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Integral equations for a fluid near a random substrate

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The fluid distribution functions near the surface of a random porous solid are investigated by the methods of liquid-state theory. The presence of the surface is taken into account by modifying the two-body interaction potential between fluid and matrix particles. Cluster expansions and Ornstein-Zernike equations for the correlation functions are derived as well as exact equations for the fluid density profile.

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Heterogeneity of solid surfaces, due to conditions of formation or subsequent treatment of the solid plays a significant role in many practical problems of adsorption and catalysis. In spite of a great deal of experimental work, progress in the theoretical description of fluids near heterogeneous surfaces is still insufficient [1]. This is mainly due to the difficulty in incorporating the chemical or geometrical randomness of the substrate into a molecular theory. Accordingly, much of the statistical mechanical treatment of the solid-fluid interface has dealt with periodic homogeneous surfaces [2] or idealized pore structures [3]. Recently, a new approach has been proposed by Madden and Glandt [4-6], which extends the methods of liquid-state theory to the study of fluids adsorbed in disordered porous materials. In particular, a description of the molecular distribution functions of quenched-annealed systems is now available, based on cluster expansions and integral equations. The most useful is a new set of Ornstein-Zernike (OZ) equations for the disorder-averaged two-body correlation functions. The exact form of these equations has been obtained by Given and Stell [7] using the continuum replica method [8]. Monte Carlo simulations for several fluid-matrix molecular models have been carried out by Vega, Kaminsky, and Monson [9] and Lomba *et al.* [10] and compared to theoretical predictions based on the Percus-Yevick and hypernetted chain approximations. The thermodynamics of these systems and the connection with the correlation function description have been investigated by Vega, Kaminsky, and Monson [9], Ford and Glandt [11], and more comprehensively by Rosinberg, Tarjus, and Stell [12]. All these studies, however, have focused on the description of statistically homogeneous systems. The present work is concerned with the extension of these methods to heterogeneous surfaces. What we have in mind is a solid surface that is planar on average (extension to more complicated geometries is straightforward) but rather corrugated on the atomic scale. This can be, for instance, the surface structure obtained from a dense random packing of hard spheres. It has been suggested that such a model may represent an important class of heterogeneous adsorbents [13,14]. Here, we show how to include the presence of this type of surface in the theoretical formalism. We give the cluster expansions of the correlation functions and the corresponding OZ equations. We also derive exact equations for the fluid density profile in the vicinity of the surface. Numerical application to model interfaces will be presented in a future publication.

We consider the same fluid-matrix system as the one studied by Madden and Glandt [4], in which the degrees of freedom of species-0 (i.e., matrix) particles are quenched, or frozen in place, whereas those of species-1 (i.e., fluid) particles are annealed. It is assumed that the structure of the matrix is that of an equilibrium system at a higher temperature, which implies that no major structural relaxation has taken place during the thermal quench. Madden and Glandt have shown how to recast the bulk problem into a mixturelike form, so that one can use the conventional techniques of topological reduction. In order to follow the same strategy, we first have to find out how to incorporate properly the presence of the interface. For the sake of simplicity, we shall assume that the heterogeneous surface has been obtained by a perfect cleavage of the porous solid so that the centers of the matrix particles are restricted to the $z>0$ half-space. In this case, pair and higher order distribution functions of the matrix particles are the same as those of the massive solid. The real situation is certainly more complicated, but it seems reasonable to start with this simplified picture. This allows us to replace the original interfacial system by an equivalent fictitious system where the matrix particles occupy the whole space but interact with the fluid only when located in the $z>0$ region. Assuming that the adsorbate-adsorbent interaction is described by the pair potential $u_{10}(r_{12})$, we thus introduce the modified potential

$$\hat{u}_{10}(1,2)=\theta(z_2)u_{10}(r_{12}) , \tag{1}$$

where $\theta(z)$ is the Heaviside step function and r_{12} is the center-to-center distance of the two particles. Since $[\theta(z)]^n=\theta(z)$, the corresponding Mayer function has the form

$$\begin{aligned}\hat{f}_{10}(1,2)&\equiv\exp[-\beta\hat{u}_{10}(1,2)]-1\\ &=\theta(z_2)f_{10}(r_{12}) ,\end{aligned} \tag{2}$$

where $\beta=(k_BT)^{-1}$, k_B is the Boltzmann constant, T is the temperature, and $f_{10}(r_{12})=\exp[-\beta u_{10}(r_{12})]-1$ is the original Mayer function. It is clear from Eq. (2) that, in all diagrammatic expansions considered by Madden Glandt, the explicit z dependence can be removed from the f_{10} bonds and transferred to the field or root points. Therefore, one can easily repeat all calculations of Ref. [4] and obtain the following cluster expansion of the disorder-averaged total correlation functions $h_{\alpha\beta}(1,2)$ $(\alpha,\beta=0,1)$:

$h_{\alpha\beta}(1,2)=$ sum of all topologically distinct, simple, connected graphs with one root point of species α, one root point of species β, some or no fluid field points weighted by $\rho_1(z)$, some or no matrix field ρ_0 points, and some or no f bonds between the appropriate pairs of points with no articulation points and no shielding sets. Matrix root and field points connected directly a fluid point are weighted by $\theta(z)$ and $\rho_0\theta(z)$, respectively. (3)

The last restriction results from the presence of the surface. We recall that a shielding set, as defined by Madden and Glandt [4], is a matrix articulation set whose removal produces unrooted, disjoint fragments containing at least one fluid field point. One then defines the direct correlation functions as

$c_{\alpha\beta}(1,2)=$ sum of all graphs in Eq. (3) with no nodal points. (4)

Using the replica trick, Given and Stell [7] have shown that in order to derive the correct OZ equations, it is necessary to divide h_{11} an c_{11} into the so-called connected and blocking parts, denoted here by h_{c11}, h_{b11}, and c_{c11}, c_{b11}, respectively. The blocking part is the subset of graphs such that all paths between the root point pass through at least one matrix field point. The introduction of the additional correlation function h_{b11} is specific to random media problems [12] and the separation of h_{11} and c_{11} into two parts prevents the occurrence of shielding sets in the OZ equations. In the present case, examination of the nodal structure of the functions $h_{\alpha\beta}(1,2)$ (or, more simply, use of the replica OZ equations) yields

$$h_{00}(r_{12})=c_{00}(r_{12})+\rho_0\int d\mathbf{r}_3c_{00}(r_{13})h_{00}(r_{32}) \tag{5}$$

$$\begin{aligned}h_{10}(z_1,z_2,R_{12})={}&c_{10}(z_1,z_2,R_{12})+\rho_0\int dz_3d\mathbf{R}_3c_{10}(z_1,z_3,R_{13})h_{00}(r_{32})\\ &+\int dz_3d\mathbf{R}_3\rho_1(z_3)c_{c11}(z_1,z_3,R_{13})h_{10}(z_3,z_2,R_{32}) ,\end{aligned} \tag{6}$$

$$\begin{aligned}h_{01}(z_1,z_2,R_{12})={}&c_{01}(z_1,z_2,R_{12})+\rho_0\int dz_3d\mathbf{R}_3c_{00}(r_{13})h_{01}(z_3,z_2,R_{32})\\ &+\int dz_3d\mathbf{R}_3\rho_1(z_3)c_{01}(z_1,z_3,R_{13})h_{c11}(z_3,z_2,R_{32}) ,\end{aligned} \tag{7}$$

$$\begin{aligned}h_{11}(z_1,z_2,R_{12})={}&c_{11}(z_1,z_2,R_{12})+\rho_0\int dz_3d\mathbf{R}_3c_{10}(z_1,z_3,R_{13})h_{01}(z_3,z_2,R_{32})\\ &+\int dz_3d\mathbf{R}_3\rho_1(z_3)c_{c11}(z_1,z_3,R_{13})h_{11}(z_3,z_2,R_{32})\\ &+\int dz_3d\mathbf{R}_3\rho_1(z_3)c_{b11}(z_1,z_3,R_{13})h_{c11}(z_3,z_2,R_{32}) ,\end{aligned} \tag{8}$$

$$h_{c11}(z_1,z_2,R_{12})=c_{c11}(z_1,z_2,R_{12})+\int dz_3d\mathbf{R}_3\rho_1(z_3)c_{c11}(z_1,z_3,R_{13})h_{c11}(z_3,z_2,R_{32}) , \tag{9}$$

where $\mathbf{r}=\{z,\mathbf{R}\}$. By symmetry, one has $h_{10}(z_1,z_2,R_{12})=h_{01}(z_2,z_1,R_{12})$ and $c_{10}(z_1,z_2,R_{12})=c_{01}(z_2,z_1,R_{12})$. Note that the equation for the matrix alone is the same as in the absence of interface (and is not influenced by the presence of fluid particles), whereas translational symmetry in the z direction is broken for the fluid-fluid and fluid-matrix correlation functions. We point out that $h_{10}(z_1,z_2,R_{12})$ and $c_{10}(z_1,z_2,R_{12})$ must be calculated in the whole space, even if there are no matrix particles in the $z_2<0$ region in the original interfacial system. Now, the set of OZ equations is not complete and we need an equation relating the fluid density distribution $\rho_1(z)$ to the pair correlation functions. When the fluid-fluid interaction is pairwise additive, the first equation of the Yvon-Born-Green (YBG) hierarchy can be easily obtained from the diagrammatic definition of $\rho_1(z)$ [4] (or, alternatively, from the corresponding equation in replica space). One finds

$$\frac{\partial \ln\rho_1(z_1)}{\partial z_1}+\beta\frac{\partial w(z_1)}{\partial z_1}=-\beta\int dz_2 d\mathbf{R}_2\rho_1(z_2)g_{11}(z_1,z_2,R_{12})\frac{\partial u_{11}(r_{12})}{\partial z_1}\ , \tag{10}$$

where $u_{11}(r_{12})$ is the pair potential between fluid particles, $g_{11}=1+h_{11}$, and $w(z)$ is an effective one-body fluid-matrix potential, which satisfies

$$\frac{\partial w(z_1)}{\partial z_1}=\rho_0\int dz_2\mathbf{R}_2 g_{10}(z_1,z_2,R_{12})\frac{\partial u_{10}(r_{12})}{\partial z_1}\theta(z_2)\ , \tag{11}$$

where $g_{10}=1+h_{10}$.

One can also derive equations similar to the Lovett-Mou-Buff-Wertheim (LMBW) equations [15,16] by taking the gradient of ln $\rho_1(z)$. In the graphical expansion of this quantity (see, for instance, Ref. [11] for the bulk case), the gradient acts only on the fluid vertices and on the matrix vertices that are connected directly to a fluid point and carry the factor $\rho_0\theta(z)$. Then, a careful examination of the diagrams shows that the derivative with respect to fluid points introduces the connected part c_{c11} of the fluid-fluid direct correlation function whereas, remarkably, the derivative with respect to matrix points introduces a subset of graphs in c_{01}, which we may loosely call also its *connected* part since it has the same topological structure as c_{c11} (i.e., the two root points are connected by at least one path that includes only fluid vertices). More precisely, one finds

$$\frac{\partial \ln\rho_1(z_1)}{\partial z_1}+\beta\frac{\partial v(z_1)}{\partial z_1}=\int dz_2 d\mathbf{R}_2 c_{c11}(z_1,z_2,R_{12})\frac{\partial\rho_1(z_2)}{\partial z_2}\ , \tag{12}$$

where $v(z)$ is another effective one-body fluid-matrix potential, which satisfies

$$\beta\frac{\partial v(z_1)}{\partial z_1}=-\rho_0\int dz_2 d\mathbf{R}_{12}\check{c}_{c10}(z_1,z_2,R_{12})\frac{\partial\theta(z_2)}{\partial z_2}=-\rho_0\int d\mathbf{R}_{12}\check{c}_{c10}(z_1,0,R_{12})\ , \tag{13}$$

where $\check{c}_{c10}$ is a continuous function defined by $c_{c10}(z_1,z_2,R_{12})=\check{c}_{c10}(z_1,z_2,R_{12})\theta(z_2)$ (indeed, $c_{c10}(z_1,z_2,R_{12})=0$ for $z_2<0$, since the matrix root point is directly connected to at least one fluid point by definition of the connected part).

Defining similarly the "connected" and "blocking" part of h_{01} (with $h_{01}=h_{c01}+h_{b01}$), one finds the additional OZ equations,

$$\begin{aligned}h_{c10}(z_1,z_2,R_{12})&=c_{c10}(z_1,z_2,R_{12})+\int dz_3 d\mathbf{R}_3\rho_1(z_3)c_{c11}(z_1,z_3,R_{13})h_{c10}(z_3,z_2,R_{32})\\&=c_{c10}(z_1,z_2,R_{12})+\int dz_3 d\mathbf{R}_3\rho_1(z_3)h_{c11}(z_1,z_3,R_{13})c_{c10}(z_3,z_2,R_{32})\ ,\end{aligned} \tag{14}$$

with $h_{c10}(z_1,z_2,R_{12})=h_{c01}(z_2,z_1,R_{12})$ by symmetry. Note that h_{b10} does not correspond to the $s=0$ limit of a correlation function between different replicas, unlike h_{b11} [7,12].

Using Eq. (9), Eq. (12) can be inverted to give

$$\frac{\partial \ln\rho_1(z_1)}{\partial z_1}+\beta\frac{\partial v(z_1)}{\partial z_1}=-\beta\int dz_2 d\mathbf{R}_{12}\rho_1(z_2)h_{c11}(z_1,z_2,R_{12})\frac{\partial v(z_2)}{\partial z_2}\ , \tag{15}$$

which can be rewritten, using Eqs. (13) and (14), as

$$\frac{\partial \ln\rho_1(z_1)}{\partial z_1}=\rho_0\int d\mathbf{R}_{12}\check{h}_{c10}(z_1,0,R_{12})\ , \tag{16}$$

where $\check{h}_{c10}$ is defined by

$$h_{c10}(z_1,z_2,R_{12})=\check{h}_{c10}(z_1,z_2,R_{12})\theta(z_2),$$

(one has also $h_{c10}(z_1,z_2,R_{12})=0$ for $z_2<0$).

If the porosity of the solid allows a significant penetration of fluid particles, $\rho_1(z)$ goes to a constant when $z\to+\infty$, which is just the averaged fluid density within the massive solid. Then Eq. (16) can be used to obtain the partition coefficient K, here defined as the ratio of the fluid density within the solid to its density in the bulk phase in equilibrium with it. One has the sum rule

$$\ln K=\rho_0\int_{-\infty}^{+\infty}dz_1\int d\mathbf{R}_{12}\check{h}_{c10}(z_1,0,\mathbf{R}_{12})\ . \tag{17}$$

This important equilibrium quantity can thus be obtained as a by-product of the solution of the inhomogeneous OZ equations, without requiring a thermodynamic integration of the Gibbs-Duhem equation, as in the bulk problem [5]. On the other hand, of course, one has to solve a rather complex set of coupled integral equations.

Generally, one will have to complement the set "OZ + BGY" or "OZ + LMBW" equations by some approximate closure equations such as the hypernetted-chain, Percus-Yevick, or reference Percus-Yevick approximations, which are well defined in replica space [10]. The closure to Eq. (14) is more problematic since h_{b10} and h_{c10} have no simple meaning in terms of replicas. However, it is easy to see that in the case of a random matrix (i.e., $u_{00}=0$), one has $c_{b10}=h_{b10}=0$ (whereas c_{b11} and $h_{b11}\neq 0$ [10]). Therefore, the closure $c_{b10}=0$ seems a reasonable approximation to start with, at least for short-ranged matrix-matrix interactions. Interestingly, the Percus-Yevick closure for c_{10}, i.e., $c_{10}(1,2)=g_{10}(1,2)(1-\exp[\beta\hat{u}_{10}(1,2)])$ implies $c_{10}(1,2)=0$ for $z_2<0$ and thus also $c_{b10}(1,2)=0$ since $c_{c10}(1,2)=0$ in this region. Numerical computations in the case of random and hard-sphere matrices will be presented in a forthcoming paper.

All the above results are explicitly written for the case of a surface that is planar on average. As mentioned earlier, the general structure of the equations remains unchanged in more complicated geometries such as the cylindrical pore geometry considered in Ref. [17]. One merely has to change the coordinate system to modify the argument of the Heaviside step function in Eq. (1) and to make the corresponding modifications in all subsequent developments. Chemical randomness of the adsorbent can also be introduced in the formalism by considering matrices composed of different particle species.

Finally, let us point out that the information obtained about the fluid structure near a random porous interface may also be useful to study transport processes. It is clear that any mass transport through a porous medium begins at the external surface of the solid. In some circumstances, this may also have considerable influence on the reaction kinetics and be the limiting rate step. With this aim in view, Monte Carlo simulations have been carried out recently to compute the fluid density near the surface of a nonrandom porous solid where solid particles are placed on a regular lattice [18]. Simulations of the interface with a random solid are in progress.

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