Statistical mechanics of homogeneous partly pinned fluid systems

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The homogeneous partly pinned fluid systems are simple models of a fluid confined in a disordered porous matrix obtained by arresting randomly chosen particles in a one-component bulk fluid or one of the two components of a binary mixture. In this paper, their configurational properties are investigated. It is shown that a peculiar complementarity exists between the mobile and immobile phases, which originates from the fact that the solid is prepared in presence of and in equilibrium with the adsorbed fluid. Simple identities follow, which connect different types of configurational averages, either relative to the fluid-matrix system or to the bulk fluid from which it is prepared. Crucial simplifications result for the computation of important structural quantities, both in computer simulations and in theoretical approaches. Finally, possible applications of the model in the field of dynamics in confinement or in strongly asymmetric mixtures are suggested.

I. INTRODUCTION

The physics of fluids under nanoscale confinement is a topic of great interest, from a fundamental, applied and interdisciplinary point of view at once (see [1–3] for reviews). This is however a rather difficult one for theorists. Indeed, since many porous solids are structurally disordered, one is usually faced with a complex interplay of finite size effects, adsorption phenomena, topology, and randomness, which is not easily captured with analytically or numerically tractable models.

In the past few years, a widely used class of models for theoretical and computational studies of fluids adsorbed in disordered porous media has been one in which the fluid molecules evolve in a statistically homogeneous random array of particles frozen in a disordered configuration sampled from a prescribed probability distribution. Recent works include investigations of the non-equilibrium phenomena in the adsorption/desorption processes [4–7], of the critical behavior at fluid-fluid transitions [8–12], and of the glassy dynamics in confinement [13–24].

The first elaborate theoretical treatment of this type of systems has been derived by Madden and Glandt [25] for the model of the so-called "quenched-annealed" (QA) binary mixture. In this model, the probability distribution of the porous matrix is chosen as the equilibrium distribution of some simple fluid system, so that the solid samples can be thought of as the results of instantaneous thermal quenches of this original equilibrium system, hence the denomination "quenched" for the matrix component. Then the fluid (the "annealed" component) equilibrates in the random potential energy landscape created by the frozen matrix particles. Thanks to the property of statistical homogeneity of the solid, Madden and Glandt have demonstrated that the QA mixture can be studied with great ease via simple and direct extensions of standard liquid-state theoretical methods. In their pioneering and subsequent works [25–28], they used diagrammatic techniques to investigate the distribution functions and thermodynamic properties of the system. Later, Stell and coworkers rederived, extended, and, in some cases,

corrected these results with the help of the replica trick [29–32]. Interesting developments in the framework of the density functional theory have been reported as well [33–36].

Following this breakthrough, other prescriptions have been put forward for the preparation of the disordered porous matrix, resulting in a variety of models. In a depleted system [37, 38], the matrix is obtained by quenching configurations of a one-component fluid and by removing at random a fraction of its particles. Strategies for a correlated depletion step have recently been suggested [39, 40]. In a templated system [41–44], the porous medium is produced by freezing configurations of a binary mixture and by removing one of its components, which acts as a template for the remaining one. In both models, the probability distribution of the solid can be explicitly and easily related to the equilibrium distribution of an underlying simple fluid system, as in the QA mixture. This needs not be the case. Indeed, for many aspects of the formalism, it has been shown that it is enough to know the structure of the solid, typically at the pair level, instead of its full statistics [27, 45]. This has allowed theoretical investigations of fluids confined in realistic porous media generated through out-of-equilibrium processes, such as the diffusion-limited cluster-cluster aggregation (DLCA) process [46].

In all the above examples, the preparation of the matrix and thus its statistical properties are independent of the fluid that will be imbibed in it. This looks like the most reasonable way to proceed, since this actually reproduces the usual experimental situation. However, a rather popular model in computer simulation studies of confined fluids does not display this feature [18, 19, 47–52]. This model is the randomly pinned (RP) system, which is considered in the present paper with one of its natural generalizations. Operationally, it can be described as follows. While exploring the configuration space of an equilibrium bulk fluid system, snapshots are selected at random times, in which a fraction of the particles is chosen randomly and pinned down, thus generating samples of rigid disordered matrices. The remaining unpinned particles then become the confined fluid phase

which evolves under the influence of the same interactions as in the original bulk system. Note that a very similar setup can be realized experimentally in two dimensions, by squeezing a binary colloidal mixture between two glass plates [53, 54].

It will be shown in the following that the RP model is actually a special case of a templated system. As such, its core physics does not display any fundamental difference compared to any other type of fluid-matrix model. But, in this specific setup, it is also clear that the fluid and matrix properties are unusually and irremediably entangled. In fact, since the porous matrix is prepared in the presence of the fluid, there is a very peculiar complementarity between the mobile and frozen phases, from which we will show that nontrivial configurational properties emerge which make the RP model worth special attention. Furthermore, among the different particle-based models of disordered porous media, the RP system is unique in allowing of an interpretation as a limiting case of an equilibrated binary mixture, whereby the mass of the pinned particles is sent to infinity (for Newtonian dynamics) or their free-diffusion coefficient to zero (for Brownian dynamics) [47–49, 52]. Its study is thus relevant for the understanding of the dynamics of mixtures with a strong dynamical asymmetry, of which it represents an asymptote.

One of the properties that will be established in the present paper has already been observed in the above-cited computer simulation studies, namely that the pair distribution functions of the bulk system on which the RP model is based are preserved after the pinning process [18, 47, 48, 50]. Up to now and depending on the authors, however, it was never clear whether this finding was reflecting an exact property of the system or was just a good approximation. The issue is settled here in favor of the first interpretation. In addition, it will be shown how other distribution functions, which are characteristic of systems with quenched disorder and usually quite difficult to compute efficiently, should be easily accessible in the very special case of the RP model.

The paper is organized as follows. In Sec. II, the RP model and a useful generalization are described with their defining probability distributions. In Sec. III, configurational identities are derived, which relate different types of averages. They are the main results of this work, whose possible applications in computer simulation studies are discussed. Their consequences for the structure at the pair level and their implications for integral equation theories are considered in Sec. IV, while a dynamical point of view is developed in Sec. V. Section VI is devoted to concluding remarks.

II. MODELS AND PROBABILITY DISTRIBUTIONS

In this section, the RP model is defined and its essential statistical properties are derived. To achieve this goal, we proceed in two steps. First, a formal link is established between the RP and templated systems, which leads to a natural generalization of the problem. Second, the relevant probability distributions are provided in this extended framework.

The simplest version of the RP model, which is sufficient to illustrate the main properties of this type of systems, derives from a one-component bulk fluid through a random pinning process, as sketched in Fig. 1 [55]. More specifically, for each configuration of the fluid which occurs with a probability distribution corresponding to a prescribed statistical ensemble, a fraction x of its particles is randomly chosen and pinned down to form a disordered porous matrix, while the complementary $1-x$ fraction remains mobile and provides the confined fluid. Different ensembles can be considered, which are all equivalent in the thermodynamic limit [32]. In existing computer simulation studies [18, 19, 47–52], both the fluid and the matrix have always been treated in the canonical ensemble, i.e., with no fluctuations in their particle numbers and thus in the pinning fraction. Here, we find more convenient to resort to a grand-canonical description in which, in particular, the pinning fraction is allowed to fluctuate around its mean value.

Accordingly, we start with a one-component bulk fluid in a volume V at temperature T (as usual, we define $\beta = 1/k_\mathrm{B}T$) and activity z. From well-known statistical mechanics [56], the configurational probability density of finding this system with N particles located at $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \equiv \mathbf{r}^N$ is

$$\mathcal{P}_\mathrm{bulk}(N, \mathbf{r}^N) = \frac{z^N e^{-\beta V_\mathrm{bulk}(N, \mathbf{r}^N)}}{\Xi_\mathrm{bulk} N!}, \qquad (1)$$

where $V_\mathrm{bulk}(N, \mathbf{r}^N)$ denotes the potential energy of the fluid. The partition function Ξ_bulk is simply

$$\Xi_\mathrm{bulk} = \mathrm{Tr}\, \frac{z^N e^{-\beta V_\mathrm{bulk}(N, \mathbf{r}^N)}}{N!}, \qquad (2)$$

where the shorthand notation for the trace operator $\mathrm{Tr} \cdots \equiv \sum_{N=0}^{+\infty} \int d\mathbf{r}^N \cdots$ is used.

During the pinning process, for every configuration of the fluid, each particle in the system might be pinned down with probability x or left mobile with probability $1 - x$. It results that the joint probability density of generating a matrix with N_m immobile particles located at $(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_{N_\mathrm{m}}) \equiv \mathbf{q}^{N_\mathrm{m}}$ while N_t unpinned particles are located at $(\mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_{N_\mathrm{t}}) \equiv \mathbf{s}^{N_\mathrm{t}}$ at the time of the pinning process, with $N_\mathrm{m} + N_\mathrm{t} = N$, is

$$\mathcal{P}_\mathrm{mt}(N_\mathrm{m}, \mathbf{q}^{N_\mathrm{m}}, N_\mathrm{t}, \mathbf{s}^{N_\mathrm{t}}) =$$
$$\frac{z^{N_\mathrm{m}+N_\mathrm{t}} x^{N_\mathrm{m}} (1-x)^{N_\mathrm{t}} e^{-\beta V_\mathrm{bulk}(N_\mathrm{m}+N_\mathrm{t}, \mathbf{q}^{N_\mathrm{m}}, \mathbf{s}^{N_\mathrm{t}})}}{\Xi_\mathrm{bulk} N_\mathrm{m}! N_\mathrm{t}!}, \quad (3)$$

which is basically Eq. (1) modified by a combinatorial factor due to the random pinning process. For clarity, different notations are used for the locations of the pinned
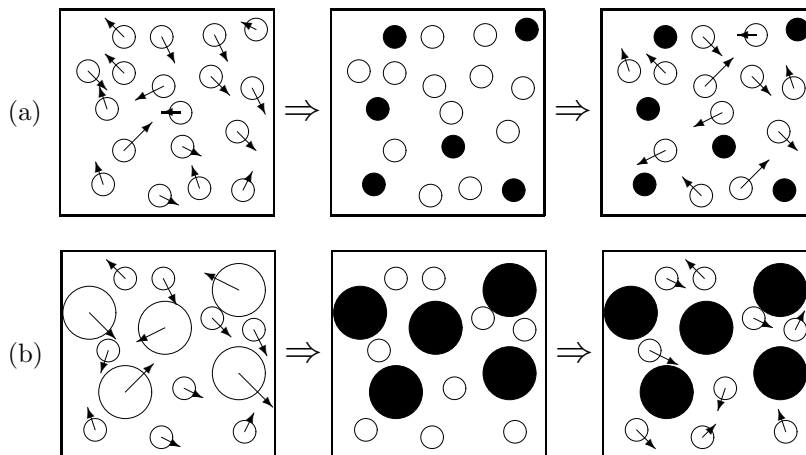
FIG. 1. Simple schematics of the fluid-matrix models studied in this work. In all panels, the immobile particles are represented in black, and the mobile ones in white, with arrows symbolizing their movement. (a) Randomly pinned system. In a precursor one-component fluid (left panel), a predefined fraction of the particles is chosen at random in an instantaneous configuration and pinned down to form the matrix (middle panel, the pinning fraction is $x = 1/3$), in which the remaining particles continue their motion (right panel). (b) Partly pinned system. Starting with an equilibrated binary mixture (left panel), one component is pinned down in an instantaneous configuration to form the matrix (middle panel), in which the other component continues its movement (right panel).

and unpinned particles, and, in anticipation of the coming interpretation, the subscripts m and t for "matrix" and "template", respectively, have been introduced. The probability density of the matrix configurations immediately follows by tracing out the unpinned particles,

$$\mathcal{P}_{\mathrm{m}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}}) = \mathrm{Tr}_{\mathrm{t}}\, \mathcal{P}_{\mathrm{mt}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}}, N_{\mathrm{t}}, \mathbf{s}^{N_{\mathrm{t}}}). \quad (4)$$

This is exactly what would be obtained for a depleted system [37, 38]. This is not surprising, since it is rather intuitive that a RP system is equivalent to a depleted system in which the depleted particles are reinjected as the confined fluid.

A similar equivalence can be established with a templated system [41–44]. Indeed, thanks to the binomial identity, Ξ_{bulk} can be rewritten as

$$\Xi_{\mathrm{bulk}} = \mathrm{Tr}_{\mathrm{m}}\, \mathrm{Tr}_{\mathrm{t}}$$
$$\frac{z^{N_{\mathrm{m}}+N_{\mathrm{t}}} x^{N_{\mathrm{m}}} (1-x)^{N_{\mathrm{t}}} e^{-\beta V_{\mathrm{bulk}}(N_{\mathrm{m}}+N_{\mathrm{t}}, \mathbf{q}^{N_{\mathrm{m}}}, \mathbf{s}^{N_{\mathrm{t}}})}}{N_{\mathrm{m}}! N_{\mathrm{t}}!}. \quad (5)$$

$\mathcal{P}_{\mathrm{mt}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}}, N_{\mathrm{t}}, \mathbf{s}^{N_{\mathrm{t}}})$ is then easily recognized as the grand-canonical configurational probability density of an ideal binary mixture, with activities $z_{\mathrm{m}} = zx$ and $z_{\mathrm{t}} = z(1-x)$ for the components m and t, respectively, and $\mathcal{P}_{\mathrm{m}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}})$ as the probability distribution of the templated matrices that can be generated from this ideal mixture, components m and t being the matrix and template components, respectively. Note that V_{bulk} appears unchanged, because the potential energy of an ideal binary mixture is, by definition, independent of its composition and thus equal to that of any one of its components alone. Therefore, a RP system with a pinning fraction x is equivalent to a templated system based on an ideal bi-

nary mixture with a matrix number fraction x, in which the template particles are reinjected as the mobile phase.

An immediate generalization of the problem follows from this equivalence, by relaxing the restriction to ideal mixtures (see Fig. 1). We call the corresponding extended class of models the partly pinned (PP) systems, which might be studied generically and only specialized afterwards to deal with the RP model. Thus, instead of Eqs. (3) and (5), we shall consider the generic expressions for templated systems, i.e.,

$$\mathcal{P}_{\mathrm{mt}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}}, N_{\mathrm{t}}, \mathbf{s}^{N_{\mathrm{t}}}) =$$
$$\frac{z_{\mathrm{m}}^{N_{\mathrm{m}}} z_{\mathrm{t}}^{N_{\mathrm{t}}} e^{-\beta\left[V_{\mathrm{mm}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}}) + V_{\mathrm{mt}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}}, N_{\mathrm{t}}, \mathbf{s}^{N_{\mathrm{t}}}) + V_{\mathrm{tt}}(N_{\mathrm{t}}, \mathbf{s}^{N_{\mathrm{t}}})\right]}}{\Xi_{\mathrm{bulk}} N_{\mathrm{m}}! N_{\mathrm{t}}!} \quad (6)$$

for the grand-canonical configurational probability distribution of the bulk matrix-template system and for the joint probability density of generating a matrix with N_{m} particles located at $\mathbf{q}^{N_{\mathrm{m}}}$ while N_{t} template particles are located at $\mathbf{s}^{N_{\mathrm{t}}}$, with

$$\Xi_{\mathrm{bulk}} = \mathrm{Tr}_{\mathrm{m}}\, \mathrm{Tr}_{\mathrm{t}}$$
$$\frac{z_{\mathrm{m}}^{N_{\mathrm{m}}} z_{\mathrm{t}}^{N_{\mathrm{t}}} e^{-\beta\left[V_{\mathrm{mm}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}}) + V_{\mathrm{mt}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}}, N_{\mathrm{t}}, \mathbf{s}^{N_{\mathrm{t}}}) + V_{\mathrm{tt}}(N_{\mathrm{t}}, \mathbf{s}^{N_{\mathrm{t}}})\right]}}{N_{\mathrm{m}}! N_{\mathrm{t}}!} \quad (7)$$

for the normalizing partition sum. Equation (4) still generates the matrix probability distribution. In the above equations, z_{m} and z_{t} are the activities of the matrix and template components in the bulk binary mixture, and $V_{\mathrm{mm}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}})$, $V_{\mathrm{mt}}(N_{\mathrm{m}}, \mathbf{q}^{N_{\mathrm{m}}}, N_{\mathrm{t}}, \mathbf{s}^{N_{\mathrm{t}}})$ and $V_{\mathrm{tt}}(N_{\mathrm{t}}, \mathbf{s}^{N_{\mathrm{t}}})$ are the matrix-matrix, matrix-template and template-

template contributions to the potential energy of the mixture, respectively.

So far, only probabilities relative to the matrix and its preparation process have been considered. We now turn to the confined fluid statistics. As mentioned above, the confined fluid is assumed to be in grand-canonical equilibrium in the presence of the porous matrix and, by construction of the model, to inherit its properties from the template. Thus, its activity z_f (the subscript f is used for properties of the confined fluid) is taken equal to the template activity z_t and, for a particular realization of the matrix with N_m particles located at $\mathbf{q}^{N_m}$, its potential energy is chosen as $V_{mt}(N_m, \mathbf{q}^{N_m}, N_f, \mathbf{r}^{N_f}) + V_{tt}(N_f, \mathbf{r}^{N_f})$, when N_f fluid particles located at $(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_f}) \equiv \mathbf{r}^{N_f}$ are present in the system. It follows that the probability density of such a configuration, which depends parametrically on the matrix configuration $(N_m, \mathbf{q}^{N_m})$, is

$$
\mathcal{P}_f(N_f, \mathbf{r}^{N_f} | N_m, \mathbf{q}^{N_m}) =
$$
$$
\frac{z_t^{N_f} e^{-\beta \left[V_{mt}(N_m, \mathbf{q}^{N_m}, N_f, \mathbf{r}^{N_f}) + V_{tt}(N_f, \mathbf{r}^{N_f}) \right]}}{\Xi_f(N_m, \mathbf{q}^{N_m}) N_f!} \quad (8)
$$

with the confined fluid partition function

$$
\Xi_f(N_m, \mathbf{q}^{N_m}) =
$$
$$
\mathrm{Tr}_f \frac{z_t^{N_f} e^{-\beta \left[V_{mt}(N_m, \mathbf{q}^{N_m}, N_f, \mathbf{r}^{N_f}) + V_{tt}(N_f, \mathbf{r}^{N_f}) \right]}}{N_f!}. \quad (9)
$$

Combining Eqs. (6) and (8), a very simple equality can be derived,

$$
\mathcal{P}_{mt}(N_m, \mathbf{q}^{N_m}, N_t, \mathbf{s}^{N_t}) \mathcal{P}_f(N_f, \mathbf{r}^{N_f} | N_m, \mathbf{q}^{N_m}) =
$$
$$
\mathcal{P}_{mt}(N_m, \mathbf{q}^{N_m}, N_f, \mathbf{r}^{N_f}) \mathcal{P}_f(N_t, \mathbf{s}^{N_t} | N_m, \mathbf{q}^{N_m}), \quad (10)
$$

which reflects the very peculiar symmetries of the system under study and will play a crucial role in the following.

Armed with these results, we might now investigate the configurational properties of the RP and PP systems.

III. CONFIGURATIONAL IDENTITIES

Dealing with quenched-disordered fluid-matrix systems, two types of configurational averages have to be considered when computing their properties [25, 27]. The first one is the ordinary thermal average denoted by $\langle \cdots \rangle$, taken for a given realization $(N_m, \mathbf{q}^{N_m})$ of the matrix with the probability density $\mathcal{P}_f(N_f, \mathbf{r}^{N_f} | N_m, \mathbf{q}^{N_m})$. The second one is the disorder average over the matrix realizations, denoted by $\overline{\cdots}$, to be taken with the probability density $\mathcal{P}_m(N_m, \mathbf{q}^{N_m})$ after the thermal average. We shall not dwell on subtleties of the physics of quenched-disordered systems, but it might be worth recalling that this average over disorder is equivalent to an average over macroscopic subparts of a macroscopic system for additive quantities, and to a volume average over a macroscopic sample for locally defined quantities [57].

These two types of averages might be combined in many different ways. For instance, computations of free energy differences typically involve expressions of the form $\ln\langle A \rangle$. Here, we shall concentrate on two specific examples for which simple results can be derived. They correspond to double averages $\overline{\langle A \rangle}$ and to products of the form $\overline{\langle A \rangle \langle B \rangle}$. Such quantities are often combined to generate correlation functions characterizing the two physically distinct types of fluctuations present in disordered systems. Thus, the typical thermal fluctuations are quantified by so-called connected averages of the form $\overline{\langle AB \rangle} - \overline{\langle A \rangle \langle B \rangle}$, while the disorder-induced fluctuations of thermal quantities are measured by so-called disconnected averages defined as $\overline{\langle A \rangle \langle B \rangle} - \overline{\langle A \rangle}\ \overline{\langle B \rangle}$. The distinction between these two types of correlation functions is an essential feature of the physics of disordered systems, whose significance is, for instance, stressed by the fact that the thermodynamic susceptibilities, such as the isothermal compressibility [28, 32], are always expressed as connected averages.

In order to shorten the equations in this rather formal section, a condensed vector notation will be used. Thus, we define $\mathbf{m} \equiv (N_m, \mathbf{q}^{N_m})$, $\mathbf{t} \equiv (N_t, \mathbf{s}^{N_t})$, and $\mathbf{f} \equiv (N_f, \mathbf{r}^{N_f})$. With these definitions, Eq. (10) now reads

$$
\mathcal{P}_{mt}(\mathbf{m}, \mathbf{t}) \mathcal{P}_f(\mathbf{f} | \mathbf{m}) = \mathcal{P}_{mt}(\mathbf{m}, \mathbf{f}) \mathcal{P}_f(\mathbf{t} | \mathbf{m}). \quad (11)
$$

Generically, a configurational variable for a quenched-disordered fluid-matrix system is a function $A(\mathbf{x}; \mathbf{m}, \mathbf{f})$ of the matrix and fluid particle numbers and coordinates, possibly with other variables (such as space variables when dealing with n-particle densities) collectively denoted by $\mathbf{x}$. Its thermal average for a given matrix realization is defined as

$$
\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle = \mathrm{Tr}_f \, \mathcal{P}_f(\mathbf{f} | \mathbf{m}) A(\mathbf{x}; \mathbf{m}, \mathbf{f}), \quad (12)
$$

so that its double average after tracing out the matrix variables reads

$$
\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle} = \mathrm{Tr}_m \, \mathcal{P}_m(\mathbf{m}) \, \mathrm{Tr}_f \, \mathcal{P}_f(\mathbf{f} | \mathbf{m}) A(\mathbf{x}; \mathbf{m}, \mathbf{f}). \quad (13)
$$

Specializing to the PP systems and introducing an explicit reference to the original matrix-template mixture, this can be rewritten as

$$
\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle} = \mathrm{Tr}_m \, \mathrm{Tr}_t \, \mathrm{Tr}_f \, \mathcal{P}_{mt}(\mathbf{m}, \mathbf{t}) \mathcal{P}_f(\mathbf{f} | \mathbf{m}) A(\mathbf{x}; \mathbf{m}, \mathbf{f}), \quad (14)
$$

which, thanks to Eq. (11), is transformed into

$$
\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle} = \mathrm{Tr}_m \, \mathrm{Tr}_t \, \mathrm{Tr}_f \, \mathcal{P}_{mt}(\mathbf{m}, \mathbf{f}) \mathcal{P}_f(\mathbf{t} | \mathbf{m}) A(\mathbf{x}; \mathbf{m}, \mathbf{f}), \quad (15)
$$

eventually leading to

$$
\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle} = \mathrm{Tr}_m \, \mathrm{Tr}_f \, \mathcal{P}_{mt}(\mathbf{m}, \mathbf{f}) A(\mathbf{x}; \mathbf{m}, \mathbf{f}), \quad (16)
$$

since $\mathrm{Tr}_t \, \mathcal{P}_f(\mathbf{t} | \mathbf{m}) = 1$ appears factorized in Eq. (15).

The right-hand side of Eq. (16) is immediately recognized as a thermal average for the bulk matrix-template

mixture, which will be denoted by $\langle \cdots \rangle_{\text{bulk}}$. So, the first sought-for configurational identity reads

$$\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle} = \langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle_{\text{bulk}}, \qquad (17)$$

i.e., the double-averaged configurational properties of a PP system coincide with the corresponding quantities in the bulk fluid on which it is based [58]. This in particular applies to the n-particle densities and distribution functions and explains past observations in computer simulation studies [18, 47, 48, 50].

There are different possible ways of taking advantage of this result in computer simulation studies. An immediate idea is that one can completely avoid the computation of double averages for the PP fluid-matrix systems. Instead, the corresponding calculations can be performed on the bulk fluid, which in any case has to be simulated in order to generate the porous samples and for which the problem is conceptually simpler (only one type of average is required and it is an ordinary thermal average) and the sampling of the configuration space is often more efficient, thanks to faster dynamics [18, 47, 48, 50–52]. Another option is to use the computation of double averages as a means to calibrate the parameters of the simulation study. Indeed, the above identity is not expected to hold on a sample-by-sample basis. It becomes valid only after the disorder average is performed. Therefore, one can use the comparison between double averages and high quality data for the bulk as a guide to estimate the minimal number of matrix realizations that is required in order to achieve a satisfactory convergence of the disorder averaging procedure.

In the case of two configurational variables $A(\mathbf{x}; \mathbf{m}, \mathbf{f})$ and $B(\mathbf{y}; \mathbf{m}, \mathbf{f})$, the typical value of the product of their thermal averages is defined as

$$\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle \langle B(\mathbf{y}; \mathbf{m}, \mathbf{f}') \rangle} = \text{Tr}_{\text{m}} \mathcal{P}_{\text{m}}(\mathbf{m})$$
$$\text{Tr}_{\text{f}} \mathcal{P}_{\text{f}}(\mathbf{f}|\mathbf{m}) A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \, \text{Tr}'_{\text{f}} \mathcal{P}_{\text{f}}(\mathbf{f}'|\mathbf{m}) B(\mathbf{y}; \mathbf{m}, \mathbf{f}'), \quad (18)$$

where Tr'_{f} simply represents the trace over primed fluid variables. Through Eq. (4), this might be rewritten for a PP system as

$$\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle \langle B(\mathbf{y}; \mathbf{m}, \mathbf{f}') \rangle} = \text{Tr}_{\text{m}} \text{Tr}_{\text{t}} \text{Tr}_{\text{f}} \text{Tr}'_{\text{f}} \mathcal{P}_{\text{mt}}(\mathbf{m}, \mathbf{t})$$
$$\mathcal{P}_{\text{f}}(\mathbf{f}|\mathbf{m}) A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \mathcal{P}_{\text{f}}(\mathbf{f}'|\mathbf{m}) B(\mathbf{y}; \mathbf{m}, \mathbf{f}'). \quad (19)$$

Thanks to Eq. (11), one can exchange the variables $\mathbf{t}$ and $\mathbf{f}'$ between $\mathcal{P}_{\text{mt}}(\mathbf{m}, \mathbf{t})$ and $\mathcal{P}_{\text{f}}(\mathbf{f}'|\mathbf{m})$ (one could choose to exchange $\mathbf{t}$ and $\mathbf{f}$ instead, but this would simply amount to an exchange of A and B which play symmetric roles in the original problem), then perform the trace Tr_{t} which reduces to a normalization condition as above. It remains

$$\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle \langle B(\mathbf{y}; \mathbf{m}, \mathbf{f}') \rangle} = \text{Tr}_{\text{m}} \text{Tr}_{\text{f}} \text{Tr}'_{\text{f}}$$
$$\mathcal{P}_{\text{mt}}(\mathbf{m}, \mathbf{f}') \mathcal{P}_{\text{f}}(\mathbf{f}|\mathbf{m}) A(\mathbf{x}; \mathbf{m}, \mathbf{f}) B(\mathbf{y}; \mathbf{m}, \mathbf{f}'), \quad (20)$$

whose meaning is illuminated by a simple change of dummy variables leading to

$$\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle \langle B(\mathbf{y}; \mathbf{m}, \mathbf{f}') \rangle} = \text{Tr}_{\text{m}} \text{Tr}_{\text{t}} \text{Tr}_{\text{f}}$$
$$\mathcal{P}_{\text{mt}}(\mathbf{m}, \mathbf{t}) \mathcal{P}_{\text{f}}(\mathbf{f}|\mathbf{m}) A(\mathbf{x}; \mathbf{m}, \mathbf{f}) B(\mathbf{y}; \mathbf{m}, \mathbf{t}). \quad (21)$$

The right-hand side of the latter equation takes the form of a double average, but now with a modified disorder average involving the matrix-template probability distribution $\mathcal{P}_{\text{mt}}(\mathbf{m}, \mathbf{t})$, which will be denoted by $\overline{\cdots}'$ in the following. Such a modification is very natural if one includes the template variables $(N_{\text{t}}, \mathbf{s}^{N_{\text{t}}})$ in the set of configurational parameters describing the system and accordingly deals with configurational variables of the form $A(\mathbf{x}; \mathbf{m}, \mathbf{t}, \mathbf{f})$. Strictly speaking, this extension is not required by the physics of the system, which can be discussed uniquely in terms of fluid and matrix parameters [27], in which case, as it should be, the modified disorder averaging procedure does not change anything, as attested by identities such as

$$\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle}' = \overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle}. \qquad (22)$$

However, the consideration of template degrees of freedom offers a very pictorial way to capture how the matrix-template and template-template correlations imprinted in the porous solid during its preparation are transferred to the fluid. It can also lead to important technical simplifications in formal developments. One example based on the interpretation of Eq. (21) will follow. Another one is provided by the integral equation theory of the generic templated systems [41–44], where the introduction of total and direct correlation functions involving the template leads to equations that preserve standard diagrammatic prescriptions (no nodal points in direct correlation functions), at variance with Madden's more compact formalism [27].

Coming back to Eq. (21), the second sought-for configurational identity thus reads

$$\overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) \rangle \langle B(\mathbf{y}; \mathbf{m}, \mathbf{f}') \rangle} = \overline{\langle A(\mathbf{x}; \mathbf{m}, \mathbf{f}) B(\mathbf{y}; \mathbf{m}, \mathbf{t}) \rangle}', \qquad (23)$$

where, since the matrix and template variables are static quantities, $B(\mathbf{y}; \mathbf{m}, \mathbf{t})$ can be placed inside or outside the thermal average. So, in a PP system, the disorder-averaged product of two thermal averages coincides with the modified double-averaged product of a fluid-matrix configurational variable with a template-matrix function. Interestingly, this result can be formulated in terms of non-equilibrium quantities as well. Indeed, since the fluid and the template components are essentially identical, the template coordinates at the time of preparation of the matrix can be considered as initial conditions for an ulterior fluid dynamics inside the matrix. So, the right-hand side of Eq. (23) can be interpreted as the correlation of a thermal average with a function of these initial conditions.

The availability of Eq. (23) represents a major simplification for computational studies of PP systems compared to other particle-based models of disordered porous media. Indeed, the modified double average on its right-hand side should be no more difficult to compute than the standard double average on fluid and matrix configurations met in all this family of systems. The only additional price to pay is to keep track of the positions

occupied by the template particles at the moment of the matrix production. Thus, through Eq. (23), quantities of the form $\overline{\langle A \rangle \langle B \rangle}$, which are required to compute the physically important connected correlations, are made numerically accessible via a simple and controlled procedure.

The relevance of this result is best illustrated through an example, which is the computation of the two-point correlation function

$$\psi(\mathbf{r}, \mathbf{r}') = \overline{\langle \hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}; \mathbf{f}) \rangle \langle \hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}'; \mathbf{f}') \rangle}, \qquad (24)$$

where $\hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}; \mathbf{f})$ is the microscopic fluid density operator

$$\hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}; \mathbf{f}) = \sum_{i=1}^{N_{\mathrm{f}}} \delta(\mathbf{r} - \mathbf{r}_i). \qquad (25)$$

For a generic fluid-matrix system, one typically has to calculate $\langle \hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}; \mathbf{f}) \rangle$ on a grid for each matrix realization and to compute the autocorrelations as sums over the grid points, before disorder averaging [59]. Unfortunately, the outcome of this procedure has been found to be marred by artifacts related to the finite size of the grid cells. Analogous difficulties are present in reciprocal space calculations of the structure factor associated with $\psi(\mathbf{r}, \mathbf{r}')$ [60]. In the case of a PP system, however, Eq. (23) can be used to obtain

$$\psi(\mathbf{r}, \mathbf{r}') = \overline{\langle \hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}; \mathbf{f}) \hat{\rho}_{\mathrm{t}}^{(1)}(\mathbf{r}'; \mathbf{t}) \rangle}', \qquad (26)$$

where $\hat{\rho}_{\mathrm{t}}^{(1)}(\mathbf{r}; \mathbf{t})$ is the template analogue of $\hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}; \mathbf{f})$. Further simplification occurs by noting that the product $\hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}; \mathbf{f}) \hat{\rho}_{\mathrm{t}}^{(1)}(\mathbf{r}'; \mathbf{t})$ is simply the two-particle fluid-template density operator $\hat{\rho}_{\mathrm{ft}}^{(2)}(\mathbf{r}, \mathbf{r}'; \mathbf{f}, \mathbf{t})$, so that eventually

$$\psi(\mathbf{r}, \mathbf{r}') = \overline{\langle \hat{\rho}_{\mathrm{ft}}^{(2)}(\mathbf{r}, \mathbf{r}'; \mathbf{f}, \mathbf{t}) \rangle}'. \qquad (27)$$

The computation of $\psi(\mathbf{r}, \mathbf{r}')$ is thus turned into the rather innocuous problem of computing the pair correlation function between the fluid particles and the template sites, which does not require the use of a grid and thus is obviously free of grid artifacts. It is interesting to note that an analogous possibility to replace the direct computation of a disconnected correlation function by the computation of an equivalent pair correlation function also exists for ideal gases in disordered environments, thanks to the fact that the connected pair correlation functions identically vanish in these systems. The case has been investigated on one specific example in Ref. [59], where it is reported that the latter strategy yields better results than the former. This clearly lends support to the suggestion that the availability of Eq. (23) and the resulting simplifications for PP systems should facilitate the accumulation of high quality computer simulation data.

Finally, the above equations, formulated in the framework of the PP systems, can be easily adapted to the case of the one-component-fluid-based RP models. In particular, using Eq. (17), the double-averaged quantities in the RP system can be related to corresponding thermal averages in the one-component bulk fluid. One only needs to revert the mapping to an ideal template-matrix mixture described in the previous section. Unfortunately, the simplicity of the above identities is lost in the process, since the dependence of the resulting expressions on the pinning fraction is found to change with the configurational variable under consideration. For this reason, we do not report any specific results for the RP model here. Some important ones will appear in the next section.

IV. PAIR CORRELATIONS AND INTEGRAL EQUATION THEORIES

The description of the structure of fluids at the pair level is a central issue of liquid state theory. In this section, we examine how the above identities impact on this problem for the PP and RP fluid-matrix models.

Since we are dealing with special cases of templated systems, the natural framework for the present study is the theory developed by Van Tassel and coworkers [41–44]. For a generic templated system with no special symmetries, they introduced eight total correlation functions in order to fully describe the structure at the pair level. Six of them are the standard functions reflecting the two-body correlations between the different types of particles involved in the model. They are the matrix-matrix, matrix-template, template-template, matrix-fluid, template-fluid, and fluid-fluid total correlation functions, denoted by $h_{\mathrm{mm}}(r)$, $h_{\mathrm{mt}}(r)$, $h_{\mathrm{tt}}(r)$, $h_{\mathrm{mf}}(r)$, $h_{\mathrm{tf}}(r)$, and $h_{\mathrm{ff}}(r)$, respectively. They can be expressed in terms of double-averaged two-particle density operators $\hat{\rho}_{ij}^{(2)}(\mathbf{r}, \mathbf{r}')$, $i, j = \mathrm{m,t,f}$ (for notational convenience, the dependence on the particle numbers and configurations is omitted here and in the following), as

$$h_{ij}(|\mathbf{r} - \mathbf{r}'|) = \frac{\overline{\langle \hat{\rho}_{ij}^{(2)}(\mathbf{r}, \mathbf{r}') \rangle}' - \rho_i \rho_j}{\rho_i \rho_j}, \qquad (28)$$

where $\rho_i = \overline{\langle \hat{\rho}_i^{(1)}(\mathbf{r}) \rangle}'$ is the number density of species i [see Eq. (25) for the expression of $\hat{\rho}_i^{(1)}(\mathbf{r})$]. Note that a modified (primed) disorder average is used, because it is required for the proper definition of quantities pertaining to template particles. When only matrix and/or fluid particles are involved, it can safely be replaced by the usual matrix average on the basis of Eq. (22). Through these averages, the statistical isotropy and homogeneity of the system are restored, hence the dependence of all pair correlation functions on the scalar $|\mathbf{r} - \mathbf{r}'|$ only.

The two remaining functions are specific to quenched-disordered systems and give an account of the correlations between the one-body fluid densities at two different points induced by the disorder. They are the blocking

or disconnected total correlation function

$$h_{\mathrm{b}}(|\mathbf{r} - \mathbf{r}'|) = \frac{\overline{\langle \hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}) \rangle \langle \hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}') \rangle} - \rho_{\mathrm{f}}^2}{\rho_{\mathrm{f}}^2}, \qquad (29)$$

and the connected total correlation function

$$h_{\mathrm{c}}(|\mathbf{r} - \mathbf{r}'|) = \frac{\overline{\langle \hat{\rho}_{\mathrm{ff}}^{(2)}(\mathbf{r}, \mathbf{r}') \rangle} - \overline{\langle \hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}) \rangle \langle \hat{\rho}_{\mathrm{f}}^{(1)}(\mathbf{r}') \rangle}}{\rho_{\mathrm{f}}^2}, \qquad (30)$$

hence the discussion of the function $\psi(\mathbf{r}, \mathbf{r}')$ in the previous section. Note that $h_{\mathrm{ff}}(r)$, $h_{\mathrm{b}}(r)$ and $h_{\mathrm{c}}(r)$ are not independent, since they obey $h_{\mathrm{ff}}(r) = h_{\mathrm{b}}(r) + h_{\mathrm{c}}(r)$.

Using diagrammatic techniques or the replica trick, Ornstein-Zernike (OZ) equations are easily derived which connect the above total correlation functions to the corresponding set of direct correlation functions, $c_{ij}(r)$, $c_{\mathrm{b}}(r)$ and $c_{\mathrm{c}}(r)$. They read (for convenience, the r dependence is omitted)

$$h_{\mathrm{mm}} = c_{\mathrm{mm}} + \rho_{\mathrm{m}} c_{\mathrm{mm}} \otimes h_{\mathrm{mm}} + \rho_{\mathrm{t}} c_{\mathrm{mt}} \otimes h_{\mathrm{mt}}, \qquad (31\mathrm{a})$$

$$h_{\mathrm{mt}} = c_{\mathrm{mt}} + \rho_{\mathrm{m}} c_{\mathrm{mm}} \otimes h_{\mathrm{mt}} + \rho_{\mathrm{t}} c_{\mathrm{mt}} \otimes h_{\mathrm{tt}}, \qquad (31\mathrm{b})$$

$$h_{\mathrm{tt}} = c_{\mathrm{tt}} + \rho_{\mathrm{m}} c_{\mathrm{mt}} \otimes h_{\mathrm{mt}} + \rho_{\mathrm{t}} c_{\mathrm{tt}} \otimes h_{\mathrm{tt}}, \qquad (31\mathrm{c})$$

$$h_{\mathrm{mf}} = c_{\mathrm{mf}} + \rho_{\mathrm{m}} c_{\mathrm{mm}} \otimes h_{\mathrm{mf}} + \rho_{\mathrm{t}} c_{\mathrm{mt}} \otimes h_{\mathrm{tf}} + \rho_{\mathrm{f}} c_{\mathrm{mf}} \otimes h_{\mathrm{c}}, \qquad (31\mathrm{d})$$

$$h_{\mathrm{tf}} = c_{\mathrm{tf}} + \rho_{\mathrm{m}} c_{\mathrm{mt}} \otimes h_{\mathrm{mf}} + \rho_{\mathrm{t}} c_{\mathrm{tt}} \otimes h_{\mathrm{tf}} + \rho_{\mathrm{f}} c_{\mathrm{tf}} \otimes h_{\mathrm{c}}, \qquad (31\mathrm{e})$$

$$h_{\mathrm{ff}} = c_{\mathrm{ff}} + \rho_{\mathrm{m}} c_{\mathrm{mf}} \otimes h_{\mathrm{mf}} + \rho_{\mathrm{t}} c_{\mathrm{tf}} \otimes h_{\mathrm{tf}} + \rho_{\mathrm{f}} c_{\mathrm{ff}} \otimes h_{\mathrm{ff}} - \rho_{\mathrm{f}} c_{\mathrm{b}} \otimes h_{\mathrm{b}}, \qquad (31\mathrm{f})$$

$$h_{\mathrm{b}} = c_{\mathrm{b}} + \rho_{\mathrm{m}} c_{\mathrm{mf}} \otimes h_{\mathrm{mf}} + \rho_{\mathrm{t}} c_{\mathrm{tf}} \otimes h_{\mathrm{tf}} + \rho_{\mathrm{f}} c_{\mathrm{c}} \otimes h_{\mathrm{b}} + \rho_{\mathrm{f}} c_{\mathrm{b}} \otimes h_{\mathrm{c}}, \qquad (31\mathrm{g})$$

$$h_{\mathrm{c}} = c_{\mathrm{c}} + \rho_{\mathrm{f}} c_{\mathrm{c}} \otimes h_{\mathrm{c}}, \qquad (31\mathrm{h})$$

where $\otimes$ represents a convolution in real space. As for the total correlation functions, one gets $c_{\mathrm{ff}}(r) = c_{\mathrm{b}}(r) + c_{\mathrm{c}}(r)$. The first three equations are simply the OZ equations for the bulk binary matrix-template mixture from which the porous medium is formed, while the others relate to the structure of the fluid adsorbed in the random solid.

Specialization to the present systems of interest is achieved by working out the consequences of the identities (17) and (23) on the one- and two-body densities. For a generic PP system, one obtains

$$\rho_{\mathrm{t}} = \rho_{\mathrm{f}}, \qquad (32\mathrm{a})$$

$$h_{\mathrm{mt}}(r) = h_{\mathrm{mf}}(r), \qquad (32\mathrm{b})$$

$$h_{\mathrm{tt}}(r) = h_{\mathrm{ff}}(r), \qquad (32\mathrm{c})$$

$$h_{\mathrm{tf}}(r) = h_{\mathrm{b}}(r), \qquad (32\mathrm{d})$$

and equivalently for the direct correlation functions, so that the OZ equations reduce to

$$h_{\mathrm{mm}} = c_{\mathrm{mm}} + \rho_{\mathrm{m}} c_{\mathrm{mm}} \otimes h_{\mathrm{mm}} + \rho_{\mathrm{f}} c_{\mathrm{mf}} \otimes h_{\mathrm{mf}}, \qquad (33\mathrm{a})$$

$$h_{\mathrm{mf}} = c_{\mathrm{mf}} + \rho_{\mathrm{m}} c_{\mathrm{mm}} \otimes h_{\mathrm{mf}} + \rho_{\mathrm{f}} c_{\mathrm{mf}} \otimes h_{\mathrm{ff}}, \qquad (33\mathrm{b})$$

$$h_{\mathrm{ff}} = c_{\mathrm{ff}} + \rho_{\mathrm{m}} c_{\mathrm{mf}} \otimes h_{\mathrm{mf}} + \rho_{\mathrm{f}} c_{\mathrm{ff}} \otimes h_{\mathrm{ff}}, \qquad (33\mathrm{c})$$

$$h_{\mathrm{b}} = c_{\mathrm{b}} + \rho_{\mathrm{m}} c_{\mathrm{mf}} \otimes h_{\mathrm{mf}} + \rho_{\mathrm{f}} c_{\mathrm{ff}} \otimes h_{\mathrm{ff}} - \rho_{\mathrm{f}} c_{\mathrm{c}} \otimes h_{\mathrm{c}}, \qquad (33\mathrm{d})$$

$$h_{\mathrm{c}} = c_{\mathrm{c}} + \rho_{\mathrm{f}} c_{\mathrm{c}} \otimes h_{\mathrm{c}}. \qquad (33\mathrm{e})$$

For a RP system with pinning fraction x based on a one-component bulk fluid with density ρ and total and direct correlation functions $h(r)$ and $c(r)$, well-known properties of ideal binary mixtures lead to

$$\rho_{\mathrm{m}} = x\rho, \qquad (34\mathrm{a})$$

$$\rho_{\mathrm{f}} = (1 - x)\rho, \qquad (34\mathrm{b})$$

$$h_{\mathrm{ff}}(r) = h_{\mathrm{mf}}(r) = h_{\mathrm{mm}}(r) = h(r), \qquad (34\mathrm{c})$$

and analogously for the direct correlation functions, so that the OZ equations become

$$h = c + \rho c \otimes h, \qquad (35\mathrm{a})$$

$$h_{\mathrm{b}} = c_{\mathrm{b}} + \rho c \otimes h - (1 - x)\rho c_{\mathrm{c}} \otimes h_{\mathrm{c}}, \qquad (35\mathrm{b})$$

$$h_{\mathrm{c}} = c_{\mathrm{c}} + (1 - x)\rho c_{\mathrm{c}} \otimes h_{\mathrm{c}}. \qquad (35\mathrm{c})$$

Some features of the above equations are very appealing with a view to developing integral-equation theoretical approaches. The most obvious one is their mere number. Indeed, not surprisingly, a significant reduction in the number of unknown functions and OZ equations linking them ensues from the special symmetries of the PP and RP systems. It is particularly drastic in the case of the RP system, where only two linearly independent OZ equations remain [remember that $h_{\mathrm{ff}}(r) = h_{\mathrm{b}}(r) + h_{\mathrm{c}}(r)$ and $c_{\mathrm{ff}}(r) = c_{\mathrm{b}}(r) + c_{\mathrm{c}}(r)$]. Since one generically needs at least two of the three functions $h_{\mathrm{ff}}(r)$, $h_{\mathrm{b}}(r)$ and $h_{\mathrm{c}}(r)$ in order to characterize the pair structure of a fluid in a statistically homogeneous disordered environment, this is actually the smallest possible number, whose only known realization so far was in the case of a Gaussian random field [61], i.e., of a non-particle-based disordered environment. Thanks to this extreme compactness of the formalism, with its minimal number of unknowns and coupled equations, one can reasonably expect that the development and the implementation of advanced integral equation theories for the present class of systems will be made much easier.

The situation is actually even more favorable than that. Indeed, from Eqs. (33) and (35), one can immediately see that the problem of computing the pair correlations between the different types of particles present in the system, which amounts to a calculation on the bulk fluid from which the confined fluid-matrix system is prepared, is completely separated from the one of obtaining the two contributions to $h_{\mathrm{ff}}(r)$ which split under the effect of randomness. Therefore, since well established integral equation schemes exist which allow one to successfully tackle the first problem for a variety of interaction potentials [56, 62], one can build on them, so that the only actual issue for the present systems of interest boils down to the computation of $h_{\mathrm{b}}(r)$ and $h_{\mathrm{c}}(r)$, $h_{\mathrm{ff}}(r)$ being considered as known.

There are different possible ways of taking advantage of this result. One of them is to note that, because of the separation of the bulk- and confinement-specific parts of the calculation, one should not feel bound to treat both problems with the same type of approximation. Therefore, for a given description of the bulk fluid system, one
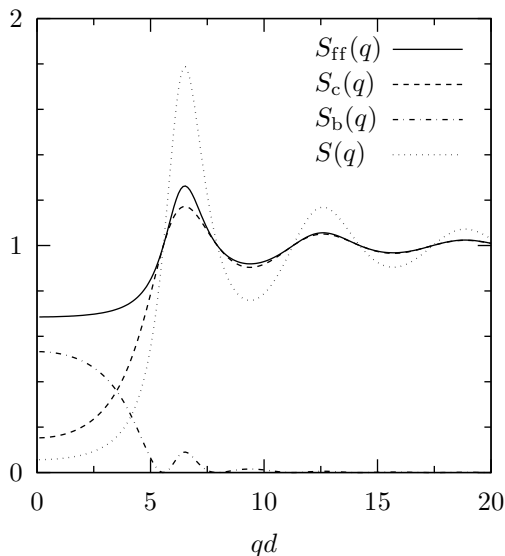
FIG. 2. Structure factors of a hard-sphere randomly pinned fluid-matrix system, obtained analytically in the Percus-Yevick approximation. $S_{\mathrm{ff}}(q)$, $S_{\mathrm{c}}(q)$, and $S_{\mathrm{b}}(q)$ are, respectively, the fluid-fluid, the connected and the blocking structure factors of the confined system, $S(q)$ is the structure factor of the bulk fluid from which the fluid-matrix system is prepared. The compacity of the original bulk system is $\phi = (\pi/6)\rho d^3 = 0.36$, with d the diameter of the spheres, and the pinning fraction is $x = 2/3$.

can freely experiment with closures for $h_{\mathrm{b}}(r)$, $h_{\mathrm{c}}(r)$, $c_{\mathrm{b}}(r)$ and $c_{\mathrm{c}}(r)$. In combination with quantitative comparisons with computer simulation data, whose accumulation is greatly facilitated by the use of Eqs. (17) and (23) (see the discussion in the previous section), this should lead to insight into this crucial but not so well understood aspect of the physics of fluids in random environments, with a real prospect that accurate theories can be developed, not only for the PP and RP systems, but for fluids in quenched disorder in general.

An alternative strategy is to use the same closure approximation for both parts of the calculation and to concentrate on integral equation theories that have analytic solutions in the bulk, trying to generate analytic solutions for the confined system as well. Such solutions are extremely scarce in the theory of fluids in disordered environments, even within basic approximation schemes. They might be useful in a number of different ways. For instance, as demonstrated by many advances in the case of bulk systems [56, 62], they might represent precious starting points for the development of more elaborate approximations. Or they might be used to produce at a minimal computational cost the large amounts of structural data that are required as input by other types of calculations, such as the prediction of dynamical phase diagrams in the framework of the mode-coupling theory [20–23].

It turns out that closures which fall in the class of the so-called Madden-Glandt approximations, i.e., char-

acterized by an identically vanishing blocking direct correlation function [29–31], are particularly well suited for such an approach. They include the Percus-Yevick (PY) and mean-spherical (MSA) approximations, for which, precisely, a number of analytic solutions for bulk systems are well known [56, 62]. As an illustration of this procedure, we report in Fig. 2 the structure factors of a hard-sphere RP system obtained analytically with the PY closure. Since $c_{\mathrm{b}}(r) = 0$ and $c_{\mathrm{c}}(r) = c(r)$ in this approximation, they are simply expressed in terms of the analytically known Fourier transform of the PY direct correlation function of the bulk hard-sphere fluid, $\tilde{c}(q)$ [$\tilde{f}(q)$ denotes the Fourier transform of $f(r)$], as

$$S(q) = 1 + \rho\tilde{h}(q) = \frac{1}{1 - \rho\tilde{c}(q)}, \tag{36a}$$

$$S_{\mathrm{ff}}(q) = 1 + \rho_{\mathrm{f}}\tilde{h}_{\mathrm{ff}}(q) = \frac{1 - x\rho\tilde{c}(q)}{1 - \rho\tilde{c}(q)}, \tag{36b}$$

$$S_{\mathrm{c}}(q) = 1 + \rho_{\mathrm{f}}\tilde{h}_{\mathrm{c}}(q) = \frac{1}{1 - (1-x)\rho\tilde{c}(q)}, \tag{36c}$$

$$S_{\mathrm{b}}(q) = \rho_{\mathrm{f}}\tilde{h}_{\mathrm{b}}(q) = \frac{x(1-x)\rho^2\tilde{c}(q)^2}{[1 - \rho\tilde{c}(q)][1 - (1-x)\rho\tilde{c}(q)]}, \tag{36d}$$

where $S(q)$ is the structure factor of the bulk fluid from which the fluid-matrix system is prepared, and $S_{\mathrm{ff}}(q)$, $S_{\mathrm{c}}(q)$, and $S_{\mathrm{b}}(q)$ are, respectively, the fluid-fluid, the connected and the blocking structure factors of the confined system.

Finally, beside integral equation theories, other liquid-state theoretical approaches could either be directly applied to the PP and RP systems or at least take advantage of their simplifying features in some parts of their development. For instance, one might turn to perturbation theory [56] and, in the same spirit as in previous work on QA systems [63] and fluids in aerogels [46], study athermal PP or RP reference systems decorated with attractive fluid-matrix and fluid-fluid interactions. One would then benefit from all the above results for the description of the reference system. Note in passing that, while integral equation theories enforce the complementarity between the fluid and the matrix at all state points and thus deal with a temperature-dependent structure of the porous solid, this would not be the case in such a perturbative scheme, where the disordered matrix exclusively inherits its properties from the reference athermal system.

V. APPLICATIONS IN DYNAMICAL STUDIES

So far, the discussion has essentially been on how the knowledge of the properties of the bulk fluid on which a PP system is based leads to considerable simplifications in the study of the confined fluid system. Then, one might wonder whether, conversely, information on the latter might help understanding aspects of the physics of the former. In this section, we show that such opportunities might exist when dealing with dynamics.

Operationally, any fluid-matrix system in which the porous solid is represented by fixed randomly placed particles can be described in dynamical terms as a binary mixture of fluid and matrix particles with, respectively, finite and infinite masses when the dynamics is Newtonian, or finite and zero free-diffusion coefficients when it is Brownian. But, in the case of the PP systems, there is more than that. Indeed, it is well known that, in classical statistical mechanics, the configurational properties of a bulk binary mixture are independent of the finite masses or free-diffusion coefficients of its two constituents. Equation (17) shows that this remains true when one mass is sent to infinity or one free-diffusion coefficient to zero, provided the averaging over the configurations of the now immobile matrix particles is performed as a disorder average or, equivalently, as a volume average over a macroscopic sample. So, a PP system can effectively be considered as an asymptotic case of a binary mixture with strong dynamical asymmetry, obtained via a well defined limiting procedure [47–49, 52]. This is a unique situation among the different particle-based models of disordered porous media, which originates in the fact that the solid matrix in a PP system is not prepared independently of the adsorbed fluid, but in its presence in equilibrium conditions.

We might now try and transport the above limiting procedure into the realm of dynamical theories. In order to do so, our starting point will be the description of the relaxation of the collective density fluctuations in bulk binary mixtures in the framework of the Mori-Zwanzig formalism [56], first for Newtonian dynamics.

So, we start with a bulk binary mixture with components labeled f and m. Their particle numbers, number fractions, number densities, and masses are denoted by N_f and N_m, x_f and x_m, ρ_f and ρ_m, m_f and m_m, respectively. The dynamical variables of interest are the Fourier components of the microscopic densities at wave vector $\mathbf{q}$ and time t, $\rho_f(\mathbf{q},t)$ and $\rho_m(\mathbf{q},t)$, from which one forms the static structure factors,

$$S_{ij}(q) = \frac{\langle \rho_i(\mathbf{q},0)\rho_j(-\mathbf{q},0)\rangle}{N_f + N_m}, \quad (37)$$

and density fluctuation autocorrelation functions,

$$F_{ij}(q,t) = \frac{\langle \rho_i(\mathbf{q},t)\rho_j(-\mathbf{q},0)\rangle}{N_f + N_m}. \quad (38)$$

Using standard projection-operator methods [56], the latter functions are shown to obey generalized Langevin equations which read in matrix form

$$\ddot{\mathbf{F}}(q,t) + \mathbf{\Omega}^2(q)\mathbf{F}(q,t) + \int_0^t d\tau \mathbf{M}(q,t-\tau)\dot{\mathbf{F}}(q,\tau) = \mathbf{0}, \quad (39)$$

with initial conditions $\mathbf{F}(q,0) = \mathbf{S}(q)$ and $\dot{\mathbf{F}}(q,0) = \mathbf{0}$. $\mathbf{M}(q,t)$ is the matrix of memory kernels and the frequency matrix $\mathbf{\Omega}^2(q)$ is given by

$$[\mathbf{\Omega}^2]_{ij}(q) = q^2 \frac{k_B T}{m_i} x_i [\mathbf{S}^{-1}]_{ij}(q), \quad (40)$$

where $\mathbf{S}^{-1}(q)$ is the matrix inverse of $\mathbf{S}(q)$.

In the limit $m_m \to +\infty$, which generates a PP system, $\rho_m(\mathbf{q},t)$ is not a dynamical variable anymore, so that $F_{mf}(q,t)[= F_{fm}(q,t)]$ and $F_{mm}(q,t)$ remain equal to the corresponding structure factors at all times [64]. As a result, the dynamical equation for $F_{ff}(q,t)$ obtained by expanding the matrix products in Eq. (39) reduces to

$$\ddot{F}_{ff}(q,t) + \Omega_{ff}^2(q)F_{ff}(q,t) + \Omega_{fm}^2(q)S_{mf}(q) +$$
$$\int_0^t d\tau M_{ff}(q,t-\tau)\dot{F}_{ff}(q,\tau) = 0, \quad (41)$$

which at infinite time leads to

$$\Omega_{ff}^2(q)f_{ff}(q) + \Omega_{fm}^2(q)S_{mf}(q) + m_{ff}(q)\left[f_{ff}(q) - S_{ff}(q)\right] = 0, \quad (42)$$

where

$$f_{ff}(q) = \lim_{t\to\infty}\lim_{m_m\to+\infty} F_{ff}(q,t), \quad (43)$$

$$m_{ff}(q) = \lim_{t\to\infty}\lim_{m_m\to+\infty} M_{ff}(q,t). \quad (44)$$

Note that the order of the limits is essential.

Our goal is to compute $m_{ff}(q)$, so it remains to evaluate $f_{ff}(q)$. If one assumes that the dynamics of the PP system is ergodic, it is expected on general grounds that

$$f_{ff}(q) = \lim_{t\to\infty} \frac{\overline{\langle \rho_f(\mathbf{q},t)\rho_f(-\mathbf{q},0)\rangle}}{N_f + N_m} =$$
$$\frac{\overline{\langle \rho_f(\mathbf{q},t)\rangle\langle \rho_f(-\mathbf{q},0)\rangle}}{N_f + N_m} = x_f\rho_f\tilde{h}_b(q), \quad (45)$$

while $S_{ff}(q) = x_f[1 + \rho_f\tilde{h}_{ff}(q)]$. Note that, compared to the previous section, additional factors x_f appear due to the use of a different normalization for the structure factors. By combining Eq. (42) with the set of OZ equations (33), it then results that

$$m_{ff}(q) = q^2 \frac{k_B T}{m_f}\rho_f\tilde{c}_b(q). \quad (46)$$

For Brownian dynamics with free-diffusion coefficients D_f^0 and D_m^0, one gets, instead of Eq. (39), the matrix equation [65]

$$\dot{\mathbf{F}}(q,t) + \mathbf{\Omega}(q)\mathbf{F}(q,t) + \int_0^t d\tau \mathbf{M}(q,t-\tau)\dot{\mathbf{F}}(q,\tau) = \mathbf{0}, \quad (47)$$

where $\mathbf{M}(q,t)$ is now the matrix of irreducible memory functions and the damping matrix $\mathbf{\Omega}(q)$ is given by

$$\Omega_{ij}(q) = q^2 D_i^0 x_i [\mathbf{S}^{-1}]_{ij}(q). \quad (48)$$

Repeating the above steps with $D_m^0 \to 0$, one obtains

$$m_{ff}(q) = q^2 D_f^0 \rho_f \tilde{c}_b(q). \quad (49)$$

Equations (46) and (49) represent bridges between the statics of the PP systems and the dynamics of the fully

annealed mixtures with a strong dynamical asymmetry. We suggest that they could be usefully incorporated into the development of phenomenological expressions for the memory kernel $M_{\mathrm{ff}}(q, t)$ reflecting the separation of time scales between the short-time relaxation due to the motion of the fast particles constrained by the nearly immobile slow ones and the long-time relaxation associated with the ultimate decorrelation of the positions of the latter. For instance, since a number of observables in dynamically asymmetric mixtures show features reminiscent of the cage effect and two-step relaxation [52], one could imagine building two-step memory kernels with a plateau value around the above determined $m_{\mathrm{ff}}(q)$.

How this should be done in practice will depend on the details of the dynamical theory at hand [56, 66] and is beyond the scope of the present paper. At this point, however, a few words of caution might be in order. First, the above argument specifically deals with one possible source of dynamical asymmetry, namely a wide separation in the kinetic parameters (masses or free-diffusion coefficients) of the mixture components [47–49, 52]. It is not clear if and how it can be transferred to cases where the dynamical asymmetry has another origin, such as size disparity in dense systems (for recent studies, see Refs. [67, 68]). Second, it is already known that not all theoretical frameworks are able to bridge between annealed mixtures and fluid-matrix systems. A prominent example is the mode-coupling theory [20–23] whose equations for these two problems have been shown to be generically incompatible [69]. In such a case, the connection described above does not bring any additional insight, neither into the dynamics of asymmetric bulk mixtures nor into that of RP and PP systems, and each problem has to be analyzed separately within the chosen theoretical framework.

Obviously, and independently of the connection suggested above, the dynamics of the RP and PP systems has an interest of its own, as a simple model of a fluid in a disordered confining environment. In particular, because the computation of static averages is made easy and well controlled in these systems thanks to the identities of Sec. III, they are very appealing models to test dynamical theories which, quite generally and as illustrated by the mode-coupling theory [20–23], require prior knowledge of a number of static properties to deliver their predictions. We stress here that the mode-coupling theory for fluids in random porous matrices [20–23] does not make any assumption on the statistics of the disordered solid (beyond statistical homogeneity) and thus applies as it stands to RP and PP systems.

These models can also be put to good use to investigate the configurational consequences of permanent trapping in systems with hard-core fluid-matrix interactions. Indeed, it is well known that, for such systems at any nonvanishing matrix density, there is always a finite probability that particles are trapped in finite domains disconnected from the rest of the matrix void space [70, 71]. This trapping phenomenon culminates in a diffusion-localization transition which coincides with the percolation transition marking the point after which the matrix void space only consists of finite disconnected domains [71–77]. Thus, the exploration of the volume accessible to the fluid is never completely ergodic and one expects to see at least quantitative differences in configurational properties depending on whether the thermal averaging is performed as an ensemble or a trajectory average, denoted by $\langle \cdots \rangle$ and $[\cdots]$, respectively. For a generic fluid-matrix system, such an investigation is hampered by a number of technical difficulties. For instance, if double averages of the form $\overline{\langle A \rangle}$ and $\overline{[A]}$ are to be compared, the estimation of the former requires the use of smart simulation methods (typically, with nonlocal updates) in order to overcome the lack of ergodicity of the system. In the case of quantities such as $\overline{\langle A \rangle \langle B \rangle}$ and $\overline{[A][B]}$, one has in addition to face the issues mentioned at the end of Sec. III for the computation of such correlation functions. Tackling the problem with a RP or a PP system does not eliminate all difficulties, but significant simplifications occur which should make the various computations much more accessible. Thus, thanks to Eq. (17), the double average $\overline{\langle A \rangle}$ can be efficiently retrieved from studies of the bulk fluid system on which the fluid-matrix model is based, in which no trapping occurs, hence with no need for special sampling techniques. Also, rather than computing $\overline{\langle A \rangle \langle B \rangle}$ and $\overline{[A][B]}$, one can follow Eq. (23) and concentrate on correlation functions involving the positions of the fluid particles at the time of the preparation of the matrix, which are much easier to compute and have essentially the same physical content.

VI. CONCLUSION

In this paper, the statistical properties of the partly pinned fluid systems, a special class of models of fluids confined in disordered porous matrices, have been studied. These systems, which in most respects are just typical examples of fluid-matrix models, are singled out by a peculiar complementarity between the mobile and immobile components, which originates from the fact that the confining random solid is prepared in presence of and in equilibrium with the adsorbed fluid. A special symmetry results, with major repercussions on the configurational properties of the system. In particular, simple identities hold, which relate different types of configurational averages, either relative to the fluid-matrix system or to the bulk fluid from which it is prepared.

By taking advantage of these identities in computer simulation studies, it seems that, with these systems, interesting opportunities are opening up for efficient and accurate computations of quantities that are usually quite difficult to estimate in generic fluid-matrix models, in particular the crucially important connected and disconnected correlation functions. In our opinion, this should make the PP fluid systems the models of choice for a number of theoretical developments in the field of fluids

adsorbed in disordered porous solids. Indeed, in many circumstances, either theories aim at predicting structural properties, as do integral equation theories, and then it is clearly an advantage that their predictions can be readily tested against high-quality simulation data, or they take structural data as input in order to predict other physical properties, such as the dynamics, and then it is extremely convenient that this input can be easily and accurately determined. In all cases, one can reasonably expect that the insight gained on the PP systems will be transferable to other types of fluid-matrix models, so that global progress can be made in our understanding of fluids in random environments.

There is however a price to pay for these conveniences. Indeed, by construction of the model, one cannot change the parameters describing the adsorbed fluid without a similar and complementary modification of the matrix. This is clearly at odd with the typical experimental situation, where, usually, the confining conditions are given and fixed and the fluid characteristics can be altered freely and independently, and might lead to difficulties

of interpretation, when evolutions of the properties of the system across its parameter space are considered.

Finally, some extensions of the present work could be of interest. One obvious direction is towards heterogeneous partly pinned fluid systems, in which all the particles of a bulk system located in a predefined spatial domain are stopped, leaving a fluid confined in a pore or in contact with a solid interface. This setup has been introduced in order to study various aspects of glass formation [78–81] and an identity analogous to Eq. (17) is known to hold [78]. Note however that, in order to prevent the invasion of the solid by the fluid, the authors of Ref. [78] mention the need to introduce a hard separation at the fluid-matrix interface which might lead to complications and approximations absent in the homogeneous case. Another possibility would be to translate the problem in the language of magnetism, where the pinning process would operate on spin variables. This would generate examples of spin systems with correlated random field and/or dilution for which suitable adaptations of Eqs. (17) and (23) would apply.

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