Nitrogen Adsorption in Carbon Aerogels: A Molecular Simulation Study

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We present a molecular model for carbon aerogel in which the mesopore space is represented by carbon spheres in a connected network. This matrix was prepared by first generating a random close-packed structure of slightly overlapping spheres, followed by removal of spheres to match the targeted porosity, while maintaining connectivity. The spheres were then replaced by a model microporous carbon generated by applying the Reverse Monte Carlo method to fit the experimental carbon radial distribution function, $g(r)$, obtained by X-ray diffraction. The resulting model aerogel had a surface area, porosity, and pore size distribution that closely matched that of the experimental material. We used a parallelized Grand Canonical Monte Carlo algorithm to study nitrogen adsorption in this model aerogel. The resulting adsorption isotherm shows satisfactory agreement with the experimental results. Adsorption occurred in the micropores at very low pressure, followed by adsorption in the mesopores, with capillary condensation occurring at the higher pressures.

I. Introduction

Aerogels consist of highly porous, nanostructured sol-gel derived materials. They were first produced in 1930 by S. S. Kistler, who performed supercritical drying of gels to avoid their collapse.1 Prior to that, subcritical drying was used with considerable shrinkage of the gel, which led to materials with lower porosity, the so-called “xerogels”.

The high porosity and the nanometer scale of the skeleton and the open pores are responsible for the most interesting properties of the aerogels, such as low thermal conductivity, slow sound propagation, and high surface area. Because of the low thermal conductivity, they can be used as thermal insulators, for example, in refrigerators or heat storage devices. The slow sound propagation in combination with the low density make them ideal for ultrasonic transducers.2 Because of their nanostructure and very large surface area, aerogels can also be used as gas filters or substrates for catalytic materials.3

There are two different groups of aerogels based on the precursor used: inorganic and organic/carbon aerogels. Silica aerogel is the most extensively studied inorganic aerogel. It is synthesized by sol-gel polymerization of silicon alkoxide, followed by drying under supercritical conditions to remove the solvent from the wet gel. Surface areas range from 600 to 1000 m²/g, with pore volumes of about 1–4 cm³/g.4 The principal applications of this material are the ones mentioned above, in addition to their use as Cherenkov detectors since they have good optical properties.5

Organic aerogels were first prepared by Pekala in 1989.6 Their synthesis involves the polymerization of a resorcinol-formaldehyde (RF) mixture diluted in water with sodium carbonate as base catalyst. The resorcinol and formaldehyde condense into polymer “clusters” that cross-link to form a gel. To obtain an aerogel, the RF gel is dried with supercritical CO₂ to avoid collapse of the structure. These RF aerogels are mesoporous materials with high surface area and relatively few micropores. The structure is composed of interconnected beads with diameters measuring 7–10 nm.6 This structure is responsible for the transparency of the organic aerogel.

Carbon aerogels are derived from the pyrolysis of RF aerogels in an inert atmosphere. During this process, volumetric shrinkage, accompanied by mass loss, occurs. The transparency is lost and the resulting aerogel appears black in color. The final structure of the carbon aerogels consists of a three-dimensional network of interconnected carbon particles measuring 5–10 nm in size. Two pore size regimes can be differentiated: (1) mesopores (2–50 nm) that span the distance between the carbon particles and (2) micropores (<2 nm) that reside within the individual carbon particles. In Figure 1, a schematic representation of the carbon aerogel structure is shown.

The principal features of carbon aerogels are a high surface area (400–900 m²/g) and a high pore volume (1–3 cm³/g).4 One of the most important properties of carbon aerogels is that they are electrically conductive. A high surface area in combination with a low resistivity makes

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them ideal for applications such as electrode materials in supercapacitors\textsuperscript{7,8} and fuel cells. Carbon aerogel based electrodes can potentially be used to remove ions from wastewater.\textsuperscript{9} Other potential applications include their use as adsorbents\textsuperscript{10,11} and as materials for chromatographic separation.

There is a wide variety of size, interpenetration, and chemical linking of the RF "clusters". As a consequence, these variations persist in the final carbon aerogel structure, depending upon reaction conditions. The influence of these conditions in the final structure has been extensively studied.\textsuperscript{10,11,12} For example, by varying the resorcinol concentration with respect to the catalyst (R/C), the carbon particle size is affected (the particle size increases with increasing R/C).\textsuperscript{11} By changing the monomer concentration of the starting solution (expressed as the mass ratio of resorcinol to formaldehyde), the aerogel density can be controlled.\textsuperscript{12} Interconnected particles are approximately the same size, independent of bulk aerogel structure, depending upon reaction conditions. The influence of these conditions in the final structure has been extensively studied.\textsuperscript{10,11} For example, by varying the resorcinol concentration with respect to the catalyst (R/C), the carbon particle size is affected (the particle size increases with increasing R/C).\textsuperscript{11} By changing the monomer concentration of the starting solution (expressed as the mass ratio of resorcinol to formaldehyde), the aerogel density can be controlled.\textsuperscript{12}

Amorphous nanoporous materials vary considerably in their microstructure and degree of regularity and are in general very difficult to characterize completely. In trying to simulate these materials, two different approaches can be taken: (1) attempt to build a model that resembles as closely as possible the real material (by studying electron micrographs and other laboratory measures) or (2) mimic by simulation the manufacturing process used to make the real material. Because of the complexity of the reactions involved in the process of generating carbon aerogels, we used the first approach in this work.

To the best of our knowledge, no attempt to model carbon aerogels has been reported before. However, different models for silica aerogels have been developed by MacElroy and co-workers\textsuperscript{14,15,16} and Monson and co-workers.\textsuperscript{17-21} Many porous materials are formed from colloidal suspensions by aggregation and gelation, such as aerogels and xerogels, which are composed of microspherical particles interlinked in a random network. Thus, such materials can be modeled as a rigid matrix of solid spheres, usually randomly arranged. This same approach is used in this work.

The rest of the paper is arranged as follows. Section II provides the experimental information for the carbon aerogel studied in this work. In Section III, the procedure to generate the molecular model is described as well as the different Monte Carlo (MC) methods used to characterize the structure generated. In section IV, results from grand canonical Monte Carlo simulations of nitrogen adsorption generated in the model are presented and compared with experiments. A brief summary and discussion are provided in section V.

II. The Carbon Aerogel

The carbon aerogel studied is one synthesized by Y. Hanzawa at Chiba University, Japan.\textsuperscript{22} This carbon aerogel is called CA-0.4, where 0.4 denotes the density (0.43 g/cm\textsuperscript{3}). The general procedure used to generate this carbon aerogel is that of Pekala. A complete detailed description of the steps and materials used is provided by Hanzawa et al.\textsuperscript{22} The particular conditions used for the reaction, as well as the temperature at which pyrolysis was performed, are listed in Table 1.

The characterization of carbon aerogel is usually based on two experimental methods: (1) transmission electron microscopy (TEM) observations and (2) nitrogen adsorption measurements. A transmission electron micrograph for CA-0.4 is shown in Figure 2a. Analysis of this image yields the carbon particle size distribution (see Figure 2b). The particle diameter distribution ranges from 4 to 10 nm with a maximum at 6 nm. It can also be seen that the carbon spheres overlap by no more than 40% of the diameter of the sphere. The adsorption isotherm is shown in Figure 3. Adsorption measurements were followed by desorption measurements under the same conditions. This isotherm is of type IV based on the IUPAC classification\textsuperscript{23} and is typical for mesoporous materials. In these materials, capillary condensation normally takes place, leading to hysteresis loops. At low relative pressures micropore filling occurs.

In Figure 4, we show the \(\alpha\)-plot for the carbon aerogel CA-0.4.\textsuperscript{22} From the \(\alpha\)-plot analysis, the mesopore surface area, micropore volume, and total surface area can be obtained.\textsuperscript{24} The results are displayed in Table 2. In this table, the total pore volume is also shown, which corresponds to the final amount of adsorption. As the adsorption isotherm at high relative pressure is almost horizontal, the pore filling is completed and the total amount adsorbed corresponds to the total pore volume. In Figure 4, it is observed that the intermediate region (dashed line), from which the mesopore surface area and the micropore volume are deduced, is quite short. This suggests that both values have a considerable error associated with them. The Dubinin–Radushkevich (14) Park, I. A.; MacElroy, J. M. D. Mol. Simul. 1989, 2, 105.
The kevitch (DR) equation can also be used to estimate the micropore volume:

\[
\frac{v_{\text{mic}}}{v_{\text{mic0}}} = \exp\left\{-\left(\frac{RT}{\beta E_0}\right)^2 \left(\ln\left(\frac{P_0}{P}\right)\right)^2\right\}
\]  

(1)

where \(v_{\text{mic}}\) is the fractional filling, \(T\) is temperature, \(E_0\) is a "characteristic energy", \(\beta\) is a scaling factor, and \(P_0/P\) is the inverse of the relative pressure. This equation was used to calculate the micropore volume \(v_{\text{mic0}}\) by assuming that no mesopore adsorption contributes to the uptake at low relative pressures. The result is shown in Table 2. We considered this value to be more realistic than the micropore volume calculated with the \(\alpha_s\)-plot and, therefore, is the one we used in this work.

There are a variety of ways we can define density in the carbon aerogel. As evident from the TEM image in Figure 2a, the carbon aerogel is a very inhomogeneous material. This leads to differences in density from one point of the structure to another. For this work, we define the following densities associated with the structure of the carbon aerogel.

**Carbon Aerogel Density.** This is the macroscopic density of the carbon aerogel determined experimentally from the weight and volume measurements of the bulk sample. The value of this density is: \(0.43 \text{ g/cm}^3\).

**Carbon Sphere Density.** This is the average carbon particle (sphere) density. We define this to be the mass of carbon in one particle divided by the volume of the particle. Therefore, this definition includes the micropores as well as the atomic framework inside the carbon particle. This density cannot be measured experimentally but can be calculated from the micropore volume, \(v_{\text{mic}}\), and the density of aggregate (explained below) using the following expression:

\[
\rho_{\text{sphere}} = \frac{\rho_{\text{aggregate}}}{1 + \frac{v_{\text{mic}}}{v_{\text{mic0}}}}
\]

(2)

The carbon sphere density calculated using the micropore volume obtained from the DR analysis is \(1.327 \text{ g/cm}^3\).

**Aggregate Density.** This is the density of the small clusters of matter inside the carbon particle. These aggregates are composed of graphite layers or crystallites and ultramicropores or closed pores. The summation of the aggregate volume and the micropore volume is equal to the volume of the carbon sphere. This density can be experimentally measured using a benzene replacement method. The value obtained is \(1.91 \text{ g/cm}^3\).

**Crystallite Density.** This is the density of the graphite. The value of this density is \(2.2 \text{ g/cm}^3\).

An illustration of these different parts of the carbon aerogel structure is shown in Figure 5.

### III. Molecular Model of Aerogel

Our molecular model consists of a three-dimensional network of connected spheres representing the carbon particles. The free space in this network represents the mesopore region of the carbon aerogel. The micropore space located inside the carbon particles is represented by an independent microporous model.

1. Generating the Mesopore Structure. The mesopores in our model consist of the interstitial space within a three-dimensional network composed of connected spheres. The spheres were all identical with a diameter of 6 nm, based on the carbon particle size distribution shown in Figure 2b. The spheres were allowed to overlap by up to 40% of their diameter. This degree of overlap is the maximum observed in the TEM images.

Preparation of the model followed a similar procedure used by Park and MacElroy. It required two steps. First, a random close-packed structure of overlapping spheres in a cubic box was generated, and then spheres were randomly removed to attain the targeted porosity.

The length of the simulation box we used was 36 nm. To reproduce the pore network in a realistic fashion, a simulation cell length of at least 4 times the average pore size of the adsorbent was needed. The mesopore porosity was calculated from the product of the carbon aerogel density (0.43 g/mL) and the mesopore volume in ml/g. The mesopore volume itself was determined by subtracting the total pore volume (1.51 mL/g), shown in Table 2, the micropore volume calculated from the DR analysis, from the volume estimated from the mass of the carbon aerogel.

The process of removing spheres was restricted by connectivity, that is, the remaining spheres all had to be connected in a single cluster. A cluster-labeling algorithm similar to that of Hoshen and Kopelman was used for this purpose. The number of spheres to be removed was determined by the porosity desired. The first step consisted of randomly removing half of the total number of spheres to be removed. Then, the remaining spheres were checked for connectivity. Small clusters were removed and only the biggest cluster was retained. The remaining spheres were removed one at a time. If isolated clusters formed after the deletion of a sphere, they were also removed until the total number of spheres to be removed was achieved. The final configuration was required to have connectivity with at least one image particle in opposite faces of the cell. This process took approximately 5 s on a 600 MHz Dec-alpha workstation. Therefore, the process could be repeated until a reasonable porosity and connectivity between opposite faces was achieved. The computation of porosity was straightforward. It could be easily done with a Monte Carlo estimation of the volume of void space accessible to a test particle (see mesopore volume in section 2.2), sized as a Lennard-Jones molecule, divided by the total volume of the system. The final structure had 169 spheres and a porosity of 0.54 (see Figure 6b).

2. Characterization of Mesopore Structure. The structural properties of the material were determined using Monte Carlo methods. These properties include mesopore surface area, mesopore volume, and pore size distribution.

a. Mesopore Surface Area. There are several different definitions of surface area. The one calculated in this work is called the accessible surface area, and it is defined as the surface that can be reached by a test particle in contact with one or more carbon spheres. This definition implies that the surface area calculation depends on the nature of the molecule used as a test particle. In this work, the test particle was always nitrogen modeled as a single nitrogen molecule.

The calculation method was a Monte Carlo integration. Test particles were placed on the surface of randomly chosen spheres. If the test particle did not overlap with any of the carbon spheres, the point was accumulated as a "miss". The fraction of misses multiplied by the total surface area of the spheres gave the accessible surface area. The experimental and the calculated values are shown in Table 3. The calculated surface area was 12% lower than the experimental one. However, this experimental value is not very reliable, as explained before, because it was derived from the slope of the intermediate region of the plot, which is not sufficiently long to give a good estimate. Taking into account that the micropore volume estimated from the plot (corresponding to the ordinate intercept of the same line with the zero value of ) is also too low compared to the one estimated from the DR analysis, it can be seen that a less steep line would provide better agreement. That is, it would yield a lower experimental surface area (because of a lower slope), as in a structure generated by a larger micropore volume (because of a higher interception with the axis), as observed from other experimental methods.

b. Mesopore Volume. There are two different interpretations of the mesopore volume. The first one is the volume


The pore size distribution was calculated by Hanzawa et al. because of the lack of reliable experimental data. The procedure was the same as that used by Gelb and Gubbins for controlled-pore glass and by Thomson and Gubbins for activated carbon. The simulation cell was divided into a 3-D grid. At each point of the grid, the largest sphere of diameter $D$ that could be enclosed was determined, taking into account that this sphere could not overlap with the pore wall. This data was accumulated in the function $V(D)$, where $D$ is the diameter of the sphere. The derivative, $-dV(D)/dD$, is proportional to the fraction of volume that can be enclosed by a sphere of diameter $D$ but not by a sphere of diameter $D + dD$. This is a direct definition of the pore size distribution.

Another point of interest is the reproducibility of these properties in different realizations (i.e., mesopore structures) for the same size. As the procedure used to generate the mesopore structure is random and only depends on one property of the material (porosity), it is useful to have a measure of the differences between realizations.

The different sizes of the simulation box studied correspond to simulation cell lengths of 36, 54, and 72 nm. Five different realizations for each box size were generated. The procedure used to generate these structures is the one explained in section 2.1. The final structures had 169, 551, and 1300 spheres, respectively.

In Figure 8, the mesopore surface area for the different simulation boxes is shown. The error bar corresponds to the standard deviation within the five realizations. It is observed that the standard deviation decreases as the simulation cell length increases, as expected. This means that on increasing the system size, better reproducibility is obtained, and thus the consistency of the method to generate the structure is improved. Another point of interest is that the mesopore surface area is sensitive to

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**Table 3. Experimental and Calculated Results for the Mesopore Surface Area and Mesopore Volume**

<table>
<thead>
<tr>
<th></th>
<th>experimental</th>
<th>calculated</th>
</tr>
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<tbody>
<tr>
<td>mesopore surface area (m²/g)</td>
<td>355</td>
<td>311</td>
</tr>
<tr>
<td>mesopore volume (ml/g)</td>
<td>1.28</td>
<td>1.25</td>
</tr>
</tbody>
</table>

* a Mesopore surface area estimated from $a_s$-plot analysis. b Mesopore volume obtained as described in section 3.1.

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**Figure 6.** Carbon aerogel model structure. (a) Close-packed configuration and (b) final configuration.

**Figure 7.** Geometric mesopore size distribution for the carbon aerogel model.

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the simulation box size. This implies that the mesopore surface area is a good structural property on which to rely in forming the model structure.

In Table 4, the mean value between all realizations of the mesopore volume for each simulation cell length is shown. The bigger the simulation box, the better the agreement between the target (1.28 mL/g) and the simulated value.

Pore size distributions for all the realizations studied are shown in Figure 9. All the realizations, regardless of the simulation box size, had the highest peak at 5 nm. This implies that the predominant pore size is independent of the simulation cell chosen.

On the other hand, an increase in the size of the simulation box yields pore size distributions that become more regular, that is, the pore size distributions are closer to each other, which means that size effects become smaller. The average pore size was calculated for each realization, and the average between realizations for each simulation box size is shown in Figure 10. The error bar represents the standard deviation within the five realizations. Differences in the average pore size between simulation box sizes are smaller than 12%.

In Figure 9a, an example of size effects can be seen. The second peak at about 6 nm was only present in two of the five realizations and had almost disappeared in the simulation box of length 54 nm. The pore size distribution of the structures with a simulation box of length 72 nm included the presence of bigger pores. Thus, a wider distribution is obtained. The presence of larger pores up to around 14 nm can be observed; such large pores were not evident in any of the smaller boxes.

3. Generating the Micropore Structure. The model for the micropores inside each carbon sphere consists of a structure composed of rigid carbon basal plates with a carbon radial distribution function (RDF) closely matching that of the real micropore adsorbent. To generate this structure, a Reverse Monte Carlo (RMC) technique was used. This method is similar to the Metropolis algorithm but instead of using the ensemble probability functions as acceptance criteria, the moves are accepted only if they improve the simulated RDF relative to the experimental input.

The first step consisted of generating an initial configuration with (1) the carbon number density equal to that of the material (in this case, this density corresponded to \( \rho_{\text{sphere}} \) as described before) and (2) the size of the plates, that is, the number of aromatic rings per plate, following a Gaussian distribution. The density of the carbon atoms in the micropore structure was taken to be 1.327 g/cm\(^3\), as calculated from eq 2. The structure was assembled in a cubic simulation cell with a length of 10 nm and with periodic boundary conditions. Once this initial configuration was generated, a RDF could be computed. Three different types of Monte Carlo moves were performed: (1) plate translation/reorientation, (2) plate creation/annihilation, and (3) ring creation/annihilation. A calculated RDF was stored before the move \( g(r)_{\text{old}} \), and a new RDF was generated after the move \( g(r)_{\text{new}} \). Both of these functions were compared to the experimental distribution function \( g(r)_{\text{exp}} \) by calculating the square deviation,

\[
\chi^2 = \sum_{i=1}^{n} (g(r_i) - g_{\text{exp}}(r_i))^2
\]

in the micropore structure was taken to be 1.327 g/cm\(^3\), as calculated from eq 2. The structure was assembled in a cubic simulation cell with a length of 10 nm and with periodic boundary conditions. Once this initial configuration was generated, a RDF could be computed. Three different types of Monte Carlo moves were performed: (1) plate translation/reorientation, (2) plate creation/annihilation, and (3) ring creation/annihilation. A calculated RDF was stored before the move \( g(r)_{\text{old}} \), and a new RDF was generated after the move \( g(r)_{\text{new}} \). Both of these functions were compared to the experimental distribution function \( g(r)_{\text{exp}} \) by calculating the square deviation,
where $n$ is the number of experimental points and $r$ is the distance from a test carbon atom. The move was accepted if

$$
\chi_{\text{new}}^2 < \chi_{\text{old}}^2
$$

In the present work, this structure was generated using experimental data provided by Professor Katsumi Kaneko (none of these data are published). The final structure had 64,165 carbon atoms and a density of 1.278 g/cm$^3$ (see Figure 11). This microporous model was used in the current work for adsorption calculation purposes, but no characterization of the structure is reported here.

**IV. Adsorption Isotherm**

The adsorption isotherm for the carbon aerogel was considered to be composed of the amount of nitrogen adsorbed in the mesopores inside the carbon spheres plus the amount of nitrogen adsorbed in the mesopores. Both quantities were calculated separately and added together to give the total adsorption isotherm.

**1. Simulation Methodology.** The intermolecular interactions are given by the Lennard-Jones (LJ) potential. The nitrogen molecule was modeled as a LJ sphere. The model potential used for the fluid–fluid interactions as well as for the carbon–fluid interactions in the microporous structure is a truncated LJ potential,

$$
U_{ij}(r) = \begin{cases} 
4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 & r \leq r_c \\
0 & r > r_c 
\end{cases}
$$

where $r$ denotes the distance between the centers of molecules $i$ and $j$. The values of the intermolecular parameters $\sigma_{ij}$ and $\epsilon_{ij}$ used in this study are shown in Table 5.32,33 The cutoff radius, $r_c$, is always 5$\sigma_{ij}$. The larger this value the more expensive the total simulation cost becomes. However, long-range corrections are negligible with this large cutoff radius.

The morphology of the mesoporous structure is a matrix of carbon spheres. To minimize the simulation cost of the calculation, the spheres were modeled as a continuum of

| $N_2$–$N_2$ | 0.375 | 95.2 |
| $N_2$–C | 0.336 | 61.4 |

Lennard-Jones potential parameters for $N_2$–$N_2$ and $N_2$–C interactions are given in Table 5.

Lennard-Jones potential for planar surfaces. It has been shown that the virial equation of state was used. The second virial coefficient was calculated from the intermolecular potential parameters in Table 5, giving a value of $-210.36$ mol/cm$^3$ at 77 K. The saturation pressure for the model adsorbate used in this study, that is, nitrogen with the intermolecular potential parameters in Table 5, was calculated using Gibbs Ensemble Monte Carlo simulations and gave a value of 1.2 atm at 77 K.

The length of the simulation box used in this work was 36 nm. Such a large system required a very large amount of computational time for the adsorption calculation. Thus, a massively parallel GCMC algorithm was used. The parallelized GCMC algorithm used in this work is the one


**Table 5. Lennard-Jones Potential Parameters for $N_2$–$N_2$ and $N_2$–C Interactions**

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$\sigma$ (nm)</th>
<th>$\epsilon/k_B$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$–$N_2$</td>
<td>0.375</td>
<td>95.2</td>
</tr>
<tr>
<td>$N_2$–C</td>
<td>0.336</td>
<td>61.4</td>
</tr>
</tbody>
</table>
suggested by Heffelfinger and Lewitt. A spatial decomposition of the system was required to implement this method. The system volume was divided into domains and each domain was assigned to a processor. In this study, the system was always divided in $3 \times 3 \times 3$ domains, that is, 27 processors. The domains were then subdivided into a fixed number of subdomains. In determining the number of subdivisions, the cutoff radius desired must be taken into account. The length of the subdomain must be equal to the cutoff radius (5σ in this work). In the mesoporous structure, the number of subdivisions was $5 \times 5 \times 5$ while in the microporous structure, because of the smaller size of the system, the number of subdivisions was $2 \times 2 \times 2$.

Each processor worked simultaneously in each subdomain, performing the three types of GCMC moves: displacement, creation, and removal. This method takes advantage of the short-range interaction potential; processors can work simultaneously in different volumes of the system as long as a distance further than the reach of the potential separates the regions in which they operate. The acceptance criteria for a proposed creation or removal is different from the one used for a single processor calculation.

The creation of a particle is accepted with a probability

$$\text{acc}(N(s) \rightarrow N(s) + 1) = \min\left[1, \frac{V(s)}{\Lambda N(s + 1)} \exp\left\{ \frac{1}{k_B T} [\mu - \Delta U(N(s) \rightarrow N(s) + 1)] \right\} \right]$$

where $N(s)$ and $V(s)$ represent the number of molecules and the volume of a subdomain $s$, respectively. In addition, $\mu$ is the chemical potential, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\Lambda$ is the de Broglie wavelength. The change of energy because of the creation of the particle is represented by $\Delta U(N(s) \rightarrow N(s)+1)$.

The removal of a particle is accepted with a probability

$$\text{acc}(N(s) \rightarrow N(s) - 1) = \min\left[1, \frac{\Lambda^3 N(s)}{V(s)} \exp\left\{ - \frac{1}{k_B T} [\mu + \Delta U(N(s) \rightarrow N(s) - 1)] \right\} \right]$$

where $\Delta U(N(s) \rightarrow N(s) - 1)$ is the energy change due to the removal of a particle.

The principal sources of inefficiency in these calculations were (1) the communication required between the processors, (2) the spatial inhomogeneity of the system, mainly in the mesoporous structure, and (3) the differences in CPU time required to perform a single Monte Carlo move. All these drawbacks caused many processors to wait for others to finish their own tasks during the simulation. This implies that a direct comparison of efficiency between a single processor code and a parallel code was meaningless.

All of the calculations were conducted on a Cray T3E at the San Diego Supercomputer Center and at the Supercomputer Center at the University of Texas.

### 2. Results and Discussion

Each simulation point started from the previous configuration at lower pressure. For the simulations in the model microporous system, each isotherm point for a relative pressure below 0.1 was equilibrated for at least 20 million moves, followed by data collection for at least 10 million more moves. For relative pressures above 0.1, 80 million moves were required to reach equilibrium and 10 more million moves were run for data collection.

For the model mesoporous system, about 1 billion MC moves were required to reach equilibrium and 10 more million moves were run for data collection. For the mesoporous system, the number of MC moves was increased up to 2 billion MC moves. Because of the magnitude of these calculations, only the adsorption branch was calculated. At each isotherm point, the average number of adsorbed nitrogen molecules was measured and converted to units of (mg N$_2$)/(g of carbon aerogel) using the carbon aerogel density (0.43 g/cm$^3$) in the mesoporous system and the carbon sphere density (1.278 g/cm$^3$) in the microporous system.

In Figure 12, results for the adsorption isotherm for the microporous structure up to a relative pressure of 10$^{-2}$ are shown. The shape of this low-pressure part of the simulated isotherm is consistent with a continuous filling description. However, in the microporous model, condensation occurred at lower relative pressure than in the experimental adsorption isotherm. Furthermore, the plateau region of the simulated isotherm was somewhat above that of the experimental curve in this pressure regime.

There are several possible reasons for this disagreement. In this work, a realistic model of the microporous structure was used, in which the carbon plates were finite. However, in the real system the carbon atoms at the edges of the carbon plates are bonded to hydrogen (or other heteroatoms if the carbon contains oxygen or other impurities), and the interaction potential between one of these atoms and a nitrogen molecule must therefore be different to that of a carbon atom in the center of a carbon plate (bonded to three other carbon atoms) and a nitrogen molecule. Nevertheless, only one set of Lennard-Jones parameters for the nitrogen–carbon interaction potential was used in this work, independent of the type of carbon atom in the plate. These parameters were obtained by fitting the simulated nitrogen adsorption on an infinite surface model to experiments performed on graphite. In addition, the density of the carbon sphere, $\rho_{\text{sphere}}$, used to generate the microporous structure is not a direct experimental measure and was calculated using eq 2. This density determined the final number of carbon atoms in the microporous structure. The adsorption at low coverage was strongly influenced by this number. If the number of carbon atoms in the micropore structure increased, condensation oc-

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Figure 13. Simulated nitrogen adsorption isotherm at 77 K for the micropore structure (squares) and experimental isotherm (diamonds) for the entire range of relative pressures. The solid line represents the micropore part of the isotherm obtained using the DR equation.

Figure 14. Nitrogen adsorption isotherms at 77 K for the model and for the experiments. Squares represent the simulated results. Diamonds represent the experimental values. The line is drawn through the experimental points and is a guide to the eye.

curred at lower relative pressure because of the increased energy exerted by the pore walls. This means that a lower value of the carbon sphere density would give better agreement in the low-pressure region. Conversely, if the carbon sphere density decreased, the number of nitrogen molecules that must be adsorbed to reach saturation in the micropores increased, leading to a higher overshoot than the one shown in Figure 12.

The results for the entire range of relative pressures are shown in Figure 13. In this figure, the experimental isotherm results and the isotherm from the DR equation is also shown. There was almost complete nitrogen uptake in the micropores occurring at a relative pressure of 0.1, and the micropore saturation is in good agreement with the results obtained from the DR equation. As the principal concern of the micropore adsorption isotherm was to reproduce the low-pressure regime but to get suitable results to be used in the mesoporous model, the agreement achieved was found to be acceptable.

The results for the total (micropore + mesopore) simulated adsorption isotherm are compared to the experimental values in Figure 14. In these calculations, the interaction between the nitrogen molecules in the mesopores and the nitrogen molecules in the micropores was neglected.

The shape of both the simulated and experimental isotherms corresponds to the type IV isotherm associated with microporosity and mesoporosity. At low relative pressures (P/P₀ < 0.01), micropore filling occurred and the amount adsorbed in the mesopore structure was almost negligible. Therefore, the initial overprediction of the adsorption was due to the poor agreement that the microporous model gave in the very low relative pressure region. Very good agreement between simulation and experimental results was obtained in the relative pressure region between 0.1 and 0.8. However, the model predicted capillary condensation at somewhat lower relative pressures than those observed experimentally. There are several possible sources for this disagreement:

1. There is an error associated with the Pₛₐₘᵣₑ value chosen. The higher the value of Pₛₐₘᵣₑ, the lower the relative pressure at which condensation takes place. As mentioned before, a direct experimental measure of this value was not provided, and the value used in these simulations was calculated from the specific micropore volume and the density of the aggregates. If instead, this density is calculated with the carbon aerogel density (0.43 g/cm³) and the specific mesopore volume (1.28 mL/g), a different value is obtained. This is evidence of the inconsistency of the experimental data for these systems, which is a major difficulty in generating molecular models of the kind used here.

2. The pore size distribution of the model mesoporous structure shows an average pore size of 5.6 nm, which is significantly lower than the 8 nm observed experimentally. The position of the capillary condensation step is strongly influenced by the size of the pores. Capillary condensation occurs at lower relative pressure for smaller size pores.

3. Finally, the simplified model system presented may not truly reflect the details of the real nitrogen–carbon aerogel system with sufficient accuracy. Many reasons may cause this disagreement, including carbon particle surface heterogeneity and particle size polydispersity. These aspects have not been taken into account in the model.

Even though this model is simplified, the results are in generally good agreement with experiments. The experimental data that is so far available do not justify a more detailed model. Snapshots of the adsorption at different relative pressures can be seen in Figure 15.

An improvement of the model would be to include the interaction between the nitrogen adsorbed in the micropores inside the carbon spheres and the nitrogen adsorbed in the mesopores. To model this interaction, eq 8 could be used. Thus, the total potential energy between a carbon sphere and a nitrogen molecule adsorbed in the mesopore would be Uₘₐ₁(r) + Uₘₐ₄(r), where Uₘₐ₁ is the energy between the carbon atoms in the carbon sphere and a nitrogen molecule adsorbed in the mesopores, calculated using eq 8, and Uₘ₄ is the energy between the nitrogen adsorbed in the micropores inside the carbon spheres and a nitrogen molecule adsorbed in the mesopores. This can be represented by

\[
Uₘ₄(r) = \frac{16}{3} \pi \epsilon \sigma_{nitrogen} R \left( \frac{r^6 + 21/5r^4R^2 + 3r^2R^4 + R^6/3}{(r^2 - R^2)^{3/2}} \right) (11)
\]

where \( \sigma_{nitrogen} \) and \( \epsilon \) are the nitrogen–nitrogen intermolecular parameters. In this case, \( \sigma_{nitrogen} \) is the average density of nitrogen adsorbed at the micropore entrance in the model system at each relative pressure. The end regions of a pore are unfavorable areas for adsorption, resulting in the formation of a meniscus in the mouth of the pore. The molecules prefer to adsorb in regions away from the pore.
mouth, where the wall fluid interactions are more favorable. The meniscus formed leads to a decrease of about 50% of the nitrogen density in the middle of the micropore. Moreover, the carbon sphere has low porosity (0.3) leading to a value of the $F_{\text{sphere}}$ much higher than the value of the $F_{\text{nitrogen}}$. As a consequence, $U_{\text{ff}}$ will be small compared to $U_{\text{sf}}$, and no significant change in the results presented here is expected.

V. Summary

We have developed a molecular model for the carbon aerogel studied by Hanzawa et al. The model consists of a network of carbon spheres representing the mesoporous structure of the material. The carbon particles themselves are microporous and a separate model was used to describe this microporosity. The method used to generate the mesoporous structure was a reconstruction method in which the model carbon was constructed using only experimental observation of the material. From TEM images, it was observed that the morphology of the material consisted of connected carbon particles, slightly overlapping and mainly spherical. On the basis of these observations, the mesoporous matrix was constructed. Only one structural property, the mesopore porosity, was required. The microporous structure was also based on a reconstruction method. In this case, a Reverse Monte Carlo technique was used to fit the experimental carbon radial distribution function, $g(r)$, obtained by X-ray scattering.

An advantage of the molecular models of porous materials is that all atomic coordinates of the porous matrix are known exactly. Thus, structural properties can be evaluated. The mesopore volume and the mesopore surface area of the model structure were calculated and agreed quantitatively with experimental results. The pore size distribution of the mesoporous structure was also generated. The average pore size was slightly smaller than the one reported experimentally. However, this value was virtually independent of the simulation box size, which means that it depends entirely on the method used to generate the structure.

In addition, nitrogen adsorption simulations were performed and compared with experiments. The total adsorption isotherm was generated by adding the contributions of the adsorbed molecules in the microporous system and the adsorbed molecules in the mesoporous system at different relative pressures. Up to a relative pressure of $P/P_0 = 0.8$, quantitative agreement was found. Capillary condensation in the model was predicted to occur at somewhat lower relative pressure than is experimentally observed. Several reasons for this disagreement have been discussed, but the most important reasons are possible errors associated with the carbon sphere density, $p_{\text{sphere}}$, and an average pore size that may be too small. A higher value of $p_{\text{sphere}}$ results in a lower relative pressure at which condensation occurs. On the other hand, as $p_{\text{sphere}}$ decreases, the amount of nitrogen adsorbed at relative pressures between 0.1 and 0.8 also decreases considerably. Although agreement between the simulation and experimental data was not quantitative, the general qualitative similarity lent credibility to the model proposed here.
There are several areas for further study. First, it would be helpful to investigate the effect of the intermolecular forces between the carbon atoms in the microporous structure and the nitrogen adsorbed. It would be useful to fit the potential parameters to get a better match with the experimental isotherm and to take into account the edge effects using a more realistic model. Second, the mesoporous structure was constructed to match the experimental mesoporosity of the material. However, one single porosity can yield several structures. It would be interesting to use a reconstruction technique based on structural information obtained experimentally, for example, from small-angle X-ray scattering (SAXS). Furthermore, SAXS experiments of the material could provide an estimation of the carbon sphere density, $\rho_{\text{sphere}}$, thereby reducing the uncertainty in choosing the value of this property. Finally, a further refinement of the model would be to include the interaction of the nitrogen adsorbed in the micropores inside the carbon spheres with the nitrogen adsorbed in the mesopores. However, since the interaction would be only with the micropore nitrogen located very near the surface of the sphere, this correction is expected to be small.

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