

Nonadditive Binary Hard Sphere Mixture in Disordered Hard Sphere Matrices: Integral Equations and Computer Simulation

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Received: May 7, 2004

We have studied adsorption of nonadditive binary symmetric hard sphere mixtures in hard sphere matrices and in templated hard sphere matrices. Adsorption is described by using replica Ornstein–Zernike integral equations complemented by Martynov–Sarkisov closure relations. This theory permits straightforward calculation of the chemical potential of fluid species and to describe equilibrium between the bulk phase in a model adsorbent body. Theoretical results for adsorption isotherms agree well with Monte Carlo computer simulation data. On the other hand, we have captured the effect of matrix modification on adsorption via templating. Finally, we have described the coexistence curve (in terms of concentration vs density and in terms of concentration vs chemical potentials of fluid species) for the demixing transition by using theoretical procedure and by semigrand computer simulation in hard sphere matrices and in corresponding templated matrices. We have shown that the explanation of the phase behavior is intrinsically related to the trends of adsorption of the model fluid in such disordered adsorbents.

1. Introduction

In recent years there has been much interest in the development of theoretical approaches to describe the structural and thermodynamic properties of fluids in disordered microporous adsorbents. Particular attention has been focused in describing the effects of disordered confinement on the phase behavior. Theoretical research in this area has been stimulated by experimental studies. In particular, the influence of highly porous gels on adsorption and phase behavior of single-component fluids has been documented by experimental results.^{1–3} From the point of view of statistical mechanics some of these combined adsorbent–adsorbate systems can be conveniently viewed as partly quenched fluids. The theoretical background to describe partly quenched systems was constructed approximately a decade ago, see, e.g., original works^{4–9} and more recent reviews.^{10,11} The problem of liquid–vapor equilibrium in disordered media has been investigated in detail by using different methods, see, e.g., refs 12–17.

Some experimental works have considered adsorption and phase behavior of mixtures in disordered media.^{18,19} Demixing of components is one of the possible phenomena occurring in certain bulk and confined mixtures. Not long ago, Gordon and Glandt have studied demixing in a binary mixture of Lennard–Jones fluids with weakened cross interaction in disordered matrices by using Monte Carlo simulation.²⁰ However, in the majority of simple fluid binary and multicomponent systems demixing occurs due to a combination of energetic and entropic effects which both contribute to thermodynamic behavior in

nontrivial manner. Entropic effects presumably dominate phase separation in mixtures at very high pressures. Some experimental studies on bulk mixtures have been focused on this subject.^{21–23} Several model fluid mixtures of statistical mechanics can induce entropically driven demixing of species which results in different phases.^{24–26} The nonadditive hard sphere (NAHS) model with a positive nonadditivity parameter is one of the simplest models that can exhibit fluid–fluid phase separation induced only by excluded volume effects. Although an experimental counterpart of the NAHS is quite difficult to identify, the model has been the focus of significant number of studies by applying theoretical^{27–29} and simulation^{30–33} procedures. However, understanding the thermodynamics of demixing in this model can be useful in studies of more complex systems. Most commonly used theoretical procedures to investigate the NAHS model employ the first-order Ornstein–Zernike (OZ) integral equation completed by a closure approximation. Since this type of theory can be applied only to homogeneous fluids, only the instability boundary and the critical (consolute) point can be obtained. A wider insight can be reached in the framework of more sophisticated approaches.

In a recent brief report, Sierra and Duda have started to investigate entropically driven demixing in the model of nonadditive hard spheres immersed in hard sphere matrices by using replica Ornstein–Zernike integral equations and semigrand computer simulation.³⁴ In this communication, our principal objective is to investigate the effect of disordered hard sphere matrices on the fluid–fluid phase separation. Namely, we would like to consider entropically driven demixing in a binary symmetric model of nonadditive hard spheres immersed into a matrix of obstacles prepared of hard spheres, in close similarity to ref 34. However, in contrast to the aforementioned study, our analysis of phase behavior is based on the adsorption isotherms for the model of NAHS in hard sphere matrices.

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Application of the closed expressions for the chemical potentials of adsorbed species is of crucial importance in this respect.

Also, we establish how the modification of matrix structure via the so-called theoretical templating procedure (see, e.g., refs 35, 36) influences adsorption of species and demixing trends in the NAHS model. Experimentally, the templating methods, to modify porous adsorbents as desired, are widely used,³⁷ but they are rather complex to mimic adequately at the present stage of this research. Here we undertake an attempt to capture the possible effects of purely “geometric” modification of the matrix structure on the properties of the NAHS model.

This study represents, in our opinion, one step forward into understanding the effects of disordered matrices on entropically driven phase separation in binary mixtures. Several issues of fundamental importance remain still unresolved, and we discuss them in more detail in the concluding part of the paper.

2. Model and Methodology

Let us consider a binary mixture of hard spheres with equal diameters, $\sigma_1 = \sigma_2$, i.e., it is a symmetric model. The cross interaction is again of hard sphere type, but is characterized by the diameter σ_{12} , where $\sigma_{12} = 0.5(\sigma_1 + \sigma_2) \times (1 + \Delta)$. The parameter Δ yielding nonadditivity of diameters is chosen to be positive and equal to 0.2 throughout this study. However, this particular choice of the value for Δ does not influence the generality of our conclusions. This nonadditive hard sphere model,

$$u_{ij}(r) = \begin{cases} \infty, & r < \sigma_{ij} \\ 0, & r > \sigma_{ij} \end{cases} \quad (1)$$

with $i, j = 1, 2$, is considered to be distributed in primitive adsorbents mimicked by the equilibrium distribution of hard spheres with a diameter σ_m at a density ρ_m . The matrix medium provides a set of obstacles for the insertion of fluid species.

It is of certain interest to investigate also how the effects of changes in the configuration of matrix species at a fixed matrix density influence adsorption. To do that we apply a theoretical model for templated matrix medium, proposed by Van Tassel et al.^{35,36} Briefly, the idea is to consider a mixture of matrix spheres and of hard spheres mimicking template. This template subsystem is characterized by the diameter of template spheres, σ_t , and by template density ρ_t . After equilibration of such a mixture, the template species are removed, and as a result one obtains a matrix with a distribution of obstacles that differs from the distribution of the same obstacles prepared, however, without template. It is assumed that the process of removal of templates does not alter configuration of matrix species.

We use Greek subscripts to denote matrix and template species in what follows. The model for interactions in nontemplated or templated adsorbent is

$$u_{\alpha\beta}(r) = \begin{cases} \infty, & r < \sigma_{\alpha\beta} \\ 0, & r > \sigma_{\alpha\beta} \end{cases} \quad (2)$$

where α, β take values m and t . Also we assume that $\sigma_{\alpha\beta} = 0.5(\sigma_\alpha + \sigma_\beta)$. Finally, the interactions between matrix species of the adsorbent and fluid particles are

$$u_{im}(r) = \begin{cases} \infty, & r < \sigma_{im} \\ 0, & r > \sigma_{im} \end{cases} \quad (3)$$

where $\sigma_{im} = 0.5(\sigma_i + \sigma_m)$. On the other hand, $u_{it}(r) = 0$ ($i = 1, 2$). Absence of interaction between fluid species and template particles mimics what in reality must be the removal of template.

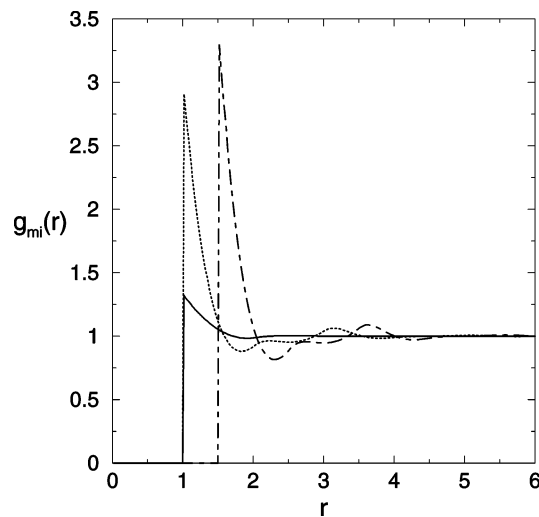


Figure 1. Pair distribution function (pdf) of matrix species at $\rho_m^* = 0.2$ (solid line), and of matrix prepared in the presence of template $\rho_m^* = 0.2$, $\rho_t^* = 0.6$ (dotted line). The pdf corresponding to matrix-template distribution in the latter case is shown by dash-dotted line.

In this work, for simplicity, we choose $\sigma_m = \sigma_1 = \sigma_2 = 1$ and $\sigma_t = 2$; all the distances are measured in units of fluid diameter. However, the *dimensionless* densities of matrix and template species will be denoted by ρ_m^* and $\rho_t^* = \rho\sigma_t^3$. The fluid subsystem is characterized by dimensionless total density ρ , $\rho = \rho_1 + \rho_2$, and by concentration $X = \rho_1/(\rho_1 + \rho_2)$.

The model is studied by using theoretical methodology and by computer simulations as explained below. To deal with the partly quenched system in question we apply replica Ornstein–Zernike (ROZ) integral equations. The matrix structure follows from the common Ornstein–Zernike equation for a mixture,

$$h_{\alpha\beta} = c_{\alpha\beta} + \sum_{\gamma} c_{\alpha\gamma} \otimes \rho_{\gamma} h_{\gamma\beta} \quad (4)$$

where \otimes denotes convolution in Fourier space and h and c are the correlation function and the direct correlation function, respectively. We have used the Percus–Yevick closure to describe the distribution function of matrix species,

$$c_{\alpha\beta}(r) = [\exp(-u_{\alpha\beta}(r)/kT) - 1][1 + h_{\alpha\beta}(r) - c_{\alpha\beta}(r)] \quad (5)$$

Actually any other closure from the liquid state theory can be used for the same purpose.

It is worth emphasizing that matrix–matrix, matrix–template, and template–template pair correlation functions are used as input to investigate the fluid–matrix and fluid–fluid correlations via ROZ equations. The pair distribution function of matrix species $g_{mm}(r)$ at $\rho_m^* = 0.2$, in the absence of template, is shown in Figure 1 by the solid line. At the same matrix density, however, in the presence of template at $\rho_t^* = 0.6$, the matrix structure is very different, see dotted line in Figure 1. The probability of finding matrix particles in contact is quite high; also from the second maximum of this function one can find evidence that matrix particles are separated by a single template particle which afterward will be removed such that a small cavity would be available for adsorption. The high probability of finding matrix particles in contact with template can be seen from the matrix–template distribution function, dash-dotted line in Figure 1. At present, we do not discuss how realistic is such a picture of preparing the adsorbent in the presence of template, satisfying ourselves by the fact that the template modifies the distribution of matrix species at a fixed matrix density.

It was common until quite recently to discuss the porosity of matrix medium, \mathcal{P} , as $\mathcal{P} = 1 - \pi\rho_m^*/6$. However, such an expression does not provide insight into changes of porosity of the adsorbent due to templating. Rather, it gives the nominal porosity as a fraction of volume in the adsorbent body available to accommodate fluid species during adsorption. We will discuss below a finer measure of porosity coming out from the chemical potential of fluid species in a matrix medium.

The essence of the ROZ theory is in the description of fluid–matrix and fluid–fluid correlations. Namely, the equations describing fluid–matrix correlations for the model in question are

$$h_{im} = c_{im} + \sum_{\gamma=m,t} c_{i\gamma} \otimes \rho_{\gamma} h_{\gamma m} + \sum_{j=1,2} c_{ij} \otimes \rho_j h_{jm} - \sum_{j=1,2} c_{ij}^{bl} \otimes \rho_j h_{jm} \quad (6)$$

A similar equation describes fluid–template correlations:

$$h_{it} = c_{it} + \sum_{\gamma=m,t} c_{i\gamma} \otimes \rho_{\gamma} h_{\gamma t} + \sum_{j=1,2} c_{ij} \otimes \rho_j h_{jt} - \sum_{j=1,2} c_{ij}^{bl} \otimes \rho_j h_{jt} \quad (7)$$

Next, we write equations describing correlations between fluid species in our binary mixture:

$$h_{ij} = c_{ij} + \sum_{\gamma=m,t} c_{i\gamma} \otimes \rho_{\gamma} h_{\gamma j} + \sum_{l=1,2} c_{il} \otimes \rho_l h_{lj} - \sum_{l=1,2} c_{il}^{bl} \otimes \rho_l h_{lj}^{bl} \quad (8)$$

and

$$h_{ij}^{bl} = c_{ij}^{bl} + \sum_{\gamma=m,t} c_{i\gamma} \otimes \rho_{\gamma} h_{\gamma j} + \sum_{l=1,2} c_{il} \otimes \rho_l h_{lj}^{bl} - \sum_{l=1,2} c_{il}^{bl} \otimes \rho_l h_{lj}^{bl} \quad (9)$$

In the above, f_{ij}^{bl} denotes the blocking part of the correlation function f_{ij} (where f stands for h or c), see, e.g., refs 3 and 4. The blocking correlation function, h_{ij}^{bl} , accounts for the correlations between fluid particles mediated by the matrix subsystem. More generally, the correlation function between fluid species can be represented as a sum of two terms:

$$c_{ij}(r) = c_{ij}^{bl}(r) + c_{ij}^{con}(r) \\ h_{ij}(r) = h_{ij}^{bl}(r) + h_{ij}^{con}(r) \quad (10)$$

where the second term in each of the sums corresponds to the connected part of the relevant correlation function. The connected part, h_{ij}^{con} , mediates correlations between a pair of fluid particles through a path involving fluid particles only. It can be convenient to use the OZ equation for the connected correlation functions,

$$h_{ij}^{con} = c_{ij}^{con} + \sum_{l=1,2} c_{il}^{con} \otimes \rho_l h_{lj}^{con} \quad (11)$$

, rather than eq 9, in conjunction with eqs 6–8 in which blocking functions can be substituted by the difference of the total and connected terms. Equation 10 is nevertheless coupled with other equations via the closure approximation.

As is common in the liquid state theory, integral equations 6–9 or 6–8 and 10 must be completed by closure relations. Actually, one can choose between the Percus–Yevick approximation or the hypernetted chain type closures to solve

replica OZ equations. It is known that the Percus–Yevick closure is quite accurate in describing the adsorption of single-component hard spheres in hard sphere matrices. The chemical potential in this case is calculated by solving relevant equations along the density path and taking the integration constant from the Carnahan–Starling type of equation of state of a hard sphere fluid mixture. On the other hand, Percus–Yevick closure assumes vanishing blocking type correlations, i.e., correlations between fluid particles mediated by matrix species. Finally, it is known that Percus–Yevick closure is not accurate in describing the demixing transition in the bulk model of nonadditive hard spheres. A reasonable alternative would be the hypernetted chain closure. It takes into account the blocking correlation functions and moreover permits to obtain the chemical potential of adsorbed species straightforwardly.³⁸ However, the HNC closure has poor performance for purely repulsive potentials and consequently in describing the bulk model of nonadditive hard sphere mixtures.

It is much better to perform approximations which include bridge functions, at least in the parametrized form, such as Martynov–Sarkisov (MS) and Verlet’s modified closures. Unfortunately, the application of Verlet’s modified approximation requires to choose several parameters according to thermodynamic consistency conditions.²⁹ This choice becomes more demanding for the problem of adsorption of a nonadditive mixture in a disordered matrix. Therefore, in the present study we resort to the MS closure, which does not require such a sophistication. On the other hand, this approximation permits us to obtain the chemical potentials of adsorbed species with reasonable accuracy. The Martynov–Sarkisov approximation reads:

$$c_{i\alpha}(r) = \exp[-\beta u_{i\alpha}(r) + \sqrt{1 + 2\gamma_{i\alpha}(r)} - 1] - 1 - \gamma_{i\alpha}(r) \quad (12)$$

where $(\alpha = m, t, u_{it} = 0)$ and

$$c_{ij}(r) = \exp[-\beta u_{ij}(r) + \sqrt{1 + 2\gamma_{ij}(r)} - 1] - 1 - \gamma_{ij}(r) \quad (13)$$

$$c_{ij}^{bl}(r) = \exp[\sqrt{1 + 2\gamma_{ij}^{bl}(r)} - 1] - 1 - \gamma_{ij}^{bl}(r) \quad (14)$$

The method to obtain the closed formula for the chemical potential is similar to that derived by one of us in the case of electrolyte solutions adsorbed in disordered matrices, see, e.g., ref 39 for a detailed description. Repeating replica trick and then taking the limit of the vanishing number of replicas, one obtains the excess chemical potentials ($\beta\mu_i = \beta\mu_i^{id} + \beta\mu_i^{ex}$) of fluid species,

$$\beta\mu_i^{ex} = - \sum_{j=1,2} \rho_j [c_{ij}(0) - c_{ij}^{bl}(0)] - \\ \sum_{\alpha=m,t} \rho_{\alpha} c_{i\alpha}(0) + \frac{1}{2} \sum_{\alpha=m,t} \rho_{\alpha} \int d\mathbf{r} h_{i\alpha}(r) \gamma_{i\alpha}(r) + \frac{1}{2} \sum_{j=1,2} \rho_j \int d\mathbf{r} [h_{ij}(r) \gamma_{ij}(r) - h_{ij}^{bl}(r) \gamma_{ij}^{bl}(r)] + \sum_{\alpha=m,t} \rho_{\alpha} \int d\mathbf{r} g_{i\alpha}(r) B_{i\alpha}(r) + \\ \sum_{j=1,2} \rho_j \int d\mathbf{r} [g_{ij}(r) B_{ij}(r) - g_{ij}^{bl}(r) B_{ij}^{bl}(r)] - \sum_{\alpha=m,t} \rho_{\alpha} \int d\mathbf{r} S_{i\alpha}(r) - \\ \sum_{j=1,2} \rho_j \int d\mathbf{r} [S_{ij}(r) - S_{ij}^{bl}(r)] \quad (15)$$

where the bridge function are $B = \sqrt{1+2\gamma} - 1 - \gamma$, $g = 1 + h$, $g_{ij}^{bl} = h_{ij}^{bl}$ (bold \mathbf{c} are the Fourier transforms of the correlation

functions), and the star functions have been calculated similar to the procedure already used by Lomba et al.,²⁹

$$S_{ij}(r) \approx \frac{h_{ij}(r)}{\gamma_{ij}(r)} \int_0^{\gamma_{ij}(r)} d\gamma'_{ij} B_{ij}(\gamma'_{ij}; r) \quad (16)$$

Integration of this formula is performed explicitly because the bridge functions are given in terms of γ .

Knowledge of the chemical potentials is an indispensable element to describe adsorption isotherms. Moreover, it permits us to describe porosity of matrix species according to the definition⁴⁰ which distinguishes between nontemplated and templated adsorbent,

$$\Pi = \exp[-\beta\mu_1(\rho_1 = 0, \rho_2 = 0, \rho_m, \rho_t)] \quad (17)$$

This expression will be used to characterize matrices of this study.

Actually, the integral equation method in the present form can be used only for homogeneous fluids. To investigate stability and phase equilibria we must restrict ourselves to the evaluation of material stability for the one-phase NAHS model mixture, i.e., of the spinodal curve. The compressibility relation is well established for partly quenched mixtures.^{6,9,41} For the binary mixture in question it reads

$$B_T = \left(\beta \frac{\partial P}{\partial \rho}\right)_T = 1 - \rho[X^2 c_{11}^{\text{con}}(k=0) + (1-X)^2 c_{22}^{\text{con}}(k=0) + 2X(1-X)c_{12}^{\text{con}}(k=0)] \quad (18)$$

where B_T is the isothermal bulk modulus. It is worth noting that only the connected parts of the correlation functions are involved in this expression. To proceed, let us introduce common structure factors of species for the fluid mixture in question,

$$\begin{aligned} S_{11}(k) &= 1 + \rho_1 h_{11}(k) = 1 + \rho_1 h_{11}^{\text{con}}(k) + \rho_1 h_{11}^{\text{bl}}(k) \\ &= S_{11}^{\text{con}}(k) + \rho_1 h_{11}^{\text{bl}}(k) = S_{11}^{\text{con}}(k) + S_{11}^{\text{bl}}(k) \end{aligned} \quad (19)$$

and

$$\begin{aligned} S_{12}(k) &= (\rho_1 \rho_2)^{1/2} h_{12}(k) = (\rho_1 \rho_2)^{1/2} h_{12}^{\text{con}}(k) + (\rho_1 \rho_2)^{1/2} h_{12}^{\text{bl}}(k) \\ &= S_{12}^{\text{con}}(k) + S_{12}^{\text{bl}}(k) \end{aligned} \quad (20)$$

The expression for $S_{22}(k)$ is similar to eq 20. Decomposition of the structure factors into the connected and blocking parts corresponds to the definition of the correlation functions. We can introduce also the connected Bhatia–Thornton structure factor,

$$S_{cc}^{\text{con}}(k)/[X(1-X)] = (1-X)S_{11}^{\text{con}}(k) + XS_{22}^{\text{con}}(k) - 2\sqrt{X(1-X)}S_{12}^{\text{con}}(k) \quad (21)$$

It comes out straightforwardly that the isothermal bulk modulus can be expressed in terms of such a structure factor via the equation

$$B_T/D(k=0) = S_{cc}^{\text{con}}(k=0)/[X(1-X)] \quad (22)$$

where

$$D(k) = [1 - \rho_1 c_{11}^{\text{con}}(k)][1 - \rho_2 c_{22}^{\text{con}}(k)] - \rho_1 \rho_2 [c_{12}^{\text{con}}(k)]^2 \quad (23)$$

High values of $S_{cc}(k=0)$ in the bulk mixtures signal strong homocoordination or, in other words, trends for separation of distinct species. Here we attempt to calculate the spinodal curve from the divergence of the concentration–concentration structure factor in the long-wavelength limit, $S_{cc}^{\text{con}}(k=0)$. If one is interested in measuring the average over disorder of thermal fluctuations in such a system, it would be useful to consider a linear combination of the blocking terms of the structure factors,

$$S_{cc}^{\text{bl}}(k)/[X(1-X)] = (1-X)S_{11}^{\text{bl}}(k) + XS_{22}^{\text{bl}}(k) - 2\sqrt{X(1-X)}S_{12}^{\text{bl}}(k) \quad (24)$$

Such a property can be obtained theoretically without difficulty. However, it is not straightforward to simulate the blocking correlation functions.⁴² In the present work we do not investigate the blocking contribution into the combined structure factor in detail.

Finally, in this part, it is worth mentioning a few technical issues. The set of ROZ/MS equations has been solved by the iteration procedure. A grid of 2^{10} points equally spaced ($\Delta r = 0.02$) has been used. A larger number of points slows down the procedure significantly without altering conclusions about the influence of matrix density and of template parameters. We have calculated adsorption isotherms and searched singularities of the structure factor $S_{cc}^{\text{con}}(k=0)$ for a sequence of states beginning from very small fluid density at fixed concentration X . Similar to the procedure described by Gazillo,²⁷ near a phase stability boundary, the density step was reduced to obtain a well pronounced divergence of the structure factor (the final value of the density step necessary to apply was of the order 10^{-5}). However, despite our efforts we were unable to obtain results for concentrations corresponding to very asymmetric mixtures, i.e., for $X < 0.25$.

Monte Carlo simulations have been performed in order to evaluate the quality of theoretically predicted adsorption isotherms and the distribution functions and also to investigate the demixing transition in the systems under study. The chemical potentials of fluid species adsorbed in the matrix for a certain state were evaluated from canonical simulation by using the Widom method.⁴³

The simulation method for evaluating the fluid–fluid equilibria was the same as that described in ref 34. Specifically, we have performed a semigrand canonical Monte Carlo simulation of a fluid in a cubic box with edge $L = 18$. In the first step, canonical simulations have been carried out to generate a matrix configuration. In the case of templated adsorbents we have simulated a two-component mixture of m and t species and afterward the t species have been discarded. In the second step we have distributed a binary mixture of fluid particles at a desired concentration in the already prepared matrix and have started usual semigrand canonical run. According to the algorithm we have applied the displacement and swap steps. Histograms of fluid composition were used to judge if a stable equilibrium was achieved. For other technical simulation details we refer the reader to ref 34. In all the runs we have performed averaging of observables over 5–8 matrix configurations. We have not encountered problems either distributing a high number of fluid particles of the mixtures in question or equilibrating them in matrices that are not dense. However, in dense matrices and for mixtures near demixing, these problems may be difficult to overcome, see, e.g., an important discussion in this respect in ref 17.

We are aware of recent developments for simulating phase equilibria in bulk nonadditive mixtures, based on invaded cluster

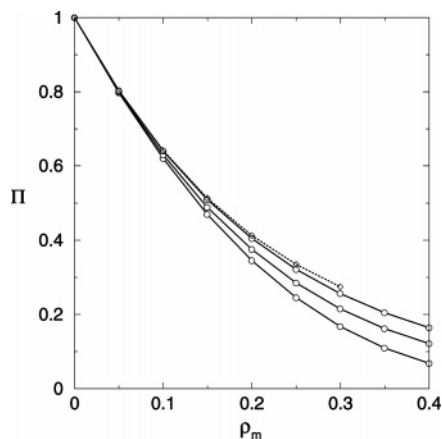


Figure 2. Theoretical results for the dependence of porosity, Π , of model porous matrices on matrix density. The solid lines with circles correspond to $\rho_t^* = 0.$, $\rho_t^* = 0.3$, and $\rho_t^* = 0.6$, from bottom to top. In all the cases $\sigma_t = 2$. The dotted line with symbols corresponds to $\rho_t^* = 0.6$ and $\sigma_t = 5$.

algorithms.^{44,45} Application of this type of approach for the study of partly quenched systems is not instantaneous.

3. Results and Discussion

We have already commented on the pair distribution functions of matrix species for nontemplated and templated adsorbent (Figure 1). However, availability of the expressions for the chemical potential permits us to discuss the dependence of porosity Π on matrix and template density (Figure 2). It is important to mention that theoretical measurement of porosity of a matrix is performed with respect to a certain fluid, in our case $\sigma_m = \sigma_f = 1$. For nontemplated material, porosity substantially decreases with increasing matrix density. The same matrix but templated with hard spheres of diameter $\sigma_t = 2$ is more porous than the corresponding nontemplated matrix. Higher density of template results in a more porous material (cf. curves corresponding to $\rho_t^* = 0.3$ and $\rho_t^* = 0.6$). However, the effects of templating become pronounced only if the matrix density is not small. Our study of adsorption is restricted to matrices with the density $\rho_m^* = 0.1$ and $\rho_m^* = 0.2$. Therefore, we expect to observe clearly the effects of template at higher matrix density. In the same figure we have shown the behavior of porosity on matrix density for large templates $\sigma_t = 5$ at $\rho_t^* = 0.6$. Porosity of matrices with such a template does not differ much in comparison to the case of $\sigma_t = 2$ at $\rho_t^* = 0.6$, seemingly because a much smaller number of large template particles are used in the preparation procedure in comparison with the case of $\sigma_t = 2$ and also because attempts for insertion are made for small fluid particles, $\sigma_f = 1$. Actually, porosity even in such a simple system depends on several parameters and can be tuned by changing any of them as convenient. Nevertheless, describing matrices in terms of nominal porosity \mathcal{P} does not provide reasonable insight in comparison to Π , in our opinion.

Next, we discuss theoretical adsorption isotherms. In Figure 3, three solid curves describe the dependence of adsorbed density on the chemical potential of fluid species in equimolar situation in matrices $\rho_m^* = 0$ and $\rho_m^* = 0.1$ and $\rho_m^* = 0.2$ (all of them have not been templated, $\rho_t^* = 0$). The higher the matrix density, the lower the adsorption, as expected for hard sphere systems. Templating of the matrix $\rho_m^* = 0.2$ ($\rho_t^* = 0.6$) has a very small effect on the adsorbed amount of fluid species. In general, configurational effects of templating influence adsorp-

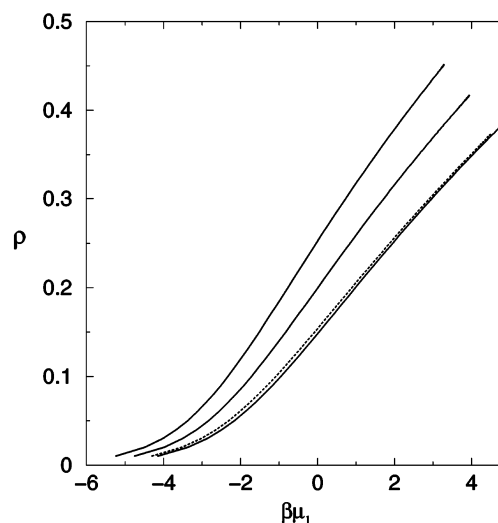


Figure 3. Theoretical results for the dependence of the total fluid density versus the chemical potential of a single component ($\rho - \beta\mu_1$) for symmetric binary mixture of nonadditive hard spheres ($\Delta = 0.2$) at equimolar concentration $-X = 0.5$, in the bulk, $\rho_m^* = 0$, and in hard sphere matrices for $\rho_m^* = 0.1$ and $\rho_m^* = 0.2$ (from top to bottom). The dotted line corresponds to the matrix ($\rho_m^* = 0.2$) prepared, however, in the presence of a hard sphere template at $\rho_t^* = 0.6$.

tion vary weakly unless one considers more dense matrices. All the curves in the figure terminate at certain values of the chemical potential and density. These points correspond to the demixing transition, as will be discussed below. At the moment, we are interested in how accurate are the adsorption isotherms obtained via ROZ/MS approximation. A comparison of the theory and simulation data is given in three panels of Figure 4. In some cases we have shown simulation results, which correspond to runs carried out for a set of different matrix realizations. The scattering of data provides insight into a range of deviations of the chemical potential values for different matrix sets. Two situations for equimolar mixtures in matrices with a more dilute template ($\rho_t^* = 0.3$) and denser template ($\rho_t^* = 0.6$) show that the agreement between theory and simulation is good (Figure 4a and 4b, respectively). Only at a high adsorbed density is some discrepancy observed, which may arise due to proximity of the system to the spinodal curve. In the situation of out of equimolarity, the agreement of theory and simulation again is very good (Figure 4c). The simulated point at the highest density studied in Figure 4b ($\rho = 0.35322$, $X = 0.5$) has been chosen to perform comparison of the simulated and theoretical structural properties. Such a comparison is performed in Figure 5a and 5b. Despite reasonable agreement around contact values of the fluid–fluid distribution function and overall qualitative agreement, we can see that there exists discrepancy in the magnitude of trends for demixing. Theoretical results indicate stronger demixing tendency in comparison to simulation data. On the other hand, the fluid–matrix distribution function agrees well with the simulation result.

It is difficult to establish the source of observed inaccuracy of the fluid–fluid distribution function in this thermodynamical state in the absence of simulation data for the blocking distribution function. Nevertheless, we suspect that the closure describing the total fluid–fluid correlation function is not as accurate as desired. To make things clearer, we have compared the distribution functions for fluid species in nontemplated and templated matrices at the fixed value of the chemical potential, $\beta\mu_1 = \beta\mu_2 = 4.297$, which yields quite similar adsorbed densities for nontemplated material ($\rho = 0.3645$) and templated

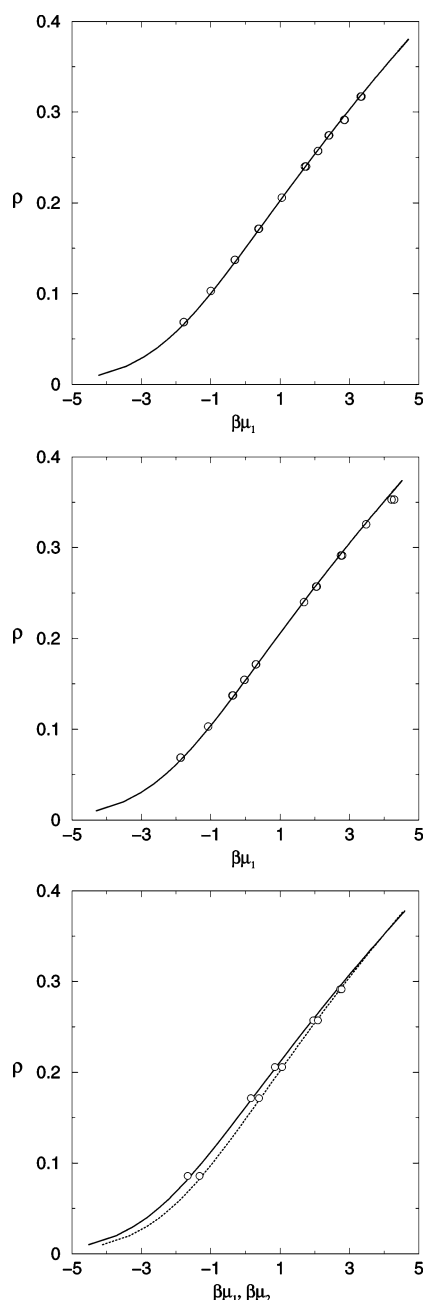


Figure 4. Comparison of theoretical adsorption isotherms (lines) with Monte Carlo computer simulation data (circles) at different conditions. Part a is for $\rho_m^* = 0.2$, $\rho_t^* = 0.3$, $X = 0.5$; part b is for $\rho_m^* = 0.2$, $\rho_t^* = 0.6$, $X = 0.5$; whereas part c is for $\rho_m^* = 0.2$, $\rho_t^* = 0.6$, $X = 0.4$. The solid and dotted lines in part c denote $\rho(\beta\mu_2)$ and $\rho(\beta\mu_1)$ dependence, respectively.

material ($\rho = 0.3668$), Figure 6a and 6b, respectively. The blocking distribution functions are shown together with the total distribution functions. We observe that the blocking contributions are big only inside the core regions, outside the core they are small and decay rapidly with increasing distance between fluid particles. Nevertheless, the blocking effects contribute to the demixing tendency for fluid species. The fluid in the templated matrix is obviously closer to the demixing transition, comparing with the fluid in nontemplated matrix.

In previous studies of demixing in the bulk models of NAHS,^{27,29} the analysis of the behavior of the determinant $D(k=0)$ has been performed. In Figure 7a, we just give a few examples of how this determinant behaves on the chemical potential of fluid species ($X = 0.5$). Such determinant approaches

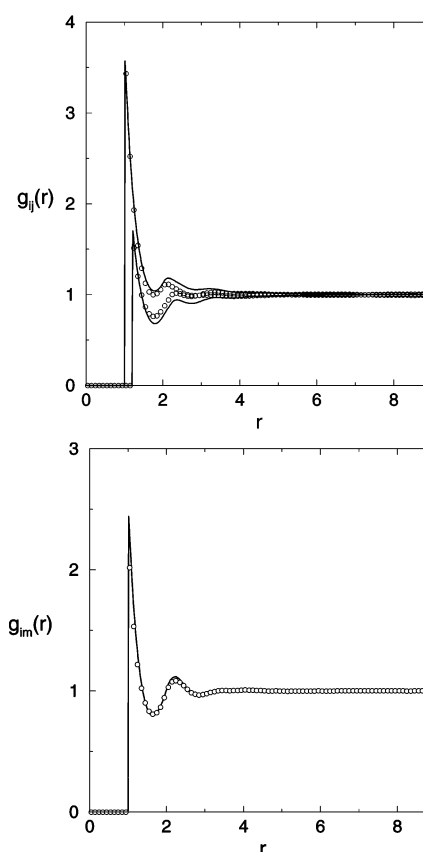


Figure 5. Comparison of the pair distribution functions coming from the theoretical procedure (solid lines) with computer simulation results (circles). The fluid model is at $\rho_m^* = 0.35322$, $X = 0.5$, confined in the matrix at $\rho_m^* = 0.2$, which has been prepared in the presence of template at $\rho_t^* = 0.6$. Part a gives the distribution functions of fluid species, $g_{11}(r)$ and $g_{12}(r)$, demonstrating tendency toward demixing, whereas part b gives the fluid-matrix distribution function $g_{1m}(r) = g_{2m}(r)$.

zero at higher values of the chemical potential if the matrix density increases. On the other hand, the effect of templating is to reduce the chemical potential for “transition”. Similar to the observation by Lomba et al.,²⁹ in our calculations via the ROZ/MS approximation $D(k=0)$ never did vanish, despite very fast decrease when approaching transition. So, the spinodal curve strictly speaking is never reached. Rather, one obtains a nonsolution boundary, which is a signature of an unstable boundary. This weakness is shared by all theoretical investigations within integral equations methodology. The incipient phase transition can be located by finding the locus at which the divergence of $S_{cc}^{con}(k=0)$ takes place. This is precisely, what we show in Figure 7b. Apparent divergence of the structure factor both for nontemplated (solid lines) and templated (dotted lines) materials is reached by very slowly increasing fluid density at a fixed composition.

Our final discussion concerns the coexistence curves. In Figure 8a we present the effect of matrix density on the ROZ/MS coexistence envelope for NAHS confined to nontemplated matrices $\rho_m^* = 0$, $\rho_m^* = 0.1$, and $\rho_m^* = 0.2$ (solid lines from top to bottom). In addition, the dotted line with symbols demonstrates coexistence for the model in templated matrix ($\rho_m^* = 0.2$, $\rho_t^* = 0.6$). Higher matrix density results in a lower critical density for demixing. However, comparing the coexistence envelope in templated and nontemplated material at the same matrix density, we observe that critical density in templated material is lower. It is straightforward to relate this behavior

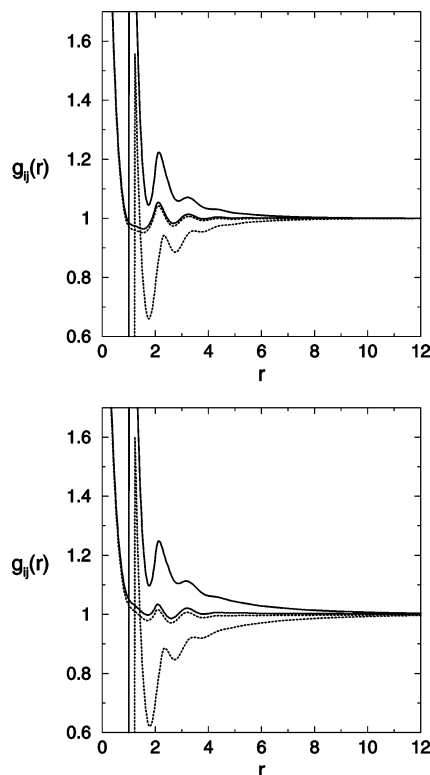


Figure 6. Comparison of the theoretical fluid–fluid pair distribution functions for an equimolar mixture at $\beta\mu_1 = 4.297$ confined in a matrix at $\rho_m^* = 0.2$. Part a gives the distribution functions of fluid species, $g_{11}(r)$ and $g_{12}(r)$, and corresponding blocking distribution functions in the case of nontemplated matrix $\rho_t^* = 0$, whereas part b gives the same functions for the case of templated matrix at $\rho_t^* = 0.6$. The curves for the blocking functions extend to $r = 0$.

with the dependence of the adsorption isotherms (cf. Figure 3). Actually in discussing critical density for demixing of the model in various matrices, the control parameter is the chemical potential of species, the resulting density is merely the result of the applied external pressure (chemical potential) of the reservoir. Demixing in the confined model occurs at higher chemical potential than in the bulk model, as one can see from Figure 8b. The higher the matrix density, the higher the value of the chemical potential at demixing transition. The templating effect of the matrix results in a lower chemical potential for demixing of the mixture in question, in comparison to the nontemplated matrix.

A comparison of the coexistence envelopes coming from the ROZ/MS approximation with semigrand computer simulation data shows qualitative agreement (Figure 9). Higher matrix density results in the lower value for the density of demixing transition. Again, lower critical density is observed for a fluid in a templated matrix, in comparison to the same fluid in a nontemplated matrix at the same matrix density. Theoretical construction overestimates the values of the critical density in comparison to simulations. However, for higher matrix density with or without templating, discrepancy between the theory and simulation is smaller than in the bulk model.

For the sake of brevity our final comment concerns the effect of template size. We have performed some additional calculations of the critical density for the model in question, by using matrices all at fixed density ($\rho_m^* = 0.2$) and by using fixed template density $\rho_t^* = 0.6$. The only parameter changing was the template diameter. We observed that the critical density for a fluid confined in templated materials with $\sigma_t = 3$ and $\sigma_t = 5$

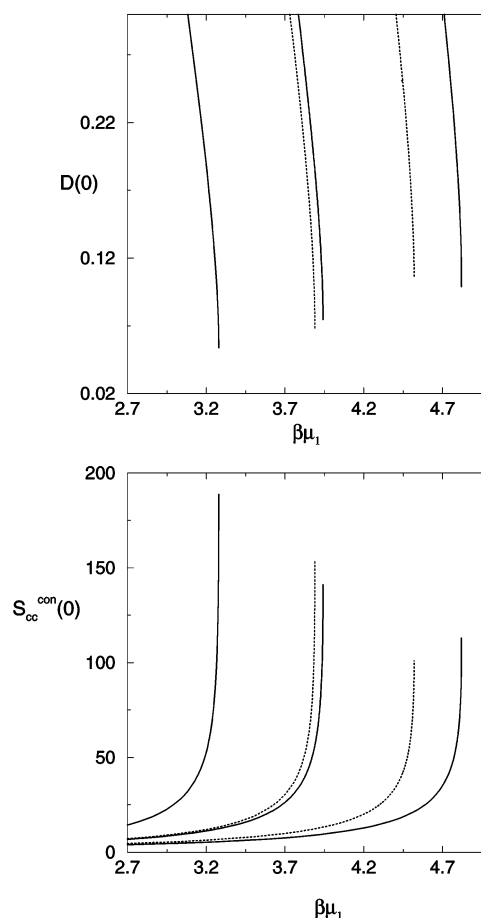


Figure 7. Part a: dependence of the determinant, $D(k = 0)$, on the chemical potential $\beta\mu_1$ for equimolar mixture, $X = 0.5$, while approaching coexistence line. Part b: dependence of the structure factor $S_{cc}^{\text{con}}(k = 0)$ on $\beta\mu_1$ close to the consolute point.

is higher comparing to the case of $\sigma_t = 2$, it grows with increasing template size at fixed template density.

To conclude, we summarize our observations. We have observed that the demixing phase transition is described qualitatively well by the replica OZ equations with Martynov–Sarkisov closure. The theory describes correctly the trends of the dependence of the coexistence curve on matrix density, on template density, and on composition. Trends of the development of demixing come from the behavior of the adsorption isotherms. Those are very well described by the applied theory in the one-phase region. The theory is attractive for systems in question because it provides explicit closed expressions for the chemical potentials of fluid species. Seemingly, a modification of the theoretical tools in the spirit of thermodynamic consistency requirements²⁹ would provide even better agreement between the theory and simulation data.

After the present work was completed and submitted for publication, there appeared a study of NAHS model in porous media by using ROZ equations and a modified Verlet closure.⁴⁶ These authors have obtained good agreement of the phase coexistence boundary between the theory and simulation. However, to reach that, a large number of adjustable parameters is required. A generalization of the applied procedure to other models may become very cumbersome.

It is of interest to extend our study to other model fluid systems such as nonsymmetric (by diameter) fluid species, multicomponent fluids, and mixtures of associating fluids. Sophistication of the matrix structure in the spirit of model gels

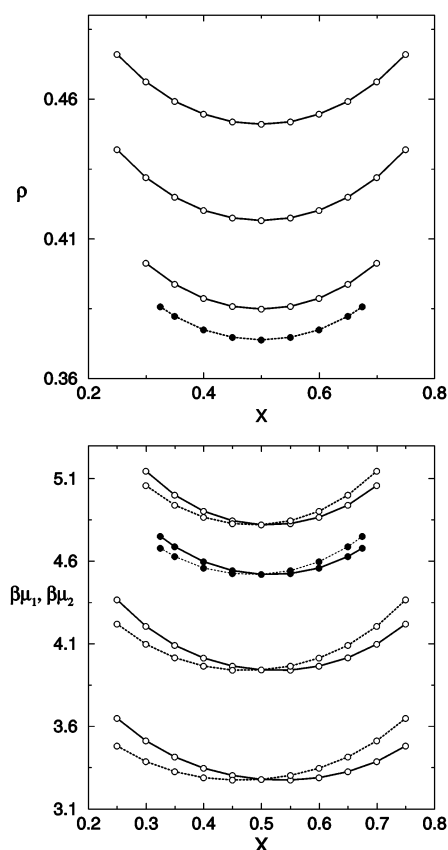


Figure 8. Part a: theoretical coexistence curves given as the dependence of total fluid density on concentration for the bulk fluid model ($\rho_m^* = 0$) and confined in matrices at $\rho_m^* = 0.1$, $\rho_m^* = 0.2$ (from top to bottom). The dotted line corresponds to the matrix ($\rho_m^* = 0.2$) prepared, however, in the presence of a hard sphere template at $\rho_t^* = 0.6$. Part b: the same as in part a but in the form of the dependence of the chemical potentials at coexistence on concentration. The lines corresponding to $\rho_m^* = 0$, $\rho_m^* = 0.1$, and $\rho_m^* = 0.2$ are from bottom to top, in contrast to part a. The coexistence for templated matrices is decorated by filled circles. In all cases solid lines are for $\beta\mu_1$ whereas the dotted lines are for $\beta\mu_2$.

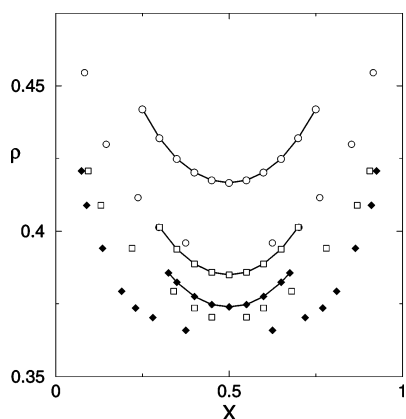


Figure 9. A comparison of the theoretical coexistence curves (lines decorated with symbols) with semigrand computer simulation results (symbols). The nomenclature of symbols is the following: circles, $\rho_m^* = 0.1$; squares, $\rho_m^* = 0.2$, $\rho_t^* = 0$; rhombs, $\rho_m^* = 0.2$, $\rho_t^* = 0.6$.

and more refined model templated microporous adsorbents would be also desired. However, both theoretical methods, as well as simulation algorithms should be then improved. Such studies would provide us wider and better understanding of possible scenarios of entropy driven phase transformations in

partly quenched fluid systems. Several important questions must be answered, however, even for the simple model under consideration. In particular, it is important to establish range of matrix densities (or porosity and pore size distribution) in conjunction with the value for the nonadditivity parameter for which one would expect that demixing may occur. On the other hand, interplay or competition between demixing and possible glass transition for a mixture in porous media has not been studied so far. We expect that some of these issues may be captured by using either the second-order ROZ integral equations, see. e.g., ref 47, or density functional type approaches rather than by employing very sophisticated closures for the singlet level integral equations.

Acknowledgment. O.P. has been supported by the CONA-CyT of Mexico under grant 37323-E and by the National University of Mexico under grant IN-113201.

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