

Theoretical model of adsorption in a templated porous material

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We introduce a theoretical description of adsorption in a templated porous material modeled as a quenched binary mixture configuration with one component removed. Using tools from equilibrium statistical mechanics, we analyze the diagrammatic structure of and derive an approximate formula for this nonequilibrium material's porosity and Henry regime selectivity. We find that templating significantly increases the porosity as well as the selectivity for the larger component of a mixture. [S1063-651X(99)51107-0]

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An emerging strategy for controlling the pore architecture of disordered porous materials is to use a sol-gel synthesis technique with a removable template [1]. One starts with a precursor solution containing polymerizable monomers and other, inert template species (sometimes covalently bonded to the monomers) around which gelation occurs. Following gelation, the template component is removed by thermal or chemical treatment. Ideally, the resulting pore architecture mimics to some extent the structure of the template. Both micro- and mesoporous materials have been formed using this technique [1]. An advantage to templated materials is that porosity and pore size are decoupled since the former is controlled by template concentration and the latter by template size [2]. For these reasons, templated materials would be ideal as adsorbents, sensors, gas separation membranes, and molecular recognition agents.

In order to develop template strategies for novel materials of diverse chemical compositions, a quantitative description is needed of the relation among template morphology and concentration, pore structure, and the behavior of molecules adsorbed in the material following synthesis. Toward this goal, we introduce in this paper (i) a simple model of a templated porous material and (ii) a theoretical treatment of the structure and Henry regime (low loading) adsorptive behavior of the model material.

Our model templated porous material is inspired by the actual formation process (see Fig. 1). One starts with a binary system of matrix and template particles. Following equilibration, the system is quenched, that is, all of the particles are frozen in space. This represents gelation. Next, the template particles are removed. The collection of matrix particles is then considered to be the porous material. A system of quenched particles (usually in an equilibrium configuration) has become a popular model for disordered porous materials [3–17]. Our model differs from these earlier description by the explicit presence of a template component. A challenge to modeling a templated material is its nonequilibrium structure. In our model, we avoid this situation by constructing a nonequilibrium configuration (the matrix particles) that has exactly the same structure as a different, equilibrium system (the matrix component of a matrix-template mixture). As detailed below, this choice allows us

to apply equilibrium statistical mechanical methods to obtain information about this nonequilibrium system.

Our theoretical treatment of this model material involves expressing the fractional porosity as a sum of Mayer diagrams and then approximating the sum using appropriately chosen combinations of correlation functions whose approximate values are known analytically. We begin by assuming that the matrix and template components of the model material interact as hard spheres. We define the porosity, Φ_1 , as the fractional available volume to a single hard sphere adsorbate of diameter σ_1 in a material following the removal of the template component. (The Henry constant for the adsorbent is then Φ_1/kT .) The porosity may be expressed using a Kirkwood-Salsburg hierarchy of integrals [18],

$$\begin{aligned} \Phi_1(1; \rho_0, \rho_{0'}) &= 1 + \sum_{s=1}^{\infty} \frac{\rho_0^2}{s!} \int d2 \cdots d(s+1) f_{01}(1,2) \cdots \\ &\quad \times f_{01}(1,s+1) g_{00 \dots}^{(s)}(2, \dots, s+1; \rho_0, \rho_{0'}), \end{aligned} \quad (1)$$

where ρ_0 is the density of matrix particles (of diameter σ_0), $\rho_{0'}$ is the density of template particles (of diameter $\sigma_{0'}$), $g_{00 \dots}^{(s)}$ is the s -body matrix correlation function for the (equilibrated) matrix-template mixture, and f_{01} is the Mayer function between a matrix (0) particle and an adsorbate (1) and has the value -1 if the two particles overlap and 0 otherwise. The vector positions \mathbf{r}_i are given as “ i .” The set of $\{f_{01}\}$ ($\{g_{00 \dots}\}$) depends additionally upon the diameters of the matrix and adsorbate (matrix and template) particles.

We note that the configuration of matrix particles “experienced” by an adsorbate is not the same as an equilibrium configuration at ρ_0 . In fact, it is out of equilibrium but possesses the structure of a different equilibrium system: the matrix-template mixture. Therefore, the $\{g_{00 \dots}\}$ is one of equilibrium correlation functions and depends on both ρ_0 and $\rho_{0'}$; although the template particles do not themselves block volume to the adsorbate (they have been removed), their presence during gelation influenced the positions of the matrix particles. A similar situation occurs for a quenched and depleted material (the special case where the template is identical to the matrix) [19,20].

Equation (1) may be expressed as a sum of Mayer diagrams consisting of a single root point connected to s field

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points by f bonds that are themselves related through $g^{(s)}$. Since the diagrammatic expansion of $\{g\}$ at equilibrium are known [21], we can write the expansion for Φ_1 as

$$\ln \Phi_1(1; \rho_0, \rho_{0'}) = \text{[diagrams]} + \dots$$

= {all connected diagrams with a single adsorbate root point (diamonds) weighted as unity, one or more matrix field points (circles) weighted as ρ_0 , some or no template field points (squares) weighted as $\rho_{0'}$, that are not connected directly to the root point, f bonds, and are free from connecting points}. (2)

In Eq. (2), the f bonds are either f_{01} , f_{00} , or $f_{00'}$, depending on whether the points connected represent matrix (0), template (0'), or adsorbate (1) particles.

It is interesting to compare the expansion in Eq. (2) to two better known cases. The porosity of an equilibrated system of like particles is just the special case where $\rho_{0'} = 0$ and all of the diagrams with square field points vanish. The porosity of a binary mixture would be given by an expansion that includes all of the diagrams of Eq. (2) plus all diagrams where at least one square field point is directly connected to the root point. Φ_1 may be obtained from the latter case when the interaction potential corresponds to the unusual Hamiltonian where the template-adsorbate interaction is that of an ideal gas, i.e., where $f_{0'1} = 0$.

We seek to estimate Φ_1 in Eq. (2) by considering the contributing diagrams. As stated above, an expansion containing only the subset of diagrams without template (square) field points yields the porosity of a single component system. This may be calculated as

$$\ln \Phi_1(1; \rho_0, \rho_{0'} = 0) = \int d2 \int_0^{\rho_0} d\rho'_0 \frac{\delta \ln \Phi_1(1; \rho_0)}{\delta \rho_0(2)} = \int d2 \int_0^{\rho_0} d\rho'_0 c_{10}(1, 2; \rho'_0), \quad (3)$$

where the last equality comes from the definition of the direct correlation function [21].

The remaining subset of diagrams, those containing at least one template field point that is not directly connected to the root point, may be approximated in the following way. We consider the product of two sets of diagrams:

$$\text{set 1: } \frac{\partial}{\partial \rho_1} [y_{00}(1, 2; \rho_0, \rho_1)]_{\rho_1 \rightarrow 0} = \frac{1}{\rho_1} \times \left[\text{[diagrams]} + \dots \right]$$

= {all connected diagrams with two unconnected matrix root points weighted as unity, one or more matrix field points (circles) weighted as ρ_0 , exactly one template field point (square) weighted as unity, f bonds, and are free from connecting points}.

$$\text{set 2: } h_{00}(1, 2; \rho_0, \rho_{0'}) - h_{00}(1, 2; \rho_0, \rho_{0'} = 0) = \text{[diagrams]} + \dots$$

= {all connected diagrams with two matrix root points weighted as unity, some or no matrix field points (circles) weighted as ρ_0 , one or more template field point (square) weighted as $\rho_{0'}$, f bonds, and that are free from connecting points}. (4)

In Eq. (4), h is the total correlation function and y is defined as $y = e^{u(r)/kT}(h + 1)$ where $u(r)$ is the hard sphere potential [21]. If one integrates the product of sets 1 and 2 over (i) one of the matrix root points and (ii) over matrix density, then lets the lone adsorbate field point become the single root point in place of the remaining matrix root point (this involves multiplying by the matrix density), and finally adjusts the symmetry number for this change so that the last two diagrams in Eq. (2) are obtained exactly, then one obtains a sum of diagrams that approximates the sum in Eq. (2). The subset of diagrams present in Eq. (2) but absent in Eq. (3) is therefore approximated as

$$\ln \frac{\Phi_1(1; \rho_0, \rho_{0'})}{\Phi_1(1; \rho_0, \rho_{0'} = 0)} = \text{[diagrams]} \approx \frac{\rho_0}{2} \int d2 \int_0^{\rho_0} d\rho'_0 \frac{\partial y_{00}}{\partial \rho_1} \Big|_{\rho_1 = 0} \times [h_{00}(1, 2; \rho'_0, \rho_{0'}) - h_{00}(1, 2; \rho'_0, \rho_{0'} = 0)]; \quad (5)$$

In Φ_1 , from Eq. (1) [or Eq. (2)], is obtained by adding the contributions in Eqs. (3) and (5). The expression at the end of Eq. (5) is of course only approximate. It is straightforward to show that the sum includes only the set of diagrams containing at least one articulation pair of matrix field points, i.e., a pair whose removal would disconnect the diagram. Diagrams containing no articulation pairs are neglected in this

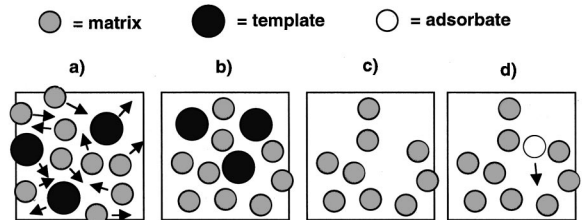


FIG. 1. Simple schematic of our proposed model for adsorption in a templated porous material. (a) The precursor fluid consists of an equilibrated mixture of matrix and template particles (the arrows crudely indicate particle motion). (b) The matrix and template particles are frozen in an equilibrium configuration. This step corresponds to gelation. (c) The template particles are then removed. The remaining matrix particles, whose arrangement reflects the earlier presence of the template, are the model of the templated porous material. (d) An adsorbate is added to the material.

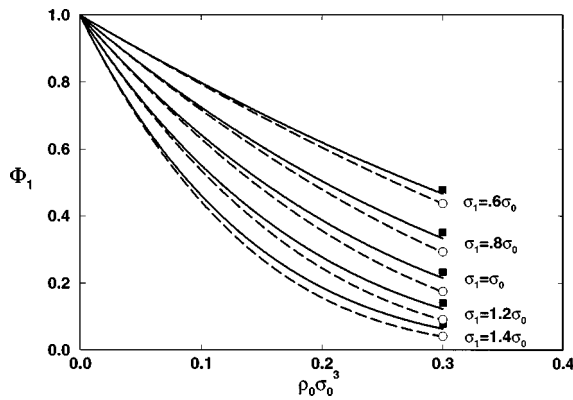


FIG. 2. Fractional porosity, Φ_1 , versus matrix density, $\rho_0 \sigma_0^3$, for hard sphere adsorbates of diameters $\sigma_1 = 0.6, 0.8, 1, 1.2,$ and $1.4 \sigma_0$. Solid lines are results from Eq. (3) for matrices formed with a template of diameter $\sigma_0' = \sigma_0$ and density $\rho_0' \sigma_0^3 = 0.6$ and the dashed lines are for matrices formed without a template. Square and circular data points are results from Monte Carlo computer simulation with and without templates, respectively.

approximation. The functions c , h , and y , needed for determining the porosity via Eqs. (3) and (5), are approximated using the analytical solution to the binary hard sphere mixture within the Percus-Yevick approximation [22].

To test this theory, we also perform a computer simulation of the system depicted in Fig. 1. A sufficient number of particles, each a sphere of diameter σ_0 , are placed in a bcc arrangement in a cubic, periodic system of length $32\sigma_0/\sqrt{3}$ so that a density of $\rho_0 + \rho_0'$ is achieved. 10^8 canonical ensemble Monte Carlo steps are applied to allow the system to reach equilibrium. A matrix configuration is generated by randomly removing particles until the density reaches ρ_0 . A spherical test particle of diameter σ_1 is then placed at random in the matrix configuration and tested for overlap with the matrix particles. Enough of these tests are conducted so that the success probability is known to within ± 0.005 . Results are then averaged over 10 configurations.

Figure 2 shows the fractional porosity as a function of matrix density for a system without a template and for one with a template. We see that the presence of the template has a significant effect on porosity even when the template has the same diameter as the matrix. The decreased porosity (and thus also Henry's constant) with increased adsorbate size is consistent with the permeation results of various adsorbates in templated silica membranes reported by Raman and Brinker [2]. Results from the Monte Carlo simulation show that the theory is quite accurate (although it slightly underpredicts the template effect).

An important adsorptive property is the selectivity of one component in a mixture over another. For a binary mixture, the selectivity is given simply by

$$\alpha_{12} = \frac{x_1/y_1}{x_2/y_2} = \frac{\Phi_1}{\Phi_2}, \quad (6)$$

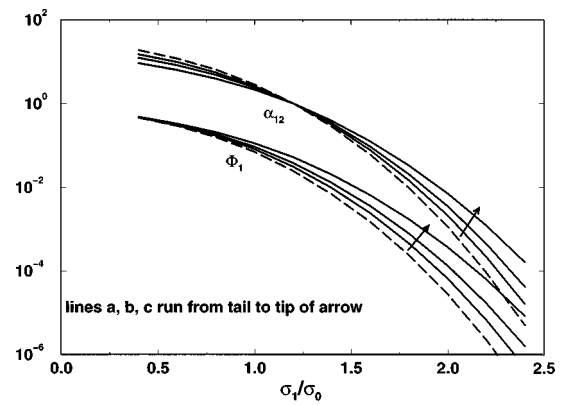


FIG. 3. Fractional porosity, Φ_1 , and Henry's regime selectivity, α_{12} , versus adsorbate diameter, σ_1/σ_0 , for $\rho_0 \sigma_0^3 = 0.4$, $\rho_0' \sigma_0^3 = 0.2$, $\sigma_2 = 1.2\sigma_0$ and (a) $\sigma_0' = \sigma_0$, (b) $\sigma_0' = 1.2\sigma_0$, and (c) $\sigma_0' = 1.4\sigma_0$. Also shown are results for a matrix of density $\rho_0 \sigma_0^3 = 0.4$ with no template (dashed lines).

where x_i , y_i , and Φ_i are the adsorbate mole fraction, the bulk mole fraction, and the porosity, respectively, of an adsorbate of diameter σ_i . (The second equality applies only in the Henry regime.) From Fig. 3 we see that selectivity and porosity decrease with adsorbate size. Additionally, increasing the size of the template molecule increases the porosity and the selectivity for the larger of adsorbate species 1 and 2. In systems employing only hard particle interactions, selectivity is always toward the smaller molecule due to its greater translational entropy. What is interesting here is that templating shifts this selectivity so that the larger component is less disfavored. In real materials, larger molecules are often selectively adsorbed due to attractive energetic interactions. In these cases, templating would enhance this selectivity by increasing the porosity. For pairs of molecules differing in diameter by a factor of 2, this shift in selectivity (over that seen in the nontemplated system) may exceed a factor of 3.

In summary, we introduce a nonequilibrium model of a templated porous material and a theoretical treatment that utilizes equilibrium statistical mechanics. We determine the porosity of Henry regime selectivity in this model system. Our analysis suggests that templating may have a significant effect on the porosity and selectivity of a material at a given matrix density. In all cases, templating appears to be an effective way to alter and perhaps "fine-tune" a material's pore structure and adsorptive ability. Our hope is that this approach will prove helpful in directing templating strategies for porous materials with specific adsorptive properties.

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