been attempts to apply DFT to fluids in random media. For instance, Menon and Dasgupta [6] have constructed a Ramakrishnan-Yussouff density functional, using the same replica trick employed in the derivation of the ROZ equations, to study the effect of pinning in the freezing of superconductor vortex lines. The same approach has been applied to study hard spheres in a quenched random gaussian potential [7]. More recently, Schmidt [8] has proposed a DFT for QA mixtures also based on the replica trick.

In Schmidt's formalism, which we will refer to as replica-DFT (or simply rDFT), the matrix is described by the equilibrium free-energy density functional corresponding to the hamiltonian modelling the matrix particles, while the behaviour of the fluid is ruled by the quenched-averaged grand potential of the QA system $\Omega_{\text{rDFT}}[\rho_1; \rho_0]$, which is written as a functional of the disorder-average density profile of the fluid, $\rho_1(\mathbf{x})$, and of the density profile of the matrix, $\rho_0(\mathbf{q})$ (which enters as a parameter). The QA character becomes explicit in the minimization principle imposed over the quenched-average grand potential, which reads as

$$\frac{\delta \Omega_{\text{rDFT}}[\rho_1; \rho_0]}{\delta \rho_1(\mathbf{x})} = 0, \quad (10)$$

where $\rho_0(\mathbf{q})$ is determined by the equation

$$\frac{\delta F_0[\rho_0]}{\delta \rho_0(\mathbf{q})} = u_0(\mathbf{q}), \quad (11)$$

$F_0[\rho_0]$ being the equilibrium free-energy functional of the pure matrix and $u_0(\mathbf{q}) \equiv \mu_0 - \varphi_0(\mathbf{q})$, with μ_0 the chemical potential of the matrix and $\varphi_0(\mathbf{q})$ the external potential acting over the matrix particles.

From $\Omega_{\text{rDFT}}[\rho_1; \rho_0]$, the free-energy functional can be defined as usual as

$$\Omega_{\text{rDFT}}[\rho_1; \rho_0] = F^{\text{id}}[\rho_1] + F_{\text{rDFT}}^{\text{ex}}[\rho_1; \rho_0] - \int d\mathbf{x} u_1(\mathbf{x}) \rho_1(\mathbf{x}), \quad (12)$$

where $F^{\text{id}}[\rho_1] = kT \int d\mathbf{x} \rho_1(\mathbf{x}) [\ln \mathcal{V}_1 \rho_1(\mathbf{x}) - 1]$ is the ideal contribution (\mathcal{V}_1 being the thermal volume of the fluid particles) and $u_1(\mathbf{x}) \equiv \mu_1 - \varphi_1(\mathbf{x})$, μ_1 being the chemical

potential of the fluid and $\varphi_1(\mathbf{x})$ the external potential on the fluid particles. The excess contribution $F_{\text{rDFT}}^{\text{ex}}[\rho_1; \rho_0]$ describes the interparticle interactions between fluid particles, and that between fluid and matrix particles.

From a practical point of view, the functional $F_{\text{rDFT}}^{\text{ex}}[\rho_1, \rho_0]$ should be approximated. Schmidt’s proposal for $F_{\text{rDFT}}^{\text{ex}}$ is based on fundamental measure theory [9, 10, 11]. This approximation has been applied to study the phase behaviour of colloid-polymer mixtures in bulk random matrices, of rods in quenched sphere matrices, of spheres in random fibre networks, and of soft-core fluids in soft-core matrices [12]. Also, with the lattice version of fundamental measure theory [13], it has been applied to study the freezing transition in a hard-core discrete fluid with different kinds of matrices [14]. Thus, as shown by its applications, rDFT is an important step forward in the study of QA systems.

This notwithstanding, the theory has a number of weak points which should be pointed out. Although the replica trick is a widely-applied method of statistical physics, it makes a few assumptions which are difficult to justify concerning the analytic continuation of the grand potential as a function of the number of replicas, and the replica symmetry or its breaking. Hence an alternative derivation of DFT for QA systems would be desirable. Moreover, contrary to what happens in classical DFT, the formulation of rDFT makes it difficult to derive the set of OZ equations for QA systems from functional relations. As a matter of fact, at present it is not at all clear what the meaning of the second derivatives of $F_{\text{rDFT}}^{\text{ex}}[\rho_1; \rho_0]$ is. These problems are the two main motivations of this paper.

The remaining of the paper is organized as follows. In section 2, we propose a DFT for QA systems based on the convexity properties of the quenched-averaged grand potential. The derivation of the formalism resembles that of classical DFT and makes no use of the replica trick. We will Legendre-transform the grand potential to obtain the quenched-average “intrinsic” free-energy functional, $\mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]$, which depends on the quenched-averaged density profile of the fluid, $\rho_1(\mathbf{x})$, on the pair distribution function of the fluid and matrix particles, $\rho_{10}(\mathbf{x}, \mathbf{q})$, and on the probability distribution of disorder \mathcal{Q} . The dependence on $\rho_{10}(\mathbf{x}, \mathbf{q})$ can be eliminated to obtain a functional only of $\rho_1(\mathbf{x})$ (for fixed fluid-matrix interaction), which will play the same role as the standard free-energy functional in classical DFT, and coincides with Schmidt’s $F_{\text{rDFT}}[\rho_1; \rho_0]$. We will then proceed with one of the most important contributions of this work: the derivation of a set of OZ equations where the direct correlation functionals are identified with second derivatives of this functional. Only equations (1–3) and (5) can be derived within this

DFT approach, but as we will discuss, these form a closed set of equations which involve all the structure information that is relevant to the thermodynamics of the system. Section 2 concludes showing how to derive the thermodynamics within this DFT approach. In section 3, we will make this formalism explicit in the case of an ideal fluid adsorbed in an arbitrary matrix. Conclusions and further discussions are gathered in section 4.

II. QUENCHED-ANNEALED DENSITY FUNCTIONAL THEORY

The system that we aim to describe consists of a fluid inside a porous matrix with which it interacts. The matrix is formed by a distribution of particles quenched at positions \mathbf{q}_i , $i = 1, \dots, M$. The fluid consists of particles, whose positions are denoted \mathbf{x}_i , $i = 1, \dots, N$, and whose interactions are described by the hamiltonian (divided by kT) $\mathcal{H}_N(\mathbf{x}_1, \dots, \mathbf{x}_N)$. These particles are in equilibrium with a thermal bath at chemical potential μ_1 and each of them undergoes the action of an external potential $\varphi_1(\mathbf{x})$. Besides, a fluid particle at position \mathbf{x} interacts with a matrix particle at position \mathbf{q} through the interaction potential $\varphi_{10}(\mathbf{x}, \mathbf{q})$. To all purposes, the total external potential acting on a fluid particle at position \mathbf{x} is

$$V_{\text{ext}}(\mathbf{x}) = \varphi_1(\mathbf{x}) + \sum_{i=1}^M \varphi_{10}(\mathbf{x}, \mathbf{q}_i).$$

The grand partition function for this system will be ($\beta = 1/kT$)

$$\begin{aligned} \Xi[u_1, u_{10}|\{\mathbf{q}_i\}] = & 1 + \sum_{N=1}^{\infty} \frac{1}{\mathcal{V}_1^N N!} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \exp \left\{ -\mathcal{H}_N(\mathbf{x}_1, \dots, \mathbf{x}_N) \right. \\ & \left. + \beta \sum_{i=1}^N \left[u_1(\mathbf{x}_i) + \sum_{j=1}^M u_{10}(\mathbf{x}_i, \mathbf{q}_j) \right] \right\}, \end{aligned} \quad (13)$$

which is a functional of $u_1(\mathbf{x}) \equiv \mu_1 - \varphi_1(\mathbf{x})$ and $u_{10}(\mathbf{x}, \mathbf{q}) \equiv -\varphi_{10}(\mathbf{x}, \mathbf{q})$, and also depends on the set $\{\mathbf{q}_i\}$. Accordingly, the grand potential will be

$$\Omega[u_1, u_{10}|\{\mathbf{q}_i\}] = -kT \ln \Xi[u_1, u_{10}|\{\mathbf{q}_i\}]. \quad (14)$$

Now we need a model for the porous matrix. The simplest model is to assume that matrix particles are placed at random positions, according to a probability density [1]. Thus the grand potential is a random variable. The hypothesis we make now is that the grand potential per unit volume, in the thermodynamic limit, is a self-averaging random variable; therefore we can obtain its value in this limit by simply averaging over

disorder (matrix particle positions). Hence the grand potential for the system in the thermodynamic limit is obtained as

$$\Omega[u_1, u_{10}; \mathcal{Q}] \equiv \overline{\Omega[u_1, u_{10} | \{\mathbf{q}_i\}]}, \quad (15)$$

where $\mathcal{Q}(\{\mathbf{q}_i\})$ is the probability density of the matrix positions, and $\overline{\cdots}$ denotes a \mathcal{Q} -average. This puts the quenched average into play.

A. Concavity of the grand potential

It is convenient to introduce the state functions

$$\hat{\rho}_N(\mathbf{x}) \equiv \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{x}_i), \quad \hat{\rho}_M^0(\mathbf{q}) \equiv \sum_{i=1}^M \delta(\mathbf{q} - \mathbf{q}_i). \quad (16)$$

In terms of them

$$\begin{aligned} \Xi[u_1, u_{10} | \{\mathbf{q}_i\}] &= 1 + \sum_{N=1}^{\infty} \frac{1}{\mathcal{V}_1^N N!} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \exp \left\{ -\mathcal{H}_N(\mathbf{x}_1, \dots, \mathbf{x}_N) \right. \\ &\quad \left. + \beta \langle u_1, \hat{\rho}_N \rangle + \beta \langle u_{10}, \hat{\rho}_N \hat{\rho}_M^0 \rangle \right\}, \end{aligned} \quad (17)$$

where

$$\langle u_1, \hat{\rho}_N \rangle \equiv \int d\mathbf{x} u_1(\mathbf{x}) \hat{\rho}_N(\mathbf{x}), \quad \langle u_{10}, \hat{\rho}_N \hat{\rho}_M^0 \rangle \equiv \int d\mathbf{x} d\mathbf{q} u_{10}(\mathbf{x}, \mathbf{q}) \hat{\rho}_N(\mathbf{x}) \hat{\rho}_M^0(\mathbf{q}). \quad (18)$$

With these definitions it is straightforward that

$$\begin{aligned} -\frac{\delta\Omega[u_1, u_{10}; \mathcal{Q}]}{\delta u_1(\mathbf{x})} &= \overline{\rho(\mathbf{x} | \{\mathbf{q}_i\})} = \rho_1(\mathbf{x}), \\ -\frac{\delta\Omega[u_1, u_{10}; \mathcal{Q}]}{\delta u_{10}(\mathbf{x}, \mathbf{q})} &= \overline{\rho(\mathbf{x} | \{\mathbf{q}_i\}) \hat{\rho}_M^0(\mathbf{q})} = \rho_{10}(\mathbf{x}, \mathbf{q}), \end{aligned} \quad (19)$$

where $\rho(\mathbf{x} | \{\mathbf{q}_i\})$ denotes the equilibrium density of the fluid for fixed positions of the matrix particles, and $\rho_1(\mathbf{x})$ is the quenched-averaged density profile of the fluid. Likewise, $\rho_{10}(\mathbf{x}, \mathbf{q})$ is the pair correlation function of the fluid and matrix particles.

On the other hand, $\Omega[u_1, u_{10}; \mathcal{Q}]$ is a concave functional of both, u_1 and u_{10} . This is easily proven by evaluating $\Xi[u_1, u_{10} | \{\mathbf{q}_i\}]$ on $u_1^{(\lambda)}(\mathbf{x}) = \lambda u_1^{(1)}(\mathbf{x}) + (1 - \lambda) u_1^{(0)}(\mathbf{x})$ ($0 < \lambda < 1$). Since

$$\exp\{\langle u_1^{(\lambda)}, \hat{\rho}_N \rangle\} = \left(\exp\{\langle u_1^{(1)}, \hat{\rho}_N \rangle\} \right)^\lambda \left(\exp\{\langle u_1^{(0)}, \hat{\rho}_N \rangle\} \right)^{1-\lambda},$$

by Hölder's inequality [15] we get

$$\Xi \left[u_1^{(\lambda)}, u_{10} \left| \{\mathbf{q}_i\} \right. \right] < \Xi \left[u_1^{(1)}, u_{10} \left| \{\mathbf{q}_i\} \right. \right]^\lambda \Xi \left[u_1^{(0)}, u_{10} \left| \{\mathbf{q}_i\} \right. \right]^{1-\lambda},$$

from which

$$\Omega \left[u_1^{(\lambda)}, u_{10} \left| \{\mathbf{q}_i\} \right. \right] > \lambda \Omega \left[u_1^{(1)}, u_{10} \left| \{\mathbf{q}_i\} \right. \right] + (1 - \lambda) \Omega \left[u_1^{(0)}, u_{10} \left| \{\mathbf{q}_i\} \right. \right],$$

and averaging over disorder,

$$\Omega \left[u_1^{(\lambda)}, u_{10}; \mathcal{Q} \right] > \lambda \Omega \left[u_1^{(1)}, u_{10}; \mathcal{Q} \right] + (1 - \lambda) \Omega \left[u_1^{(0)}, u_{10}; \mathcal{Q} \right].$$

Clearly the same holds for u_{10} . Because of this, equations (19) define a one-to-one correspondence between the pair $\{\rho_1, \rho_{10}\}$ and the pair $\{u_1, u_{10}\}$ (i.e. the equations can be inverted) [15].

B. Free-energy functional and minimum principle

Let us now introduce the Legendre transform of $\Omega[u_1, u_{10}; \mathcal{Q}]$ with respect to its two arguments

$$\mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}] \equiv \Omega[u_1, u_{10}; \mathcal{Q}] + \langle u_1, \rho_1 \rangle + \langle u_{10}, \rho_{10} \rangle, \quad (20)$$

where $u_1(\mathbf{x})$ and $u_{10}(\mathbf{x}, \mathbf{q})$ are the solution of Eqs. (19) for fixed $\rho_1(\mathbf{x})$ and $\rho_{10}(\mathbf{x}, \mathbf{q})$. Because of the properties of the Legendre transform [15]

- (a) $\mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]$ is a *convex* functional of both $\rho_1(\mathbf{x})$ and $\rho_{10}(\mathbf{x}, \mathbf{q})$;
- (b) the equilibrium $\rho_1(\mathbf{x})$ and $\rho_{10}(\mathbf{x}, \mathbf{q})$ are the absolute minimum of the functional

$$\tilde{\Omega}[\rho_1, \rho_{10}; \mathcal{Q}] \equiv \mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}] - \langle u_1, \rho_1 \rangle - \langle u_{10}, \rho_{10} \rangle, \quad (21)$$

for fixed $u_1(\mathbf{x})$ and $u_{10}(\mathbf{x}, \mathbf{q})$, and therefore

- (c) they can be obtained by solving the equations

$$\frac{\delta \mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]}{\delta \rho_1(\mathbf{x})} = u_1(\mathbf{x}), \quad \frac{\delta \mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]}{\delta \rho_{10}(\mathbf{x}, \mathbf{q})} = u_{10}(\mathbf{x}, \mathbf{q}). \quad (22)$$

As for the meaning of the functional \mathcal{F} , let us adopt a different point of view on the system: let us think of the porous matrix as an external potential acting on the fluid

particles. Then the “intrinsic” free-energy functional is obtained as

$$\begin{aligned}\mathcal{F}[\rho] &= \Omega[u_1, u_{10}|\{\mathbf{q}_i\}] + \int d\mathbf{x} \rho(\mathbf{x}|\{\mathbf{q}_i\}) \left\{ u_1(\mathbf{x}) + \sum_{i=1}^m u_{10}(\mathbf{x}, \mathbf{q}_i) \right\} \\ &= \Omega[u_1, u_{10}|\{\mathbf{q}_i\}] + \int d\mathbf{x} \rho(\mathbf{x}|\{\mathbf{q}_i\}) u_1(\mathbf{x}) + \int d\mathbf{x} d\mathbf{q} \rho(\mathbf{x}|\{\mathbf{q}_i\}) \hat{\rho}_M^0(\mathbf{q}) u_{10}(\mathbf{x}, \mathbf{q}),\end{aligned}$$

and is, of course, a functional of $\rho(\mathbf{x}|\{\mathbf{q}_i\})$. If we now average this functional over disorder we obtain, making use of Eqs. (15), (19) and (20),

$$\overline{\mathcal{F}[\rho]} = \mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]. \quad (23)$$

This equation reveals the physical meaning of functional $\mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]$ as the intrinsic free energy of the fluid undergoing the presence of a porous matrix, averaged over disorder. But the fact that this functional depends on both $\rho_1(\mathbf{x})$ and $\rho_{10}(\mathbf{x}, \mathbf{q})$ makes it rather inconvenient to use it as the basis for a QA-DFT (notice that this functional is the same for any fluid-matrix interaction, so it is far too general).

Of course, one can assume $u_{10}(\mathbf{x}, \mathbf{q})$ fixed and Legendre-transform only with respect to $u_1(\mathbf{x})$ to obtain the alternative functional

$$F[\rho_1; \mathcal{Q}] = \Omega[u_1, u_{10}; \mathcal{Q}] + \langle u_1, \rho_1 \rangle. \quad (24)$$

This is [for fixed $u_{10}(\mathbf{x}, \mathbf{q})$ and \mathcal{Q}] a functional of $\rho_1(\mathbf{x})$ alone, and fulfils the Euler-Lagrange equation

$$\frac{\delta F[\rho_1; \mathcal{Q}]}{\delta \rho_1(\mathbf{x})} = u_1(\mathbf{x}). \quad (25)$$

Comparing with (20) and recalling that $u_{10}(\mathbf{x}, \mathbf{q}) = -\varphi_{10}(\mathbf{x}, \mathbf{q})$,

$$F[\rho_1; \mathcal{Q}] = \mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}] + \langle \varphi_{10}, \rho_{10} \rangle, \quad (26)$$

the intrinsic free energy of the fluid *plus* the interaction energy with the porous matrix. As we will show in Sec. II C, this one and not $\mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]$ is the functional that plays a similar role in QA-DFT as the standard free-energy functional does in classical DFT, and in fact coincides with the functional $F_{\text{TDFT}}[\rho_1]$ derived from the replica formalism.

C. Replica Ornstein-Zernike equations

Let us work out the identity

$$\delta(\mathbf{x} - \mathbf{x}') = \frac{\delta \rho_1(\mathbf{x})}{\delta \rho_1(\mathbf{x}')} = \int d\mathbf{y} \frac{\delta \rho_1(\mathbf{x})}{\delta u_1(\mathbf{y})} \frac{\delta u_1(\mathbf{y})}{\delta \rho_1(\mathbf{x}')} = - \int d\mathbf{y} \frac{\delta^2 \Omega[u_1, u_{10}; \mathcal{Q}]}{\delta u_1(\mathbf{x}) \delta u_1(\mathbf{y})} \frac{\delta^2 F[\rho_1; \mathcal{Q}]}{\delta \rho_1(\mathbf{y}) \rho_1(\mathbf{x}')}. \quad (27)$$

This is one of the replica Ornstein-Zernike (ROZ) equations, namely Eq. (5). To see it let us compute

$$\begin{aligned} -kT \frac{\delta^2 \Omega[u_1, u_{10}; \mathcal{Q}]}{\delta u_1(\mathbf{x}) \delta u_1(\mathbf{y})} &= \frac{\rho_{11}(\mathbf{x}, \mathbf{y} | \{\mathbf{q}_i\}) - \rho_1(\mathbf{x} | \{\mathbf{q}_i\}) \rho_1(\mathbf{y} | \{\mathbf{q}_i\}) - \delta(\mathbf{x} - \mathbf{y}) \rho_1(\mathbf{x} | \{\mathbf{q}_i\})}{\rho_1(\mathbf{x}) \rho_1(\mathbf{y}) h_c(\mathbf{x}, \mathbf{y}) - \delta(\mathbf{x}, \mathbf{y}) \rho_1(\mathbf{x})}, \end{aligned} \quad (28)$$

where we have made use of Eq. (8). Introducing this expression into Eq. (27) we are immediately led to the identification

$$-\beta \frac{\delta^2 F^{\text{ex}}[\rho_1; \mathcal{Q}]}{\delta \rho_1(\mathbf{x}) \delta \rho_1(\mathbf{x}')} = c_c(\mathbf{x}, \mathbf{x}'; [\rho_1; \mathcal{Q}]), \quad (29)$$

where $F^{\text{ex}}[\rho_1; \mathcal{Q}]$ is the excess (over the ideal) part of the functional $F[\rho_1; \mathcal{Q}]$.

In order to obtain Eqs. (1–3) we must set \mathcal{Q} as the probability distribution of a grand-canonical ensemble at temperature T_0 , chemical potential μ_0 and external potential $\varphi_0(\mathbf{q})$. Thus, if we define as usual $u_0(\mathbf{q}) \equiv \mu_0 - \varphi_0(\mathbf{q})$, the probability of finding the matrix configuration $\{M; \mathbf{q}_1, \dots, \mathbf{q}_M\}$ is given by $\mathcal{Q} = \{P_M(\mathbf{q}_1, \dots, \mathbf{q}_M)\}_{M \geq 0}$, where

$$P_M(\mathbf{q}_1, \dots, \mathbf{q}_M) = \frac{1}{\Xi_0[u_0]} \frac{1}{\mathcal{V}_0^M M!} \exp \left\{ -\mathcal{H}_M^0(\mathbf{q}_1, \dots, \mathbf{q}_M) + \langle u_0, \hat{\rho}_M^0 \rangle \right\}, \quad (30)$$

$\mathcal{H}_M^0(\mathbf{q}_1, \dots, \mathbf{q}_M)$ being the hamiltonian which models the interaction between matrix particles (divided by kT_0) and $\Xi_0[u_0]$ the grand partition function

$$\Xi_0[u_0] = 1 + \sum_{M=1}^{\infty} \frac{1}{\mathcal{V}_0^M M!} \int d\mathbf{q}_1 \cdots d\mathbf{q}_M \exp \left\{ -\mathcal{H}_M^0(\mathbf{q}_1, \dots, \mathbf{q}_M) + \langle u_0, \hat{\rho}_M^0 \rangle \right\} \quad (31)$$

(\mathcal{V}_0 is the thermal volume of the matrix fluid). From classical DFT we know that for each external potential $u_0(\mathbf{q})$ there exists a unique equilibrium density profile $\rho_0(\mathbf{q})$ and the system can be described alternatively in terms of any of them. Therefore, if the hamiltonian $\mathcal{H}_M^0(\mathbf{q}_1, \dots, \mathbf{q}_M)$ and temperature T_0 remain fixed, the dependence of the functionals $\Omega[u_1; \mathcal{Q}]$ and $F[\rho_1; \mathcal{Q}]$ on the disorder is actually a dependence on either $u_0(\mathbf{q})$ or $\rho_0(\mathbf{q})$. Hereafter, we will make explicit this dependence by writing this functional as $F[\rho_1; \rho_0]$ and the grand potential as $\Omega[u_1; u_0]$.

Now, Eq. (1) is just the identity

$$\delta(\mathbf{q} - \mathbf{q}') = \frac{\delta \rho_0(\mathbf{q})}{\delta \rho_0(\mathbf{q}')} = \int d\mathbf{s} \frac{\delta \rho_0(\mathbf{q})}{\delta u_0(\mathbf{s})} \frac{\delta u_0(\mathbf{s})}{\delta \rho_0(\mathbf{q}')} = - \int d\mathbf{s} \frac{\delta^2 \Omega_0[u_0]}{\delta u_0(\mathbf{q}) \delta u_0(\mathbf{s})} \frac{\delta^2 F_0[\rho_0]}{\delta \rho_0(\mathbf{s}) \delta \rho_0(\mathbf{q}')}, \quad (32)$$

where $\Omega_0[u_0] = -kT_0 \ln \Xi_0[\rho_0]$ is the grand potential of the matrix and $F_0[\rho_0]$ the corresponding free-energy functional. Finally, to obtain Eqs. (2) and (3), we will notice that

the QA system can be described in terms of any of the following pairs of independent functions $\{u_1(\mathbf{x}), u_0(\mathbf{q})\}$ or $\{\rho_1(\mathbf{x}), \rho_0(\mathbf{q})\}$. Then, both ROZ equations can be identified, respectively, with the identities

$$\begin{aligned} 0 = \frac{\delta u_1(\mathbf{x})}{\delta u_0(\mathbf{q})} &= \int d\mathbf{y} \frac{\delta u_1(\mathbf{x})}{\delta \rho_1(\mathbf{y})} \frac{\delta \rho_1(\mathbf{y})}{\delta u_0(\mathbf{q})} + \int d\mathbf{s} \frac{\delta u_1(\mathbf{x})}{\delta \rho_0(\mathbf{s})} \frac{\delta \rho_0(\mathbf{s})}{\delta u_0(\mathbf{q})} \\ &= - \int d\mathbf{y} \frac{\delta^2 F[\rho_1; \rho_0]}{\delta \rho_1(\mathbf{x}) \delta \rho_1(\mathbf{y})} \frac{\delta^2 \Omega[u_1; u_0]}{\delta u_1(\mathbf{y}) \delta u_0(\mathbf{q})} - \int d\mathbf{s} \frac{\delta^2 F[\rho_1; \rho_0]}{\delta \rho_1(\mathbf{x}) \delta \rho_0(\mathbf{s})} \frac{\delta^2 \Omega_0[u_0]}{\delta u_0(\mathbf{s}) \delta u_0(\mathbf{q})}, \end{aligned} \quad (33)$$

$$\begin{aligned} 0 = \frac{\delta \rho_1(\mathbf{x})}{\delta \rho_0(\mathbf{q})} &= - \int d\mathbf{y} \frac{\delta \rho_1(\mathbf{x})}{\delta u_1(\mathbf{y})} \frac{\delta u_1(\mathbf{y})}{\delta \rho_0(\mathbf{q})} - \int d\mathbf{s} \frac{\delta \rho_1(\mathbf{x})}{\delta u_0(\mathbf{s})} \frac{\delta u_0(\mathbf{s})}{\delta \rho_0(\mathbf{q})} \\ &= - \int d\mathbf{y} \frac{\delta^2 \Omega[u_1; u_0]}{\delta u_1(\mathbf{x}) \delta u_1(\mathbf{y})} \frac{\delta^2 F[\rho_1; \rho_0]}{\delta \rho_1(\mathbf{y}) \delta \rho_0(\mathbf{q})} - \int d\mathbf{s} \frac{\delta^2 \Omega[u_1; u_0]}{\delta u_1(\mathbf{x}) \delta u_0(\mathbf{s})} \frac{\delta^2 F_0[u_0]}{\delta \rho_0(\mathbf{s}) \delta \rho_0(\mathbf{q})}, \end{aligned} \quad (34)$$

where we have used Eqs. (19) and (25) for the QA system, and their counterparts for the matrix. To complete the identification of these identities with the corresponding OZ equations, we have to take into account the expression (28) as well as

$$-kT \frac{\delta^2 \Omega[u_1; u_0]}{\delta u_1(\mathbf{x}) \delta u_0(\mathbf{q})} = \rho_1(\mathbf{x}) \rho_0(\mathbf{q}) h_{10}(\mathbf{x}, \mathbf{q}), \quad (35)$$

and to make the identification

$$-\beta \frac{\delta^2 F[\rho_1; \rho_0]}{\delta \rho_1(\mathbf{x}) \delta \rho_0(\mathbf{q})} = c_{10}(\mathbf{x}, \mathbf{q}; [\rho_1; \rho_0]). \quad (36)$$

At this point, it is important to notice that the set of OZ equations that we have obtained within the DFT approach is self-contained. This means that if we have the functionals $F_0[\rho_0]$ and $F[\rho_1; \rho_0]$, we can derive from them the direct correlation functionals c_{00} , c_c and c_{10} , and using them as inputs in the OZ Eqs. (1), (2) and (5) to obtain h_{00} , h_{10} and h_c . Moreover, both Eqs. (1) and (5) can be solved independently and their solutions can be used to solve Eq. (2). This situation is remarkably different from the one we find in the integral equation framework. In that case, although the OZ equation for the matrix [Eq. (1)] is independent of all the others, the remaining ones [Eqs. (2), (4) and (5)] form a coupled system. The reason for this difference is that in the case of integral equation theory, the direct correlation functions are also unknown and the ROZ equations must be complemented with closure relations. This additional equations are derived from exact relations between the interaction potentials between particles and the correlation functions, with one equation for each potential. Thus, in our case, we would have two

new equations which would involve $\{h_{10}, c_{10}\}$ and $\{h_{11}, c_{11}\}$, respectively. The absence of a closure relation for $\{h_c, c_c\}$ is what keeps the set of Eqs. (2), (4) and (5), the two closure relations, and one of Eqs. (6) or (7), coupled.

We should remark that in the QA-DFT the blocking parts are absent. Nevertheless, contrary to what happens with integral equation theory, we are able to compute all the structure functions that are relevant to the thermodynamics without the blocking correlations.

D. Thermodynamics

We will finish this section showing how all the thermodynamics can be derived from the functional $F[\rho_1; \rho_0]$. The starting point will be the relation proved by Rosinberg et al. [5]

$$\overline{\Omega[u_1|\{\mathbf{q}_i\}]} = \Omega[u_1; u_0] = -pV, \quad (37)$$

where p is the thermodynamic pressure and V the volume of the system (see Refs. [16] and [17] for a discussion about the definition of the thermodynamic pressure and the difference between this one and the mechanical pressure). Now, as the functional $F[\rho_1; \rho_0]$ is related to the quenched-averaged grand potential $\Omega[u_1; u_0]$ [Eq. (24)] in the same way as the standard free-energy functional with the grand potential in classical DFT, and as this formal equivalence is also found in the relation (25) between $F[\rho_1; \rho_0]$ and the chemical potential, we can conclude that all the thermodynamic relations we found in classical DFT remain formally identical in the QA-DFT, with c_c playing the role of the direct correlation because of Eq. (29).

III. AN EXACT MODEL: IDEAL FLUID IN AN ARBITRARY MATRIX

As the simplest example let us consider the only known example which can be exactly solved in this formalism: an ideal fluid in an arbitrary porous matrix. As a QA system, the matrix is taken to be a configuration of a grand-canonical ensemble of a certain fluid at temperature T_0 , chemical potential μ_0 , and external potential $\varphi_0(\mathbf{q})$ [let us also define $u_0(\mathbf{q}) \equiv \mu_0 - \varphi_0(\mathbf{q})$]. The grand partition function, grand potential and free energy of this fluid will be denoted, respectively, $\Xi_0[u_0]$, $\Omega_0[u_0]$ and $F_0[\rho_0]$, $\rho_0(\mathbf{q})$ being the corresponding equilibrium density profile.

For the ideal gas $\mathcal{H}_N = 0$, so the grand partition function of the fluid becomes

$$\begin{aligned}\Xi[u_1, u_{10}|\{\mathbf{q}_i\}] &= 1 + \sum_{N=1}^{\infty} \frac{1}{\mathcal{V}_1^N N!} \left\{ \int d\mathbf{x} \exp \left[\beta u_1(\mathbf{x}) + \sum_{i=1}^M \beta u_{10}(\mathbf{x}, \mathbf{q}_i) \right] \right\}^N \\ &= \exp \left\{ \frac{1}{\mathcal{V}_1} \int d\mathbf{x} \exp \left[\beta u_1(\mathbf{x}) + \sum_{i=1}^M \beta u_{10}(\mathbf{x}, \mathbf{q}_i) \right] \right\}.\end{aligned}\quad (38)$$

Thus,

$$\Omega[u_1, u_{10}|\{\mathbf{q}_i\}] = -\frac{kT}{\mathcal{V}_1} \int d\mathbf{x} \exp \left[\beta u_1(\mathbf{x}) + \sum_{j=1}^M \beta u_{10}(\mathbf{x}, \mathbf{q}_j) \right], \quad (39)$$

and therefore

$$\begin{aligned}\Omega[u_1, u_{10}; \mathcal{Q}] &= -\frac{kT}{\mathcal{V}_1} \int d\mathbf{x} e^{\beta u_1(\mathbf{x})} \frac{\Xi_0[\tilde{u}_0(\mathbf{x}, \cdot)]}{\Xi_0[u_0]} \\ &= -\frac{kT}{\mathcal{V}_1} \int d\mathbf{x} e^{\beta u_1(\mathbf{x}) - \beta_0 \Delta \Omega_0(\mathbf{x})}.\end{aligned}\quad (40)$$

In this expressions $\Xi_0[\tilde{u}_0(\mathbf{x}, \cdot)]$ stands for the grand partition function of the matrix fluid undergoing an external potential $\tilde{u}_0(\mathbf{x}, \mathbf{q}) \equiv u_0(\mathbf{q}) + (T_0/T)u_{10}(\mathbf{x}, \mathbf{q})$, \mathbf{x} being the position of a fixed fluid particle, and $\Delta \Omega_0(\mathbf{x}) \equiv \Omega_0[\tilde{u}_0(\mathbf{x}, \cdot)] - \Omega_0[u_0]$.

From the first of Eqs. (19) it follows that

$$\rho_1(\mathbf{x}) = \frac{1}{\mathcal{V}_1} e^{\beta u_1(\mathbf{x}) - \beta_0 \Delta \Omega_0(\mathbf{x})}, \quad (41)$$

an interesting equation which tells us that the average equilibrium density profile of the fluid is given by the barometric law corrected with the probability of inserting a fluid particle in the matrix fluid at position \mathbf{x} , namely $e^{-\beta_0 \Delta \Omega_0(\mathbf{x})}$.

From the second of Eqs. (19) it follows that

$$\rho_{10}(\mathbf{x}, \mathbf{q}) = \frac{1}{\mathcal{V}_1} e^{\beta u_1(\mathbf{x})} \frac{kT_0}{\Xi_0[u_0]} \frac{\delta \Xi_0[\tilde{u}_0(\mathbf{x}, \cdot)]}{\delta \tilde{u}_0(\mathbf{x}, \mathbf{q})}. \quad (42)$$

Dividing this equation by Eq. (41) leads to

$$\frac{\rho_{10}(\mathbf{x}, \mathbf{q})}{\rho_1(\mathbf{x})} = -\frac{\delta \Omega_0[\tilde{u}_0(\mathbf{x}, \cdot)]}{\delta \tilde{u}_0(\mathbf{x}, \mathbf{q})} = \rho_0(\mathbf{x}, \mathbf{q}), \quad (43)$$

where $\rho_0(\mathbf{x}, \mathbf{q})$ is the equilibrium density profile of the matrix fluid corresponding to the external potential $\tilde{u}_0(\mathbf{x}, \mathbf{q})$ created by a fluid particle placed at \mathbf{x} .

Because of Eq. (41), Eq. (40) simply becomes

$$\Omega[u_1, u_{10}; \mathcal{Q}] = -kT \int d\mathbf{x} \rho_1(\mathbf{x}), \quad (44)$$

the equation of state of the ideal gas. On the other hand, eliminating $u_1(\mathbf{x})$ from Eq. (41),

$$u_1(\mathbf{x}) = kT \ln \left(\mathcal{V}_1 \rho_1(\mathbf{x}) \right) + \frac{T}{T_0} \Delta \Omega_0(\mathbf{x}), \quad (45)$$

so Eq. (20) becomes

$$\begin{aligned} \mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}] &= F^{\text{id}}[\rho_1] + \frac{T}{T_0} \int d\mathbf{x} \left\{ \rho_1(\mathbf{x}) \Omega_0[\tilde{u}_0(\mathbf{x}, \cdot)] - \rho_1(\mathbf{x}) \Omega_0[u_0] \right\} \\ &\quad + \int d\mathbf{x} \int d\mathbf{q} u_{10}(\mathbf{x}, \mathbf{q}) \rho_{10}(\mathbf{x}, \mathbf{q}), \end{aligned} \quad (46)$$

where $u_{10}(\mathbf{x}, \mathbf{q})$ is the solution to Eq. (43) and

$$F^{\text{id}}[\rho_1] = kT \int d\mathbf{x} \rho_1(\mathbf{x}) \left\{ \ln \left(\mathcal{V}_1 \rho_1(\mathbf{x}) \right) - 1 \right\}. \quad (47)$$

Adding and subtracting

$$\frac{T}{T_0} \int d\mathbf{x} \rho_1(\mathbf{x}) \left\{ \int d\mathbf{q} u_0(\mathbf{q}) \left(\rho_0(\mathbf{q}) - \rho_0(\mathbf{x}, \mathbf{q}) \right) \right\}$$

to Eq. (46) and using Eq. (43) yields

$$\begin{aligned} \mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}] &= F^{\text{id}}[\rho_1] + \frac{T}{T_0} \int d\mathbf{x} \rho_1(\mathbf{x}) \left\{ \int d\mathbf{q} u_0(\mathbf{q}) \left(\rho_0(\mathbf{q}) - \rho_0(\mathbf{x}, \mathbf{q}) \right) \right\} \\ &\quad + \frac{T}{T_0} \int d\mathbf{x} \rho_1(\mathbf{x}) \left\{ \Omega_0[\tilde{u}_0(\mathbf{x}, \cdot)] + \int d\mathbf{q} \tilde{u}_0(\mathbf{x}, \mathbf{q}) \rho_0(\mathbf{x}, \mathbf{q}) \right\} \\ &\quad - \frac{T}{T_0} \int d\mathbf{x} \rho_1(\mathbf{x}) \left\{ \Omega_0[u_0] + \int d\mathbf{q} u_0(\mathbf{q}) \rho_0(\mathbf{x}) \right\}. \end{aligned} \quad (48)$$

One can recognize in the brackets above the Legendre transforms of the grand potential of the matrix fluid; thus the final expression for the functional can be written as

$$\begin{aligned} \mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}] &= F^{\text{id}}[\rho_1] + \frac{T}{T_0} \int d\mathbf{x} \rho_1(\mathbf{x}) \left\{ F_0[\rho_{10}(\mathbf{x}, \cdot)/\rho_1(\mathbf{x})] - F_0[\rho_0] \right\} \\ &\quad + \frac{T}{T_0} \int d\mathbf{x} \int d\mathbf{q} \frac{\delta F_0[\rho_0]}{\delta \rho_0(\mathbf{q})} \left\{ \rho_1(\mathbf{x}) \rho_0(\mathbf{q}) - \rho_{10}(\mathbf{x}, \mathbf{q}) \right\}. \end{aligned} \quad (49)$$

Notice that, apart from the standard ideal free-energy functional, there is a non-trivial term arising from the interaction between the fluid and the matrix.

So far for the intrinsic free-energy functional. Now to obtain the functional $F[\rho_1; \mathcal{Q}]$ — or, considering that we are describing a QA system, better $F[\rho_1; \rho_0]$ — we make a Legendre transformation of $\Omega[u_1, u_{10}; \mathcal{Q}]$ only w.r.t. u_1 (u_{10} is assumed fixed) to obtain

$$\begin{aligned} F[\rho_1; \rho_0] &= F^{\text{id}}[\rho_1] + \frac{T}{T_0} \int d\mathbf{x} \rho_1(\mathbf{x}) \left\{ F_0[\rho_0(\mathbf{x}, \cdot)] - F_0[\rho_0] \right\} \\ &\quad + \frac{T}{T_0} \int d\mathbf{x} \rho_1(\mathbf{x}) \int d\mathbf{q} \left\{ \rho_0(\mathbf{q}) \frac{\delta F_0[\rho_0]}{\delta \rho_0(\mathbf{q})} - \rho_0(\mathbf{x}, \mathbf{q}) \frac{\delta F_0[\rho_0(\mathbf{x}, \cdot)]}{\delta \rho_0(\mathbf{x}, \mathbf{q})} \right\}. \end{aligned} \quad (50)$$

A. The special case of an ideal matrix

One particular case which has received some attention in the literature [3, 5, 18] is the case in which the matrix is also ideal. The reason is that the ROZ equations for this system can be exactly solved (when u_{10} is a hard-sphere potential), and, in spite of its simplicity, the blocking part of the direct correlation function is non-zero.

If the matrix is a configuration of an ideal gas at temperature T_0 , then

$$F_0[\rho_0] = kT_0 \int d\mathbf{q} \rho_0(\mathbf{q}) \left\{ \ln \left(\mathcal{V}_0 \rho_0(\mathbf{q}) \right) - 1 \right\}. \quad (51)$$

Substituting this F_0 in the expressions of the previous section one gets

$$\begin{aligned} \rho_0(\mathbf{q}) &= \frac{e^{\beta_0 u_0(\mathbf{q})}}{\mathcal{V}_0}, \\ \rho_0(\mathbf{x}, \mathbf{q}) &= \frac{e^{\beta_0 u_0(\mathbf{q}) + \beta u_{10}(\mathbf{x}, \mathbf{q})}}{\mathcal{V}_0} = \rho_0(\mathbf{q}) e^{\beta u_{10}(\mathbf{x}, \mathbf{q})}; \end{aligned} \quad (52)$$

therefore

$$F[\rho_1; \rho_0] = F^{\text{id}}[\rho_1] - kT \int d\mathbf{x} \int d\mathbf{q} \rho_1(\mathbf{x}) \rho_0(\mathbf{q}) f_{10}(\mathbf{x}, \mathbf{q}), \quad (53)$$

$$f_{10}(\mathbf{x}, \mathbf{q}) \equiv e^{\beta u_{10}(\mathbf{x}, \mathbf{q})} - 1, \quad (54)$$

and

$$\rho_1(\mathbf{x}) = \frac{e^{\beta u_1(\mathbf{x})}}{\mathcal{V}_1} \exp \left\{ \int d\mathbf{q} \rho_0(\mathbf{q}) f_{10}(\mathbf{x}, \mathbf{q}) \right\}. \quad (55)$$

A simple inspection of the exact functional (53) for an ideal fluid in an ideal matrix reveals that the non-ideal term is quadratic, so the only second derivative that is nonzero is $c_{10} = f_{10}$. Nevertheless, as mentioned above, this system has a non-trivial c_b [3, 5, 18], which certainly cannot be derived from (53) by any functional differentiation. In spite of this, the functional (53) contains all the equilibrium thermodynamics of the system.

IV. DISCUSSION AND CONCLUSIONS

We have made a first-principles derivation of a density functional formalism for fluids inside quenched disorder matrices without resorting to the replica trick. The main conclusion is that, for fixed interaction potential between the fluid particles, $\mathcal{H}_N(\mathbf{x}_1, \dots, \mathbf{x}_N)$, and fixed distribution of the disorder, there exist a unique functional $\mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]$ from which all the equilibrium structure information and thermodynamics

can be derived. Given the generalized external potential acting on the fluid particles, $u_1(\mathbf{x}) = \mu_1 - \varphi_1(\mathbf{x})$, and the interaction potential between the fluid and matrix particles, $u_{10}(\mathbf{x}, \mathbf{q}) = -\varphi_{10}(\mathbf{x}, \mathbf{q})$, the disorder-average of the equilibrium density profile of the fluid, $\rho_1^{\text{eq}}(\mathbf{x})$, and the fluid-matrix pair distribution $\rho_{10}^{\text{eq}}(\mathbf{x}, \mathbf{q})$ can be derived from Eqs. (22). Once we have $\rho_1^{\text{eq}}(\mathbf{x})$ and $\rho_{10}^{\text{eq}}(\mathbf{x}, \mathbf{q})$, the average of the “intrinsic” free-energy of the system is given by $\mathcal{F}[\rho_1^{\text{eq}}, \rho_{10}^{\text{eq}}; \mathcal{Q}]$, and the grand potential by

$$\begin{aligned} \bar{\Omega} = & \mathcal{F}[\rho_1^{\text{eq}}, \rho_{10}^{\text{eq}}; \mathcal{Q}] - \int d\mathbf{x} \left. \frac{\delta \mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]}{\delta \rho_1(\mathbf{x})} \right|_{\substack{\rho_1 = \rho_1^{\text{eq}} \\ \rho_{10} = \rho_{10}^{\text{eq}}}} \rho_1^{\text{eq}}(\mathbf{x}) \\ & - \int d\mathbf{x} d\mathbf{q} \left. \frac{\delta \mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]}{\delta \rho_{10}(\mathbf{x}, \mathbf{q})} \right|_{\substack{\rho_1 = \rho_1^{\text{eq}} \\ \rho_{10} = \rho_{10}^{\text{eq}}}} \rho_{10}^{\text{eq}}(\mathbf{x}, \mathbf{q}). \end{aligned} \quad (56)$$

Although for the ideal fluid in a quenched matrix we have been able to derive the explicit form of $\mathcal{F}[\rho_1, \rho_{10}; \mathcal{Q}]$, this is a formidable task for an arbitrary system. Note that this functional is valid for *any* interaction potential between the fluid and matrix particles and if we had it, then we would have solved a very general problem. Thus, it is more practical to turn to a less general functional, $F[\rho_1; \mathcal{Q}]$, which will be a functional only of $\rho_1(\mathbf{x})$ and whose functional form will depend on $u_{10}(\mathbf{x}, \mathbf{q})$. Again, we have an Euler-Lagrange equation to obtain the equilibrium properties for a given generalized external potential $u_1(\mathbf{x})$ [Eq. (25)], but now $F[\rho_1^{\text{eq}}; \mathcal{Q}]$ is not just the average over disorder of the “intrinsic” free energy, but it also contains an additional contribution due to the quenched-average of the interaction energy between the fluid and matrix particles, $-\int d\mathbf{x} d\mathbf{q} u_{10}(\mathbf{x}, \mathbf{q}) \rho_{10}^{\text{eq}}(\mathbf{x}, \mathbf{q})$, where $\rho_{10}^{\text{eq}}(\mathbf{x}, \mathbf{q})$ can be obtained from the OZ Eq. (2).

One of the most relevant contributions of this work is the identification of the direct correlation functionals appearing in the ROZ equations with second functional derivatives of $F[\rho_1; \mathcal{Q}]$ [Eqs. (29) and (36)]. It is worth mentioning that, in contrast to the case of classical DFT, the second derivative of $F^{\text{ex}}[\rho_1; \mathcal{Q}]$ with respect to $\rho_1(\mathbf{x})$ and $\rho_1(\mathbf{x}')$ is not $c_{11}(\mathbf{x}, \mathbf{x}'; [\rho_1; \mathcal{Q}])$ but only its connected part. Notwithstanding, the formalism is closed in the set of correlation functionals $\{(c_{00}, h_{00}), (c_{10}, h_{10}), (c_{01}, h_{01}), (h_c, c_c)\}$, since the *direct* correlation functionals are obtained by simple functional differentiations of $F[\rho_1; \mathcal{Q}]$ and the *total* correlation ones can be derived from the ROZ Eqs. (1–3), and (5), which have been obtained as functional identities in the QA-DFT presented in this work.

As we have discussed previously, the blocking parts h_b and c_b do not enter anywhere in the formalism. The fact that the QA-DFT does not contain these correlations and that the thermodynamics can be entirely derived from it implies that the blocking correlations

are not relevant for the thermodynamics. In this respect, we would like to mention that mode-coupling theory has been recently extended to QA systems [19] in order to study the dynamics of confined glass-forming liquids, and the only equilibrium structural information needed to obtain the relaxing density fluctuations is the set $\{c_c, c_{10}, c_0\}$. Thus even the liquid-glass transition can be determined if we know the functional $F[\rho_1; \mathcal{Q}]$. Also notice that in Refs. [6, 7], where freezing is studied with a Ramakrishnan-Yussouff density functional, the direct correlation employed in its construction (which is derived with the replica trick) is c_c , not c_{11} .

Finally, as it happens in classical DFT, there are few systems for which $F[\rho_1; \mathcal{Q}]$ can be obtained exactly (in this case only ideal fluids in arbitrary matrices, as far as we know). Therefore, this formalism should be complemented with approximations for $F^{\text{ex}}[\rho_1; \mathcal{Q}]$. In this line are the works by Schmidt and collaborators [8, 12, 14], which make use of the constructing principle of fundamental measure theory [9, 10, 11, 13], namely the exact result for a 0D cavity (a cavity which can hold at most either a fluid or a matrix particle) to approximate $F[\rho_1; \mathcal{Q}]$. Although the results obtained seem promising, we think that the extension of fundamental measure theory to QA systems involves subtleties concerning the correlations between fluid and matrix particles that are difficult to deal with, and further study is required.

Another research line worth exploring is, in analogy to the development of classical DF approximations, to study the extension of those approximation based on the thermodynamics and structural information of the uniform fluid (usually obtained from integral equation theory) such as the weighted density or the effective liquid approximations [20]. This will be the subject of a forthcoming work.

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