Advantages of QSDFT for Pore Size Analysis of Carbons

Relevant for: carbon, activated carbon, pore size analysis

Quenched solid density functional theory methods that take into account the heterogeneity / surface roughness of carbons were developed and validated and are available in the Anton Paar software for pore size analysis. Methods exist for varying pore geometry and examples for activated carbons, templated mesoporous carbons, and hierarchical carbons are given.

1　Introduction

Significant progress has been made in understanding the underlying mechanisms of gas adsorption in micro- and mesoporous materials for their structural characterization. Contributions from density functional theory (DFT), which describes the molecular level adsorption and phase behavior of fluids, aid pore size analysis. Applied DFT methods give an accurate pore size distribution (PSD) and provide pore size and volume information over the complete range of micro- and mesopores using a single method. Non-local DFT (NLDFT) methods were developed for reliable characterization of siliceous/oxidic materials and zeolites. Our instruments are equipped with a library of these NLDFT methods (which are recommended by standards organizations such as IUPAC, ISO, and ASTM).

While NLDFT is reliable for oxidic materials, pore size analysis of carbonaceous materials with heterogeneous surfaces and disordered or ordered pore structures is still challenging. NLDFT methods are available for carbon materials based on a model of independent, slit-shaped pores with ideal, graphitic walls; however, significant errors occur when applied to carbons with highly heterogeneous (rough)

surfaces. Starting from pore widths of more than a few molecular diameters, theoretical adsorption isotherms making up an NLDFT model exhibit multiple steps associated with layering transitions. Experimentally, step-wise adsorption isotherms are only observed for fluids adsorbed onto molecularly smooth surfaces (such as mica or graphite). However, in carbon materials with heterogeneous surfaces (i.e., activated carbons, templated carbons), layering transitions do not exist because of inherent energetics and geometrical heterogeneities. This mismatch between the theoretical NLDFT and experimental isotherms causes artifacts in the calculated PSD. This problem is especially pronounced for porous materials with a broad PSD, which is typical for many activated carbons.

1.1　QSDFT

To account for the heterogeneity in carbon materials, we have developed quenched solid DFT (QSDFT), which introduces heterogeneity and surface roughness into the model. QSDFT models are available for both N_2 at 77 K and Ar at 87 K adsorption for various pore geometries including slit-shaped micropores (typical of activated carbons), cylindrical pores (typical of channel like micro- and mesopores), and spherical shaped pore (typical of some templated carbons). Details of these models can be found in the literature [1-3].

2　Examples

2.1　NLDFT vs QSDFT on Activated Carbon Fiber

Figure 1 shows the experimental N_2 isotherm on an activated carbon fiber (ACF) sample, along with the corresponding theoretical fitted isotherm from both NLDFT and QSDFT. The QSDFT approach leads to a significantly better agreement between the experimental and theoretical isotherms, specifically in the low pressure micropore region. The NLDFT step-

wise theoretical isotherm assumed a monolayer transition, which is eliminated by QSDFT. As a consequence, the resulting QSDFT PSD is more reliable. Specifically, the sharp minimum in the NLDFT PSD curve at ~10 Å is absent in the QSDFT PSD (Figure 1).
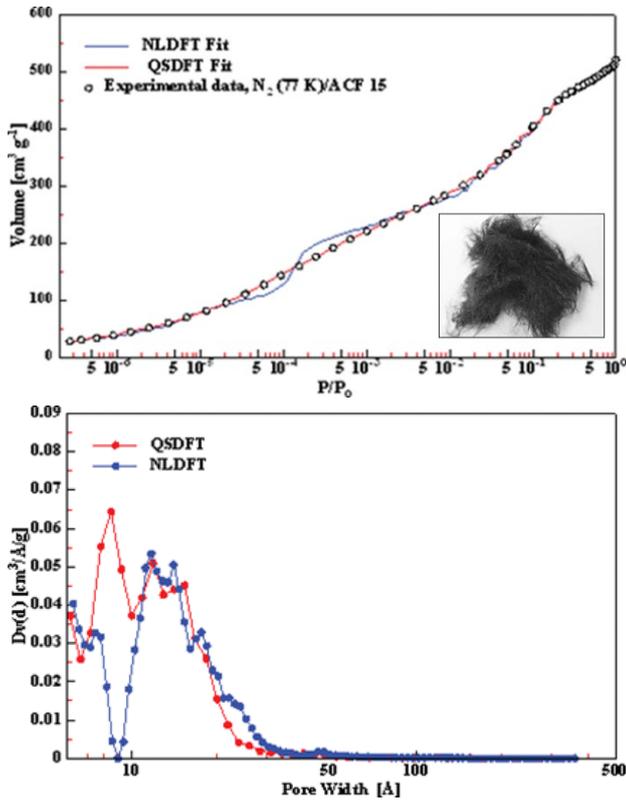

Figure 1: N_2 isotherm on an activated carbon fiber with the NLDFT and QSDFT theoretical fitted isotherms (top) and the corresponding NLDFT and QSDFT PSDs (bottom) illustrating the artifact in the NLDFT fitted isotherm and PSD that is eliminated with QSDFT.

2.2 Templated 3DOm Carbons

Carbons containing spherical pores templated using 30 nm and 40 nm silica nanoparticles were characterized by a spherical mesopore QSDFT model for N_2 adsorption at 77 K (Figure 2) [4]. The spherical pore QSDFT model is a hybrid model that assumes spherical pore geometry in the relative pressure range of hysteresis ($P/P_0 > 0.5$) and cylindrical pore geometry in the low pressure region ($P/P_0 < 0.5$). In the case of spherical pores, the desorption is often affected by a pore blocking mechanism (entrance diameter is smaller than the internal pore diameter) and the pore size can only be obtained from the adsorption branch of the isotherm using a QSDFT model which correctly takes into account the delay in condensation in spherical pores. The mode pore size for these two carbons matched closely with the expected template size and the pore sizes measured

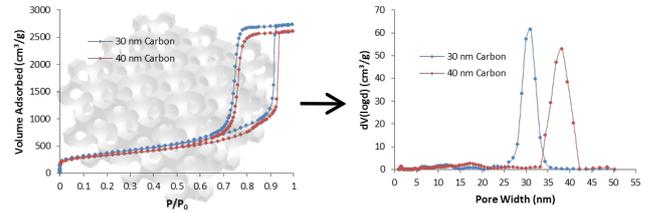independently using scanning electron microscopy (SEM).

Figure 2: N_2 adsorption isotherms on 3DOm carbons template from 30 and 40 nm nanoparticles (left) and corresponding QSDFT PSD calculated assuming a spherical mesopore geometry (right).

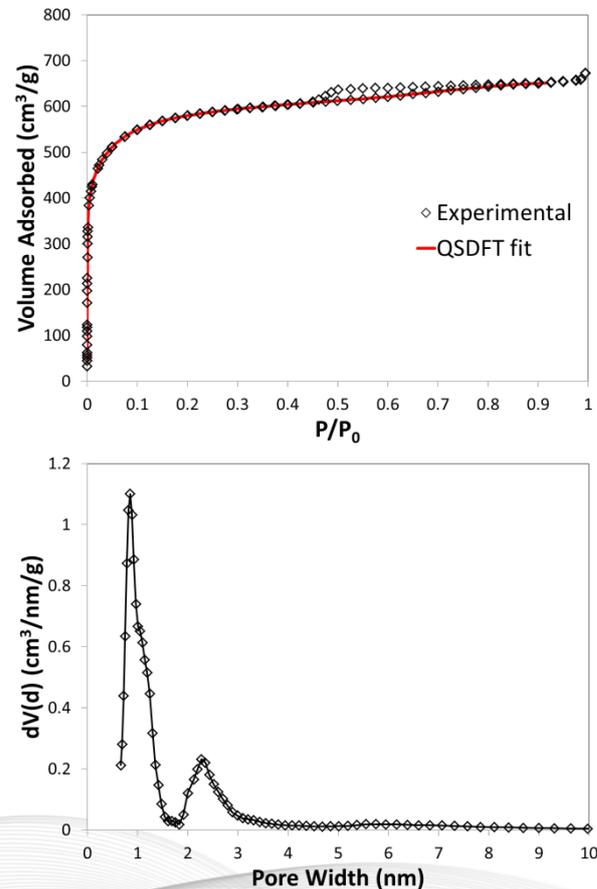## 2.3 Hierarchical Carbons by Calcination, Carbonization, Pyrolysis, or Templating

Figure 3: Experimental N_2 (77 K) isotherm of a micro-mesoporous carbon together with a slit/cylindrical model QSDFT theoretical adsorption branch isotherm (top) and differential pore size distribution curve obtained from the slit/cylindrical QSDFT model (bottom).

Carbons often contain a mixture of inherent microporosity and introduced mesoporosity. Anton Paar also offers hybrid QSDFT models that apply the correct pore geometry in the correct region (micro- or mesopore) of the isotherm. For example, QSDFT models for adsorption in activated carbons

with slit pores in the low pressure region (micropores) and cylindrical-like pores in the high pressure region (mesopores) are available and have been applied to carbons such as micro-mesoporous carbon derived from lignocellulosic precursors, carbide-derived carbons, and FDU-14-15 carbons, among others. One such example is shown in Figure 3 [5].

3   Conclusions

QSDFT leads to significant improvement in the accuracy of DFT pore size distribution analyses of carbon materials from N_2 and Ar isotherms. In contrast to NLDFT methods, QSDFT takes into account the effects of surface roughness and heterogeneity. QSDFT eliminates the artificial gaps in the pore size distributions typical of NLDFT on carbons. A library of QSDFT methods for both N_2 and Ar is available in Anton Paar gas sorption instrumentation software for slit, cylindrical, and spherical-shaped carbon pores. Hybrid models for more complex and hierarchical carbon materials, which take into account different pore geometries in different regions of the isotherm, are also available.

4   References

1. A.V. Neimark, Y. Lin, P.I. Ravikovitch, M.Thommes. Quenched Solid Density Functional Theory and Pore Size Analysis of Micro-Mesoporous Carbons. Carbon, 2009, 47, 1617-1628.

2. G.Y. Gor, M. Thommes, K.A. Cychosz, A.V. Neimark. Quenched Solid Density Functional Theory Method for Characterization of Mesoporous Carbon by Nitrogen Adsorption. Carbon, 2012, 50, 1583-1590.

3. J. Landers, G.Y. Gor, A.V. Neimark. Density Functional Theory Methods for Characterization of Porous Materials. Colloids Surfaces A, 2013, 437, 3-32.

4. K.A. Cychosz, X. Guo, W. Fan, R. Cimino, G.Y. Gor, M. Tsapatsis, A.V. Neimark, M. Thommes. Characterization of the Pore Structure of Three-Dimensional Ordered Mesoporous Carbons Using High Resolution Gas Sorption. Langmuir, 2012, 28, 12647-12654.

5. M. Thommes, K.A. Cychosz, A.V. Neimark. Advanced Physical Adsorption Characterization of Nanoporous Carbons. Novel Carbon Adsorbents, ed. J.M.D. Tascón, Elsevier, Oxford, 2012, p 107-145.