POWDER TECH NOTE 40

APPLICATION OF QSDFT (QUENCHED SOLID DENSITY FUNCTIONAL THEORY) - A NOVEL DENSITY FUNCTIONAL THEORY FOR AN ACCURATE PORE SIZE ANALYSIS OF DISORDERED POROUS CARBONS

Quantachrome introduces a new DFT method (i.e. QSDFT) for the pore size analysis of geometrically and chemically disordered micro-mesoporous carbons, which allows the calculation of pore size distributions from ca. 0.5 nm up to ca. 40 nm. This new DFT

Activated Carbon Fiber ACF15

method complements Quantachrome's comprehensive existing library of NLDFT and GCMC methods, and allows for a major improvement of the accuracy of DFT pore size distribution analyses of disordered carbon materials from low-temperature nitrogen adsorption isotherms. In contrast to the previous NLDFT models that assumed flat, structureless, graphitic pore walls the QSDFT method takes into account the effects of surface roughness and heterogeneity explicitly.

Backgound

In recent years, significant progress has been achieved in understanding the underlying mechanisms of adsorption in micro- and mesoporous solids which has led to major progress in the textural characterization of porous materials by gas adsorption. This progress has been related, to a large extent, to the application of microscopic methods such as the non-local density functional theory (NLDFT) of inhomogeneous fluids, which allow one to describe adsorption and phase behavior of fluids in pores on a molecular level [1 - 3]. The application of such NLDFT methods allows not only an accurate pore size analysis for many materials, but also provides
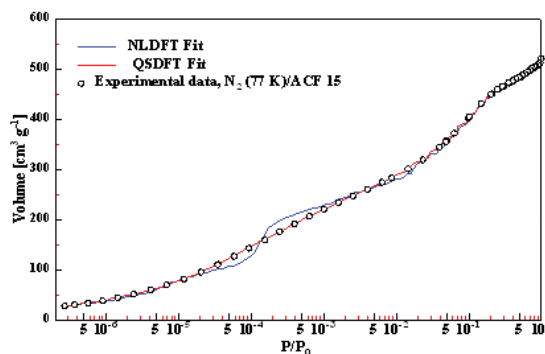
Figure 1a. Experimental N_2 (77K) isotherm (in semi-logarithmic scale) on an activated carbon fiber together with NLDFT and QSDFT theoretical isotherms.

the possibility to obtain pore size, porosity and surface area information over the complete range of micro- and mesopores.

The NLDFT approach had been validated by comparing with the known pore sizes of micro-and mesoporous molecular sieves. This is demonstrated in numerous scientific papers, published within the last decade (for a review see, e.g. [4]). These studies also clearly revealed that classical, macroscopic, thermodynamic methods for pore size analysis may underestimate the pore size in the pore diameter range < 10 nm up to 30 % [1, 2, 4]. Quantachrome has commercialized a comprehensive library of NLDFT and GCMC (Grand Canonical Monte Carlo Simulation) methods for the interpretation of experimental data and the calculation of pore size distributions for various types of materials (see table). The NLDFT method is now widely applied and is featured in a recent standard by ISO (*ISO- 15901-3: Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption – Part 3: Analysis of micropores by gas adsorption*).

While NLDFT has been demonstrated to be a reliable method for characterization of ordered siliceous materials and zeolites, pore size analysis of carbons with hetero- geneous surfaces and disordered pore structure remains difficult. Although the first DFT methods were suggested for activated carbons [5,6] inherent complexity and heterogeneity of pore structures in many carbonaceous materials make the development of improved adsorption isotherm models and new characterization methods a topical problem.

Current implementations of NLDFT for carbon materials are based on a model of independent, slit-shaped pores with ideal, graphitic walls [7, 8]. Such a model has a significant drawback if applied to disordered carbons with highly heterogeneous surfaces; starting from pore widths of more than a few
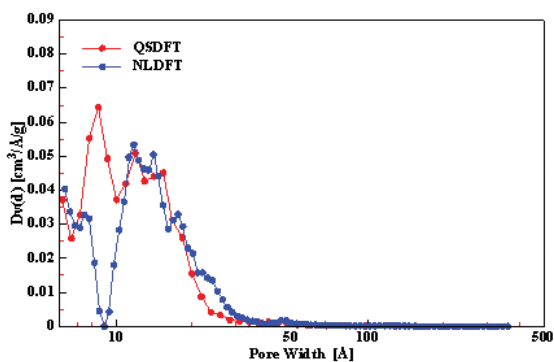
Figure 1b. Differential pore size distribution curves obtained by applying NLDFT and QSDFT on the adsorption isotherm shown in Fig. 2a.
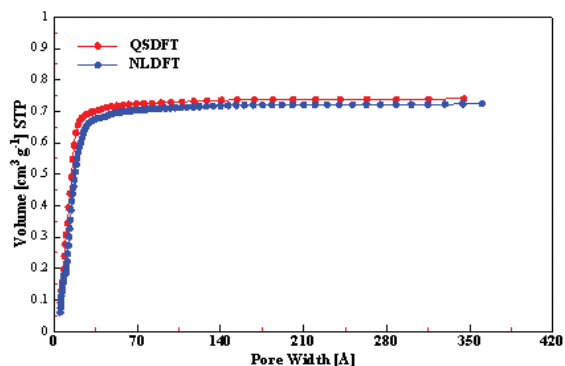

Figure 1c. Cumulative pore volume obtained by applying NLDFT and QSDFT on the adsorption isotherm shown in Fig. 1a.

molecular diameters; theoretical adsorption isotherms exhibit multiple steps associated with layering transitions related to the formation of a monolayer, second adsorbed layer, and so on. Experimentally, stepwise adsorption isotherms are observed only at low temperatures for fluids adsorbed onto molecularly smooth surfaces (such as mica or graphite). However, in carbon materials with heterogeneous surface chemistry (e.g. some activated carbons), layering transitions are hindered due to inherent energetic and geometrical heterogeneities of real surfaces. This mismatch between the assumed theoretical isotherms in the NLDFT kernels (i.e. layering), and the experimental situation can cause artifactual gaps in the calculated pore size distributions. For example, in the case of nitrogen at 77K on graphite, the monolayer formation step in NLDFT occurs at the same pressure as the pore filling in ~1 nm wide slit pore, which results in a prominent false gap in the pore size distribution histograms [8, 9]. This problem is especially pronounced for porous materials with a broad pore size distribution that is typical for many activated carbon materials.

Application of QSDFT (Quenched Solid Density Functional Theory)

These problems in the pore size analysis of disordered carbon samples have been known for many years, but just recently some progress has been made in order to overcome them and to take into account the heterogeneity of carbon materials. Within the framework of the standard slit-pore model of carbons, variability of pore wall thickness has been introduced [10, 11], but it led to just a marginal improvement over the standard NLDFT approach. Other approaches are based on a fit to the reference isotherm of non-graphitized carbon black, and the resulting NLDFT method was found
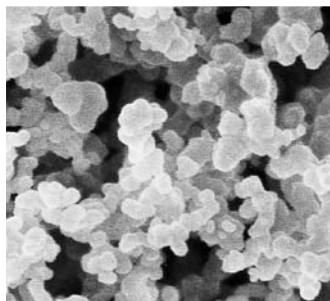
Carbon Black

(based on a limited number of examples) to produce the pore size distributions without a false gap at ~1 nm [12, 13].

More recently, Ravikovitch and Neimark have suggested a new DFT model of adsorption in pores with heterogeneous walls, named the quenched solid density functional theory (QSDFT) [14]. The extension of this method to nitrogen adsorption (at 77.4K) on heterogeneous carbon materials with slit pore geometry [15, 16] has now been commercialized within Quantachrome's data reduction software. The method allows reliable pore size, porosity and surface area characteristics to be calculated in the pore width range from 0.35 nm to ca. 40 nm. Details of the method are described in ref. [14 - 16], but the main idea is to use a multi-component DFT, in which the solid is treated as one of the components with a fixed spatially distributed density. In the QSDFT [14] the solid is modeled using the distribution of solid atoms rather than the source of the external potential field. This allows for the effects of heterogeneity due to the surface roughness to be accounted for explicitly, improving the previous NLDFT models for carbons that assumed flat, structureless, graphitic pore walls. The parameters of the fluid-fluid interactions have been determined so as to reproduce bulk thermodynamic equilibria of nitrogen at low temperatures. The model of the solid, the extent of pore wall roughness/corrugation, and fluid-solid interaction parameters have been determined from the fit of the reference experimental adsorption isotherms on graphitized and non-graphitized carbon blacks [16]. The reference surface has been chosen as that of the carbon blacks with a *partial* degree of graphitization.

We applied the QSDFT model to several typical carbons, and selected examples for two different active carbon fibers are
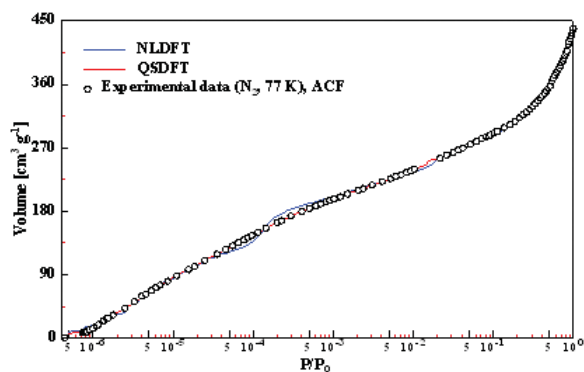
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Figure 2a. Experimental N₂ (77K) isotherm (in semi-logarithmic scale) on a pitch-based activated carbon fiber together with NLDFT and QSDFT theoretical isotherms.
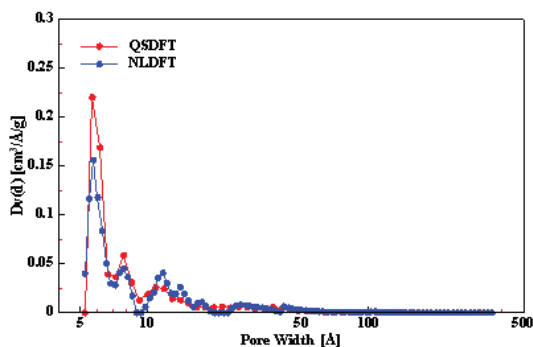

Figure 2b. Differential pore size distribution curves obtained by applying NLDFT and QSDFT on the adsorption isotherm shown in Fig. 2a.

which occurs at the same pressure as the pore filling in ~1nm slit pores.

Summary and Conclusions

The new QSDFT method leads to a significant improvement in the accuracy of DFT pore size distribution analyses of disordered carbon materials from low-temperature nitrogen adsorption isotherms. In contrast to the previous NLDFT models that assumed flat, structureless graphitic pore walls, the QSDFT method takes into account the effects of surface roughness and heterogeneity explicitly. We demonstrate that the QSDFT method eliminates artificial gaps in the pore size distributions typical for NLDFT calculations.

Quantachrome's library of DFT/GCMC kernels now offers methods for carbon pore size analysis with different degree of surface heterogeneity. The methods based on NLDFT are more accurate for the pore size analysis of more ordered carbon materials whereas the QSDFT method is of advantage for geometrically and chemically disordered carbons. Furthermore, the option of applying DFT methods for carbon pore size analysis based on the same pore geometry (slit-pore), but assuming different surface chemistry, allows one to assess the reliability of the pore size analysis of unknown carbon samples.

presented below in comparison with the results obtained by NLDFT (see for instance ref. [15]). These examples demonstrate that the novel QSDFT approach leads to a *significant* improvement in the agreement between the experimental and the theoretical isotherms, in particular in the low pressure range of the micropore filling. The prominent step peculiar to theoretical NLDFT isotherms, due to a monolayer transition,

Figure 2c. Cumulative pore volume obtained by applying NLDFT and QSDFT on the adsorption isotherm shown in

has been completely eliminated. As a consequence, the resulting QSDFT pore size distributions are more reliable. Specifically, the sharp (zero) minimum in the NLDFT pore size distribution curve at ~1nm no longer appears in the results of QSDFT calculations. This confirms that this minimum (in the differential NLDFT pore size distribution) is indeed an artifact caused by the monolayer step in NLDFT approach,
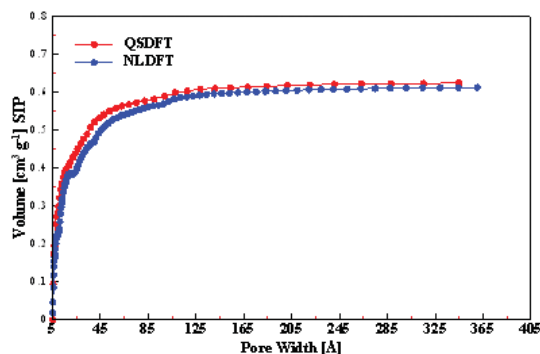
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LIBRARY OF DFT AND GCMC METHODS IN QUANTACHROME'S DATA REDUCTION SOFTWARE

DFT / GCMC Kernel File	Applicable Pore Width Range	Examples
NLDFT– N_2 - carbon equilibrium transition kernel at 77K based on a *slit-pore model*.	0.35nm - 40 nm	Activated carbons, activated carbon fibers, novel micro/mesoporous carbons of type CMK-1 etc.
NLDFT-N_2 -carbon equilibrium transition kernel kernel.	0.35nm - 40 nm	Novel micro/mesoporous carbons (e.g. CMK-3, carbon nanotubes, carbon aerogels) etc.
NLDFT– N_2 - carbon equilibrium transition kernel at 77K based on a *slit-pore model for pore widths < 2nm, and a cylindrical model for pore widths > 2nm*	0.35nm - 40nm	Novel micro/mesoporous carbons (some CMK's), certain activated carbons.
NLDFT– N_2 – silica equilibrium transition kernel at 77K based on a *cylindrical pore model*.	0.35nm-100 nm	Siliceous materials, e.g.some types of silica gels, porous glasses, MCM-41, SBA-15, MCM-48 and other adsorbents which show type H1 sorption hysteresis.
NLDFT-N_2 -silica adsorption branch kernel at 77K based on a *cylindrical pore model* for pores of diameter < 5 nm, *and spherical pores* of diameter > 5nm.	0.35nm - 40 nm	Novel siliceous materials with hierachically ordered pore structure, SBA-16 silica, some types of porous glasses and some types of silica gels.
NLDFT– N_2 - silica adsorption branch kernel at 77K based on a *cylindrical pore model*.	0.35nm-100nm	Siliceous materials such as controlled pore glasses,MCM-41, SBA-15, MCM-48 and others. Produces an accurate pore size distribution even in cases of type H2 sorption hysteresis.
NLDFT–Ar zeolite/silica equilibrium transition kernel at 87K based on a *cylindrical pore model*.	0.35nm -100nm	Zeolites with cylindrical pore channels such as ZSM5, mordenite, and mesoporous siliceous materials e.g., MCM-41, SBA-15, MCM-48, some porous glasses (e.g. CPG) and silica gels which show type H1 sorption hysteresis.
NLDFT – Ar-zeolite/silica adsorption branch kernel at 87K based on a *cylindrical pore model*.	0.35nm-100nm	Zeolites with cylindrical pore channels such as ZSM5, mordenite etc., mesoporous siliceous materials such as MCM-41, SBA-15, MCM-48, porous glasses and some silica gels etc. Produces an accurate pore size distribution even in cases of H2 sorption hysteresis.
NLDFT – Ar-zeolite/silica equilibrium transition kernel at 87K based on a *spherical pore model* (pore diameter < 2nm) and *cylindrical pore model* (pore diameter > 2 nm).	0.35nm-100nm	Zeolites with cage-like structures such as faujasite, 13X etc.
NLDFT – Ar-zeolite/silica adsorption branch kernel at 87K based on a *spherical pore model* (pore diameter < 2 nm) and *cylindrical pore model* (pore diameter > 2 nm).	0.35nm-100nm	Zeolites with cage-like structures such as faujasite, 13X etc.
NLDFT Ar-carbon equilibrium transition kernel at 87K based on a *cylindrical pore model*.	0.35nm - 40 nm	Novel micro/mesoporous carbons (e.g. CMK-3), carbon nanotubes, carbon aerogels and others.
NLDFT – Ar - carbon equilibrium transition kernel at 77K based on a *slit-pore model*.	0.35 nm - 7 nm	Activated carbons,activated carbon fibers, novel micro/mesoporous carbons of type CMK-1 and others.
NLDFT – Ar - carbon equilibrium transition kernel at 87K based on a *slit-pore model*.	0.35nm – 40 nm	Activated carbons, activated carbon fibers, novel micro/mesoporous carbons of type CMK-1 and others.
NLDFT - CO_2 - carbon equilibrium transition kernel at 273K based on a *slit-pore model*.	0.35nm-1.5 nm	Ultra-microporous activated carbons, activated carbon fibers.
GCMC-CO_2 -carbon equilibrium transition kernel at 273K based on a *slit-pore model*.	0.35nm-1.5 nm	Ultra-microporous activated carbons, activated carbon fibers.
QSDFT N_2-carbon equilibrium transition kernel 77K based on a *slit-pore model*.	0.35- 40 nm	Disordered micro/mesoporous carbons with heterogeneous surface chemistry (eg. activated carbons, activated carbon fibers).

NLDFT = non local density functional theory, QSDT = quenched solid density functional theory, GCMC = grand canonical Monte Carlo