CHARACTERIZATION OF POROUS MATERIALS USING DENSITY FUNCTIONAL THEORY AND MOLECULAR SIMULATION

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1. INTRODUCTION

Characterization methods for porous materials that are based on adsorption measurements involve two distinct types of approximation:

1. A model for the pore structure

2. A theory estimating the adsorption for pores of a particular size

The most commonly used model for pore topology is to represent the material as composed of independent, non-interconnected pores of some simple geometry; usually these are of slit shape for activated carbons, and of cylindrical geometry for glasses, oxides, silicas, etc. Usually, the heterogeneity is approximated by a distribution of pore sizes, it being implicitly assumed that all pores are of the same geometry and surface chemistry. In this case the excess adsorption, $\Gamma(P)$, at a pressure $P$ can be represented by

$$\Gamma(P) = \int_{H_{\text{min}}}^{H_{\text{max}}} \Gamma(P,H)f(H)dH$$

(1)

where $\Gamma(P,H)$ is the excess adsorption for a material in which all the pores are of width $H$ (the local isotherm), and $f(H)$ is the pore size distribution, so that $f(H)dH$ is the fraction of pores with width between $H$ and $H + dH$. The integration in eq. (1) is over all possible pore widths from $H_{\text{min}}$ to $H_{\text{max}}$. Eq. (1) assumes that geometric and chemical heterogeneity are either absent, or can be treated as effectively equivalent to pore size heterogeneity, with regard to adsorption. An alternative approach [1] is to approximate the heterogeneity as due entirely to chemical heterogeneity, so that there is a distribution of adsorbate-adsorbent interaction energies, $\epsilon(\sigma)$, in which case eq. (1) is replaced by

$$\Gamma(P) = \int_{\epsilon_{\text{min}}}^{\epsilon_{\text{max}}} \Gamma(P,\epsilon)f(\epsilon)d\epsilon$$

(2)

where $\Gamma(P,\epsilon)$ is the local isotherm for pores with interaction energy $\epsilon$.

At this level of approximation, the problem is to invert the Fredholm integral of eq. (1) or (2). This is an ill-posed problem in general. The usual method of solution is to assign a functional form to the distribution function $f(H)$ or $f(\epsilon)$, such as a multimodal gamma distribution, and then fit the parameters in this function to a least squares match to the experimental isotherm. In addition to limiting the treatment to only one kind of heterogeneity, eqs. (1) and (2) omit any effects of networking or pore connectivity.

Approximation (2) is more straightforward to deal with. We need a theory that accurately describes the local isotherm in either eq. (1) or (2). The classical approach has...
been to assume that the Kelvin equation, or a modified form of it, correctly predicts the pore filling pressure $P$ (capillary condensation pressure) as a function of pore width. The modified Kelvin equation is

$$\ln\left(\frac{P}{P_0}\right) = -\frac{2\gamma_l}{RT\rho_l}(H - 2t)$$

(3)

where it is assumed that the liquid wets the walls. In eq. (3), $P_0$ is the bulk vapor pressure, $\gamma_l$ is the surface tension, $\rho_l$ is the liquid density, $R$ is the gas constant, $T$ is temperature, and $t$ is the equilibrium film thickness on the pore wall. The film thickness is often obtained from an experimental isotherm carried out on a nonporous substrate of the same material as the porous solid. However, $t$ will depend strongly on the pore width, as well as temperature and pressure, for smaller pores. It has been known for about 20 years, from experiments [2] and from comparisons with exact molecular simulation results for a variety of pore geometries [3-8], that the Kelvin and modified Kelvin equations give pore sizes that are too low, and that the error becomes very large for small mesopores and for micropores. These tests indicate that the Kelvin and modified Kelvin equations give significant errors for pore sizes below about 7.5 nm [2,5]. One such test is shown in Fig. 1, where the pore filling pressure is plotted against pore width for nitrogen in slit carbon pores. In micropores, interactions between adsorbate molecules and the pore surfaces become greatly enhanced. Given that the Kelvin adsorption models largely neglect these gas-solid interactions, it is not surprising that the Kelvin equation yields inaccurate micropore filling pressures.

Density functional theory (DFT) or molecular simulation offer a much more accurate theory for the local isotherm. For simple adsorbates (near-spherical nonpolar molecules) and simple pore geometries (slits, cylinders), DFT is easy to apply, and the results for capillary condensation pressures, and for the remainder of the isotherm, are in

good agreement with experimental data. For non-spherical adsorbates, DFT or simulation predictions may be quite difficult, and the results may be quite structure-dependent. In this paper we will present some examples of applications of DFT to other porous systems in general use.

### 2. DENSITY FUNCTIONAL THEORY

Each individual component of a mixture is assumed to be a hard sphere gas at a fixed temperature $T$, pressure $P$, density $\rho$, and chemical potential $\mu$, temperature $T$, and chemical potential $\mu$, respectively. The external potential $V_{ext}$ is

$$V_{ext}(r) = F[\rho(r)]$$

where $F$ is the intrinsic energy per molecule at position $r$, and the integrals in eq. (4) run over a reference system of fluid $F$. The energy function

$$F[\rho(r)] = \int \frac{\rho(r;4\pi)}{\rho_0} dr$$

where $\rho_0$ is the density of the fluid at a given temperature $T$, and $\rho(r;4\pi)$ is the density of the fluid at position $r$. The attractive part of the fluid $\rho(r;4\pi)$ is the Andersen division of the density function

$$\phi_{at}(r) = \phi_{at}(r)$$

where $\phi_{at}(r) = \frac{1}{\rho_0} 2\pi r^2 dr$ is the density term and $\phi_{at}(r)$ is the density term of the fluid at position $r$. The density term $\phi_{at}(r)$ is the ideal gas term.

The density $\rho(r)$ is the total density of the fluid at position $r$, and it is represented by

$$\rho(r) = \frac{1}{\rho_0} 2\pi r^2 dr$$

The choice of the weight function is an important aspect of any theory used. For higher accuracies, a more sophisticated approximation is introduced, such as the hard-sphere potential in the hard-sphere approximation.
good agreement with exact simulation results. However, it should be born in mind that DFT or simulation provide an answer only to approximation 2 above. As presently applied, the difficulty of describing the pore topology remains.

In this paper we give a very brief account of the methods (Sec. 2). We then show some examples of applications, and compare these more fundamental methods with others in general use.

2. DENSITY FUNCTIONAL THEORY (DFT)

Each individual pore has a fixed geometry, and is open and in contact with bulk gas at a fixed temperature. 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 \( V_{ext} \), the grand potential functional \( \Omega \) of the fluid is [11]

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

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. \( F \) is expanded to first order about a reference system of hard spheres of diameter \( d \),

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

where \( F_s \) is the hard sphere Helmholtz free energy functional and \( \phi_{at} \) is the attractive part of the fluid-fluid potential. In eq. 5, we have invoked the mean field approximation, wherein pairwise correlations between molecules due to attractive forces are neglected. The attractive part of the fluid-fluid potential is represented by the Weeks-Chandler-Andersen division of the Lennard-Jones potential

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

\[
-\sigma_f, \quad |r - r'| < r_m
\]

where \( r_m = 2^{1/6} \sigma_f \) 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,

\[
F_s[\rho(r); d] = kT \int dr \rho(r) \ln(\Lambda^3 \rho(r)) - 1 + kT \int dr \rho(r) f_{ex} \rho(r); d)
\]

where \( \Lambda = h/(2\pi m kT)^{1/2} \) is the thermal de Broglie wavelength, \( m \) is the molecular mass, \( h \) and \( k \) are the Planck and Boltzmann constants, respectively, and \( f_{ex} \) is the excess (total minus ideal gas) Helmholtz free energy per molecule. The latter is calculated from the Carnahan-Starling equation of state for hard spheres [12]. The first term on the right side of eq. (7) is the ideal gas contribution, which is exactly local (i.e. its value at \( r \) depends only on \( \rho(r) \)); the second term on the right is the excess contribution, which is nonlocal.

The density \( \tilde{\rho}(r) \) that appears in the last term of (12) is the smoothed or nonlocal density, and it represents a suitable weighted average of the local density \( \rho(r) \),

\[
\tilde{\rho}(r) = \int d\rho' \rho' w(|r - r'|, \rho(r))
\]

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. Tarazona's model [13] is the one most commonly 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

$$w[r - r_i^\Psi \rho(r)] = \sum_{i=0}^{2} w_i(r - r_i)\rho(r)^i$$

(9)

Expressions for the weighting coefficients $w_i$ are given by Tarazona et al. [13].

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

$$\frac{\delta \Omega(r)}{\delta \rho(r)} = 0 \quad \text{at} \quad \rho = \rho_{eq}$$

(10)

A numerical iteration scheme is used to solve this minimization condition for $\rho_{eq}(r)$ for each set of values of $(T, \mu, H)$. The hard sphere diameter is determined from the Barker-Henderson prescription [14] for each temperature.

3. COMPARISONS OF DFT AND OTHER PORE FILLING MODELS

Several independent studies support the conclusion that DFT is a better model for adsorption in micropores than classical thermodynamics models. Because a detailed knowledge of the morphology of porous adsorbents is usually not available, molecular simulation results for ideal model adsorbents have frequently been used as a standard for evaluating the relative merits of the different pore filling models. One such comparison is shown in Fig. 1 for nitrogen adsorption on model carbon slit pores at 77 K. The modified Kelvin method severely overestimates the micropore filling pressures, whereas the DFT method yields a pore filling correlation that is in very close agreement with the "exact" molecular simulation results. Also shown in Fig. 1 is the Horvath-Kawazoe (HK) pore filling correlation, an analytic adsorption model often used for micropore PSD analysis [15]. The HK method gives a more realistic micropore filling correlation than the Kelvin-based methods; however, the HK model still substantially overestimates micropore filling pressures, as shown by comparison to simulation results. The principal shortcoming of the HK model is that it assumes the adsorbate density is uniform everywhere in the slit pore. In fact, the density profile of a confined fluid is highly structured, and this error leads to an underestimation of the heat of adsorption in the HK model, and consequently an overestimation of the pore filling pressures.

An additional test of the robustness of the DFT method is the consistency of PSDs calculated from adsorption experiments using different adsorbates to probe the pore volume. The mean pore diameters of activated carbons obtained from nitrogen and argon porosimetry have been found to agree to within about 10% using DFT as the pore filling model [16]. One such comparison is shown in Fig. 2. Another study [17] reported greater differences in the PSDs computed from DFT models of nitrogen sorption on carbons at 77 K and high-pressure methane sorption at 313 K. The differences were attributed to the quadrupolar interactions of nitrogen with defect sites or heteroatoms on the carbon surface.

In another investigation [19], HK and DFT methods were used for a different activation temperature dependence of DFT and DFT methods correlation of carbon slit pores, while the DFT method was generally found to be more accurate. Gaussian distribution could be used to predict the adsorption pressure at best in recovering the data from the measured data.

Pore filling models

The inside pore diameter of an adsorbent is a degree of consistency for the model [20]. By combining the data on the pore structure, a model was used to determine the best theoretical model. The Kelvin model is the best used in comparison of condensation pressures.

4. APPLICATIONS

DFT and molecular adsorption models can be used to provide a local isotherm or energy distribution on the adsorbent. The energy distribution of the nitrogen sorption isotherm is given by

In applications to adsorption, an adsorbent is generally a porous material. In cases where MCM-41 pore diameters are at temperatures [20-21], helium [22] at 77 K and carbon dioxide at temperatures over 300 K, adsorption effects of slow mass transfer can be avoided. The disadvantages of using nitrogen at supercritical temperature provide a distinct advantage in these cases.
In another investigation [18], the PSDs obtained using the Dubinin-Stoeckli (DS) [19], HK and DFT methods were compared for a series of activated carbons with different activation times (the longer the time, the greater the microporosity). The HK and DFT methods correctly predict an increase in the micropore PSD as activation time increases, while the DS method does not. The authors ran a second test, in which a mock isotherm was generated via molecular simulation for a graphitic carbon having a Gaussian distribution of pore sizes. The three models were applied to this "experimental" data to see if the original PSD could be recovered (Fig. 3). In most cases, the shape of the Gaussian PSD was not reproduced by the analysis routines. However, DFT performed the best in recovering the PSD maxima for distributions centered in the micropore range.

Pore filling model comparisons have also been reported for other porous solids. The inside pore diameters of MCM-41 type adsorbents have been calculated to a high degree of consistency from nitrogen and argon porosimetry (Fig. 4) by using a DFT model of gas adsorption in cylindrical oxide pores to interpret the experimental isotherms [20]. By combining the DFT analysis of the sorption isotherm with X-ray diffraction data on the pore spacing, the pore wall thicknesses of a set of MCM-class adsorbents were determined. These thicknesses were found to be consistent across the set of adsorbents, which lends further strong evidence to the validity of the DFT adsorption model. The Kelvin and modified Kelvin equations, by contrast, overestimate the condensation pressures of nitrogen in cylindrical oxide pores [21].

4. APPLICATIONS OF DFT/MOLECULAR SIMULATION TO PSD ANALYSIS

DFT and molecular simulation methods have been applied to the analysis of adsorbents in two main capacities. For nonporous adsorbents, DFT can be used to provide a local isotherm \(\Gamma(P, e)\) in order to solve eq. (2) for the distribution of site energies on the adsorbent surface [1]. A sample result is shown in Fig. 5 for the site energy distribution of a heterogeneous activated carbon obtained from DFT analysis of the nitrogen sorption isotherm.

In applications of DFT to the characterization of porous solids, the surface of the adsorbent is generally assumed to be chemically homogeneous, and the PSD of the adsorbent is then obtained from solution of eq. (1). Results have been reported for MCM-41 pore diameters using nitrogen or argon as the adsorptive at cryogenic temperatures [20-21]; and for activated carbon PSDs using nitrogen [6,17], argon [16], or helium [22] at 77 K and carbon dioxide at 273 K [23]. Monte Carlo molecular simulation has also been employed to interpret PSDs from supercritical adsorption isotherms of methane and other gases on activated carbons [24-25]. The advantage of using high-temperature (>300 K) isotherms for PSD analysis is that the potentially complicating effects of slow mass transfer and multipole interactions at low temperatures can be avoided. The disadvantage is that the isotherms for mesopores become indistinguishable at supercritical temperatures, whereas at cryogenic temperatures, capillary condensation provides a distinct "fingerprint" of mesopore size.
5. CONCLUSIONS

It is important to note that frequent use of Kelvin-Fourier geometry, chemical holograms is the best available method for molecular simulation and filling in chemically heterogeneous systems.

DFT and molecular statics based methods have become popular in recent years, but they involve more complex calculations. These methods are more convenient to use than the latter. However, we note that molecular statics and complicated adsorbate systems are not the case for most adsorbates. Other properties besides adsorbed gas or neutron diffraction, such as the use of isosteric heats of adsorption.

As noted in the introduction, the isosteric heat of adsorption is an ill-defined concept and is sensitive to perturbations in the data. We have therefore used regularized nonlinear least squares to fit isosteric heats of adsorption to the DFT data. The use of such a well-defined problem is important in ensuring the accuracy of the results.

To avoid such confusion, we have proposed a new method for determining the isosteric heat of adsorption. This method involves fitting the DFT data to a theoretical model, which is then used to predict the isosteric heat of adsorption. This approach has been shown to be more accurate and reliable than previous methods.

Since the DFT is a computationally expensive method, the use of approximations is helpful. One approach is to use a combination of DFT and empirical methods. Another approach is to use experimental data to help guide the calculations.

We have discussed the current state of the art in isosteric heat of adsorption and the challenges that remain. We have also proposed a new method for determining the isosteric heat of adsorption. This method has been shown to be more accurate and reliable than previous methods. We believe that further work in this area is necessary to fully understand the behavior of adsorption systems.
5. CONCLUSIONS

It is important to bear in mind that the pore filling models currently in most frequent use (Kelvin, HK, DFT) are all limited by the same assumptions regarding pore geometry, chemical homogeneity, neglect of connectivity, and so forth. At present, DFT is the best available model for the determination of micropore PSDs. Validation against molecular simulation results has established that DFT offers a realistic model of pore filling in chemically homogeneous solids with simple pore geometries.

DFT and molecular simulation provide much improved accuracy in predicting the local isotherms in eqs. (1) and (2). They give good results for a wide range of temperatures (including supercritical) and over the full pressure range, in contrast to methods based on the modified Kelvin equation or Horvath-Kawazoe model. However, they involve more computational effort than the older methods. At the present time, DFT is more convenient to use than simulation, because of the computational demands of the latter. However, we expect this situation to change fairly rapidly as computer power increases. Molecular simulation has the advantage that it can be readily applied to more complicated adsorbate molecules, and particularly to more complex pore topologies [26]. This is not the case for DFT. In addition, it may be valuable to apply these methods to other properties besides adsorption isotherms, e.g. structure factor measurements by x-ray or neutron diffraction, and heats of adsorption. Nicholson and Quirke [27] have shown that the use of isosteric heat data provides more reliable PSD determinations.

As noted in the introduction, the solution of the Fredholm integral of eqs. (1) and (2) is an ill-posed inverse problem. Consequently, the solution to the PSD can be very sensitive to perturbations in the experimental adsorption data [26]. Some investigators have therefore used regularization to recast the ill-posed adsorption integral of eq. (1) into a well-posed problem. This is done mathematically by introducing additional constraints into the solution technique (e.g. least-squares minimization) to find the PSD. The effect of introducing regularization is to "smooth out" the PSD, as shown in Fig. 6 for a range of smoothing parameter values employed in fitting the PSD of activated carbon to methane adsorption data. An apparent lack of agreement between two reported PSDs for a given material, therefore, may depend as much on whether regularization techniques were used in finding the PSD, as on what pore filling model was used in solving eq. (1). To avoid such confusion, a standard protocol for the use of regularization in PSD analysis should in the near future be developed for the characterization of porous solids.

Since the DFT and molecular simulation methods provide an effective solution to approximation 2 of the introduction, the major challenge facing characterization methods is how to develop improved models for the pore topology (approximation 1). Most of the current methods omit effects of heterogeneity other than pore size, as well as connectivity effects. The latter are likely to prove important, since there is evidence that phase transitions such as capillary condensation are strongly affected by networking. A method of simultaneously determining the PSD and network connectivity of a porous solid has recently been suggested, in which adsorption isotherms from a battery of probe gas experiments involving different adsorbates are measured [25]. Each adsorbate probes a different region of pore volume, based on steric exclusion in the micropores, as shown in Fig. 7. By combining the PSD results for the individual probe gases with a percolation model, an estimate of the mean connectivity number of the network can be obtained.
New approaches based on novel molecular simulation techniques are now emerging which are able to provide much more realistic models of the porous structures. These may be classified into two types: (a) those in which the experimental procedures used to fabricate the material are mimicked in the simulation, and (b) methods based on the use of experimental structural data (small angle scattering data, TEM, etc.) to build model structures that are significantly more sophisticated than simple slit and cylindrical pore models. An example of the first approach is the recent use of quench MD methods to mimic the spinodal decomposition of a liquid mixture of oxides to produce porous silica glasses (controlled pore glass and Vycor) [9,10]. The resulting glasses have a pore topology, pore size distribution, porosity, surface area and adsorption isotherm behavior that closely match those of experimental glasses. An example of approach (b) is the use of off-lattice reconstruction methods [28,29] with TEM data to build more realistic models of porous glasses. In this method a model material is constructed based on the volume autocorrelation function obtained from TEM data. A method that is similar to this in spirit is the use of Reverse Monte Carlo techniques to match the structure of model activated carbons to that obtained from small angle x-ray or neutron data [30].

Method (a) has the advantage that it gives a unique structure, but it requires a different approach for each new class of materials. Method (b) can be applied to a range of materials, but does not yield a unique structure in general. How important this non-uniqueness is for adsorption work remains to be evaluated. It may be possible to alleviate the non-uniqueness problem by using more than one experimental property in the structure determination. At present these methods are in the earliest stage of development, and are highly computer intensive. However, the computer effort needed will decrease rapidly over the next few years as computers become faster.

Such more realistic existing characterization data do not need to know the location of every pore. By simulating adsorption and inverting the isotherm, we can use the new method. Such a test for a (geometric) PSD is considered a key test for any method, which is based on the statistical adsorption approach to building new adsorption models to fit experimental adsorption data. A new method is introduced by fitting the statistical adsorbed fraction curves with a reference model (or a class of models).
Development of these methods for a range of types of porous materials could lead to much more sophisticated characterization methods in the next decade. In the case of a particular class of materials, such as porous silica glasses, it would be straightforward to prepare a range of material samples with differing mean pore size and porosity, and to simulate a variety of adsorption and structural experiments on these. The computer could then match the properties of a given experimental material against those of the model materials in the data bank. Provided the models are realistic this should produce an accurate characterization: structure factor, TEM images, mean pore size, surface area, porosity and so on would be available for the model material. The resulting model material could then be used to predict other adsorption properties. Under such a scenario no knowledge of advanced simulation techniques or of statistical mechanics would be needed on the part of the user.

Such more realistic models of porous materials can also be used to rigorously test existing characterization methods. The model material is precisely characterized (we know the location of every atom in the material, hence the pore sizes, surface area and so on). By simulating adsorption of simple molecules in the material model and then inverting the isotherm, we can obtain a pore size distribution for any particular theory or method. Such a test for porous glasses is shown in Figure 8, where the exactly known (geometric) PSD is compared to that predicted by the Barrett-Joyner-Halenda (BJH) method, which is based on the modified Kelvin equation.

Finally, we note in closing it may be possible to retool some of the simpler adsorption models to improve their predictive capabilities for modeling micropore adsorption. A new method, combining the Kelvin equation with an improved model of the statistical adsorbed film thickness or “t-curve”, has recently been proposed [31]. This

Figure 8: PSDs for model porous silica glasses [10]. A, B, C, D are sample glasses prepared by Quench Molecular Dynamics, and differ in mean pore size and porosity. The solid curves are the exact geometric PSDs for the models; the dashed lines are PSDs predicted by analyzing simulated nitrogen adsorption isotherms for these materials using the BJH method (a form of the modified Kelvin equation). The BJH method gives mean pore sizes that are too small by about 1 nm in each case.
computationally efficient method yields pore filling pressures in remarkably close agreement with DFT results, except for very narrow micropores. A problem, however, is that such “fixes” are likely to be strongly dependent on the materials and adsorbates used.

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REFERENCES