The effective interaction between colloidal hard sphere particles in disordered microporous media

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Using the replica Ornstein-Zernike (ROZ) integral equations, the effective interaction between hard sphere colloidal particles in the presence of a hard sphere solvent, both dispersed either in a disordered quenched matrix of hard spheres is analyzed in this work. The ROZ equations are complemented by the Percus-Yevick (PY) closure. The presence of a disordered matrix is manifested in the attractive minima of the colloid-colloid potential of mean force (PMF), in addition to a set of minima due to the presence of solvent species. The effects of matrix porosity and solvent density on the PMF are investigated.

Keywords: Potential of mean force; replica Ornstein-Zernike equations; porous media

En este trabajo analizamos la interacción efectiva entre partículas coloidales de esfera dura en presencia de solvente de esferas duras, dispersadas en una matriz desordenada de esferas duras fijas. Para ello usamos las ecuaciones integrales de réplica de Ornstein-Zernike (ROZ). Para resolver las ecuaciones de ROZ usamos la cerradura de Percus-Yevick. La presencia de la matriz desordenada se pone de manifiesto con un mínimo atractivo en el potencial de fuerza promedio (PFP) entre los coloides, además de un conjunto de mínimos adicionales debidos al solvente. Investigamos los efectos en el PFP debidos a cambios en la porosidad de la matriz y la densidad del solvente.

Descriptores: Potencial de fuerza promedio; ecuaciones de réplica de Ornstein-Zernike; medios porosos

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1. Introduction

The study of adsorption of fluids in disordered porous media is very interesting from theoretical and practical point of view. The statistical mechanical theory of quenched-annealed (partly quenched) systems that consist of a microporous medium prepared, for example, by thermal quench, and of annealed fluid or a mixture, *i.e.* of the one that reaches thermal equilibrium in the presence of rigidly fixed disordered adsorbent (matrix) has been initiated by Madden and Glandt [1, 2]. Subsequent theoretical development of Given and Stell [3–5] have provided the exact replica Ornstein-Zernike (ROZ) equations to study partly quenched systems. A model for one-component hard spheres adsorbed in a *disordered* (hard spheres) and *random* (freely overlapping spheres) matrices has been the focus of several recent studies using the ROZ equations and computer simulation [6–9]. However, the adsorption of even simple mixtures has been much less investigated [10–12]. Moreover, simpler theoretical tools than the ROZ equations, have been employed to study the adsorption of mixtures [10, 11].

Our principal objective in the present work is to begin a systematic investigation of the adsorption of mixtures in disordered microporous environment in the framework of integral equation method for partly quenched systems. Namely, we are interested in the adsorption of model mixtures that include large and small hard spheres mimicking, in a simplified manner, a colloidal dispersion. It is of much interest to describe the effective pair interaction between colloidal particles in the adsorbed mixtures, because the structural, thermodynamic and dynamic properties of colloidal dispersions are mostly determined by these interactions.

There have been much investigation previously in the intercolloidal effective forces and related phenomena in colloidal dispersions in the framework of the model of hard spheres and of Ornstein-Zernike integral equation for mixtures [13–15]. It was found that there is an attractive well in the effective interaction between colloids due to the depletion effect. The depths of the atractive wells depends on the solvent concentration. When the concentration is high enough the effective interaction becomes oscillatory indicating the layering phenomenon of the solvent species between to large colloidal particles. This theoretical predictions are in qualitative agreement with the experimental observations for the force acting between colloids in dispersions. In particular, the mean force potential acting between colloids in the presence of dilute rigidly fixed subsystem of obstacles has been studied experimentally for quasi two-dimensional model in works from the group of M. Medina Noyola from the Institute of Physics at San Luis Potosí University [13, 14].

As a natural extension of previous efforts in the theory of colloidal dispersions, in this study we apply the ROZ equations for adsorbed colloidal solutions. The present work represents only the first step of a larger project; we discuss extensions of the model and of the theory for further research in the conclusions of this study.

2. Theoretical model

Let us first investigate a two-component fluid mixture adsorbed in a disordered quenched matrix (M). The matrix (a set of obstacles) is assumed to correspond to an equilibrium configuration of hard spheres at packing fraction $\eta_M = \pi\rho_M\sigma_M^3/6$, where ρ_M is the matrix density, σ_M is the diameter of matrix particles. A disordered hard sphere matrix also can be characterized by the value of microporosity, p, $p = 1 - \eta_M$, *i.e.* by the fraction of volume available to accommodate fluid particles. The fluid is a mixture consisting of a hard sphere solvent species of diameter σ_s, considered at a dimensionless density $\rho_s^* = \rho_s\sigma_s^3$ (ρ_s is the solvent density) and hard spheres of a larger diameter σ_c mimicking colloidal particles. In what follows, without loss of generality, we assume $\sigma_s = 1$. The colloids are considered at density $\rho_c^* = \rho_c\sigma_c^3$. Our consideration is restricted to a region of a low concentration of colloidal particles in a solution, such that $\rho_c^* \ll \rho_s^*$.

At this initial stage of investigation of adsorbed colloidal solutions we assume a simple model for interparticle interactions between species,

$$U_{ij}(r) = \begin{cases} \infty, & r < \sigma_{ij} = 0.5(\sigma_i + \sigma_j) \\ 0, & r > \sigma_{ij} \end{cases}, \qquad (1)$$

where i, j take values s, c, M.

Let us proceed now with the equations necessary to solve the problem for quenched-annealed mixture in which, most importantly, fluid species do not have influence on the quenched matrix structure. According to the assumption of an equilibrium distribution of hard sphere species mimicking a disordered matrix we describe its structure in terms of the pair correlation function (pcf) $h_{MM}(r)$. The pcf $h_{MM}(r)$ is obtained by using customary Ornstein-Zernike integral equation

$$h_{MM} - c_{MM} = c_{MM} \otimes \rho_M h_{MM}, \qquad (2)$$

with the Percus-Yevick closure

$$c_{MM}(r) = \{\exp[-\beta U_{MM}(r)] - 1\}\{1 + h_{MM}(r) - c_{MM}(r)\}, \qquad (3)$$

where $U_{MM}(r)$ is a hard sphere interaction between matrix species. In Eq. (2), and in what follows, the symbol $\otimes$ denotes convolution and r-dependencies are omitted for the sake of brevity.

Let us now proceed with the ROZ equations for the description of fluid-matrix and matrix-matrix correlations. In the framework of the ROZ formalism, both the fluid-fluid pair correlation functions, $h_{ij}(r)$, and the direct correlation functions, $c_{ij}(r)$ (with i, j taking values c, s) consist of the connected and blocking parts, *i.e.* $h_{ij}(r) = h_{ij}^{\text{con}}(r) + h_{ij}^{\text{bl}}(r)$, $c_{ij}(r) = c_{ij}^{\text{con}}(r) + c_{ij}^{\text{bl}}(r)$. The blocking parts describe a set of correlations between fluid particles via matrix subsystem [3–5]. The blocking contribution into the direct correlation functions $c_{ij}(r)$ $(i, j = c, s)$ is neglected within the Madden-Glandt approximation (MGOZ), *i.e.* if one works, for example, in the framework of the Percus-Yevick closure [1–5].

The ROZ equations, written in the MGOZ form, are the following:

$$h_{iM} - c_{iM} = c_{iM} \otimes \rho_M h_{MM} + \sum_{j=c,s} c_{ij} \otimes \rho_j h_{jM}, \qquad (4)$$

for the fluid-matrix correlations, and

$$h_{ij} - c_{ij} = c_{iM} \otimes \rho_M h_{jM} + \sum_{l=c,s} c_{il} \otimes \rho_l h_{lj}, \qquad (5)$$

for a set of fluid-fluid correlations. The function $h_{MM}(r)$ serves as an input into Eq. (4) that must be solved in conjunction with Eqs. (5).

In this work we solve the ROZ equations supplementing them by the PY approximation. The PY approximation has been used previously for hard sphere type models for colloidal mixtures [15–18] and for quenched-annealed systems as well.

The PY closure for the problem in question reads

$$c_{iM}(r) = \{\exp[-\beta U_{iM}(r)] - 1\}\{1 + h_{iM}(r) - c_{iM}(r)\},$$
$$c_{ij}(r) = \{\exp[-\beta U_{ij}(r)] - 1\}\{1 + h_{ij}(r) - c_{ij}(r)\}, \qquad (6)$$

where the subscripts i, j take values s and c, and the interactions are given by Eq. (1). The system of equations (4)–(6) has been solved numerically by direct iterations.

We would like to comment briefly one important issue relevant to the presented study. It seems natural to require that the theory must be tested versus computer simulation of the model. However, the model in question is difficult to simulate for several reasons. First, it requires grand canonical ensemble simulation of a mixture consisting of particles with large difference of diameters. This is a difficult problem in any ensemble. A smart displacement algorithm is necessary to employ [19]. The attempts to create large colloidal spheres in a matrix in grand canonical simulation, are hardly expected successful. Common regime of colloidal suspensions is characterized by a very low number of colloidal particles compared to the number of solvents. That makes statistics of pairwise properties of colloidal species poor. For example, in the canonical ensemble simulations of Biben *et al.* [19] only ten large spheres has been used to mimic colloidal subsystem. Moreover, to describe the adsorption of a mixture in disordered porous medium requires the results from a set of simulation experiments (each experiment must be performed at a given, but different, statistically independent, matrix configuration). Next, the results must be averaged over different matrix configurations. To summarize this discussion, the simulation of colloidal dispersions in disordered porous media represents a scientific problem on its own. Having these difficulties in mind, we restrict ourselves, for the moment, to theoretical developments. Nevertheless, previous experience accumulated in the investigation of colloidal suspensions in the absence of matrix species via integral equation method, makes us confident that our results are at least qualitatively correct.

We postpone a detailed description of thermodynamic properties of adsorbed colloid-solvent mixtures, in the framework of the model in question and more sophisticated models, to our future work, which is now in progress. There we will discuss, in particular, the adsorption isotherms and the compressibility of adsorbed mixture. Our focus in the present study is in the structural properties, in the potential of the mean force between colloidal species and forces acting between them.

3. Results

The structural properties of adsorbed colloidal mixtures in terms of the distribution functions, $g_{ij}(r) = 1+h_{ij}(r)$, where i, j stand for s, c and M, are of some interest. However, in the case of colloidal mixtures a more common interpretation of the results is given in terms of the PMF, $-\beta W_{cc}(r)$:

$$-\beta W_{cc}(r) = \ln[1 + h_{cc}(r)]; \tag{7}$$

besides the pair distribution functions $g_{cM}(r)$, $g_{sM}(r)$, $g_{cs}(r)$ and $g_{ss}(r)$. We are looking how the shape of PMF depends on the matrix microporosity and on the density of the supporting solvent. The fluid-matrix correlations play an important role in the microscopic description of partly quenched systems, besides the fluid-fluid correlations.Therefore, in addition to the PMF defined by Eq. (7), we also interpret the fluid-matrix correlations in terms of the corresponding PMF. It is defined similar to Eq. (7),

$$-\beta W_{cM}(r) = \ln[1 + h_{cM}(r)]. \tag{8}$$

On the other hand, the derivative of the PMF's yields the force acting between colloids, *i.e.*, the so called solvation force and the force acting on a colloids with respect to the fixed matrix particle. Namely,

$$\beta F_{ij}(r) = -\frac{d\beta W_{ij}(r)}{dr}. \tag{9}$$

The parameters of the model in this study are the following. Throughout our study, we choose the diameter of matrix particles seven times larger than of the solvent species, $\sigma_M = 7, \sigma_s = 1$. One of the reasons of this choice is that in a successful model for adsorption of methane in a model silica xerogel of Kaminsky and Monson [20] the size ratio is like that. On the other hand, in previous studies of hard sphere colloid-solvent mixtures [13–15], it has been assumed that the size ratio of colloids and solvent particles is of the order 10:1. In this work we have chosen this diameter ratio.

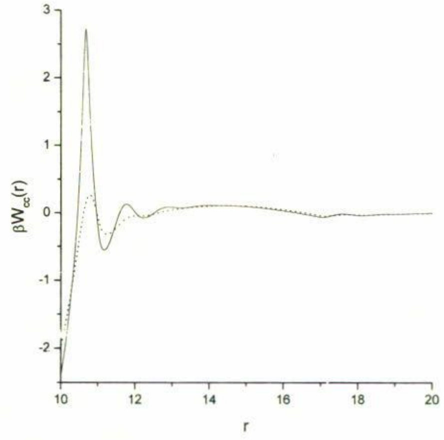

FIGURE 1. Colloid-Colloid PMF with diameter $\sigma_c = 10$ at the low packing fraction, $\eta_c = \pi\rho_c\sigma_c^3/6 = 5.2 \times 10^{-5}$. The packing fraction corresponding to the matrix particles is $\eta_M = 0.209$. The solvent density is considered in the intermediate range, $\rho_s^* = \rho_s\sigma_s^3 = 0.25$ (dot line) and $\rho_s^* = 0.36$ (solid line).

Let us discuss now the most interesting results, obtained by using the PY approximation. We begin with the presentation of the PMF for the case of a matrix at microporosity, $p = 0.791$ ($\eta_M = 0.209$) (Fig. 1). The large particles mimicking colloids with the diameter $\sigma_c = 10$ are considered at fixed, low packing fraction, $\eta_c = \pi\rho_c\sigma_c^3/6 = 5.2 \times 10^{-5}$. The solvent density is considered in the intermediate range, $\rho_s^* = \rho_s\sigma_s^3 = 0.25$ and $\rho_s^* = 0.36$. We observe that the magnitude and range of the oscillations of the PMF increase with increasing solvent density. The contact attraction between large spheres also increases with augmenting solvent density. At a higher solvent density we observe that the repulsive maxima correspond to one or two or three layers of solvent particles between two colloidal spheres. In addition, we observe a small cusp of attraction at distances corresponding to matrix-separated colloidal spheres. However, the magnitude of effects due to the presence of rigidly fixed matrix species is small, in comparison with the effects of solvent species.

In Fig. 2 we present the solvation force acting between colloidal particles. This is the measurable quantity in experiments, and, therefore, is of particular interest. There is a cusp in the repulsive region at $\sigma_c + 1$ for a hard sphere solvent. At larger distances, repulsive force changes smoothly. The amplitude of the oscillations of the solvation force essentially increases with increasing solvent density. The effect of matrix species in the attractive force is very small. In Figs. 3 and 4, we shown the PMF corresponding to the colloid-matrix correlations and the corresponding force, respectively. The colloid-matrix PMF is of smaller magnitude comparing to the colloid-colloid one. The reason is that the matrix particles are rigidly fixed in a disordered configuration. However, the effect of layering of solvent species in between the matrix and colloidal particles is well pronounced (Fig. 3). Trends for layering augment with increasing solvent

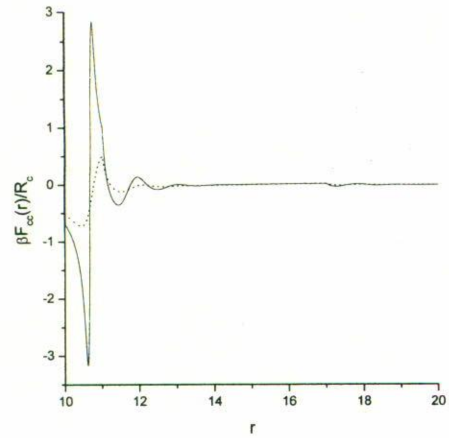

FIGURE 2. Solvation force acting between colloidal particles with $\eta_c = \pi\rho_c\sigma_c^3/6 = 5.2 \times 10^{-5}$ and $\eta_M = 0.209$. The dot line corresponds to a solvent density $\rho_s^* = 0.25$, and the solid line is for $\rho_s^* = 0.36$. Here $R_c = \sigma_c/2$.

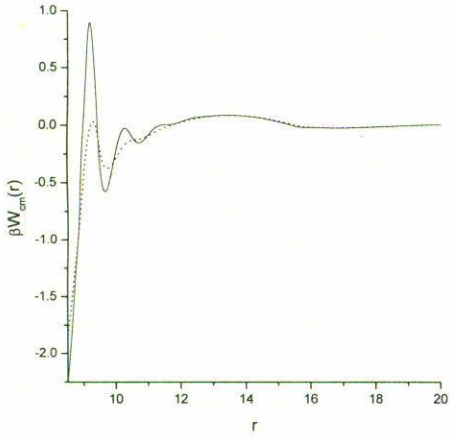

FIGURE 3. The same as in Fig. 1 but now for Colloid-Matrix interaction with $R_{\rm cm} = (\sigma_c + \sigma_m)/2$.

density. We do not observe any cusp, but a continuous change of shape at large colloid-matrix separations (corresponding to matrix-matrix-colloid configuration) in this PMF even at a quite high density, $\rho_s^* = 0.36$. This behavior serves as manifestation that the configurations like colloid-matrix-matrix can occur in the system, but with a low probability. The solvation, fluid-matrix, force reflects trends of behavior of the corresponding PMF. The amplitude of the this solvation force is much less than for colloid-colloid force, as expected, Fig. 4. The matrix particles are unmovable and the force originates from the pressure that exhibit solvent species on a colloid, trying to put a colloid closer to the matrix particle. The applicability of the PY approximation is commonly restricted by the maximal density at which the PY yields an entirely positive pair distribution function between large species (colloids). For higher densities of the solvent, one needs to apply a more sophisticated closure, probably the hypernetted chain (HNC) one, or a combined PY-HNC closure, as has been used previously in the studies of unconfined colloidal dispersions in the framework of a hard sphere model. The density $\rho_s^* = 0.36$ is exactly the highest solvent density at which the colloidal pair distribution function is entirely positive for the model in question.

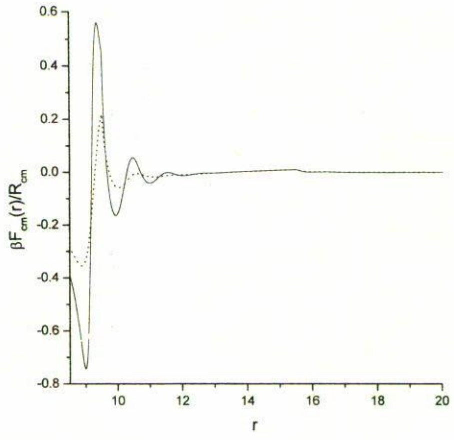

FIGURE 4. The same as in Fig. 2 but now for Colloid-Matrix interaction.

After discussing the effect of solvent density, we would like to elucidate the effect of matrix microporosity. Now, let us proceed to the matrix with a higher packing fraction, *i.e.* with a lower microporosity, $p = 0.614$ ($\eta_M = 0.386$). The value of microporosity corresponds to the nominal value of porosity of the silica xerogel in the model of Kaminsky and Monson [20]. The large particles mimicking colloids with the diameter $\sigma_c = 10$ are considered at $\eta_c = 5.2 \times 10^{-5}$, as in the previous case. The solvent density range is smaller now, the densities in question are $\rho_s^* = 0.15$, 0.2 and 0.23. This latter value is the highest solvent density at which we have obtained entirely positive pair distribution function between colloidal species, $g_{cc}(r)$. At a higher value of solvent density, to use the PY approximation does not make sense.

The colloid-colloid PMF, shown in Fig. 5, exhibits similar trends to those discussed in the case of a more microporous matrix (Fig. 1). However, the effect of the presence of the matrix of obstacles becomes much more pronounced. The effective attraction between matrix-separated colloids becomes of the order of the secondary attractive minimum due to solvent species. Moreover, the oscillatory behavior of the PMF at large distances reflects attraction between matrix-separated colloids in which either of species (matrix or colloids) are covered by a layer of solvent species. The matrix particles also contribute into the formation of the effective repulsion between colloids at distances less than the matrix species diameter. This repulsion plays role of important background effect that can be modulated by the solvent density, however, the effective interaction remains repulsive at these distances. The effect of stronger confinement, *i.e.*, of higher matrix density also can be seen in the solvation force (Fig. 6). The solvation force between colloids has similar shape to the one given in Fig. 2. However, the amplitude of all the effects is approx-

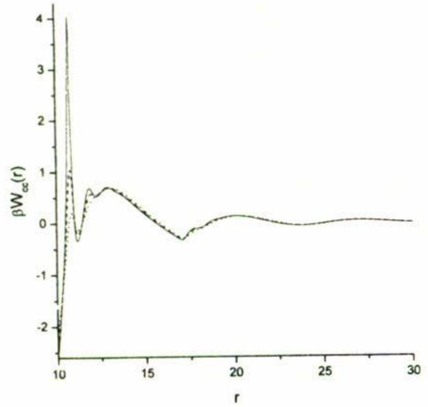

FIGURE 5. Colloid-Colloid PMF at the packing fraction $\eta_c = \pi\rho_c\sigma_c^3/6 = 5.2 \times 10^{-5}$ and $\eta_M = 0.386$ with $\sigma_c = 10$. The solvent density stands for $\rho_s^* = 0.15$ (dot line), $\rho_s^* = 0.2$ (dash line) and $\rho_s^* = 0.23$ (solid line).

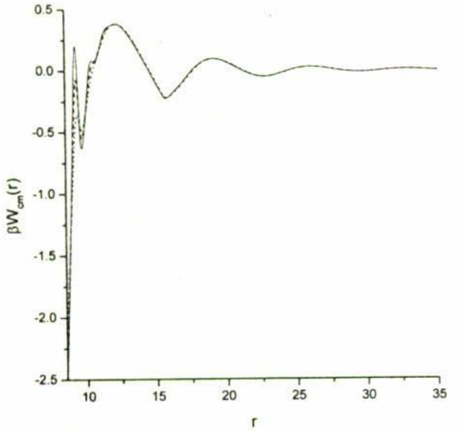

FIGURE 7. The same as in Fig. 5 but now for Colloid-Matrix interaction, again $R_{cm} = (\sigma_c + \sigma_m)/2$.

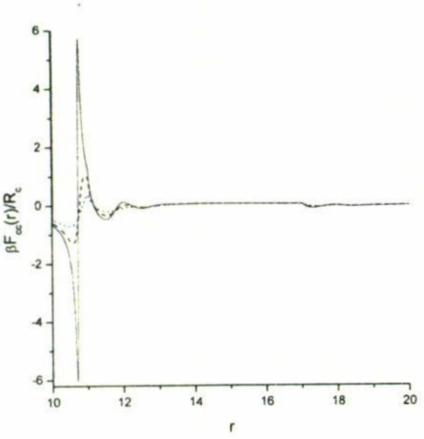

FIGURE 6. Solvation force acting between colloidal particles for the data of Fig. 5, with $R_c = \sigma_c/2$.

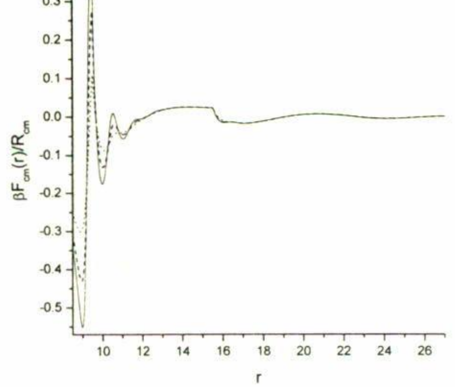

FIGURE 8. The same as in Fig. 6 but now for Colloid-Matrix interaction.

imately twice larger (note different scales in Figs. 2 and 6). Nevertheless, we would like to emphasize that the solvent subsystem plays an overwhelmingly important role in the formation of the solvation force, such that the matrix confinement is manifested mostly in the magnitude of the effects rather than introducing peculiarities of the shape of the force. On the other hand, the influence of the matrix confinement is quite strongly pronounced in the colloid-matrix correlations. We observe a strongly modulated shape of the colloid-matrix PMF (Fig. 7), such that the modulating influence due to matrix species is of similar importance to the one due to solvent particles. Probable colloid-matrix configurations are contact pairs as well as such that there is one solvent layer between them. Next, at low matrix microporosity the configurations of the type matrix-matrix-colloid can be found also. The solvation force, following from this PMF is shown in Fig. 8. Most importantly, is that there appears a repulsive shoulder of the range of matrix species diameter, in the colloid-matrix solvation force. The oscillatory behavior of this force extends to larger separations.

In addition to the trends discussed above, we observe that the solvent effects are well pronounced even at a low nominal solvent density. This is a clear manifestation of the influence of the matrix confinement corresponding to low microporosity.

To conclude, in the present work we have considered the problem of the description of the potential of mean force acting between colloidal particles in dispersions adsorbed in microporous disordered media. Our theoretical analysis is based methodologically on the replica Ornstein-Zernike equations. The model, that has been studied, is the simplest one. However, it permits several extensions to make it closer with experimentally relevant systems. In particular, it is of interest to consider a model with long-range repulsive interaction between colloids. It would be also necessary to involve more sophisticated approximations, rather than the most popular Percus-Yevick closure used in this work. This issue would be particularly important to study segregation phenomena in adsorbed colloidal dispersions. Moreover, the calculations of the adsorption isotherms would be of primary importance in a future work, to perform comparisons of the structure of dispersions in different matrices and in the bulk colloidal solutions.

Our major findings are nevertheless the following. The ROZ integral equations provide an adequate tool for the problem of description of the structure of adsorbed colloidal dispersions in microporous media. We have observed that, in addition to the effect of modulation of the PMF due to solvent species, there arises the effect of modulation of the mean force potential due to rigidly fixed disordered confining medium. An attractive minimum on the PMF at distances between colloids, slightly larger than the matrix particle diameter, can be observed for different values of adsorbent microporosity. This attraction can be attributed to the confinement effects of the matrix species. The effects of disordered matrix media also influence the value of the repulsive barrier between colloids separated by a single layer of solvent particles. We have observed that changes of the matrix microporosity have substantial influence on the colloid-matrix correlations. The solvent effects even at low nominal density are very well pronounced in matrices at low microporosity.

Acknowledgments

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