Structure of Porous Adsorbents: Analysis Using Density Functional Theory and Molecular Simulation

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Abstract

The pore size distribution (PSD) analysis method based on nonlocal density functional theory (DFT) and on molecular simulation is reviewed and compared with classical PSD methods. Applications to carbons and oxides are given. The DFT method offers several advantages over classical methods: (a) a valid and accurate description for small pores; (b) a description of the full adsorption isotherm (not just the capillary condensation pressure), as well as other properties such as heats of adsorption; (c) it can be used for supercritical conditions; (d) it accounts for effects of pore shape; (e) it can be improved in a systematic way, since it rests on fundamental statistical mechanics. A critique of the method as currently applied is also offered. In common with most other PSD methods, the model neglects connectivity and pore blocking, and changes in pore size and geometry with pressure and temperature, and assumes that heterogeneity due to differences in pore shape and surface chemical groups can be approximated by an effective porous material, in which all heterogeneity is due to a distribution in pore sizes. Additional tests, using molecular simulation and experiment, are needed to determine whether these neglected effects exhibit signatures in experimental results that are distinct from the PSD effects. Molecular simulation studies of pore connectivity effects have been made for a simple network model; the model seems able to provide a detailed molecular explanation for the several hysteresis types found in Type IV and V isotherms.

1. Introduction

Classical methods [1] for determining the pore size distribution (PSD) from nitrogen adsorption isotherms have relied on thermodynamic models based on the Kelvin equation for the capillary condensation pressure, or on semi-empirical treatments such as that of Horvath and Kawazoe (HK) [2] for slit pores, or of Saito and Foley (SF) [3] for cylindrical pores. The Kelvin-based methods are only applicable for large pores; while the HK and SF methods have a better range of application, they also underpredict pore sizes and break down for small pores. Methods based in statistical mechanics are much more accurate, and provide the full isotherm for pores of all sizes. Our recent work [4-8] in developing an accurate method for analysis of pore size distributions is aimed at replacing the phenomenological methods with a more rigorous approach based on density functional theory (DFT). In this paper we review the DFT method and show some recent applications to pore size distribution analysis.

In both the classical and DFT approaches, the adsorption Ï(Î) at pressure Î is usually approximated as
\[ \Gamma(P) = \int_{\gamma_{\text{m}}}^{\gamma_{\text{m}}^*} \Gamma(P, H) f(H) dH \]  

(1)

where \( H \) is pore size (e.g. width for slit pores, diameter for cylinders), \( f(H) \) is the pore size distribution, and \( \Gamma(P, H) \) is the adsorption for a material whose pores are all of width \( H \). The latter is calculated from the macroscopic correlation or theory. Equation (1) does not explicitly account for many effects present in real porous materials, such as pore networking and blocking, heterogeneity due to chemical groups on the surface, or variation in pore shape. The inclusion of all these effects is not practical at the present time. The use of eqn. (1) replaces the real material by an effective porous material, in which all the heterogeneity of the real material is approximated by a distribution of pore sizes [7].

2. Classical Methods

The experimental nitrogen isotherm is a composite of the individual adsorption isotherms of the various sizes and types (shapes, surface chemical nature) of pores present in the sorbent. Historically, the Kelvin equation has been the most commonly employed model to describe capillary condensation in pores of a given size and geometry. The Kelvin equation is derived from classical thermodynamics and is accurate in the limit of large pores for temperatures that are sufficiently below critical that the gas phase can be treated as ideal. It is based on the assumptions that there is a definable gas-liquid interfacial region, and that the liquid phase is incompressible. Since it only accounts for the effect of surface curvature on gas-liquid surface tension, it does not take into account the influence of fluid-wall forces, wetting, etc. In an attempt to roughly account for these wall effects, it is common to use a modified form of the Kelvin equation, in which the pore width \( H \) is replaced by \( H - 2t \), where \( t \) is the adsorbed film thickness at the pore condensation pressure \( P_c \).

\[ \ln \left( \frac{P_c}{P_0} \right) = -2\gamma_l / R T \rho_l (H - 2t) \]  

(2)

where \( P_c \) is the vapor pressure of the bulk fluid, \( \gamma_l \) and \( \rho_l \) are the gas-liquid surface tension and liquid phase density, \( R \) is gas constant and \( T \) is absolute temperature. In practice, the film thickness \( t \) is usually estimated from a standard isotherm, or "t-curve", measured on a nonporous surface of the same chemical type. While this equation works satisfactorily for large pores, it fails for small mesopores and for micropores, due to the failure to account properly for fluid-wall interaction effects, and the highly inhomogeneous nature of the pore fluid. These effects lead to enhanced adsorption at a given pressure, so that the Kelvin and modified forms overestimate the capillary condensation pressure; this leads to pore size predictions that are too low. Simulation studies [9] indicate that 75 Å is the approximate lower bound of pore size that can be determined from such methods (see also Fig. 1).

An alternative method, originating from the microporosity model put forth by Everett and Powl [10], is to calculate an average potential function inside the micropore. Using thermodynamic arguments, this average potential can be related to the free energy change of adsorption, yielding a relation between filling pressure and pore width. This approach was developed for slitlike pores by Horvath and Kawazoe [2], and later extended to cylindrical pores by Saito and Foley [3]. For nitrogen adsorption in carbon slit pores, the Horvath-Kawazoe (HK) relation between filling pressure and slit width is

\[ \ln \left( \frac{P_c}{P_0} \right) = \frac{N_A (A_N)}{RT} \times \left( \frac{10}{9} \right)^9 \frac{\kappa^{10}}{CN^9} \]

where \( N_A \) is Avogadro's number for carbon, \( C_{\text{m}} \) and \( C_{\text{N}} \) are nitrogen and nitrogen-12, and \( \kappa \) is the zero-energy attractive force in microns of the Dubinin-Asakhow model. A simplified view of this model is below its filling pressure, where pore filling is in fact a condensation occurring prior to pore filling.

Several more experimental gas isotherms for microporous sorbents, such as those for the Dubinin-Asakhow model, show that the adsorbed volume is smaller than assumed Gaussian model. Several models have been put forth to improve this: it consists of a mesopore filling that requires the use of empirical corrections.

![Figure 1. Filling of pores with nitrogen adsorption](image-url)
\[
\ln\left(\frac{P_c}{P_0}\right) = \frac{N_A}{RT\kappa^4(H-2\sigma_{CN})} \left[ \frac{\kappa^{10}}{9\sigma_{CN}^2} - \frac{\kappa^4}{3\sigma_{CN}^2} - \frac{\kappa^{10}}{9(H-\sigma_{CN})^9} + \frac{\kappa^4}{3(H-\sigma_{CN})^3} \right]
\]

where \(N_A\) is Avogadro's number, \(A_N\) and \(A_C\) are the monolayer areas of nitrogen and carbon, \(\sigma_{NN}\) and \(\sigma_{CN}\) are the Kirkwood-Müller dispersion constants for nitrogen-nitrogen and nitrogen-carbon interactions, \(\sigma_{CN}\) is the mean nitrogen-carbon diameter and \(\kappa\) is the zero-energy adsorbate-surface separation distance. The HK method is an improvement over the Kelvin approach, in that it accounts for the strong solid-fluid attractive forces in micropores. However, it gives poor results for mesopore PSDs, as it does not account for pore wetting, and it must be combined with a Kelvin-type method to describe the full PSD (Fig. 1). Furthermore, the HK method has an oversimplified view of pore filling, in that it assumes a pore is completely empty if it is below its filling pressure and completely full is above its filling pressure. Since pore filling is in fact a continuous process, with monolayer and multilayer formation occurring prior to pore condensation, this assumption leads to inaccuracies in the HK model.

Several more empirical methods have been proposed to determine the PSD of microporous sorbents. An example is the Dubinin-Stoeckli equation [11], in which the Dubinin-Astakhov equation for estimating micropore volume is combined with an assumed Gaussian micropore size distribution. This method has two principal drawbacks: it constrains the PSD to an arbitrarily chosen functional form, and it requires the use of empirical energy parameters in the solution of the PSD.

![Figure 1. Filling pressures \(P_c\) predicted by the modified Kelvin equation (MK), the Horváth-Kawazoe equation (HK), density functional theory (DFT), and molecular simulation (points) for nitrogen adsorption in a carbon slit pore at 77 K.](image-url)
Attempts to analyze hysteresis loops in type IV isotherms have been largely confined to percolation theory methods [12-18]. In percolation theory, individual pores are regarded as bonds on a lattice, and percolation of the system occurs when a connected cluster of pores containing vapor spans the lattice. Application of this probabilistic method to experimental desorption data yields estimates of the mean connectivity in porous materials. The utility of the percolation approach is limited, however, as this model cannot be used to examine the dynamic aspects of desorption at the molecular level.

3. The Model

Many porous materials contain an interconnected network of pores, each with its own shape, size and heterogeneity. While we cannot hope to realistically model such a complicated structure in its entirety, we can reduce the problem to a more tractable form by assuming that (1) the pores have a simple geometry (e.g. slits or cylinders), (2) the aspect ratio of pore length to width is large, so that pore junction effects can be neglected, and (3) the concentration of surface functional groups is either uniformly distributed or low enough to be disregarded. With these assumptions, the task of determining the pore size distribution reduces to the solution of eqn. (1).

To model nitrogen adsorption on activated carbon, a slit pore geometry is chosen for the individual pores. Each pore is bounded by two semi-infinite parallel graphite slabs separated by a physical width \( H \), the distance between the centers of the surface carbon atoms (Figure 2). The graphite layers in each slab are separated by a uniform spacing \( \Delta \). The fluid-fluid interaction potential is modeled using the Lennard-Jones 12-6 pairwise potential, with parameters fitted to the bulk fluid properties of nitrogen. The solid-fluid interaction potential \( \phi_d \) for nitrogen interacting with a single graphite slab is described by the Steele 10-4-3 potential [19]

\[
\phi_d = 2ne_d \rho_s \sigma_d^3 \Delta \left[ \frac{2}{3} \left( \frac{\sigma_d}{z} \right)^6 - \frac{1}{2} \left( \frac{\sigma_d}{z} \right)^4 - \frac{1}{3 \Delta (z + 0.61 \Delta)^3} \right]
\]

where \( z \) is the distance from the graphite surface, \( \rho_s \) is the solid number density, and \( \sigma_d \) and \( \sigma_d \) are fitted parameters for the nitrogen-carbon well depth and intermolecular diameter. We take \( \rho_s = 0.114 \text{ \AA}^{-3} \) and \( \Delta = 0.35 \text{ \AA} \) [19]. The 10-4-3 potential is obtained by integrating the Lennard-Jones potential between one fluid molecule and a carbon atom over the individual carbon atoms in one graphite plane, and then summing over all planes. The “10” and “4” terms represent the repulsive

![Figure 2. Schematic of model carbon slit pore.](image)

and attractive interactions, whereas the “3” term results from the interaction between the remaining layers of the graphite surface and the subsurface graphite. The fluid molecule interacts with

\[
V_{ef}(z) = \phi_d(z) + \phi_d(F)
\]

To model nitrogen adsorption, it is assumed that the pore walls are cylindrical pores of various structures, structureless solid slabs, adsorbate molecules as well as heterogeneous (e.g. exchanged zeolites), nonpolar, and hence for nonpolar adsorbate, expected to dictate the adsorption.

The fluid-sorbate interaction potential for an unstructured oxide has the form of a simple unstructured pore of physical radius \( R \), oxide surface atoms) is

\[
\phi_e(r) = \frac{\sigma_d}{r} \left[ 1 - \frac{3}{2} \left( \frac{\sigma_d}{r} \right)^2 \right]
\]

where \( r \) is the distance from the pore to the oxide in the solid (0.07 A) and \( \beta \) is a constant.

\[
I_e(z) = \int_0^\infty d\theta (-x \cos \theta)
\]

The “9” and “3” terms in the fluid-particle interaction potential represent adsorption with the oxide.

Fluid-fluid interaction potentials to the bulk thermodynamic limit for nitrogen at its normal boiling point were obtained using the “t-curve” method [18]. The solid-fluid potential parameters for nonporous material are given in Table 1. Using the “t-curve” method and for the oxides it is found in this way are:

<table>
<thead>
<tr>
<th>Type</th>
<th>( \varepsilon_{ef} \langle k \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbons:</td>
<td>( 3.5 )</td>
</tr>
<tr>
<td>Oxides:</td>
<td>( 1.5 )</td>
</tr>
</tbody>
</table>
and attractive interactions of the fluid molecule with the surface graphitic plane, while the "3" term results from the summation of the attractive part of the potential over the remaining layers of the solid. (The repulsive interactions of the fluid molecule with the subsurface graphite planes are small and therefore neglected.) For a slit pore, the fluid molecule interacts with two graphite slabs; hence, the full external potential \( V_{\text{ext}} \) is

\[
V_{\text{ext}}(z) = \phi_{\text{r}}(z) + \phi_{\text{d}}(H - z)
\]

To model nitrogen adsorption on silica and other aluminosilicates, it is assumed that the pore network is composed of an array of non-interconnected cylindrical pores of varying radius. Each individual pore is bounded by an infinite structureless solid slab. It is further assumed that any cation interactions with the adsorbate molecules are small and may be neglected. This premise, which is no doubt inaccurate for sorbents with strong localized charge centers (e.g. cation-exchanged zeolites), nonetheless provides a practical starting point for the analysis. Usually, the cation species are situated beneath the surface oxide layer of the solid, and hence for nonpolar adsorbates the oxide interactions with the sorbate can be expected to dictate the filling behavior.

The fluid-sorbent potential for nitrogen interacting with a semi-infinite slab of unstructured oxide has been derived by Peterson et al. [20]; the external field for a pore of physical radius \( R \) (the distance from the pore centerline to the center of the oxide surface atoms) is of the 9-3 form

\[
\phi_{\text{d}} = \varphi_{\text{d}} \sigma_{\text{d}}^3 \left[ \frac{\sigma_{\text{d}}}{r} \right]^3 \frac{7}{32} \left( \frac{\sigma_{\text{d}}}{r} \right)^6 I_4 \left( \frac{\sigma_{\text{d}}}{r} \right) - I_3 \left( \frac{\sigma_{\text{d}}}{r} \right)
\]

where \( r \) is the distance from the centerline of the pore, \( \varphi_{\text{d}} \) is the number density of the oxide in the solid (0.0706 Å\(^{-3}\) for alumina), and

\[
I_n(x) = \int_{0}^{\infty} d\theta (-x \cos \theta + (1 - x^2 \sin^2 \theta)^{1/2})^n
\]

The "9" and "3" terms represent the repulsive and attractive interactions of the adsorbate with the oxide solid.

Fluid-fluid interaction parameters were obtained by fitting the DFT predictions to the bulk thermodynamic data (liquid density and pressure) for saturated liquid nitrogen at its normal boiling point; this gives \( \varepsilon_{\text{d}}/k = 93.98 \) K and \( \sigma_{\text{d}} = 3.572 \) Å. The solid-fluid potential parameters are fitted so as to reproduce the nitrogen isotherm on a nonporous material of the same composition as the porous materials of interest, using the "t-curve" method [21]. For carbons the nonporous material was Vulcan, and for the oxides it was a nonporous NBS alumina. The solid-fluid parameters found in this way are:

- **Carbons:** \( \varepsilon_{\text{d}}/k = 53.22 \) K, \( \sigma_{\text{d}} = 3.494 \) Å
- **Oxides:** \( \varepsilon_{\text{d}}/k = 193.6 \) K, \( \sigma_{\text{d}} = 3.166 \) Å
4. Density Functional Theory

Each individual pore has a fixed geometry, and is open and in contact with bulk nitrogen. The temperature is fixed at the nitrogen boiling point. For this system, the grand canonical ensemble provides the appropriate description of the thermodynamics. In this ensemble, the chemical potential \( \mu \), temperature \( T \), and pore volume \( V \) are specified. In the presence of a spatially varying external potential \( V_{\text{ext}} \), the grand potential functional \( \Omega \) of the fluid is

\[
\Omega[\rho(r)] = F[\rho(r)] - \int dr \rho(r) [\mu - V_{\text{ext}}(r)]
\]

where \( F \) is the intrinsic Helmholtz free energy functional, \( \rho(r) \) is the local fluid density at position \( r \), and the integration is over the pore volume. An analytic equation of state for \( F \) is not available for the Lennard-Jones fluid; hence, \( F \) is expanded to first order about a reference system of hard spheres of diameter \( d \),

\[
F[\rho(r)] = F_s[\rho(r);d] + \frac{1}{2} \int dr dr' \rho^{(2)}(r,r') \phi_{\text{at}}(|r-r'|)
\]

where \( F_s \) is the hard sphere Helmholtz free energy functional, \( \rho^{(2)} \) is the pair distribution function, and \( \phi_{\text{at}} \) is the attractive part of the fluid-fluid potential. In principle, the pair distribution function of the reference fluid is known, the second term on the right hand side can be evaluated numerically. It is usual, however, to invoke mean field approximation, wherein correlations due to attractive forces are neglected (i.e. the two-body correlation function \( g^{(2)}(r,r') \) is set equal to unity). The mean field density functional is thus

\[
F[\rho(r)] = F_s[\rho(r);d] + \frac{1}{2} \int dr dr' \rho(r) \rho(r') \phi_{\text{at}}(|r-r'|)
\]

The attractive part of the fluid-fluid potential is represented by the Weeks-Chandler-Andersen division of the Lennard-Jones potential

\[
\phi_{\text{at}}(|r-r'|) = \phi_{\text{at}}(|r-r'|), \quad |r-r'| > r_m
\]

\[
-\epsilon_{\text{at}}, \quad |r-r'| < r_m
\]

where \( r_m = \frac{1}{2} \sigma_m \) is the location of the minimum of the Lennard-Jones potential. The hard sphere term \( F_s \) can be written as the sum of two terms,

\[
F_s[\rho(r);d] = kT \int dr \rho(r) \ln(\lambda \rho(r)) - 1 + kT \int dr \rho(r) f_{\text{at}}[\rho(r);d]
\]

where \( \lambda = \hbar / (2\pi mkT)^{1/2} \) is the thermal de Broglie wavelength, \( m \) is the molecular mass, \( k \) is the Boltzmann constant, and \( f_{\text{at}} \) is the excess (total minus ideal gas) Helmholtz free energy per hard sphere molecule. The latter is calculated from the Carnahan-Starling equation of state for hard spheres [22]. The first term on the right side of (12) is the ideal gas contribution, which is exactly local (i.e. its value at \( r \) depends only on \( \rho(r) \) at \( r \)), while the second term on the right is the excess contribution, which is nonlocal.

The density \( \rho(r) \) is related to the nonlocal density, and

\[
\rho(r) = \int dr' \rho(r') w(|r-r'|)
\]

The choice of the weight function is crucial to the theory used. For high density approximations, \( w(r) \) gives a good description of the density profile of a uniform fluid over a wide range of densities, while \( \rho \) is used for the weighting function. Agreement with simulations of fluids near attractive walls and in pores uses a power series expansion for \( \rho \)

\[
w(|r-r'|) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{d^n}{dr^n} (\frac{\rho}{\rho_0})^n
\]

Expressions for the weight function \( w \) are available.

The equilibrium condition

\[
\frac{\delta \Omega[(\rho(r))]}{\delta \rho(r)} = 0
\]

A numerical iteration scheme can be used to find \( \rho_{\text{eq}}(r) \) for each set of equilibrium properties, where the difference with respect to the bulk properties is related to the bulk properties of the fluid

\[
F(\rho) = R_s(\rho) - \frac{a k T \rho}{2}
\]

where \( a \) is a van der Waals parameter. When more than one equilibrium state is possible, the one with the lowest potential energy is the stable state. When the potential energy is zero, the state is said to occur.

In subsequent calculations, the enthalpy

\[
H^* = H / \sigma \quad T^* = T / \sigma
\]
The density $\rho(r)$ that appears in the last term of (12) is the smoothed or nonlocal density, and represents a suitable weighted average of the local density $\rho(r)$,

$$
\bar{\rho}(r) = \int dr' \rho(r') w(|r - r'|, \bar{\rho}(r))
$$

(13)

The choice of the weighting function $w$ depends on the version of density functional theory used. For highly inhomogeneous confined fluids, a smoothed or nonlocal density approximation is introduced, in which the weighting function is chosen to give a good description of the hard sphere direct pair correlation function for the uniform fluid over a wide range of densities. In this work, Tarazona’s model [23] is used for the weighting function. This model has been shown to give very good agreement with simulation results for the density profile and surface tension of LJ fluids near attractive walls. The Tarazona prescription for the weighting functions uses a power series expansion in the smoothed density. Truncating the expansion at second order yields

$$
w(|r - r'|, \bar{\rho}(r)) = \sum_{i=0}^{2} w_i(|r - r'|, \bar{\rho}(r))
$$

(14)

Expressions for the weighting coefficients $w_i$ are given by Tarazona et al. [23].

The equilibrium density profile is determined by minimizing the grand potential functional with respect to the local density,

$$
\delta Q(\rho(r)) = 0 \quad \text{at } \rho = \rho_{es}
$$

(15)

A numerical iteration scheme is used to solve this minimization condition for $\rho_{es}(r)$ for each set of values of $(T, \mu, \lambda)$; the hard sphere diameter is determined from the Barker-Henderson prescription [24] for each temperature. The chemical potential is related to the bulk pressure through the bulk fluid equation of state,

$$
P(\rho) = P_\phi(\rho) - \frac{akT\rho^2}{2}
$$

(16)

where $a$ is a van der Waals interaction parameter given by

$$
a = 4\pi \int_0^\infty \phi_{sw}(r)r^2dr
$$

(17)

For large pores, two minimum density profiles often arise; these are the liquid and vapor branches associated with thermodynamic hysteresis in individual slit pores. When more than one minimum exists, the density profile which has the lower grand potential energy is the stable branch. The chemical potential at which condensation occurs is the value for which the two minima have the same grand potential energy.

In subsequent sections, the following dimensionless quantities are used:

$$
H^* = H/\sigma, \quad T^* = kT/\epsilon, \quad \rho^* = \rho\sigma^3, \quad z^* = z/\sigma
$$
5. Molecular Simulation

To check the accuracy of the density functional theory results, adsorption
isotherms have been calculated using Gibbs ensemble simulation. The Gibbs
ensemble method provides a direct route to the determination of the phase coexistence
properties of a fluid, by Monte Carlo simulation of the fluid in two distinct physical
regions that are in thermal, mechanical and material contact. Gibbs simulation was
originally developed to determine phase equilibria in bulk fluids [25] and in fluids
adsorbed in cylindrical pores [26]. In order to test the theory, Gibbs ensemble
calculations are performed for fluid adsorption in the slit pore geometry of Figure 2.
Two types of Gibbs simulation are performed: pore-pore and pore-fluid. The pore-
pore calculations yield the coexisting liquid and vapor densities at the filling pressures
of pores in which capillary condensation occurs. A schematic of the pore-pore
simulation method is shown in Figure 3. The fluid molecules are confined in the slit
pore geometry of each of the two simulation cells, designated regions I and II. At
each simulation step, one of three perturbations is attempted: (a) particle displacement
in each region; (b) particle interchange between the two regions; and (c) exchange of
pore surface area between the two regions, such that the total surface area remains
constant. The acceptance probability for each of these moves is chosen in a way that
ensures that the system obeys the laws of equilibrium statistical mechanics [8,25,26].
Sampling configurations using these three perturbations ultimately brings the two
regions into thermal, material and mechanical equilibrium. Such a state is phase-
equilibrated, and thus the Gibbs method yields the equilibrium densities of the
coexisting liquid and vapor phases. The potentials described in Section 3 are used to
model the fluid-fluid and fluid-solid interactions. Starting from an initial face-
centered cubic lattice configuration in each region, the system is equilibrated by
successive perturbations over a sufficient number of configurations. Additional
configurations are then sampled to measure the properties of the equilibrated phases.

Figure 3. Schematic of Gibbs ensemble Monte Carlo simulation
method for pore-pore equilibria calculations in slit-shaped pores.
Solid lines denote pore walls; dashed lines denote periodic boundaries.
A typical calculation requires approximately 1.5 million configurations for equilibration and an additional 1.5 million configurations for collecting property data.

For the inhomogeneous confined fluid, long range corrections are not computed because of the associated computational difficulties. However, the system size is chosen so that the minimum edge length of the pore surface is 10σ, (i.e. all molecular interactions up to a distance of 5σ are explicitly included in the calculations). This cutoff is presumed to be large enough so that long range corrections may be neglected.

While the pore-pore calculation yields the equilibrium vapor and liquid states that coexist in a pore of specified width, it does not specify the pressure at which the equilibrium state occurs, nor does it indicate the amount adsorbed at pressures below and above the equilibrium pressure. Therefore, the filling pressure and the state points along the vapor and liquid branches of the adsorption isotherm are calculated using the Gibbs pore-fluid ensemble. In this variation of the Gibbs ensemble method, the fluid in region I is again confined in a slit pore, but region II is a homogeneous bulk fluid (all boundaries are periodic). In the pore-fluid calculation, no exchanges of pore volume are attempted, since the condition for mechanical equilibrium is automatically satisfied if the chemical potentials in regions I and II are equal (i.e. material equilibrium is achieved) [27]. Hence, only displacement and particle interchange steps are performed, with the same acceptance probabilities as stated for the aforementioned pore-pore simulation. In calculating the bulk fluid properties, a long range correction for the cubic simulation cell geometry is included [25,28]. At equilibrium, the adsorbed fluid density corresponding to the bulk fluid pressure is obtained. To facilitate comparison of theory and experiment, the bulk pressure is scaled with respect to the saturation pressure P_{s} of the bulk Lennard-Jones fluid, given by the modified Benedict-Webb-Rubin equation of state [29]. To determine the pressure at which condensation occurs, the vapor coexistence density from the pore-

![Figure 4. Surface area measurement of Vulcan nonporous carbon. The slope of the linear region of the plot is the specific surface area of the sorbent.](image)
pore calculation is interpolated so that it coincides with the vapor branch of the isotherm constructed from the pore-fluid results.


Calculations using several different values of the solid-fluid potential strength \( \varepsilon_{sf}/k \) showed that the pressure at which the monolayer forms, and the pore filling pressure for micropores, are both sensitive to this value, but the general form of the isotherm is not much affected. The solid-fluid potential strength was fitted to adsorption data for a nonporous material of the same chemical structure as the porous material. For carbons this was a Vulcan provided by BP Research. The surface area \( A \) of this material was estimated using the method of deBoer et al. [21], from the slope of the plot of volumetric uptake against the universal film thickness, or “i-curve” (see Figure 4); \( A \) is related to the slope \( S_m \) of the linear region as

\[
A = \frac{S_m}{(\rho_{sat} S_{TP})}
\]

(18)

where \( \rho_{sat} \) is the density of the adsorbed film, and \( S_{TP} \) is the molar volume of nitrogen at standard conditions. Here \( \rho_{sat} \) is usually taken to be the bulk saturated liquid nitrogen density. This procedure leads to \( A=78.6 \text{ m}^2 \), as compared to \( A=71.76 \text{ m}^2 \) from BET measurement. The ratio \( A/A_{BET}=1.10 \) is consistent with deBoer’s results for Graphon and Spheron carbon blacks. The solid-fluid potential parameter \( \varepsilon_{sf}/k \) was then estimated by fitting the mean nitrogen density in a large mesopore, \( \rho_{DFT} \), as calculated from the DFT theory, to experimental data, using the relation

\[
V_{sat} = \frac{1}{2} \rho_{DFT} H V_{TP}
\]

where \( V_{sat} \) is the uptake value of \( \varepsilon_{sf}/k=53.22 \) forms. For oxide materials, \( V_{sat} \) is given for a nonporous NB.

With these parameter values generated using nitrogen, measurements were taken from \( H^*=1.68 \text{ to 100} \text{ Å} \) for mesoporous carbon at IV capillary condensation pressure is increased. The condensation pressure compression of the nitrogen in the condensation pressure consideration of the pore in Figure 7. As the slit width of the pore, where \( V_{sat} \) throughout the pore 

Figure 5. Nontlocal theory isotherms for nitrogen adsorbed in carbon mesopores at 77 K. The pore widths, reading from left to right, are: \( H^*=6, 7, 8, 9, 10, 12, 14, 20, 40, 60, \) and 100.

Figure 6. Nonlocal theory isotherms for supermicropores are: \( H^*=3.75, 4, 5 \text{ Å} \).
\[ V_{ad} = \frac{1}{2} \rho_{DF} H A V_{STP} \]

where \( V_{ad} \) is the uptake of nitrogen (cm\(^3\) at STP/g of carbon). This procedure gave a value of \( \varepsilon / k = 53.22 \) K as the one best fitting the pressure at which the monolayer forms. For oxide materials a similar procedure was followed, using adsorption data for a nonporous NBS alumina [8].

With these fitted potential parameters, individual pore isotherms were generated using nonlocal theory for a range of pore sizes. For carbons these ranged from \( H^* = 1.68 \) to 100 (6.0 Å to 357 Å) at \( T = 77 \) K. Nitrogen adsorption isotherms in mesoporous carbon slits are shown in Figure 5. Pores in this size range exhibit type IV capillary condensation behavior. At low pressures, a monolayer is formed; as the pressure is increased, additional multilayers are adsorbed, until the condensation pressure is reached, whereupon a phase transition to the liquid state occurs. Above the condensation pressure, there is a gradual increase in the mean density due to compression of the nitrogen in the liquid-filled pore. As the pore width is reduced, the condensation pressure decreases, as shown in Figure 6. This follows from consideration of the solid-fluid slit potentials, shown for several pore widths in Figure 7. As the slit walls move closer together, the bulk-like region in the center of the pore, where \( V_{ad} \) is approximately zero, disappears, and adsorption is enhanced throughout the pore space. In addition, the proximity of the adsorbed fluid layers on opposing walls increases fluid-fluid interactions, and further promotes the adsorption of multilayers. A transition from capillary condensation to continuous filling occurs at a critical width of \( H^* = 3.8 \), or 13.6 Å (e.g. isotherm \( H^* = 3.75 \) in Figure 6). Interestingly, there is a second region of discontinuous pore filling in the nonlocal theory isotherms, separate from the condensation region, at pore widths below the critical width \( H^* = 3.8 \). From Fig. 8 we see that for pore widths between \( H^* = 2.55 \) (9.1 Å) and \( H^* = 3.6 \) (12.8 Å), a 0→1 monolayer transition occurs wherein the

![Figure 6. Nonlocal theory isotherms for nitrogen adsorbed in carbon supermicropores at 77 K. The pore widths, reading from left to right, are: \( H^* = 3.75, 4, 4.25, 4.5, 5, \) and 6.](image-url)
Figure 7. Wall-fluid potentials for nitrogen on graphite for selected slit pore widths $H^*$ (indicated by the numerals). The wall-fluid potential $V_{w-f} = V_{w-f}/\varepsilon_H$ is plotted as a function of position in the pore.

Figure 8. Nonlocal theory isotherms for nitrogen adsorbed in carbon supermicropores at 77 K. The pore widths, reading from left to right, are: $H^*$=2.5, 2.6, 2.75, 3, 3.25, 3.5, and 3.75.

Figure 9. Nonlocal theory isotherms for nitrogen adsorbed in ultramicropores and supermicropores at 77 K. The pore widths are shown from left to right, with pore widths smaller than $H^*=1.69$ (6.0 Å). The pore space is inaccessible.
incomplete monolayer on each pore wall abruptly fills to completion. At T=77 K there is a narrow band of continuously filling pores between H₂* and H₃*. Although the pores in the size range from H₃* to H₂* fall within the IUPAC supermicropore classification (9.1 to 13.6 Å), the phase transition in these slits is atypical of the continuous filling normally expected for such pores. However, Gibbs ensemble Monte Carlo simulations (Section 5) confirm the presence of a 0→1 monolayer transition in pores that can accommodate approximately two complete layers of adsorbate.

For still smaller pore widths, a return to continuous pore filling is observed (Figure 9). Pores of this size, corresponding to the IUPAC ultramicropore range, are too narrow to accommodate more than a single layer of adsorbate. The shape of the ultramicropore isotherms are similar to the IUPAC Type I isotherm, characteristic of micropore adsorption, although the IUPAC representation uses a linear rather than a logarithmic pressure axis. As Figure 7 illustrates, the two minima of the solid-fluid potential coalesce into a single minimum at a pore width of H*=2.25 (8.0 Å). This enhances the potential well strength, which is maximized to roughly double its original depth at a pore width of H*=1.94, or 6.9 Å. A corresponding reduction in the filling pressures is seen, with the minimum (at H*=1.94) occurring at approximately P/P₀=10⁻¹⁰, a pressure on the order of 0.1 microtorr. As the pore width is reduced beyond this minimum, the repulsive portions of the opposing wall potentials begin to overlap. Hence, there is a rapid rise in filling pressure as pore width decreases below H*=1.94 (Fig. 9). For pores with physical width narrower than H*=1.69 (6.0 Å), the entire solid-fluid slit potential is repulsive, and thus the pore space is inaccessible to nitrogen and no adsorption occurs. It is observed that

![Figure 9. Nonlocal theory isotherms for nitrogen adsorbed in carbon ultramicropores at 77 K. The pore widths, reading the solid lines from left to right, are: H*=1.94, 2.25, and 2.5. For pore widths smaller than H*=1.94, the filling pressure increases with decreasing width, as shown by the dashed lines, reading from left to right: H*=1.8, 1.75, 1.72, 1.7, and 1.69.](image)
the mean density of nitrogen in the ultramicropores (H less than 9.1 Å) is considerably reduced, due to exclusion of the adsorbate from the region near the slit walls. Only in the largest mesopores (e.g. Fig. 5) does the mean fluid density in the pore approach the bulk saturated liquid density of $\rho^*=0.792$. Although the IUPAC designation of pore sizes is a useful guide to anticipating pore filling behavior, it is evident from the results presented in this section that the nature of the adsorption depends as much upon the adsorbate characteristics as it does upon the structure of the absorbent. For example, if the size of the adsorbate molecule was increased, and all other potential parameters were held constant, some of the slits that exhibited capillary condensation for the original value of $\sigma_k$ would fill continuously were they to adsorb the larger fluid molecules. Therefore, it is more relevant to devise a classification scheme that uses a pore size scaled with respect to the adsorbate molecular diameter, and that also accounts for the influence of temperature.

A comparison of the filling behavior predicted by nonlocal theory and Gibbs ensemble Monte Carlo shows good agreement for both the density profiles in the pore and the adsorption isotherms, for the whole range of pore widths from the ultramicropore region to large mesopores. The Gibbs result also verifies the presence of the 0→1 monolayer transition found in the theoretical isotherms for supermicropore-sized slits. Adsorption isotherms calculated from theory and simulation are compared in Figure 10, for a range of pore widths. In each case, the filling pressures predicted by nonlocal theory and Gibbs simulation are in excellent agreement. Further, the simulation isotherms are consistent with the IUPAC “stepped” or IUPAC “staircase” models for the adsorption of simple gases on carbon (still subcritical) and the Lennard-Jones fluid on a lower reduced temperature and the phase splitting in the Gibbs simulation is quantitatively accurate.

The variation studied [6] for the adsorption of the are also temperature dependent on temperature, with a change in range of pore widths from 1.1 to 5.0 Å (“stepped” or IUPAC “staircase” models for the adsorption of simple gases on carbon) and a change in the Lennard-Jones fluid on a lower reduced temperature.) The results suggest that an upper limit to the adsorption should be sought at the intermediate between the three-dimensional $\langle \rho k \rangle$ and the two-dimensional $\langle \rho k \rangle$ respectively. The pore volume is controlled by the number of adsorbate molecules in the pore; in the case of the slit pores, it is not strictly two-dimensional.

7. Pore Size Distribution

The overall pore size distribution of the slit pores is given by a lognormal distribution, where the parameters that define the lognormal distribution and the probability density function are used to represent the size distribution of the slit pores.

$$f(H) = \frac{n}{\sum_{i=1}^{n} \alpha_i H_i^2} \frac{2}{\pi} \sum_{i=1}^{n} \frac{\alpha_i}{\gamma_i} H_i (2\pi)^{1/2}$$

where $n$ is the number of slit pores, and $\gamma_i$ are used to represent the size distribution of the slit pores.

To determine the accuracy of the adsorption data, the theoretical pressure function of pressure...
agreement. Furthermore, the vapor and liquid branches of the theoretical and simulation isotherms agree quantitatively over the range of pressures sampled. There are some differences between theory and simulation for the adsorbed densities in smaller pores; this may arise because mean-field density functional theory predicts a higher bulk fluid critical temperature $T_c$ than is obtained from simulation results for the Lennard-Jones fluid [30]. Hence, the nonlocal theory isotherms at $T=77$ K are at a lower reduced temperature $T/T_c$ than the corresponding Gibbs simulation isotherms, and the phase splitting in the theoretical calculation is therefore more pronounced than in the Gibbs simulation. Overall, however, the nonlocal theory provides a quantitatively accurate description of pore filling.

The variation of the adsorption isotherm with temperature has also been studied [6] for the range 70–85 K. The critical slit widths, $H_{14}^*$, $H_{15}^*$ and $H_{13}^*$ depend on temperature. At 70 K there are no continuously filling pores, but rather a range of pore widths which exhibit two discontinuous jumps in the isotherm. These "stepped" or IUPAC Type VI isotherms are typical of low temperature adsorption of simple gases on carbon surfaces [4,19]. At the higher temperature of 85 K (which is still subcritical) the range of continuous filling is broader than at 77 K. The results suggest that an upper critical temperature for the monolayer transition in nitrogen adsorption should occur slightly below $T_{cr}^*=1.0$ (94 K). This critical temperature lies intermediate between the bulk Lennard-Jones fluid two-dimensional [31] and three-dimensional [32] critical temperatures of $T_{cr}^*=0.515$ and $T_{cr}^*=1.316$, respectively. The pores which exhibit the 0-1 monolayer transition condense two layers of adsorbate, one on each surface. Thus, it follows that $T_{cr}<T_{cr}$ due to the effect of confinement, and also $T_{cr}>T_{cr}$. Since the adsorbed molecules interact with molecules in the opposing film layer as well as those in their own layer (i.e. the fluid is not strictly two-dimensional).

7. Pore Size Distribution: Slit Carbon Pores

The overall sorbent structure is envisioned as an array of noninteracting individual slit pores with a distribution of pore widths described by a function $f(H)$. Clearly this distribution function must be non-negative for all pore widths $H$. For amorphous sorbents such as carbons, it is reasonable to assume also that $f(H)$ is continuous. Two functions which satisfy these requirements are the gamma distribution and the lognormal distribution. The gamma distribution is

$$f(H) = \sum_{i=1}^{m} \alpha_i (\gamma H)^{\beta_i} \frac{1}{(\beta_i)H} \exp(-\gamma H)$$

while the lognormal distribution is

$$f(H) = \sum_{i=1}^{m} \frac{\alpha_i}{\sqrt{2\pi} H} \exp \left( -\frac{(\ln H - \beta_i)^2}{2\gamma_i^2} \right)$$

where $m$ is the number of modes of the distribution, and $\alpha_i$, $\beta_i$, and $\gamma_i$ are adjustable parameters that define the amplitude, mean and variance of mode $i$. These equations are used to represent the PSD in the fitting of adsorption integral. The choice of the PSD function is discussed at greater length below.

To determine the PSDs of porous carbons from experimental nitrogen adsorption data, the set of model isotherms presented in Section 6 are correlated as a function of pressure and pore width. The adsorption integral, equation (1), is then

\[\text{isotherms calculated for absorption in carbon fiber isotherms for } 2.5, 3, 3.75, 5, 8\text{ from pore-pore interaction results.}\]
solved numerically, inserting one of the model pore size distribution functions (equations (20) and (21)) and employing a simple minimization algorithm to optimize the parameters $\alpha$, $\beta$, and $\gamma$ of the PSD function. A least squares error minimization criterion is used to determine the optimum fit. The choice of the number of modes in the PSD function is arbitrary, provided that enough are used to give $f(H)$ sufficient flexibility. In practice, the number of inflection points in the experimental isotherm can be used as an estimate of the number of modes required to yield an acceptable fit. This assertion is made on the basis of the one-to-one correspondence of filling pressure to pore width in the nonlocal theory results in Figure 1 (excluding the special case of the ultramicropores, with $H<6.9$ Å). All PSD results that follow were obtained using a trimodal gamma distribution, eqn. (20) with $m=3$, except where otherwise noted.

The PSDs of three carbons have been fitted using this method. The standard pretreatment for all of the samples was a bakeout at 300°C for 16 hours at 10⁻⁵ torr. The nitrogen uptake data was collected by static flow measurement on a Coulter Omnisorp. In Fig. 11 and Fig. 12 we present the isotherm and calculated PSD for carbon CXV, a micro/mesoporous carbon. The Kelvin-type models yield predictions of unphysical pore widths, and are clearly not applicable in this pore range. The PSD from the HK method is offset to lower pore sizes relative to the nonlocal DFT results, due to differences in the predicted micropore filling pressures. The DFT isotherm is in good agreement with the experimental data. There is some deviation around $P/P_o = 10^4$, which is thought to arise from the mean-field approximation of equation (10). In the present version of nonlocal theory used, it is not possible to reproduce the large uptake near the saturation pressure without slightly overestimating the uptake at the monolayer filling pressure. It is known that density functional theory predicts a higher bulk fluid critical temperature than is found from comparable Lennard-Jones molecular simulations. Therefore, at subcritical temperatures, the nonlocal theory exhibits too sharp a rise in the isotherm at the monolayer pressure, as is seen in Figure 11. Nonetheless, since nonlocal theory gives a reasonably good description of micropore filling, the nonlocal results are considered the most realistic interpretation of the PSD.

In Figs. 13 through 16 we show the isotherms and PSDs for two highly microporous carbons, AC610 and AX21. Nonlocal theory again gives a good fit over the full pressure range of the experimental isotherm. The PSDs which correspond to these isotherm fits are also shown in these figures. Only the DFT and HK results are shown, since the Kelvin-based methods give non-physical results for such small pores. Although the Horvath-Kawazoe method was specifically developed for interpreting the PSDs of microporous carbons, and gives a plausible fit to the experimental sorbent isotherms, the HK theory consistently underpredicts the position of the maximum in the PSD relative to the DFT results, due to differences in the predicted micropore filling pressures from the two theories. Since DFT is the most realistic model of pore filling, the DFT results are the most reliable. Comparisons of these predictions for the isotherms and PSDs with those calculated from the local form of DFT [33] have also been made and described elsewhere [7]. The local theory is based on the approximation that the free energy density depends only on the local density at the point of interest, i.e., $\bar{\rho}(r) = \rho(r)$ in eqn. (12). It yields PSDs that have too sharp a peak in the micropore region for all three carbons; for CXV local theory also gives this peak at too small a pore size.
The distribution functions in an algorithm to optimize the least squares error of the number of points in the experimental results required to yield an s-to-one correspondence is in Figure 1 (excluding PSD results that follow (20) with m=3, except for the standard 16 hours at 10^-4 torr. measurement on a Coulter and calculated PSD for models yield predictions in pore range. The PSD nonlocal DFT results, 1. The DFT isotherm is deviation around P/P_e of equation (10). In order to reproduce the large data the uptake at the isotherm theory predicts a substantial Lennard-Jones repulsion, the nonlocal theory the pressure, as is seen in an ably good description of the most reliable 20 PSDs for two highly again gives a good fit in. The PSDs which agrees. Only the DFT and non-physical results for specifically developed gives a plausible fit to the density underpredicts the results, due to differences in energies. Since DFT is the are the most reliable, it is with those calculated described elsewhere (7). energy density depends on {\rho}(r) in eqn. (12). It is on for all three carbons; size.

Figure 11. Nitrogen adsorption on microporous carbon CXV at 77 K. Symbols denote the experimental uptake measurement; the solid, short-dashed and long-dashed lines indicate the fitted isotherms from nonlocal theory, the HK equation, and the Kelvin equation.

Figure 12. Pore size distribution of carbon CXV. The solid, long-dashed, and short-dashed lines indicate the fitted distributions from nonlocal theory, the HK equation, and the Kelvin equation.
Figure 13. Nitrogen adsorption on microporous carbon AC610 at 77 K. Symbols denote the experimental uptake measurement; the solid and dashed lines indicate the fitted isotherms from nonlocal theory and the HK equation.

Figure 14. Pore size distribution of carbon AC610. The solid and dashed lines indicate the fitted distributions from nonlocal theory and the HK equation.

Figure 15. Nitrogen adsorption on microporous carbon AC610 at 77 K. Symbols denote the experimental uptake measurement; the solid and dashed lines indicate the fitted isotherms from nonlocal theory and the HK equation.

Figure 16. Pore size distribution of carbon AC610. The solid and dashed lines indicate the fitted distributions from nonlocal theory and the HK equation.
Figure 15. Nitrogen adsorption on microporous carbon AX21 at 77 K. Symbols denote the experimental uptake measurement; the solid and dashed lines indicate the fitted isotherms from nonlocal theory and the HK equation.

Figure 16. Pore size distribution of carbon AX21. The solid and dashed lines indicate the fitted distributions from nonlocal theory and the HK equation.
8: Pore Size Distributions: Cylindrical Aluminosilicates and Oxide Pores

The density functional theory model and pore size analysis method described in previous sections have been extended to the interpretation of the isotherms of aluminosilicate-based sorbents (e.g., silicas, aluminas, zeolites). As discussed in Section 3, aluminosilicate pore channels are of first approximation cylindrical in shape, in contrast to the slit pore geometry of carbon sorbents. The pore size distributions vary considerably within the aluminosilicate family, from the highly discrete pore geometries typical of zeolites and aluminophosphates to the disordered network of pore channels characteristic of amorphous sorbents such as a-alumina. Characterization of amorphous microporous aluminosilicates presents similar challenges to the analysis of microporous carbons.

As in the carbon pore size analysis, nonlocal density functional theory is used to generate model isotherms for the pore fitting analysis of silicas. Aside from the change in geometry from a slit pore to a cylindrical pore, and from a carbon surface to an oxide surface, the density functional procedure is identical in all respects to the method outlined in the previous section.

Nonlocal density functional theory isotherms were calculated for pore radii ranging from R*=2 to 50 (7.0 Å to 179 Å) at T=77 K. Both the theory and simulation produced the same filling features: monolayer adsorption at P/P₀=10⁻¹⁴; multilayer formation at P/P₀ =0.05; and capillary condensation slightly below P/P₀ =0.2. For the micropores, some discrepancies are evident, as nonlocal theory predicts a smaller

critical pore radius compared to the continuous filling. This transition should occur for the corresponding Giinter equation. The nonlocal theory and simulation predict a higher bulk filling, but the nonlocal theory does not require a free energy function. The nonlocal model is more accurate for narrow pores, which gives a progressively lower bound on the pore size, a lower bound on the carbon.

In Figure 17 the experimental data is compared to the nonlocal theory, as well as to simulation. The filling pressures are estimated from the isotherms.

The density functional theory also agrees in general, whereas the simulation data shows a slight shift in the capillary filling pressure. For example, according to simulation the first capillary condensation occurs at P/P₀=0.0013; for the same system, nonlocal theory predicts it at a filling pressure of P/P₀=0.002. As the pore size increases, the deviation between the two theories increases. Below 20 Å, the adsorption proceeds almost linearly, which fills with nitrogen. The pore width for which the nonlocal theory, however, is 30 Å.

The DFT model illustrates the difference between the experimental adsorption data and the simulation. The experimental carbon pore size analysis is used to optimize the coefficients of the empirical equation provided by Orvath and Kawazoe(2). The result for the Saito-Foley line-averaged case overlaps closely with the Kelvin equation curve.

Figure 17: Filling pressures predicted by the Kelvin equation (K), the Saito-Foley equation (SF), density functional theory (DFT) and molecular simulation (points) for nitrogen adsorption in cylindrical oxide pores at 77 K. The Saito-Foley results are calculated from the area-averaged case(8) using the sorbent oxide ion parameters reported in the original paper(3) and the sorbate nitrogen parameters reported by Horvath and Kawazoe(2). The result for the Saito-Foley line-averaged case overlaps closely with the Kelvin equation curve.
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critical pore radius than simulation for the transition from capillary condensation to
continuous filling. For example, nonlocal theory suggests that a vapor-liquid phase
transition should occur in the oxide pore of radius R*=2.5, whereas Gibbs simulation
indicates that no such transition occurs. The micropore filling differences between
theory and simulation may arise in part because mean-field density functional theory
predicts a higher bulk critical temperature T\(_{c}\) than is obtained from simulation; thus,
the nonlocal theory isotherms are at lower reduced temperature T/T\(_{c}\) than the
Gibbs simulation isotherms. Also, in the limit of small pore radius, nonlocal theory
does not produce the correct one-dimensional limit of the
free energy functional in contrast to the two-dimensional case where the theory is
accurate for narrow slit pores. Hence, as the pore radius is reduced, nonlocal theory
gives a progressively poorer representation of the pore filling behavior. This imposes
a lower bound on the pore size range for which the nonlocal theory results are valid.

In Figure 17 the capillary filling pressures predicted by Gibbs simulation and
nonlocal theory, as well as by the Kelvin equation and the Saito-Foley method, are
compared. The filling pressures of pores that do not undergo a phase transition are
estimated from the inflection point in the adsorption isotherm.

The density functional theory and Gibbs simulation filling pressures are in close
agreement, whereas the Kelvin and Saito-Foley relations both overestimate the
capillary filling pressures relative to the statistical mechanics calculations. For
example, according to nonlocal theory, a 9 Å radius oxide pore condenses nitrogen at
P/P\(_0\)=0.005; for the same pore size the Saito-Foley correlation reports a much higher
filling pressure of P/P\(_0\)=0.1. As the pore radius decreases, the disparity between the
theories increases. Because the classical methods overestimate the filling pressures of
the pores, these adsorption models will underestimate the mean pore size distribution.
Another example illustrates this point: according to the Saito-Foley model, a pore
which fills with nitrogen at pressure P/P\(_0\)=0.01 has a radius of approximately 6 Å.
Nonlocal theory, however, interprets the pore size in this case to be 10.5 Å.

The DFT model isotherms for N\(_2\) in cylindrical pores have been used to fit
experimental adsorption data for sorbents which have oxide surfaces. As in the
carbon pore size analysis a least-squares minimization algorithm is employed to
optimize the coefficients of a multimodal gamma distribution, equation 20, which is
chosen to represent the sorbent PSD function. The adsorption integral, equation 1,
provides the appropriate minimization criterion. The fitted isotherm of a
meso/macroporous silica is shown in Figure 18.

The experimental isotherm is reasonably well fitted by the theoretical model. The
nonlocal theory pore size distribution is shown in Figure 19. The silica has a
mesopore peak at 70 Å and a broad macropore band which extends beyond the
resolution of the nitrogen adsorption measurement.

These results indicate that the nonlocal theory pore filling model can interpret
adsorption data for a wide spectrum of pore sizes. It should also be applicable to the
pore size analysis of other aluminosilicates such as activated alumina and pillared
clays.
9. Simulation Studies of Carbon

In previous theories, the thermodynamic hysteresis of uniform size, which are believed to affect adsorbents which have a pore size distribution, describe much of the adsorbed isotherms. Nevertheless, it is important for some isotherms that have been obtained, the shape of the isotherms attributed to connectivities.

In our studies of the carbon, Figure 20 is used to calculate the volume is situated be truncated to produce a cavity potential is obtained. The nitrogen-nitrogen potential is described in section 4.

In both the narrow width approximately the initial monolayer of the cavity adjacent to adsorbing molecules, and thus the filling pressure of the narrow pore.

In order to reproduce the technique is required to produce a metastable liquid phase and the surface area for the simplified model for the simplified model.

The feasibility of gas transport by Cielinski and Qadri simulation was concluded from grand canonical depletion was small; every time a molecule molecules were chosen to maintain the temperature maintained.

GCMC methods[3] were successfully in a
9. Simulation Studies of Pore Blocking Hysteresis in Model Porous Carbon

In previous theoretical[7], simulation[34,35] and experimental[36] studies, thermodynamic hysteresis has been observed to arise from fluid metastability in pores of uniform size, where pore blocking cannot occur. Connectivity effects, however, are believed to account for the desorption hysteresis observed in experiments on sorbents which have a size distribution of multiply connected pores[5]. When the pore size distribution is accounted for, the independent pore model of section 3 can describe much of the qualitative behavior of experimentally measured sorption isotherms. Nevertheless, pore blocking and networking effects are believed to be important for some adsorption classes, particularly types IV and V. Type IV isotherms have been divided into four subclasses in the IUPAC scheme[1], based upon the shape of the hysteresis loop; the variations in the shape of the loop are attributed to connectivity effects between pores of different size.

In our studies of the effect of connectivity, the simplified slit pore junction model of Figure 20 is used to model nitrogen adsorption in porous carbon at 77 K. The pore volume is situated between two semi-infinite graphite slabs, with the innermost slab truncated to produce a cavity connected to the pore channel as shown in Figure 21. The lateral boundaries of the simulation cell are periodic. The graphite layers are assumed to be smooth and structureless, and are held rigid, the nitrogen-wall potential is obtained by summing over all carbon atoms in the cavity/pore regions[8]. The nitrogen-nitrogen pair interaction is modeled using the Lennard-Jones potential described in section 3.

In both the narrow channel region (slit width approximately \( 4.5 \) \( \sigma_n \)) and the larger cavity region (slit width approximately \( 6.5 \) \( \sigma_n \)) there is a potential well, adjacent to each pore wall, where the initial monolayer forms. Additional low energy regions are located at the corners of the cavity adjacent to each graphitic half-plane; these sites are particularly attractive to adsorbing molecules. The external potential is weakest at the center of the cavity, and thus the filling pressure of the cavity can be expected to be higher than the filling pressure of the narrow channel.

In order to reproduce pore blocking (a non-equilibrium process) a simulation technique is required which maintains phase equilibrium between the bulk vapor phase and the surface-connected pores, while allowing the development of a metastable liquid phase in the blocked interior pores. In the current study we choose to do this using a grand canonical molecular dynamics (GCMD) method[8], adapted for the simplified model pore junction geometry of Figure 20.

The feasibility of grand canonical molecular dynamics GCMD was first demonstrated by Cielinski and Quirke in 1985[37]. They tested an ad hoc GCMD method for the properties of bulk LJ fluids. The chemical potential of a molecular dynamics simulation was controlled by superimposing the particle insertion and deletion step from grand canonical Monte Carlo simulation. As long as the number of creations and deletions was small, thermodynamic and transport properties (diffusion coefficients) were accurately predicted. In their work a trial insertion and deletion was attempted every time a molecule crossed the periodic boundaries. The velocities of the inserted molecules were chosen from a Maxwell-Boltzmann distribution and the overall temperature maintained by temperature scaling. Later workers have developed other GCMD methods[38,39]. The Cielinski and Quirke method has recently been used successfully in a study of nonequilibrium mass transport in micropores[38].
For the present model, the phase is maintained by buffer zone between the interior cavity can open the liquid-filled cavity regions, and pore blocks.

During the GCMD the blocks be large enough to equilibrate the molecules are under For bulk systems it have be set equal to the fluid cell. However it for inhomogeneous system, with pore diffusion a low insertion/deletion.

Figure 22: Hysteresis carbon network adsorption simulation. The desorption results predicted by nonlocal in a carbon slit pore isotherm. The data (left) and adsorption.
For the present model pore junction, contact between the pore network and a bulk phase is maintained by partitioning the narrow pore into two regions, as shown in Figure 21: A "bulk" region, of length \( L_x \), spanning the periodic boundary in the x-direction and a "pore" region, of length \( L_p \), adjacent to the junction with the cavity region, where \( L_p = L_z = 3 \sigma_c \). In the cavity region and the pore region normal canonical (constant NVT) molecular dynamics employed. In the bulk region the chemical potential is maintained at a fixed value using GCMD. In order that a metastable liquid state can develop within the interior cavity during desorption, the geometric parameter \( L_p \) is assigned a sufficiently large value (here \( 3 \sigma_c \)) to produce a buffer zone between the cavity region and the bulk/equilibrated region. Thus the interior cavity can only adsorb and desorb molecules by diffusion across the pore region of Figure 21. If GCMD were imposed in both the bulk and the pore region, the liquid-filled cavity could equilibrate at the interface between the pore and cavity regions, and pore blocking would not occur.

During the GCMD the rate of insertion/deletion attempts must be carefully selected to be large enough to equilibrate the bulk region, but not so large that the trajectories of the molecules are unduly influenced by large fluctuations in the number of molecules. For bulk systems it has been shown [40] that the rate of insertion/deletion attempts can be set equal to the flux of molecules across the periodic boundaries of the simulation cell. However it is found that this procedure is ineffective for GCMD simulation of inhomogeneous systems (see also [41]). Because of the low flux rates associated with pore diffusion a substantial drift from the bulk-equilibrated state occurs; i.e., for low insertion/deletion rates, the system becomes uncoupled from the mass reservoir.

![Figure 22: Hysteresis loop for nitrogen adsorption isotherm in porous carbon network of Figure 20 at 77 K, calculated from GCMD simulation. The open and solid circles denote the adsorption and desorption results, respectively. The spinodal limits of stability predicted by nonlocal density functional theory for nitrogen adsorption in a carbon slit pore of width \( \sigma_c \) = 6 are superimposed on the junction isotherm. The dashed lines show the spinodal limits for desorption (left) and adsorption (right).](image-url)
and a constant chemical potential is not maintained in the bulk region. In this work the insertion/deletion trial rate varies between 25 to 50 trials per timestep, with more trials made at higher densities due to the decreased acceptance probability. At this rate, the measured chemical potential in the bulk region (by test-particle methods) was found to be consistent with the imposed chemical potential.

Figure 22 reports results for the adsorption and desorption of nitrogen in the carbon pore junction model of Figure 20 using CQ-GCMD simulation[8]. The reduced chemical potential $\mu^r=\mu/\varepsilon_p$ is increased from a low initial value in increments of 0.5, each increase followed by an equilibration period. The desorption isotherm is similarly obtained by step decreases of 0.5 starting from the saturated liquid state. The complete sorption isotherm required 3.5 million timesteps due to the slow diffusion in the cavity region.

The spinodal adsorption limit $\mu^*=6.38$ and desorption limit $\mu^*=6.94$ from nonlocal theory are superimposed on the network isotherm. Spontaneous adsorption and desorption occurs when the respective limits of thermodynamic stability are crossed. This hysteresis loop resembles IUPAC type H4, representative of porous sorbents which have a significant fraction of large pores, coupled with some much smaller pores. Because the filling pressure of the small pores is very low (Figure 1), the fluid in the large pore reaches its spinodal pressure before emptying occurs in the small pores. Immediate vaporization occurs in the large pore, driving liquid out of the smaller connecting pores and yielding a hysteresis loop of type H4.

By suitable variation of the pore junction geometry, the other IUPAC hysteresis subclasses should be reproducible. Larger pore network dimensions are expected to yield the H1, H2 and H3 subclasses, while increasing the pore width ratio Hc/Hp is likely to produce a more pronounced type H4 loop.

Future work will address the relation between the network geometry and the observed hysteresis behavior.

10. Discussion and Critique of Method

Error in the PSD calculation can arise from three sources: (1) the experimental uptake data $\Gamma(P)$; (2) the model used for the adsorption isotherms; and, (3) mathematical uncertainties associated with the selection of the PSD function $f(H)$ and the solution of the adsorption integral. We briefly consider each of these factors in turn.

10.1. Experimental Limitations

The characterization of strongly adsorbing materials such as carbons and oxides requires careful measurement of the low pressure isotherm. If such pressures cannot be attained, the PSD calculation must necessarily be truncated at the experimentally imposed lower bound. For the fitting procedure, the full range of pore widths is employed in the calculations, since changes in the density of the liquid-filled micropores contribute to the overall isotherm. It is only after the optimum PSD is determined that the distribution is truncated. For porous graphitic carbon, the theoretical calculations suggest that the minimum filling pressure is approximately $10^{-16}P_0$, or $10^{-7}$ torr. The experimental isotherms presented in this work sample pressures as low as $10^{-10}P_0$. Thus a portion of the ultramicropore range is not accessible using these measurement. Recently, we have been able to modify the Coulter Sorptometer to achieve relative pressures $P/P_0$ down to less than $10^{-7}$, and to

determine adsorption methods that include this low pressure.

When calculating adsorption, it is important to allow for slow rates of diffusion. This may be evaluated through uptake measurements and the use of an automated flow system. In a limited micropore volume, improperly equilibrated samples may underestimate the population.

For all of the isotherms, the desorption branch, as well as the adsorption branch, due to pore blocking, due to network hysteresis. For the blocking moves the entire isotherm, with the adsorption pressure, which will incorrectly skew the results.

10.2. Accurate Data

A crucial step in obtaining the best possible data is to fit the surface which closely determined. The work with Vulcan carbon or a N2 adsorption on sample or the porous surface. While the data of physisorbed gases, the results would require elevated pressures [11]. Hence, it is more realistic effective potential of a sample is that the surface contact is used.

Several key aspects are implicit in the model. In the individual pore shapes, as in the condition of adjacent pore shapes, the solution of the adsorption appearing.

PSD results are obtained for cylindrical-shaped geometry, and information about the shape, heterogeneity, and the use of triangular-5 for microporous carbons. The pore shape is thus an isotropic heat of adsorption, and model structure.
determine adsorption isotherms for nitrogen and methane on nonporous carbons that include this low pressure range [33].

When calculating PSDs for microporous sorbents such as AX21 or AC610, it is important to allow for kinetic limitations in the adsorption measurement due to the slow rates of diffusion through the narrow pores. For AC610, for example, static uptake measurements showed a markedly increased adsorption at low pressure over automated flow measurements using the Coulter Sorptometer, since the diffusion-limited micropore volume fills at these pressures [7]. The implication is that improperly equilibrated flow adsorption measurements will yield PSDs that underestimate the population of micropores in the sorbent.

For all of the PSD fitting analysis, only the adsorption branch of the sorbent isotherm is used in the solution of the adsorption integral. We avoid fitting the desorption branch, as there may be hysteresis effects in this branch associated with pore blocking, due to the connectivity of the pore structure. This type of blocking, termed network hysteresis, is commonly observed in mesoporous sorbents. Pore blocking moves the desorption branch to an emptying pressure below that of the adsorption pressure. Consequently, fitting the PSD to the desorption isotherm would incorrectly skew the PSD to smaller pore widths.

10.2. Accuracy of the adsorption model

A crucial step in assembling accurate model isotherms from nonlocal theory is to obtain the best possible estimate of the solid-fluid potential parameters. To do so, it is desirable to fit the parameters to the isotherm of a nonporous sorbent that has a surface which closely resembles that of the porous specimens whose PSDs are to be determined. The work presented here uses a nonporous isotherm measured on Vulcan carbon or a NBS alumina. Clearly it is unlikely that either the nonporous sample or the porous materials considered in Sections 7 and 8 actually have ideal surfaces. While the pretreatment conditions should be sufficient to remove any physically adsorbed gases, the removal of chemisorbed species such as carbon monoxide would require elevated temperatures that could alter the pore structure of the sorbent [11]. Hence, it is more accurate to view the solid-fluid parameters as representing the effective potential of a graphite-like surface. The main assumption in the model, then, is that the surface concentration of functional groups is the same for pores of all widths. These factors may account for the differences in the nonlocal theory fit to the CXV isotherm at the monolayer filling pressure.

Several key assumptions concerning the structure of the porous material are implicit in the model. One is the neglect of connectivity in the modeling of adsorption in the individual pores. If the aspect ratio of pore length to pore width is not large, then it is possible, in fact likely, that the adsorption in a pore would be influenced by the condition of adjacent pores. This type of pore-pore correlation would make the solution of the adsorption integral difficult. A second assumption is that, because the PSD results are obtained by assuming that all of the pores have either a slit- or cylinder-shaped geometry, it is not possible to infer from the PSD additional information about the true morphology of the sorbent. In principle, it is possible to add shape heterogeneity to the modeling of the pore structure, although this necessarily complicates the solution of the adsorption integral. For carbon pores there is experimental evidence [10] that suggests a slit-like geometry. Alternatively, the use of triangular-shaped pores of uniform size has been proposed [42] as a model for microporous carbon. This geometry introduces an energetic heterogeneity due to the pore shape, which gives better agreement to experimental measurements of the isosteric heat of adsorption than is obtained using uniformly sized slit pores as the model structure. However, it has been demonstrated [43] that it is possible to model
the molar heat of adsorption of methane on carbon by using a size distribution of slit shaped pores, a similar approach as is used in this work for modeling nitrogen adsorption. By using a distribution of pore sizes, a different sort of heterogeneity is introduced, which nonetheless seems equally capable of modeling calorimetric data for porous carbons. A third assumption is that the pore size and geometry is not changed on changing the pressure or temperature (no pore swelling, etc.).

There is no theoretical limitation to modeling the PSD using supercritical adsorption data, in place of the subcritical isotherms presented in this analysis. Indeed, it would be advantageous to compare, for consistency, the PSD results calculated from measurements at multiple temperatures. However, the interpretation of supercritical isotherms may prove more difficult, as the filling transitions in these isotherms tend to be less distinct than the condensation jumps observed in subcritical isotherms.

A further limitation of the model is the use of simplified intermolecular potentials to describe both the fluid-fluid and fluid-solid intermolecular potentials. More accurate nitrogen-nitrogen potentials are available, based on site-site LJ terms with or without the addition of quadrupole forces [e.g. 44]. As pointed out by Nicholson [45], these models are effective potentials, so that in fitting parameters to data multibody effects are incorporated in some way; it is likely that such potentials optimized using bulk fluid data may require some modification for confined fluids. Nevertheless they provide a suitable starting point, and potential parameters can be refined as needed through comparisons with low pressure adsorption data. More sophisticated models are also available for fluid-solid interactions; these will vary with the material considered, but should include both direct and induced electrostatic interactions between nitrogen and the wall atoms. For the direct electrostatic interactions between the fluid molecules and the carbon surface electric field, the use of surface quadrupoles located in the carbon basal plane has been suggested by Vernov and Steele [46], and further studied by Bruch [47]. The influence of induction effects, due to interaction between charges or multipoles on the fluid molecules with the induced dipole in the graphite can be included using image methods [e.g. 48,49]. For oxides, aluminoisicates and similar materials, a sum of atom-atom potentials (LJ and Coulombic terms) can be used to approximate the dispersion, repulsion and direct electrostatic terms, with image terms for induction forces.

10.3 Mathematical considerations

The solution of the adsorption integral presents a difficulty in that one is attempting to construct part of an integrand, f(H), from information about the integral \( \Gamma(P) \). In principle, this mathematical problem is ill-posed and will not give a unique solution for f(H) unless an infinite number of data points \( \Gamma(P) \) are available [50]. In practice, however, it is found that a sufficiently large sample of data (typically thirty to fifty points) constrains the shape of f(H) such that the numerical values of the pore size distribution are unique, provided a sufficiently flexible functional form is chosen for the PSD. The functional form of f(H) itself is arbitrary; any description that is suitably flexible to model the carbon PSD is acceptable, provided that the function is nonnegative over all pore widths. To check the uniqueness of the numerical values of the PSDs, the fitting process was attempted using the trinodal lognormal distribution, equation (21), in place of the trinodal gamma distribution. It is found that the lognormal distribution results are essentially indistinguishable from the gamma distribution results [7].
There are some small fluctuations of the fitted isotherms about the experimental isotherms that might suggest a constraint imposed by the fitting procedure, given that the nonlocal theory model of adsorption otherwise seems accurate. Other convolution techniques can be adapted to the solution of the adsorption integral; a review of regularization methods is presented by Szombathy et al. [50].

11. Conclusions

The DFT pore size distribution analysis method presented in this work offers a more quantitatively accurate method for predicting the adsorption behavior for pores of well-defined geometry, and since it is based in fundamental statistical mechanics, offers the possibility of systematic improvement, through the use of more sophisticated potential models, more flexible models for pore structure, etc. Future work is needed to explore the influence of using more accurate potentials for the fluid-fluid and fluid-solid interactions, and to account for networking effects and changes in pore structure under pressure. Further systematic experimental work is needed using different adsorbate gases and different temperatures to see if consistent PSD results can be obtained for selected test adsorbents. Careful attention will be needed to the low pressure part of the isotherm, and to determination of fluid-solid potential parameters from such data. Such experimental studies, when combined with appropriate molecular simulations, are also needed to determine whether such neglected effects as pore shape and chemical heterogeneity exhibit signatures in experimental results that are distinct from the PSD effects.

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