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Diffusion of fluids in disordered pore matrices

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Diffusion of different fluids was studied in disordered pore matrices by computer simulations. The matrices were formed using zeolite parameters with two distinct methods. In the first method, the matrix was prepared from a set of particles with a fixed density and, after equilibration, the matrix structure was taken from the last configuration of the particles. In the second method, the porous matrix was prepared from a binary mixture where the first and the second components are particles of a template material and the matrix, respectively. The final matrix structure was obtained by removing the template particles from the equilibrated mixture. Therefore we were able to investigate the behavior of the diffusion of Ar, Kr, and $\mathrm{CO_2}$ fluids as a function of the matrix preparation method. The results show that, when matrices were prepared without a template, the diffusion is higher than in matrices prepared with a template. This can be explained in terms of the cavities formed in the matrices when they were prepared.

Keywords: Diffusion; porous matrix structure; porosity; computer simulation.

En este artículo se estudia el coeficiente de difusión para diferentes fluidos en matrices porosas desordenadas usando simulaciones por computadora. Las matrices fueron preparadas usando parámetros de una zeolita con dos métodos distintos. En el primer método, la matriz se prepara con un conjunto de partículas a una densidad fija y, después de equilibrar el sistema la estructura, de la matriz se toma de la última configuración. El segundo método utiliza una mezcla binaria donde un componente son partículas de un substrato y el segundo componente son partículas de la matriz. La estructura de la matriz se toma después de equilibrar el sistema y de quitar las partículas del substrato. Así entonces, se investiga el coeficiente de difusión de los fluidos de Ar, Kr, and $\mathrm{CO_2}$ como función del método de preparación de la matriz. Los resultados muestran que la difusión es mayor en las matrices preparadas sin un substrato. Estos resultados se pueden entender en términos de las cavidades que se forman en las matrices al momento de prepararse.

Descriptores: Difusión; estructura de poros; porosidad; simulaciones por computadora.

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1. Introduction

Understanding the behavior of fluids confined in small pores has been the subject of much interest over the last years. These studies have been motivated not only for their scientific importance but also for their practical applications in heterogeneous catalysis, petroleum recovery, membrane separation processes, etc.

The most common pore models used have ranged from simple geometries such as slit pores [1] or cylindrical pores [2], to more complex structures such as disordered matrices [3]. In particular, one popular model for disordered matrices is that consisting of a system of quenched particles, usually in an equilibrium configuration [3–5]. However, a new method inspired by the actual formation process has been employed for the last few years [6, 7]. The model considers the explicit presence of a template material, *i.e.* the system is composed of a binary system where one species is the matrix and the other is the template [8, 9]. Once the system is equilibrated in one particular thermodynamic state, it is frozen and the template particles are removed. Thus the remaining particles form the pore matrix.

From the theoretical point of view, people have investigated fluids in equilibrium within a disordered porous matrix using extensions of liquid-state theories [4, 10]. In the same approximations, other authors have investigated density distributions, flow through matrices [11], porosity and adsorption in porous matrices [12, 13].

Of particular interest is the study of the diffusion of fluids inside the porous cavities. These studies have been carried out with several experimental techniques [14] and using also several computational methods [8,15,16]. From macroscopic measurements, the diffusion coefficient can be obtained with the help of Fick's law. From the microscopic point of view, one can measure the mean square displacement of the particles and, by using Einstein's relations, the diffusion coefficient is calculated. On the other hand, there are also models developed from lattice theory to study diffusion of fluids in zeolites and other nanoporous materials [17]; in the case of 2D, some computer simulations of lattice gas have also been performed [18].

In spite of the work performed on diffusion in pores, there are works to investigate how the diffusion coefficient depends on the pore matrix structure or on the pore-fluid interaction [18,19]. People have seen, for instance, a maximum in the self-diffusion in confined fluids for particles with diameter sizes comparable to the cavities of porous material. This is known as the ”levitation effect” [20, 21], which presents two regimes: a linear regime when diffusion has a linear proportionality with the inverse square diameter of the fluid particle (the fluid particle diameter size is smaller than the void sizes in the matrix), and an anomalous regime characterized by a peak in the diffusion when the fluid particle diameter size is big. Therefore, there are nice works investigating diffusion in terms of fluid-pore interactions or fluid-pore void diameter ratio [18–22]. However, how the presence of a template material, in the preparation of pore matrices, affects diffusion is a subject that has not been extensively investigated.

The model of a template material using computer simulations was previously investigated by Van Tassel few years ago [8,9]. However, that research was done when the systems were prepared with hard spheres. In those studies they found that porosity was higher in matrices prepared with a template than in those prepared without any template material.

In a previous paper, we started our studies on diffusion inside porous matrices [23]. The principal goal of that paper was to understand how the interactions between particles affect the structure of the pore matrix during its preparation, using repulsive and attractive potentials. In those studies, the fluid and the matrix particles had the same Lennard Jones parameters (well-depth potential and molecular diameter); however, this situation is not always true in real experiments. In this paper, we present a series of computational experiments where two different disordered porous matrices were prepared, with and without template particles, and we investigate the role of the template in the diffusion coefficient of actual fluids such as Ar, Kr and $\mathrm{CO_2}$ in the different matrix structures.

2. Computational method and model

The disordered porous matrix model consisted of particles located in a cubic box of lengths $X = Y = Z = 15.9285\sigma$. The particles interacted each other with the well known Lennard Jones potential (LJ) [Eq. (1)]

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (1)$$

The ϵ and σ parameters were chosen to mimic a zeolite material [24, 25]. As is common in computer simulations, reduced units were employed [26], and in the present simulations the zeolite parameters were used to reduce the units (r^*, T^*, ρ_m^*, etc.).

Simulations were carried out using the Molecular Dynamics (MD) method with a cut and shifted potential of r^* = 4.0. The equations of motion in the MD were solved using the leap-frog method with a reduced time step of t^* = 0.005. Then, simulations at two different reduced temperatures, T^* = 0.8 and T^* = 1.5, were performed where all velocities were rescaled at each time to the desired temperature.

The porous matrices were prepared by two different procedures, with and without template particles.

In the first procedure, a given number of particles were placed randomly in the simulation box with the number of particles fixed to have a reduced density of ρ_m^* = 0.3. Then, the system was equilibrated for 50 000 time steps, and the final matrix structure was obtained from the last configuration of the particles after another run of 80 000 time steps. These simulations were performed at T^* = 0.8 and T^* = 1.5, *i.e.* we had two matrix configurations.

In the second method we used template particles. Here the porous matrix was prepared from a binary mixture where the components of the mixture had the same LJ parameters. In order to differentiate the components of the mixture we used labels, where species 1 was the template and species 2 was the matrix. In this case, both the template and the matrix particles were chosen to have a density of $\rho_t^* = \rho_m^*$ = 0.3. The initial system consisted of random particles of species 1 located in the box, then particles of species 2 were randomly added to have a binary mixture with total density ρ^* = 0.6. The system was first run for 50 000 MD steps for equilibration and 80 000 steps for collecting data. The final porous matrix configuration was obtained by removing the template particles (the first species), keeping a disordered matrix with density ρ_m^* = 0.3. Once again this system was simulated at two reduced temperatures, T^* = 0.8 and T^* = 1.5.

At this point we have prepared four different pore matrices with the same densities but with different structures.

Finally, we studied the diffusion of different fluids, Ar, Kr and $\mathrm{CO_2}$, immersed in the matrices already described. For each fluid we conducted simulations at different reduced densities, ρ_f^* = 0.1, 0.2, 0.3, 0.4. For these simulations, the matrix particles were frozen and did not interact with each other. The matrix particle-fluid particle and the fluid particle-fluid particle interactions were given by Eq. (1), for which the LJ parameters of the fluids are shown in Table I [27], and the Lorentz-Berthelot rules were used for the unlike particles.

3. Results

In the next subsections, we present the results obtained from our simulations. The structure and the porosity of the matrices are analyzed in terms of the preparation method. Finally, results of the diffusion coefficient for different fluids adsorbed in the different matrices are presented.

3.1. Matrix structure

Firstly, the matrix structure was studied in terms of the vacancies or voids formed in the disordered matrix. This analysis was performed by the Voronio-Delaunay tessellation method, which it has been previously used to study the structure of Lennard Jones and hard sphere fluids [28,29]. In our case,

TABLE I. Lennard Jones Parameters σ and ϵ. The unlike interactions were calculated using the Lorentz-Berthelot mixture rules

	σ/ Å	ϵ/ K
Ar	3.405	119.8
Kr	3.636	166.4
$\mathrm{CO_2}$	3.673	241.7
Zeolite	12.0	62.89

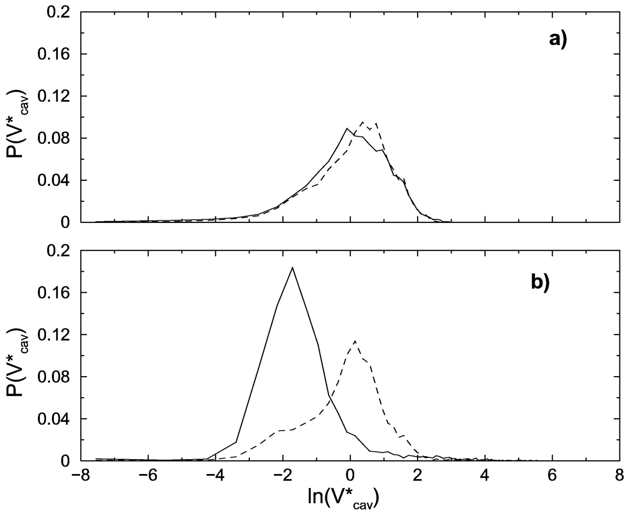

FIGURE 1. Void size distributions of matrices at a) T^* = 1.5 and b) T^* = 0.8. Solid lines are for matrices without a template and dashed lines for matrices with one.

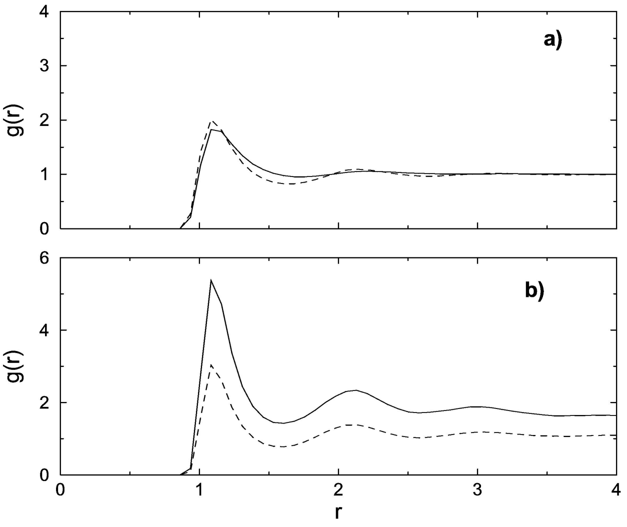

FIGURE 2. g(r) for the matrix at a) T^* = 1.5 and b) T^* = 0.8. Solid lines are for matrices without a template and dashed lines for matrices with one.

having all the matrix particles, we calculated the Voronoi vertices to define the center of the voids. The size of a void (cavity) was calculated by growing a sphere (increasing its radius) from the void center until it overlapped with a matrix particle [30]. Therefore, a cavity (V^*_{cav}) was expressed in terms of volumes of spheres of different diameters. This procedure was performed for all the void centers inside the simulation box to calculate a void size distribution. Although this volume might not represent the exact volume of a cavity, it gives us good insight into the distribution of the cavity sizes in the matrix.

In Fig. 1, the void size distributions for the four different matrices are shown. For all panels, the matrix density was ρ^*_m = 0.3. In Fig. 1a the matrix was prepared with and without template particles at a reduced temperature of T^* = 1.5. The x-axis in the figure is given in terms of $ln(V^*_{vac})$ to enhance the features. From these plots we observed that the distribution of the matrices with and without a template are alike; moreover, the maximum volume is nearly of the same size in both matrices. The maximum void sizes are $V^*_{vac} \approx$ 18.8 and 14.1 for the matrix without and with a template, respectively.

In Fig. 1b, a different feature is observed. Here the matrices were prepared at temperature T^* = 0.8 and the void distributions have different values. When the matrix is constructed with a template, the maximum void size is up to $V^*_{vac} \approx$ 137.3, whereas when the matrix is prepared without a template, the maximum volume is $V^*_{vac} \approx$ 268.1. The temperature seems to have an effect on the production of voids in the structure of the matrix. It seems that at a low temperature there are much bigger voids regardless of whether or not the matrix was prepared with template particles. On the other hand, at low temperatures there is also an effect of using template particles which is not observed at high temperatures.

Analyzing the void distributions, we have at T^* = 1.5 standard deviations of Σ^2 = 4.09 and 3.028 for matrices without and with the template, respectively, and the maximum peaks are located at $V^*_{vac} \approx$ 0.91 and 1.43 for the matrix without and with the template, respectively. At T^* = 0.8 we have Σ^2 = 0.03 and 1.18 without and with a template, respectively whereas the maximum peaks in the distributions are at $V^*_{vac} \approx$ 0.18 and 1.15 for the matrix without and with template respectively. The results showed sharper distributions (particularly for the matrix without a template) at a low temperature compared to those at a high temperature. These results and those of maximum size of the voids suggest that at a low temperature the matrix has some voids of a small size and few voids of a large size. However, at a high temperature there are more regular and uniform void sizes.

The porous structure was also analyzed in terms of the pair distribution function of the matrix particles (g(r)). In Fig. 2a we have the g(r) for the matrix prepared with and without template particles at T^* = 1.5. Both graphs are similar, indicating that the structures are basically the same, *i.e.* at a high temperature the structure does not change depending on whether or not template particles are employed. However, at a low temperature, T^* = 0.8, the g(r) are clearly different (Fig. 2b). The g(r) of the matrix without a template is dominated by the first peak, and it does not oscillate around unity but has a slope towards it, *i.e.*, the g(r) presents the typical behavior of a low density fluid. Therefore, it seems that the matrix particles aggregate in small clusters, leading to large voids in the volume. When template particles were used in the system, the matrix particles were more uniformly distributed and the g(r) that of a denser liquid, *i.e.* the porous matrix presents a more uniform distribution. As a general feature we can also observe that matrices prepared at a low temperature have a more structured g(r) than those prepared at a high temperature.

Porosity is also an important factor in characterizing the porous media. This quantity can be measured in experiments by adsorption techniques. In the present work of computer simulation, porosity was measured by random insertions of a test spherical particle of diameter σ_t into the matrix, checking for any overlap with the matrix particles. Then the porosity was calculated using the ratio

$$P = \Phi_0/\Phi, \tag{2}$$

where Φ was the total number of insertions and Φ_0 was the number of no overlaps.

For the test particles, we used the diameters of the Ar, Kr, and CO_2 particles (see Table I). Although these particle diameters are nearly the same, we can observe some features in the porosity. In Fig. 3, porosity is shown as a function of the test particle diameters. The first thing to observe is the reduction in porosity as the test particle diameter increases, as expected. When the matrix is prepared at T^* = 1.5, with and without template particles, porosity is almost the same. When the temperature preparation is reduced to T^* = 0.8, the porosity shows a drastic change. When template particles are not used in the construction of the matrix, the porosity is much higher than when template particles are used. Nevertheless, these results with a template show that porosity at this temperature is just slightly higher than at T^* = 1.5. As a general trend, porosity increases as we find greater maximum void sizes in the matrix.

We recall that previous simulations of similar systems using hard spheres showed that porosity was higher in porous prepared with template particles than that in matrices prepared without a template [8]. However, in these simulations using attractive potentials, the opposite trend is observed (which is more remarkable at a low temperature), *i.e.* matrices constructed without a template show higher porosity than matrices with a template.

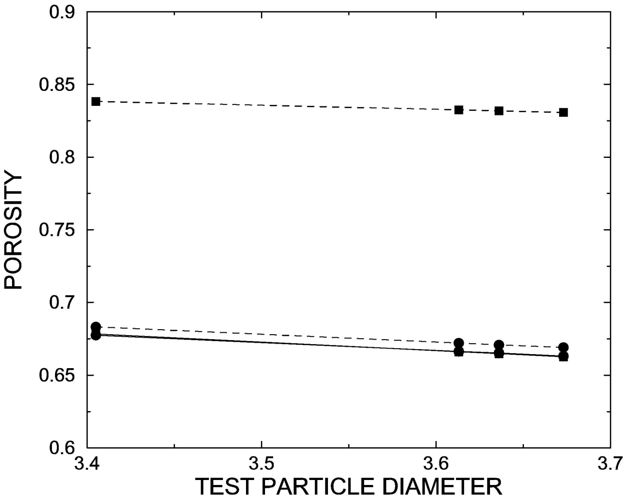

FIGURE 3. Matrix porosity as a function of the test particle diameter (σ_t in Å) at T^* = 1.5 (solid lines) and T^* = 0.8 (dashed lines) prepared with (circle) and without (square) a template. The symbols at T^* = 1.5 overlap. The lines are just given as a guide.

3.2. Diffusion coefficient

Finally, we investigated how the diffusion of fluids is affected by the matrix structure. The fluid in the matrices was modeled by inserting random particles until we reached a fluid with four different densities, *i.e.* ρ_f^* = 0.1, 0.2, 0.3 and 0.4. As mentioned above, the matrix particles were fixed and the interactions fluid particle - fluid particle and matrix particle - fluid particle were LJ [Eq. (1)]. There was no matrix particle - matrix particle interaction. The molecular dynamics simulations for these calculations were carried out a long enough time (at least 120 000 time steps) to let the particles visit most of the matrix regions.

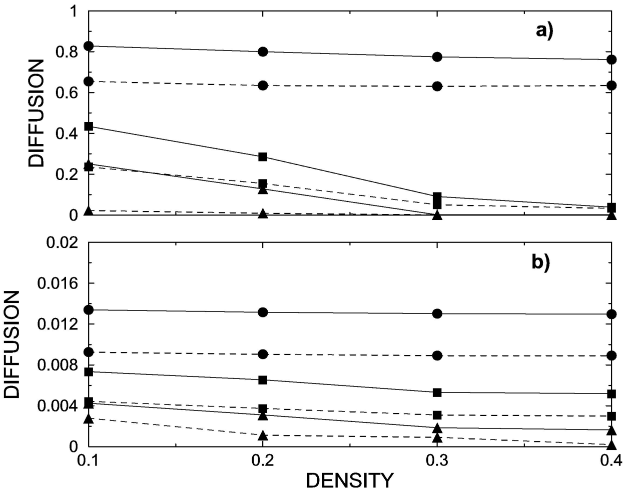

FIGURE 4. Diffusion coefficient of Ar (circle), Kr (square) and CO_2 (triangle) at a fluid temperature of a) T^* = 1.5 and b) T^* = 0.8. The matrix was prepared without (solid line) and with (dashed line) a template at T^* = 0.8. The lines are just given as a guide.

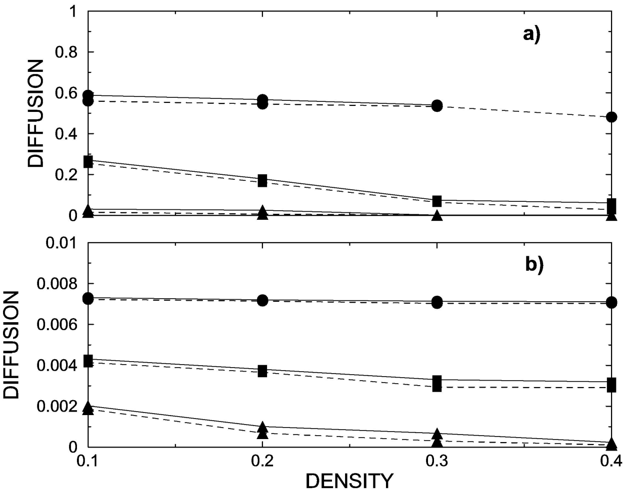

FIGURE 5. Diffusion coefficient of Ar (circle), Kr (square) and CO_2 (triangle) at fluid temperature of a) T^* = 1.5 and b) T^* = 0.8. The matrix was prepared without (solid line) and with (dashed line) a template at T^* = 1.5. The lines are just given as a guide.

The diffusion coefficient was calculated by the mean square displacement, using the Einstein relation,

$$2tD = \frac{1}{3}\langle[r(t) - r(0)]^2\rangle \tag{3}$$

Figures 4 and 5 show the plots for the diffusion coefficient, in reduced units, for the fluids in all matrices.

In these simulations, the fluid temperature was T^* = 1.5 and T^* = 0.8 and, as observed, the diffusion decayed in all cases the fluid density increased. Previous simulations of nitrogen in nanopore models and a lattice theory model showed in some cases a similar tendency [17, 31], *i.e.* the diffusivity decreases with loading, although interesting cases are also observed in which diffusion can also present a maximum. In the present work, we did not see any maximum; however, in some cases (data for Ar), the values of diffusion are nearly the same for all the densities studied.

When the fluids are immersed in matrices prepared at T^* = 0.8, different features are observed. Here, in the matrix prepared without a template there are larger cavities in the matrix and it is easier for a fluid to travel inside it. Thus, in general, it is possible to observe a higher diffusion in matrices without a template than in matrices with one (Fig. 4a). The diffusion coefficient is governed basically by the fluid temperature; *i.e.* if the fluid temperature is high, T^* = 1.5, there is more kinetic energy and the diffusion is higher than that at a low fluid temperature, T^* = 0.8, as shown in Figs. 4a and 4b. The increase in diffusion as the temperature increases has been also observed from other simulations and theoretical results. For instance, Kamat and Keffer, from a lattice theory, observed that diffusion increased as a function of the temperature [17]. The same trend was found in simulations of nitrogen in nanoporous carbon [31].

In Fig. 5a, the diffusion of the different fluids is shown at temperature T^* = 1.5, immersed in matrices prepared at T^* = 1.5, with and without a template. Since in this case the voids and porosity are similar in matrices with and without a template, the diffusion coefficients do not present much change. Nevertheless, the values of the fluid diffusion inside the matrices prepared without a template are slightly higher than the diffusion in matrices prepared with one. The same tendency is displayed when the fluid temperature drops to T^* = 0.8; the diffusion is slightly higher when the fluid is in the matrix without a template. However, in this case all the values of the diffusion are much smaller than those at the fluid temperature of T^* = 1.5.

In a recent paper on hard fluid particles in a disordered medium composed of hard sphere particles [22], the authors found that, if the ratio of diameters of the fluid particle to that of the matrix particle is greater than one, the diffusion increases as the fluid density increases, whereas if the ratio of diameters is smaller than one, this trend is reversed. It seems that the fluid-matrix particle diameter ratio plays a role in defining the tendency of the diffusion coefficient in disordered porous media. In our study, the matrix - fluid particle interaction includes attraction, and the fluid particle diameter is much smaller than the matrix particle diameter; therefore, the diffusion decreases as the fluid density increases in agreement with those results shown in Ref. 22, even when only hard sphere potentials are used.

Since we have only three fluid particle diameters, it is not possible to calculate an accurate relation to determine if our system presents the levitation effect. Nevertheless, since we have small particle diameters compared with the cavity sizes, and the diffusion data increase with the inverse of the square particle diameter (plot not shown), we believe that we are in the linear regime described by some authors [20, 21].

It is worth mentioning that diffusion always seems to be higher in matrices prepared without a template than that in matrices with one. In a previous paper [30], we observed that, at a high temperatures, the diffusion seems to be higher in matrices with a template than in matrices without one. However, those matrices were prepared with a different template particle density; therefore porosity and the cavities have a different tendency to those observed in this work. Also, the fluid and the matrix particles were of the same size, which might be the reason why diffusion shows a different behavior from that observed here.

3.3. Conclusions

We have presented a series of computer experiments to show the behavior of different fluids inside disordered pore matrices. We found that, when matrices are prepared without a template at a low temperature they present high porosity and form large cavities. These results can give us insight into which parameters are important to control in order to prepare disordered porous matrices. As a general trend, we observed that the porosity is higher when the matrices are prepared without template particles at a low temperature. When the matrices are prepared at a high temperature, the porosity is practically the same, regardless of whether they were constructed with a template or not. The voids in the matrices had different sizes; however, in some cases, they were approximately 26 times as large as the size of the fluid particle diameter (in real units we have cavities up to 10 nanometers in diameter) when the matrix was prepared without a template at T^* = 0.8. In general, it was found that matrices at a low temperature have more structure [shown by the g(r)] than those at a high temperature, where they have also more uniform and regular void sizes. Previous works on hard sphere systems observed that there is greater porosity in matrices with a template than in matrices without one [8]; however, we observed the opposite trend. In seems that attractive forces, particularly at a low temperature, produce more and greater voids in the porous matrix, thus increasing the porosity and the size of the cavities.

The diffusion coefficient of different fluids inside the matrices was also studied, and the diffusion decreased as the fluid density increased. Also, in agreement with the results of porosity and void distributions, the highest diffusion is found in matrices prepared without a template at a low temperature.

It is well known that the properties of confined fluids are very different from those in bulk. The combined effect of the pore-fluid forces and the finite size can modify the structure, dynamics and thermodynamics of the fluids. For instance, it has been observed that the phase diagram of a confined fluid is shifted with respect to that in bulk (*e.g.* capillary condensation is observed) [32, 33]. In our case, we have a confined fluid which should have a different phase diagram compared to that in bulk, although we are not interested in its determination in this work. The confinement effect, however, is observed in the reduction of the diffusion coefficients of the fluids compared to those in bulk. From our simulations (data not shown here), the diffusion coefficients are significantly lower for fluids inside matrices than those in bulk.

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