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# Characterization of activated carbons with low-temperature hydrogen adsorption

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ABSTRACT

Low-temperature nitrogen adsorption isotherms are widely used for characterization of carbon materials. However, quite complex physical mechanism of interaction of nitrogen with graphite and micropores hinders a reliable pore size distribution (PSD) analysis. This situation is worsening by a strong regularization procedure which effect on the PSD function is basically unknown. In the present paper we propose a new method of the PSD analysis of activated carbons in the micropore range using hydrogen adsorption isotherms at 77 K. We relied on the kinetic Monte Carlo simulation and accurately accounted for the McLachlan surface mediation, quantum correction of the $H_2 - C$ potential, and the reduced carbon collision diameter (0.26 nm) determined previously (Ustinov E. Carbon 2016; 100: 52). Analysis of PSDs of several samples of activated carbons has shown that the microporous structure of investigated materials consists of discrete number of slit micropores of specified width. We noted that a population of micropores having width of 0.67–0.69 nm is often observed. This suggests that this group of pores can appear due to burn-off of one layer in the graphite lattice. The kernel for the PSD analysis is presented in the form of regression equation which can be used by researches independently.

## 1. Introduction

In the past few decades, a considerable development of methods for the pore size distribution (PSD) analysis of nanoporous materials is indicated. It is now commonly known that the structure in the microporous region (where pore size is conventionally bounded by 2 nm) can only be disclosed with molecular approaches such as Monte Carlo method, molecular dynamics, and non-local density functional theory (NLDFT). The latter has being predominantly developed for the practical use and widely applied to nitrogen adsorption isotherms at 77 K. As applied to carbon materials first papers on this matter appeared in the literature in early 90s [1–7]. Then the energetic and structural heterogeneity was taken into account [8,9]. Further refinement of the PSD analysis was made by accounting for the distribution of the pore wall thickness [10–12]. The authors have analyzed the effect of burn-off on the pore wall thickness distribution and their results were in consistency with X-ray diffraction data. It was also shown that the non-additivity of pair potentials plays a significant role in adsorption phenomena [13,14]. Thus, in the contact layer the non-additivity factor decreases the fluid – fluid attractive component of the potential up to 23%, which is the source of errors up to 40% when the standard NLDFT is applied to fitting adsorption isotherms on graphite. The Axilrod – Teller equation was, therefore, incorporated into the NLDFT model. However, even such a complication proved to be not enough to properly describe experimental nitrogen and argon adsorption isotherms on graphitized carbon black. It turned out that it can be only done with an additional assumption that the solid – fluid collision diameter is 0.272 nm for nitrogen and 0.286 nm for argon. Assuming that the Lorentz – Berthelot mixing rule is valid, this gives the carbon – carbon collision diameter of about 0.26 nm instead of 0.34 nm according to Steele [15].

Despite significant efforts to improve description of adsorption isotherms on the reference surface and nanoporous solids they were not very successful and, therefore, the PSDs of activated carbons restored with the NLDFT did not look entirely convincing. Thus, nearly all PSDs included a gap around the pore width of 1 nm

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regardless of the precursor and methods of the carbonization and activation which looked quite questionable. To resolve this problem Jagiello and Olivier [16] turned to modeling of gas adsorption in finite slit pores formed by parallel disks. They found that in this case the pores fill with the adsorbate more gradually than homogeneous infinitely extended slit pores. As a result, the simulated adsorption isotherms and the PSDs became smoother. Recently the same authors developed a new model which accounts for the energetic heterogeneity and geometrical corrugation of the pore walls [17,18]. This model is in accord with latest results of STEM investigation of activated carbons [19]. The authors have shown that building blocks of the pore walls are randomly wrinkled graphene sheets having nonhexagonal defect rings of carbon atoms which produce curvature of graphenes. The problem is, however, that the NLDFT must be extended to two-dimensional space, which makes the simulation much more time-consuming. Besides, it is necessary to define the ratio between the pore width and the pore wall size, which is one more adjusting parameter. Another way to increase accuracy of fitting experimental adsorption isotherms is to exchange the reference system. To this end, we replaced the graphite surface by that of nongraphitized carbon black Cabot BP-280 [9]. The Tarazona version of NLDFT [20,21] was modified to account for the contribution of the solid atoms to the increase of the effective smoothed density within a solid – fluid transition zone [22,23]. In other words, the repulsive potential of solid atoms in the diffuse zone additionally increases the Helmholtz free energy in the proximity of the solid. Application of the approach to the PSD analysis of activated carbons has shown that fitting of the isotherms are much better than that in the case of the standard NLDFT, with the PSDs becoming smoother and simpler. A similar idea was proposed by Neimark and coworkers [24–27] on the basis of Rosenfeld fundamental measure theory [28,29]. In the framework of this approach, the so-called quenched solid density functional theory (QSDFT), the solid and the fluid are considered as a mixture in the diffuse zone near the surface. The fitting of experimental adsorption isotherms in this case is also good and the QSDFT is now widely used for the PSD analysis of micro- and mesoporous materials. It should be kept in mind however that various conceptually different approaches could provide a very good fitting of experimental adsorption isotherms producing totally different PSDs. As an example, one could mention the Horvath and Kawazoe method [30] where the isotherm is presented as unrealistic superposition of Heaviside step functions always providing its precise fitting without a regularization procedure. This means that the appropriate fitting of experimental adsorption isotherm is not a guarantee that the corresponding PSD reflects the real structure of the sample.

An important condition of a correct PSD analysis is ability of the theory to correctly describe a reference system without resorting to additional assumptions taken in an *ad hoc* manner. This raises the question whether NLDFT can adequately describe the system nitrogen – graphite at 77 K. Thorough inspection of attempts to do this by means of NLDFT published in the literature gives the negative answer. Rigorous analysis of this system with Monte Carlo simulation [28] shows that it is necessary to account for (i) the quadrupole – quadrupole interaction of nitrogen molecules, (ii) the surface mediation using a well-grounded approach like the McLachlan theory [31–34], (iii) anisotropy of the carbon – nitrogen potential [35], (iv) the realistic solid – fluid potential which decays along the normal to the surface much faster than it is predicted by the Steele equation due to the smaller collision diameter of the carbon atom (0.26 nm instead 0.34 nm) [14,31,36,37]. Besides, the theory must reproduce the crystallization of nitrogen adsorbed on graphite at 77 K and a pressure of about 1 kPa and the formation of the monolayer structure commensurate with that of graphite. All these features are beyond limits of the NLDFT and therefore, its ability to disclose the structure of nanoporous solids, which are far more complex systems than graphite, is questionable.

In view of the fact that simulation of nitrogen adsorption in a confined pore volume of nanoporous carbons and generation of the corresponding kernel for the pore size distribution analysis is a quite challenged and time-consuming task, we find reasonable to turn to the hydrogen adsorption at 77 K on graphite and in slit micropores. The advantage of this choice is that hydrogen does not crystallize at 77 K and, therefore, the disordered hydrogen monolayer does not form a structure commensurate with the graphite or the pore wall surface. In this case the effect of anisotropy of the carbon – hydrogen atom disappears. Second, due to 77 K is far beyond the hydrogen critical temperature, the potential of the hydrogen molecule can be treated as the one-center Lennard-Jones (LJ) potential. The contribution of quadrupole – quadrupole interactions to the $H_2 - H_2$ interaction is relatively small [38] and can be neglected. Besides, hydrogen molecule is smaller than nitrogen and can be adsorbed in micropores inaccessible to nitrogen or argon. From experimental viewpoint hydrogen adsorption is less affected by the kinetic limitation which is a serious additional advantage. The hydrogen adsorption in nanoporous solids has been mainly considered from the viewpoint of hydrogen storage and only a few papers published in the literature are devoted to characterization of carbon materials using hydrogen adsorption isotherms. Thus, Jagiello and co-authors [39–41] used a combined PSD analysis of various carbons based on nitrogen, argon, carbon dioxide, and hydrogen adsorption isotherms. They noted that using hydrogen adsorption isotherms allowed them to increase the range of the PSDs toward smaller size of micropores. In all cases the authors relied on the standard NLDFT and used the effective pore width, i.e., the distance between the planes passed through the centers of carbon atoms of outmost layers of the opposite pore walls minus 0.34 nm, which is the collision diameter of the carbon atom according to Steele [15]. The Lennard-Jones parameters for hydrogen were taken by the authors from Ref. [42] as 0.2958 nm and 36.7 K for the $H_2$ collision diameter and the potential well depth, respectively. The LJ solid – fluid parameters were determined with the Lorentz – Berthelot mixing rule using the Steele LJ parameters for the carbon atom. Thus, the $C - H_2$ collision diameter $\sigma_{sf}$ used in the DFT simulation of the kernel for the PSD analysis was taken as 0.3179 nm. The consequence is that the minimum of the graphene – hydrogen potential is located at a distance of 0.318 nm from the graphene. However, the quantum density functional theory shows that this distance is significantly shorter and equals approximately to 0.28 nm [43]. This difference is extremely important for the PSD analysis because the overestimation of the solid – fluid repulsive potential leads to overestimation of the pore widths and the decrease of calculated specific surface area of the sample. The previous finding that the collision diameter of carbon atom is 0.26 nm instead of the commonly used value 0.34 nm [31] improves the situation with the graphite – hydrogen system. Given the Lorentz – Berthelot mixing rule, we obtain the value 0.278 nm for the minimum $C - H_2$ potential, which practically coincides with that obtained with the quantum thermodynamic approach [43]. This strongly supports the conclusion derived from the analysis of the $N_2$ – graphite system [31] that the carbon collision diameter $\sigma_{CC}$ should be taken as 0.26 nm rather than 0.34 nm. Of course, there is no any direct link between $\sigma_{CC}$ and the interlayer distance $\Delta$ of 0.335 nm. The latter value can be explained in the framework of quantum mechanics rather than via the empirical 12-6 LJ potential. However, the LJ potential can be effectively used for modeling gas – graphite interaction basing on the parameter $\sigma_{CC} = 0.26$ nm. This motivates reconsidering of methods for the PSD analysis which is the aim of this study. In spite of the evidence of complex structure