

# APPLICATION OF A NOVEL DENSITY FUNCTIONAL THEORY TO THE PORE SIZE ANALYSIS OF MICRO/MESOPOROUS CARBONS

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## ***Abstract***

Recently, we have suggested a model of adsorption in pores with amorphous and microporous solids walls, named the quenched solid density functional theory (QSDFT), that had been successfully applied to modeling adsorption in pores of siliceous materials [1]. This novel approach, which takes into account roughness and corrugation of pore walls, has been extended to carbon adsorbents. QSDFT represents a multicomponent non-local density functional theory (NLDFT), in which the solid is treated as a quenched component with a fixed spatially distributed density. In this paper, we have applied the QSDFT model to calculations of pore size distributions in various carbons (e.g. active carbons, active carbon fibers, ordered mesoporous carbons such as CMK1). We demonstrate that the account for surface heterogeneity improves significantly the reliability of pore size analysis of carbon materials.

## ***Introduction***

Over the last decade, a significant progress has been achieved in understanding the underlying mechanisms of adsorption in micro- and mesoporous solids and, consequently, in elaborating the theoretical foundations of adsorption characterization. This progress has been related, to a large extent, to the application of microscopic methods such as the density functional theory (DFT) of inhomogeneous fluids, which allow one to describe adsorption and phase behavior of fluids in pores on a molecular level. DFT has helped qualitatively classify the specifics of adsorption and capillary condensation in pores of different geometries. Moreover, it has been shown that the non-local density functional theory (NLDFT) with suitably chosen parameters of fluid-fluid and fluid-solid interactions quantitatively predicts the positions of capillary condensation and evaporation transitions of argon and nitrogen in cylindrical and spherical pores of ordered mesoporous molecular sieves such as MCM-41, SBA-15, SBA-16, and silica [2,3]. The NLDFT methods have been already commercialized by the producers of adsorption equipment for the interpretation of experimental data and the calculation of pore size distributions from adsorption isotherms. The NLDFT method is meanwhile widely applied, and it 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 silica materials, pore size analysis of carbons remains difficult. Although the first DFT methods were suggested for activated carbons [4-6], inherent complexity and heterogeneity of pore structures in 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. Such a model has a significant drawback; starting from pore widths of more than a few 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 disordered carbon materials (e.g. active carbons, activated carbon fibers etc), layering transitions are hindered due to inherent

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energetic and geometrical heterogeneities of real surfaces. The layering steps on the theoretical isotherms cause artificial gaps on the calculated pore size distributions, because the computational scheme, which fits the experimental isotherm as a linear combination of the theoretical isotherms in individual pores, attribute a layering step to a pore filling step in a pore of a certain size. 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  $\sim 1$  nm wide slit pore, which results in a prominent false gap on the pore size distribution histograms [7, 8]. The problems associated with this mismatch between the theoretical assumption of a smooth and homogeneous surface and the experimental situation is especially pronounced for porous materials with a broad pore size distribution that is typical for many microporous carbons. In addition, the fit of the low-pressure part of experimental isotherms is rarely satisfactory.

Several new approaches have been considered to account for the heterogeneity of carbon materials. New molecular structural models of porous carbons have been developed [9]. Although very promising, these models are too complex to be easily implemented for routine pore size analyses. Within the framework of the standard slit-pore model of carbons, variability of pore wall thickness has been introduced [10 - 12], but it led to just a marginal improvement over the standard NLDFT approach.

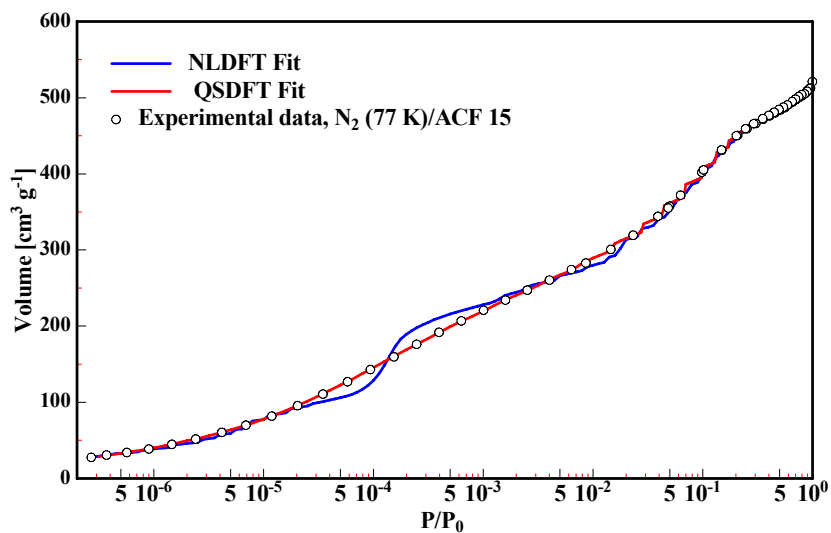
Molecular simulations have demonstrated that the surface roughness and defects affect significantly the shape of adsorption isotherms on heterogeneous surfaces [13 - 16]. Ustinov et al [16] suggested a modification of the Tarazona version of NLDFT, which is capable of generating smooth adsorption isotherms. They developed a model for the pore size analysis of carbons, which is based on a fit to the reference isotherm on nongraphitized carbon black (Ustinov et al, 2005). Based on a limited number of examples, the method was found to produce the pore size distributions without a false gap at  $\sim 1$  nm.

Recently, two of us have suggested a new DFT model of adsorption in pores, named the quenched solid density functional theory (QSDFT) [1]. This new theory is suitable for modeling adsorption in heterogeneous materials with corrugated amorphous walls. It has been successfully applied to siliceous materials of MCM-41 and SBA-15 type [1]. In this work, this novel approach is extended to carbon adsorbents. The main idea is to use a multicomponent DFT, in which the solid is treated as one of the components with a fixed spatially distributed density. In the QSDFT [1, 17], 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.

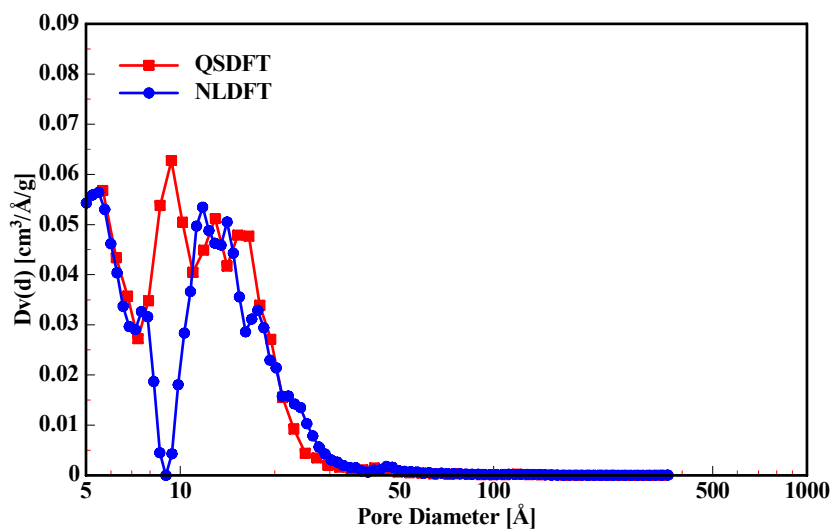
As in NLDFT, the parameters of the model are the fluid-fluid and the solid-fluid interaction potentials. In addition, QSDFT includes a solid density distribution. The parameters of the fluid-fluid interactions have been determined to reproduce bulk thermodynamic equilibria of nitrogen at low temperatures. The model of the solid, the extent of pore wall corrugations, and the fluid-solid interaction parameters have been determined by fitting reference experimental adsorption isotherms on graphitized and non-graphitized carbon blacks [18, 19]. It is important to emphasize that by varying the solid density distribution the QSDFT model is capable of describing adsorption isotherms on carbon materials with various degree of pore wall roughness/corrugation and/or surface defects. In this work, the reference surface has been chosen as that of carbon blacks with a partial degree of graphitization.

### *Application Examples*

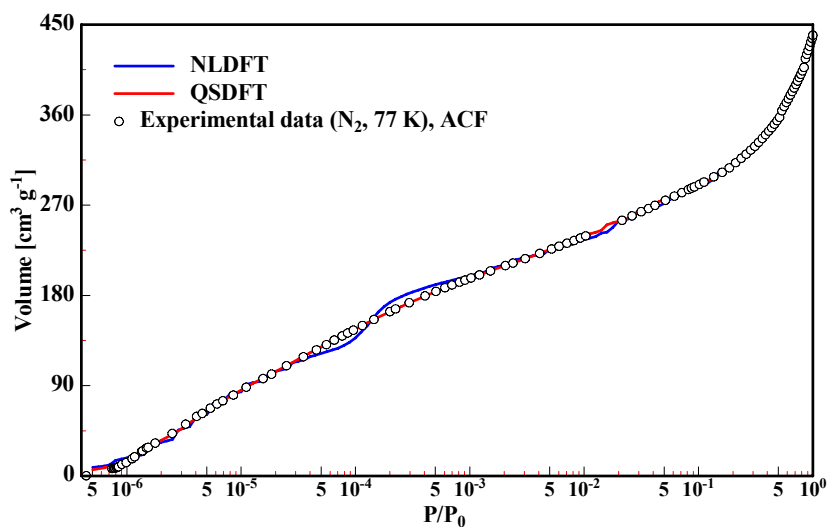
We applied the QSDFT model to several typical carbons. Two selected examples of active carbon fiber are presented below and compared with the results obtained by NLDFT. These examples demonstrate that the novel QSDFT approach leads to a significant improvement in the agreement between the experimental and the theoretical isotherms, in particular in the low pressure range of the micropore filling. The prominent step characteristic to the theoretical NLDFT isotherms, which is due to monolayer transition, has been completely eliminated. As a consequence, resulting QSDFT pore size distributions are more reliable. In particular, a sharp minimum in the NLDFT pore size distribution curve at  $\sim 1$  nm (which is typical to NLDFT pore size distribution curves for many active carbon materials) does not appear anymore in 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, which occurs at the same pressure as the pore filling in  $\sim 1$  nm slit pore.



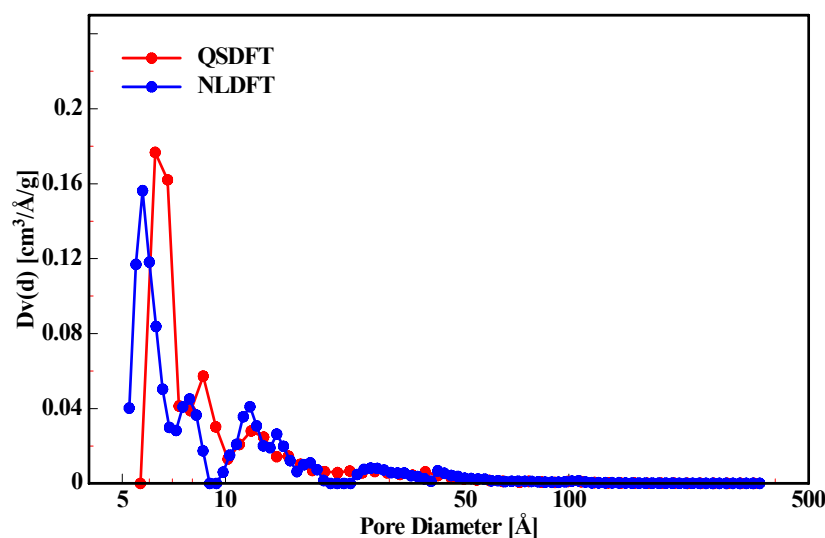
**Figure 1a.** Experimental N<sub>2</sub> (77 K) isotherm (in semi-logarithmic scale) on activated carbon fiber ACF-15 (sample obtained from Osaka Gas, Japan) together with NLDFT and QSDFT theoretical isotherms.



**Figure 1b.** Differential pore size distribution curves obtained by applying NLDFT and QSDFT on the adsorption isotherm shown in Fig. 1a



**Figure 2a.** Experimental N<sub>2</sub> (77 K) isotherm (in semi-logarithmic scale) on pitch-based activated carbon fiber P10 (experimental data from ref. [8]) 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.

### *Summary and Conclusions*

The proposed QSDFT method leads to a definitive improvement of the accuracy of DFT pore size distribution analyses 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 on the [pore size distributions typical for NLDFT calculations.

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