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Thermodynamics of fluids in quenched disordered matrices

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Using the replica method, we derive the thermodynamic relations for a fluid in equilibrium with a quenched porous matrix. In particular, the appropriate Gibbs-Duhem equation is obtained as well as the equivalence between grand canonical and canonical ensembles. The exact compressibility and virial equations are derived. Whereas the compressibility equation remains a direct and practical way to obtain the adsorption isotherm, the virial equation involves terms which do not relate easily to the properties of the fluid/matrix system. This explains the inconsistency between previous theoretical predictions and computer simulation results.

I. INTRODUCTION

The effects of quenched disorder on the thermodynamic properties of condensed systems have received increased experimental and theoretical attention in recent years. In particular, it has been suggested [1] (and observed experimentally [2]) that because of the geometrical and chemical randomness of the porous network, the critical behavior of fluid mixtures imbibed in porous media like glasses and gels is related to that of the random-field Ising model [3]. This is, however, an oversimplified representation of real systems (especially away from criticality) because the structure of porous materials produced by a quench from an equilibrium distribution at some higher temperature is not completely random. Moreover, a lattice-gas model cannot provide a faithful description of the effects of packing constraints on the density profiles of fluids confined in narrow pores. A continuum description of such fluid/matrix systems is therefore highly desirable. This has been done recently by Madden and Glandt [4, 5] who used the conventional techniques of liquid-state physics to obtain rigorous cluster expansions for the structure and the thermodynamics of a mobile fluid in equilibrium with a matrix of rigid obstacles (the *quenched* particles). They also derived a set of Ornstein-Zernike (OZ) equations for the interparticle distribution functions, which can be solved, at least in principle, with some appropriate closure. An important application of this formalism would be the calculation of the thermodynamic properties of the two-phase system, in particular the adsorption isotherm which describes the variations of the average density of the fluid in the porous solid as a function of the pressure or the chemical potential of the fluid in the bulk at constant temperature. Fanti *et al.* [6, 7] have suggested that an appropriate route to this is to calculate the pressure of the fluid in the matrix by using an analog of the virial equation for equilibrium mixtures [5] and then to obtain the chemical potential by integration of the isothermal Gibbs-Duhem equation. Such a study has

been performed for hard spheres in porous matrices of randomly distributed spheres ("random sphere matrix") and quenched hard sphere structures ("hard-sphere matrix"), using a Percus-Yevick (PY) closure for the OZ equations. However, as pointed out very recently by Vega *et al.* [8], the adsorption isotherm obtained via this route is inconsistent with the Monte Carlo simulation results for a specific example of hard sphere system. The origin of this discrepancy does not lie in the OZ equations nor in the approximate method of solution. Although the equations given in reference [4] are not the exact OZ equations associated with the cluster expansion, as shown by Given and Stell [9], they predict with good accuracy within the PY closure the fluid-fluid and fluid-matrix correlation functions of the hard sphere system considered by Vega *et al.* Therefore, one has to question the validity of the virial and/or Gibbs-Duhem equations used by Fanti *et al.* More generally, this motivates a careful study of the thermodynamics of fluids in equilibrium with quenched disordered matrices. As we show in the following, this can be done in a straightforward way by using the extension of the replica method to liquid-state [10].

II. THERMODYNAMICS FROM REPLICAS

A. Pressure and Gibbs-Duhem equation

Consider a two species-system in a volume V in which the species-0 (i.e. matrix) particles are quenched, or frozen in place, and the species-1 (i.e. fluid) particles are allowed to equilibrate with some specified activity z_1 and inverse temperature $\beta_1 = (k_B T_1)^{-1}$. To facilitate further analysis, we assume that the N_0 matrix particles are distributed according to a *canonical* equilibrium distribution established at some inverse temperature $\beta_0 = (k_B T_0)^{-1}$

$$P_0(\mathbf{q}^{N_0}) = Z_0^{-1} \exp[-\beta_0 H_{00}(\mathbf{q}^{N_0})] \quad (1)$$

where $\mathbf{q}^{N_0} = \{\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_{N_0}\}$ denotes the positions of the matrix particles in a particular realization, H_{00} is the potential energy of the N_0 particles, and $Z_0 = \frac{1}{N_0!} \int d\mathbf{q}^{N_0} \exp[-\beta_0 H_{00}(\mathbf{q}^{N_0})]$ is the canonical partition function. For a specified realization of the matrix, the conditional probability density that the system contains N_1 fluid particles is given by a *grand canonical* distribution

$$P_1(\mathbf{r}^{N_1} | \mathbf{q}^{N_0}) = \Xi_1(\mathbf{q}^{N_0})^{-1} z_1^{N_1} \exp[-\beta_1 [H_{01}(\mathbf{r}^{N_1}; \mathbf{q}^{N_0}) + H_{11}(\mathbf{r}^{N_1})]] \quad (2)$$

where $\mathbf{r}^{N_1} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_1}\}$ denotes the positions of the N_1 particles, $H_{01} + H_{11}$ is the potential energy of the N_1 fluid particles in presence of the N_0 matrix particles and $\Xi_1(\mathbf{q}^{N_0}) = \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int d\mathbf{r}^{N_1} \exp[-\beta_1 [H_{01}(\mathbf{r}^{N_1}; \mathbf{q}^{N_0}) + H_{11}(\mathbf{r}^{N_1})]]$ is the matrix-dependent grand partition function. We could have also considered a grand canonical distribution for the matrix and a canonical distribution for the fluid. However, the present choice is dictated by the experimental situation in which a fluid (gas or liquid) in contact with a reservoir which fixes the chemical potential penetrates a matrix characterized by its average density $\rho_0 = N_0/V$. Therefore, there is no need to bother with fluctuations in the number of matrix particles. On the other hand, it is important to study the fluctuations in the number of fluid particles and to state the thermodynamic equivalence between the canonical and grand canonical ensembles for the fluid in the matrix.

Any quantity $\langle X(z_1, T_1, V; \mathbf{q}^{N_0}) \rangle$ which is defined in a particular realization \mathbf{q}^{N_0} of the matrix by taking a thermal average over the fluid variables can be further averaged over the disorder matrix variables to give $X(z_1, T_1, \rho_0, T_0, V) = \overline{\langle X(z_1, T_1, V; \mathbf{q}^{N_0}) \rangle}$. If X is a self-averaging quantity (generally the density of an extensive quantity), it has a well-defined limit in the thermodynamic limit. The presence of two different temperatures may have some consequences on the thermodynamics of the two-species systems. However, this problem will not be addressed in

the following since we only consider random or hard sphere matrices for which β_0 can be equally well replaced by $\beta_1 (= \beta)$. We are especially interested in the average value of the grand potential $-\beta\Omega_1(z_1, T, V; \mathbf{q}^{N_0})$,

$$-\beta\bar{\Omega}_1 = \frac{1}{Z_0 N_0!} \int d\mathbf{q}^{N_0} \exp[-\beta H_{00}(\mathbf{q}^{N_0})] \ln \Xi_1(\mathbf{q}^{N_0}) \quad (3)$$

This is a quenched average so that the usual interrelationships between statistical mechanics and thermodynamics [11] cannot be taken for granted. However, following Given [10], we can use the continuum generalization of the replica trick [12] to obtain $\bar{\Omega}_1$ as the continuation at $s = 0$ of the annealed averages of the moments Ξ_1^s ,

$$-\beta\bar{\Omega}_1 = \frac{1}{Z_0} \lim_{s \rightarrow 0} \frac{d}{ds} \Xi^{rep}(s) \quad (4)$$

with

$$\begin{aligned} \Xi^{rep}(s) = \frac{1}{N_0!} \sum_{N_1, N_2, \dots, N_s} \frac{z_1^{N_1 + N_2 + \dots + N_s}}{N_1! N_2! \dots N_s!} \int d\mathbf{q}^{N_0} d\mathbf{r}^{N_1} \dots d\mathbf{r}^{N_s} \exp[-\beta \{ H_{00}(\mathbf{q}^{N_0}) \\ + \sum_{i=1}^s (H_{0i}(\mathbf{r}^{N_i}; \mathbf{q}^{N_0}) + H_{ii}(\mathbf{r}^{N_i})) \}] \end{aligned} \quad (5)$$

where we have introduced s replicas of the fluid with the same activity z_1 (or chemical potential μ_1). We are now dealing with the *equilibrium* partition function of an $(s+1)$ -component mixture in which there is no interaction between particles of components i and j ($1 \leq i \neq j \leq s$). More precisely, we are considering a grand partition ensemble for the replicas and a canonical ensemble for the matrix. Therefore, the change in $\Omega^{rep}(s) = -k_B T \ln \Xi^{rep}(s)$ associated with any infinitesimal change in thermodynamic state is

$$\begin{aligned} d\Omega^{rep}(s) &= -P^{rep}(s) dV - S^{rep}(s) dT - s N_1^{rep}(s) d\mu_1 + \mu_0^{rep}(s) dN_0 \\ &= [-P^{rep}(s) + \rho_0 \mu_0^{rep}(s)] dV - S^{rep}(s) dT - s N_1^{rep}(s) d\mu_1 \\ &\quad + \mu_0^{rep}(s) V d\rho_0 \end{aligned} \quad (6)$$

where we have explicitly indicated that the pressure P^{rep} , the entropy S^{rep} , the number of particles N_1^{rep} in each replica (all replicas are equivalent), and the chemical potential μ_0^{rep} of the matrix depend on the number of replicas. Here and in the following, we assume that there is no replica symmetry breaking when $s \rightarrow 0$.

Using Eq.(4), we readily obtain the corresponding equation for the original quenched-annealed mixture

$$d\bar{\Omega}_1 = \lim_{s \rightarrow 0} \left[-\frac{dP^{rep}(s)}{ds} + \rho_0 \frac{d\mu_0^{rep}(s)}{ds} \right] dV - \lim_{s \rightarrow 0} \frac{dS^{rep}(s)}{ds} dT - N_1^{rep}(s=0) d\mu_1 + \lim_{s \rightarrow 0} \frac{d\mu_0^{rep}(s)}{ds} V d\rho_0 \quad (7)$$

from which we get

$$P_1 \equiv - \left. \frac{\partial \bar{\Omega}_1}{\partial V} \right|_{T, \mu_1, \rho_0} = \lim_{s \rightarrow 0} \frac{d}{ds} [P^{rep}(s) - \rho_0 \mu_0^{rep}(s)] \quad (8)$$

$$S_1 \equiv - \left. \frac{\partial \bar{\Omega}_1}{\partial T} \right|_{V, \mu_1, \rho_0} = \lim_{s \rightarrow 0} \frac{dS^{rep}(s)}{ds} \quad (9)$$

$$N_1 \equiv - \left. \frac{\partial \bar{\Omega}_1}{\partial \mu_1} \right|_{V, T, \rho_0} = N_1^{rep}(s=0) \quad (10)$$

and

$$X_1 \equiv \frac{1}{V} \left. \frac{\partial \bar{\Omega}_1}{\partial \rho_0} \right|_{V, T, \mu_1} = \lim_{s \rightarrow 0} \frac{d\mu_0^{rep}(s)}{ds} \quad (11)$$

Note that the thermodynamic quantities P_1, S_1, N_1 for the fluid inside the matrix are defined *at constant density of the matrix*. This is indeed the correct definition: for instance, to calculate the pressure by changing the volume, one does not want to modify the average distribution of the matrix particles. For several models of porous media, the density of the matrix is related in a simple way to the porosity ϕ , i.e. the fraction of space not occupied by the solid [13].

Finally, from the Gibbs-Duhem equation for the $s + 1$ mixture,

$$\begin{aligned} 0 &= -VdP^{rep}(s) + S^{rep}(s)dT + sN_1^{rep}(s)d\mu_1 + N_0d\mu_0^{rep}(s) \\ &= -Vd[P^{rep}(s) - \rho_0\mu_0^{rep}(s)] + S^{rep}(s)dT + sN_1^{rep}(s)d\mu_1 - V\mu_0^{rep}(s)d\rho_0 \end{aligned} \quad (12)$$

we get the Gibbs-Duhem equation for the fluid inside the matrix

$$0 = -VdP_1 + S_1dT + N_1d\mu_1 - VX_1d\rho_0 \quad (13)$$

and thus, by using Eqs. (7-11) and integrating $d\bar{\Omega}_1$,

$$\bar{\Omega}_1 = -P_1V \quad (14)$$

which shows that this standard thermodynamic relation remains valid for the fluid inside the matrix. Accordingly, $-X_1$, defined by Eq.(11), is the partial derivative of the fluid pressure P_1 with respect to the matrix density ρ_0 when T and μ_1 are kept constant.

B. Fluctuations and equivalence of ensembles

Consider now the fluctuations in the fluid particle number about its average value. There are two types of fluctuations, thermal fluctuations for a given realization of the matrix, and fluctuations induced by disorder. Therefore, we have to consider the two different variances

$$\begin{aligned} \sigma_{th}^2 &= \overline{\langle N_1(\mathbf{q}^{N_0})^2 \rangle} - \overline{\langle N_1(\mathbf{q}^{N_0}) \rangle^2} \\ \sigma_d^2 &= \overline{\langle N_1(\mathbf{q}^{N_0}) \rangle^2} - \overline{\langle N_1(\mathbf{q}^{N_0}) \rangle}^2 \end{aligned} \quad (15)$$

which measure, respectively, the average over disorder of thermal fluctuations, and the fluctuations of the thermal average induced by disorder. We expect $\langle N_1(\mathbf{q}^{N_0}) \rangle / V$ to be a self-averaging quantity, i.e. $\sigma_d/N_1 \rightarrow 0$ in the thermodynamic limit. From Eqs.(3) and (10), we find that

$$\begin{aligned} \left. \frac{\partial \overline{\langle N_1 \rangle}}{\partial(\beta\mu_1)} \right|_{V,T,\rho_0} &= \frac{1}{Z_0 N_0!} \int d\mathbf{q}^{N_0} \exp[-\beta H_{00}(\mathbf{q}^{N_0})] \frac{\partial^2 \ln \Xi_1(\mathbf{q}^{N_0})}{\partial(\beta\mu_1)^2} \\ &= \overline{\langle N_1^2 \rangle} - \overline{\langle N_1 \rangle}^2 \end{aligned} \quad (16)$$

It follows from Eq. (16) and the Gibbs-Duhem relation, Eq. (13), that the isothermal compressibility χ_1 of the fluid in the matrix is given by

$$\rho_1 k_B T \chi_1 = \frac{\sigma_{th}^2}{N_1} \quad (17)$$

where $\rho_1 = N_1/V$ and $N_1 = \overline{\langle N_1 \rangle}$.

The transition from the grand canonical ensemble to the canonical ensemble for the fluid can be easily proved by using replicas. We have

$$\Xi^{rep}(s) = \sum_{N_1, N_2, \dots, N_s} \exp[\beta\mu_1(N_1 + N_2 + \dots + N_s)] Z^{rep}(N_0, N_1, \dots, N_s, V, T) \quad (18)$$

where $Z^{rep}(s)$ is the canonical partition function for the replicated $(s+1)$ -species system. The most probable value of N_1, N_2, \dots, N_s is then $N_1^{rep}(s)$, found from the maximum-term procedure, i.e.

$$\left. \frac{\partial(\exp[\beta\mu_1(N_1 + N_2 + \dots + N_s)] Z^{rep}(s))}{\partial N_1} \right|_{\mu_1, N_0, N_2, \dots, N_s, V, T} = 0 \quad (19)$$

or

$$-\beta\mu_1 = \left. \frac{\partial \ln Z^{rep}(s)}{\partial N_1} \right|_{N_0, N_2, \dots, N_s, V, T} \quad (20)$$

This is also the relation that defines the chemical potential in the canonical ensemble where all replicas have the same number of particles $N_1^{rep}(s)$ since

$$\frac{\partial \ln Z^{rep}(N_1 = N_2 = \dots = N_s = N_1^{rep}(s))}{\partial(sN_1^{rep}(s))} = \left. \frac{\partial \ln Z^{rep}(N_1, N_2, \dots, N_s)}{\partial N_1} \right|_{N_1 = N_2 = \dots = N_s = N_1^{rep}(s)} \quad (21)$$

Then from

$$\Xi^{rep}(s) = \exp[s\beta\mu_1 N_1^{rep}(s)] Z^{rep}(N_1 = N_2 = \dots = N_s = N_1^{rep}(s)) \quad (22)$$

we deduce

$$\begin{aligned} F^{rep}(s) &= -k_B T \ln Z^{rep}(s) \\ &= -P^{rep}(s)V + \mu_0(s)N_0 + s\mu_1 N_1^{rep}(s) \end{aligned} \quad (23)$$

and finally

$$\begin{aligned} \bar{F}_1 &= \lim_{s \rightarrow 0} \frac{d}{ds} F^{rep}(s) \\ &= -P_1 V + \mu_1 N_1 \end{aligned} \quad (24)$$

as expected.

C. Correlations, compressibility and virial equations

By definition, the pair density $\rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ for the mobile phase is the average of $\rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0})$ over all realizations of the matrix. One then defines the total correlation function $h_{11}(\mathbf{r}_1, \mathbf{r}_2)$ by [4]

$$\rho_1(\mathbf{r}_1)\rho_1(\mathbf{r}_2)h_{11}(\mathbf{r}_1, \mathbf{r}_2) = \rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho_1(\mathbf{r}_1)\rho_1(\mathbf{r}_2) \quad (25)$$

Since the matrix structure is statistically homogeneous, $\rho_1(\mathbf{r}_1) = \rho_1$ and $h_{11}(\mathbf{r}_1, \mathbf{r}_2) = h_{11}(|\mathbf{r}_1 - \mathbf{r}_2| \equiv r_{12})$ in the absence of external potential. One can also consider the average over disorder of the *connected* pair density $\rho_{11,c}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0}) = \rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0}) - \rho_1(\mathbf{r}_1; \mathbf{q}^{N_0})\rho_1(\mathbf{r}_2; \mathbf{q}^{N_0})$. ~~As in the case of~~ ^{as in the case of} spin systems in the presence of quenched random magnetic fields [14], this leads to define two additional correlation functions h_c and h_b by

$$\begin{aligned} \rho_1^2 h_c(r_{12}) &= \overline{\rho_{11,c}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0})} \\ &= \overline{\rho_{11}^{(2)}(r_{12})} - \overline{\rho_1(\mathbf{r}_1; \mathbf{q}^{N_0})\rho_1(\mathbf{r}_2; \mathbf{q}^{N_0})} \end{aligned} \quad (26)$$

and

$$\rho_1^2 h_b(r_{12}) = \overline{\rho_1(\mathbf{r}_1; \mathbf{q}^{N_0}) \rho_1(\mathbf{r}_2; \mathbf{q}^{N_0})} - \rho_1^2 \quad (27)$$

such that

$$h_{11}(r_{12}) = h_c(r_{12}) + h_b(r_{12}) \quad (28)$$

For a given realization of the matrix, we have the usual normalisation in the grand canonical ensemble [11]

$$\begin{aligned} \int \rho_1(\mathbf{r}_1; \mathbf{q}^{N_0}) d\mathbf{r}_1 &= \langle N_1(\mathbf{q}^{N_0}) \rangle \\ \int \rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0}) d\mathbf{r}_1 d\mathbf{r}_2 &= \langle N_1(\mathbf{q}^{N_0})^2 \rangle - \langle N_1(\mathbf{q}^{N_0}) \rangle^2 \end{aligned} \quad (29)$$

Then, by averaging over disorder, we readily obtain the two relations

$$\begin{aligned} 1 + \rho_1 \int h_c(r_{12}) d\mathbf{r}_{12} &= \frac{\sigma_d^2}{N_1} \\ &= \rho_1 k_B T \chi_1 \end{aligned} \quad (30)$$

and

$$\rho_1 \int h_b(r_{12}) d\mathbf{r}_{12} = \frac{\sigma_d^2}{N_1} \quad (31)$$

where the second equality in Eq.(30) derives from Eq.(17). Eq.(30) is the compressibility equation for the fluid in the matrix.

The correlation functions h_c and h_b can be also related to correlation functions in the replicated ($s + 1$)-species system. Assuming that the fluid-fluid interaction potential is a sum of pairwise interactions $\phi_{11}(\mathbf{r}_i, \mathbf{r}_j)$, one can use the functional relation [15]

$$\rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0}) = -2k_B T \frac{\delta \ln \Xi_1(\mathbf{q}^{N_0})}{\delta \phi_{11}(\mathbf{r}_1, \mathbf{r}_2)} \quad (32)$$

to find

$$\begin{aligned}
\rho_{11}^{(2)}(r_{12}) &= 2 \frac{\delta \bar{\Omega}_1}{\delta \phi_{11}(\mathbf{r}_1, \mathbf{r}_2)} \\
&= 2 \lim_{s \rightarrow 0} \frac{d}{ds} \frac{\delta \Omega^{rep}(s)}{\delta \phi_{11}(\mathbf{r}_1, \mathbf{r}_2)} \\
&= \rho_{11}^{(2)rep}(r_{12}; s = 0)
\end{aligned} \tag{33}$$

where we have considered the fact that there are s identical replicas which do not interact to obtain the last equality. Thus

$$h_{11}(r_{12}) = h_{11}^{rep}(r_{12}; s = 0) \tag{34}$$

On the other hand, using the functional relation [15]

$$\mathcal{G}_{11}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0}) = \frac{\delta^2 \ln \Xi_1(\mathbf{q}^{N_0})}{\delta[\beta(\mu_1 - u_1(\mathbf{r}_1))] \delta[\beta(\mu_1 - u_1(\mathbf{r}_2))]} \tag{35}$$

where $\mathcal{G}_{11}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0}) = \rho_{11,c}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0}) + \rho_1(\mathbf{r}_1; \mathbf{q}^{N_0})\delta(\mathbf{r}_1 - \mathbf{r}_2)$ is the density-density correlation function of the fluid for a given realization of the matrix and $u_1(\mathbf{r})$ is some external potential acting only on the fluid molecules, we get the following expression for $\mathcal{G}_{11}(r_{12}) = \overline{\mathcal{G}_{11}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0})}$:

$$\begin{aligned}
\mathcal{G}_{11}(r_{12}) &= - \left. \frac{\delta^2[\beta \bar{\Omega}_1]}{\delta[\beta(\mu_1 - u_1(\mathbf{r}_1))] \delta[\beta(\mu_1 - u_1(\mathbf{r}_2))]} \right|_{u_1=0} \\
&= - \lim_{s \rightarrow 0} \frac{d}{ds} \frac{\delta^2[\beta \Omega^{rep}(s)]}{\delta[\beta(\mu_1 - u_1(\mathbf{r}_1))] \delta[\beta(\mu_1 - u_1(\mathbf{r}_2))]} \\
&= \lim_{s \rightarrow 0} \frac{d}{ds} [s \mathcal{G}_{11}^{rep}(r_{12}; s) + s(s-1) \rho_{12}^{(2)rep}(r_{12}; s)] \\
&= \rho_{11,c}^{(2)rep}(r_{12}; s = 0) + \rho_1^{rep}(s = 0) \delta(\mathbf{r}_1 - \mathbf{r}_2) - \rho_{12}^{(2)rep}(r_{12}; s = 0)
\end{aligned} \tag{36}$$

where $\rho_{11,c}^{(2)rep}(r_{12}; s) = \rho_{11}^{(2)rep}(r_{12}; s) - \rho_1^{rep}(s)^2$ and $\rho_{12}^{(2)rep}(r_{12}; s)$ is the pair density for two different replicas (we recall that although replicas do not interact directly, they couple via the interactions with the matrix). Thus, from Eq.(26),

$$h_c(r_{12}) = h_{11}^{rep}(r_{12}; s = 0) - h_{12}^{rep}(r_{12}; s = 0) \tag{37}$$

This is precisely the definition of the *connected* correlation function h_c introduced by Given and Stell [9]. Accordingly, the function h_b defined by Eq.(27) can be identified with the so-called *blocking* part of h_{11} introduced in that reference. The two correlation functions h_c and h_b can be also defined by their diagrammatic expansion [9], h_b being the subset of graphs of h_{11} such that all paths between the fluid root points pass through at least one $-\rho_0$ field point. It is easy to check that this is in agreement with the exact graphical expansion of our Eqs. (26) and (27).

Defining the direct correlation function c_{11} as the sum of all graphs in h_{11} with no nodal points, and introducing the total and direct pair correlation functions h_{00}, h_{01}, h_{10} and c_{00}, c_{01}, c_{10} , Madden and Glandt [4] have derived a set of OZ equations for the quenched-annealed mixture. However, as pointed out by Given and Stell [9], these equations correspond to an approximation in which a certain class of terms is neglected in the cluster expansion of c_{11} . The exact equations (called the replica Ornstein-Zernike (ROZ) equations in ref. [9]) can be easily obtained by using the replica trick. Indeed, h_{00}, h_{01}, h_{10} are related to their counterparts in the replicated system by equations similar to Eq. (34), and one finds

$$h_{00} = c_{00} + \rho_0 c_{00} \otimes h_{00} \quad (38)$$

$$h_{10} = c_{10} + \rho_0 c_{10} \otimes h_{00} + \rho_1 c_c \otimes h_{10} \quad (39)$$

$$h_{11} = c_{11} + \rho_0 c_{10} \otimes h_{01} + \rho_1 c_c \otimes h_{11} + \rho_1 c_b \otimes h_c \quad (40)$$

$$h_c = c_c + \rho_1 c_c \otimes h_c \quad (41)$$

where the symbol \otimes denotes a convolution, $h_{01} = h_{10}$ and $c_{01} = c_{10}$ by symmetry, and

$$c_{11}(r_{12}) = c_c(r_{12}) + c_b(r_{12}) \quad (42)$$

with

$$\begin{aligned} c_b(r_{12}) &= c_{12}^{rep}(r_{12}; s = 0) \\ c_c(r_{12}) &= c_{11}^{rep}(r_{12}; s = 0) - c_{12}^{rep}(r_{12}; s = 0) \end{aligned} \quad (43)$$

Several closures to these equations have been tested against numerical simulations for various models of porous media by Vega *et al.* [8] and Lomba *et al.* [17]. The Madden-Glandt approximation [4] consists in setting $c_b = 0$. As will be discussed elsewhere [18], these equations can be also used to extract some interesting information about the critical behavior of the fluid inside the porous matrix.

From Eqs.(30) and (41) we have

$$\frac{\beta}{\rho_1 \chi_1} = 1 - \rho_1 \int c_c(r_{12}) dr_{12} \quad (44)$$

which is the expression of the compressibility equation derived independently by Ford and Glandt [16] from a graphical analysis. A similar equation was suggested as an approximation by Vega *et al.* [8], with the full c_{11} instead of the correct c_c . However, within the PY approximation used by Vega *et al.*, this difference disappears [9] and the approximate equation yields good predictions for the adsorption isotherm of the hard-sphere fluid/hard-sphere matrix system studied in that reference. On the other hand, as noted by Vega *et al.*, use of the virial equation of Fanti *et al.* [7] and Madden [5], which is quite analogous to the familiar equation of the virial pressure for an equilibrium mixture (without the contribution of the matrix-matrix interactions), is inconsistent with the simulation results. This equation is indeed incorrect, as we now show by using replicas.

In the replicated system (which is a true equilibrium mixture), the virial equation writes

$$\beta P^{rep}(s) = \rho_0 + s\rho_1 - \frac{\beta}{6} \int dr r [\rho_0^2 \phi'_{00}(r) g_{00}^{rep}(r; s) + s\rho_1^2 \phi'_{11}(r) g_{11}^{rep}(r; s) + 2s\rho_0\rho_1 \phi'_{01}(r) g_{01}^{rep}(r; s)] \quad (45)$$

where $g_{ij}^{rep}(r; s)$ and $\phi_{ij}(r)$ denote, respectively, the pair correlation function and the pair interaction for particles belonging to species i and j , and $\phi'_{ij}(r) \equiv d\phi_{ij}(r)/dr$. Hence, from Eqs.(8) and (11) and the relation between the pair correlation functions in the fluid/matrix system and their counterparts in the replicated system, we derive

$$\beta P_1 - \rho_0 \left. \frac{\partial(\beta P_1)}{\partial \rho_0} \right|_{T, \mu_1} = \rho_1 - \frac{\beta}{6} \int dr r [\rho_0^2 \phi'_{00}(r) \lim_{s \rightarrow 0} \frac{dg_{00}^{rep}(r; s)}{ds} + \rho_1^2 \phi'_{11}(r) g_{11}(r) + 2\rho_0\rho_1 \phi'_{01}(r) g_{01}(r)] \quad (46)$$

In particular, for hard-core interactions characterized by the diameters σ_{00}, σ_{01} and σ_{11} , this equation reduces to

$$\frac{\beta P_1}{\rho_1} - \frac{\rho_0}{\rho_1} \left. \frac{\partial(\beta P_1)}{\partial \rho_0} \right|_{\mu_1} = 1 + \frac{2\pi}{3} \frac{\rho_0^2}{\rho_1} \sigma_{00}^3 \lim_{s \rightarrow 0} \frac{dg_{00}^{rep}(\sigma_{00}; s)}{ds} + \frac{2\pi}{3} \rho_1 \sigma_{11}^3 g_{11}(\sigma_{11}) + \frac{4\pi}{3} \rho_0 \sigma_{01}^3 g_{01}(\sigma_{01}) \quad (47)$$

Neither the term $\rho_0 \left. \frac{\partial(\beta P_1)}{\partial \rho_0} \right|_{T, \mu_1}$ nor the one involving $\frac{dg_{00}^{rep}(r; s)}{ds}$ are present in the equation of Fanti *et al.* [7] and Madden [5]. The first term comes from the chosen definition of the fluid pressure at constant matrix density. It is, however, only with this definition that one can apply the Gibbs-Duhem relation, Eq. (13). The other additional term, which is not simply related to any physical quantity of the quenched-annealed mixture, is only zero when the matrix-matrix interactions are ideal, i.e. $\sigma_{00} = 0$ (random sphere matrix). Therefore, at first sight, Eq.(46) does not seem to be a very useful route to the thermodynamics of the system. However, a careful analysis of the graphical expansion of $g_{00}^{rep}(r; s)$ shows that

$$\lim_{s \rightarrow 0} \frac{dg_{00}^{rep}(r; s)}{ds} = g_{00}^{rep}(r; s = 0) [W_{00}^{rep}(r; s = 1) - W_{00}^{rep}(r; s = 0) + \mathcal{O}(\rho_0 \rho_1^2)] \quad (48)$$

where $-k_B T W_{00}^{rep}(r; s)$ is the excess potential of mean force which is related to the pair correlation function $g_{00}^{rep}(r; s)$ according to

$$W_{00}^{rep}(r; s) = \ln g_{00}^{rep}(r; s) + \beta \phi_{00}(r) \quad (49)$$

A similar relation holds for the derivative of the chemical potential $\mu_0^{rep}(s)$, so that

$$\begin{aligned} - \left. \frac{\partial P_1}{\partial \rho_0} \right|_{T, \mu_1} &= \lim_{s \rightarrow 0} \frac{d\mu_0^{rep}(s)}{ds} \\ &= \mu_0^{rep}(s=1) - \mu_0^{rep}(s=0) + \mathcal{O}(\rho_0 \rho_1^2) \end{aligned} \quad (50)$$

Neglecting the contributions of order $\rho_0 \rho_1^2$ in Eqs. (48) and (50) may then provide a practical way to evaluate the fluid pressure P_1 by means of the virial equation. All quantities that appear in addition to the pair correlation functions of the fluid/matrix system can indeed be obtained by considering equilibrium ensembles formed by either matrix particles alone ($s=0$) or a binary mixture of matrix and fluid particles ($s=1$).

Finally, it is worth noting that there is a nontrivial cancellation of diagrams in Eq. (46) which leads to $\beta P_1 / \rho_1 \rightarrow 1$ when $\rho_1 \rightarrow 0$, as it should be (this is not the case with the equation of Fanti *et al.* [7] and Madden [5]).

III. CONCLUDING REMARKS

By applying the replica method, we have derived the thermodynamic relations for a fluid in equilibrium with a quenched porous matrix and established the connection between statistical mechanics and thermodynamics. In particular, the appropriate Gibbs-Duhem relation has been obtained as well as the equivalence between grand canonical and canonical ensembles. In addition, the two traditional routes that allow to relate the thermodynamic properties of equilibrium systems to the pair correlation functions, namely the compressibility and the virial equations, have been investigated. We have shown that, whereas the compressibility equation remains a direct

and practical way to obtain the adsorption isotherm, the virial equation involves terms which do not relate easily to the properties of the fluid/matrix system. We have proposed, however, simple approximations to these terms which remain to be tested on specific examples. It is worth stressing that although it provides an efficient way to express the thermodynamic and structural relations of the fluid/matrix system, the replica method may not always be of practical use for explicit calculations. The equilibrium replicated system may indeed be more complicated than the original quenched-annealed system because the pairwise interactions in the replicas/matrix mixture are highly non-additive. This is strikingly illustrated by the simple case of an ideal gas in a random sphere matrix (i.e. $\sigma_{00} = \sigma_{11} = 0$ and $\sigma_{01} \neq 0$). This is the quenched-annealed version of the Widom-Rowlinson penetrable-sphere model [19]. The replicated system is then equivalent to an equilibrium binary mixture of matrix particles at a density ρ_0 and ideal fluid particles at density $\rho = s\rho_1$. Its thermodynamics is far from obvious [19] whereas the quenched-annealed system can be exactly treated. Indeed, taking the $s = 0$ limit amounts to retaining only the first terms in the virial expansions in $\rho = s\rho_1$. Using the results of section II, one readily obtain that $\beta P_1 = \rho_1$: as expected, the fluid remains ideal in the matrix (even though h_{11} is non-zero [4, 17]).

The description of the fluid structure in the porous matrix requires two distinct pair correlation functions, h_c and h_b . This is a direct consequence of the randomness induced by the porous medium. It may be noticed that the definitions of h_c and h_b that are given in this paper, Eqs. (26) and (27), are valid even if the matrix is not a quenched equilibrium configuration, as for instance if it is obtained by a Random Sequential Addition (RSA) [10, 20]. In this case, the replica Ornstein-Zernike equations, Eqs. (38-42), are no longer valid: their derivation indeed requires that the pair correlation function for the matrix alone satisfies a simple OZ equation,

which is wrong for the RSA as well as for many other non-equilibrium systems [21]. Thus, contrary to Madden's claim [5], the ROZ equations or their Madden-Glandt approximation apply essentially to matrices obtained from a thermal quench.

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