On the Pore Size Distributions of Carbonaceous Catalysts and Adsorbents

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Abstract

The modeling of a low temperature nitrogen adsorption in graphite mesopores with rectangular sections having the aspect ratio of the side lengths more than 7 : 1 has been executed by using the grand canonical Monte Carlo (GCMC) method. The adsorption branches of obtained GCMC isotherms were processed with the purpose of calculation of the formal pore size distributions (PSDs) by the nonlocal density functional theory (NLDFT) and Derjaguin-Broekhoff-de Boer (D-BdB) method. It is shown that NLDFT underestimates the sizes of the model rectangular mesopores though gives good estimations of specific surface area and volume of the pores. Also, it is shown that D-BdB method very strongly underestimates specific surface area and overestimates total volume of pores. PSDs obtained from D-BdB method have a very wide distributive interval of apparent sizes and brightly expressed bimodal forms. Such completely wrong information about the size of the investigated model pores is a consequence of the macroscopic assumption of the D-BdB theory about the constancy of the capillary condensate density in pores at various pressures.

INTRODUCTION

The carbonaceous materials (CM) and activated carbons in particular are of common interest for clearing, storage and transportation of gases, separation of liquid and gas mixtures, and also for some catalytic processes. Their properties in such applications in many respects depend on the size of pores present in a material. At an estimation of PSD by adsorption methods, the porous space of CM usually represents as ensemble of slit-like (or slit-shaped) pores with parallel graphite-like walls infinite in lateral directions. However, even the experimental research of the structures of graphitized carbon blacks shows that they appear to be made up of graphitic blocks packed together in a chaotic manner [1]. This assumes that the real CM contain "corners" where the carbon planes meet and probably the interpretation based on the ideal slit-shaped pores can result in errors.

In 1998 grand canonical Monte Carlo (GCMC) comparisons of the adsorption of argon at 80 K [2] and methane at 308 K [3] for the first time were carried out in slit-like square-shaped and rectangular-shaped pores, and the essential distinction in their adsorption behaviour was established. In 2002 A. Malanoski and F. van Swol [4] studied low-temperature adsorption of lattice gas in rectangular pores of the different size with the different aspect ratios of cross sections. They came to a conclusion that if to fix the smaller side of mesopore rectangular section (pore size) and to increase the length of the other side, the value of filling pressure for this pore at first grows but then is stabilized achieving a limit, and this limit is not equal to filling pressure for a usual slit-like pore of the same size [4]. In spite of the fact that this result was obtained with the help of rather rough version of the lattice density functional theory, it will be well coordinated to a macroscopic thermodynamic reason according to which in corners of a mesopore the meniscii should arise and develop. At achievement of the sufficiently high pressure such meniscii should lose the

thermodynamic stability and a pore will be filled with a condensate. It is completely obvious therefore that the process of adsorption filling of a rectangular-shaped capillary with the infinitely large aspect ratio should be thermodynamically identical to filling of a infinitely deep crack with "bottom". The shape of an evolution meniscus at such pore filling should be described by the equations deduced by Derjaguin-Broekhoff-de Boer (D-BdB) for a semi-infinite slit-like pore within the framework of the concept of "disjoining" pressure (or "adsorption potential") [5, 6].

The purpose of the given work is to simulate adsorption and capillary condensation of nitrogen at 77 K in rather small rectangular mesopores with the large aspect ratios of cross sections by grand canonical Monte Carlo (GCMC) method and to check up as far as it is well possible to estimate the sizes, surface areas and volumes of these pores by nonlocal density functional theory (NLDFT) and Derjaguin-Broekhoff-de Boer (D-BdB) calculations.

METHODS

Adsorption experiments

The choice of realistic parameters for potentials of interaction between molecules is a major stage of any molecular simulation. One of the correctness criteria of such a choice for adsorption modeling in pores is the good coordination of a model adsorption isotherm for an opened surface with an experimental isotherm obtained by adsorption measurements on a nonporous reference material. During last 20 years the most popular nonporous standard for CM was the carbon black Vulcan (S_{BET} ~ 76 m^2/g). However, M. Sweatman and N. Quirke have shown in their recent work [7] that this carbon black contains micropores and its use as the nonporous reference solid is not expedient.

In this connection we have carried out (with the help of the automated unit Sorptomatic-1900) series of measurements of nitrogen adsorption at 77.4 K for the industrial graphitized carbon black TG-10 (S_{BET} ~ 7 m^2/g). The obtained data have appeared to be in excellent conformity with the data for the carbon black Sterling-FTG (S_{BET} ~ 11 m^2/g) [8] and were used by us for specification of necessary molecular parameters. Both experimental isotherms TG-10 and Sterling-FTG are shown in Fig. 1 together with numerical GCMC-isotherms. It was supposed during the generation of the GCMC isotherm that a pair of nitrogen molecules interacts by means of well-known Lennard–Jones 12-6 potential having a well depth ε_{ff} = 96.04 K, interaction diameter σ_{ff} = 0.394 nm, and radius of potential truncation, R_c = 2 nm. It is necessary to note that the pressures marked along the horizontal axis in Fig. 1 were calculated with the use of four virial coefficients of the Lennard–Jones gas [9] having above-mentioned values of ε_{ff} and σ_{ff}, and of course that only an excess of adsorption values was employed

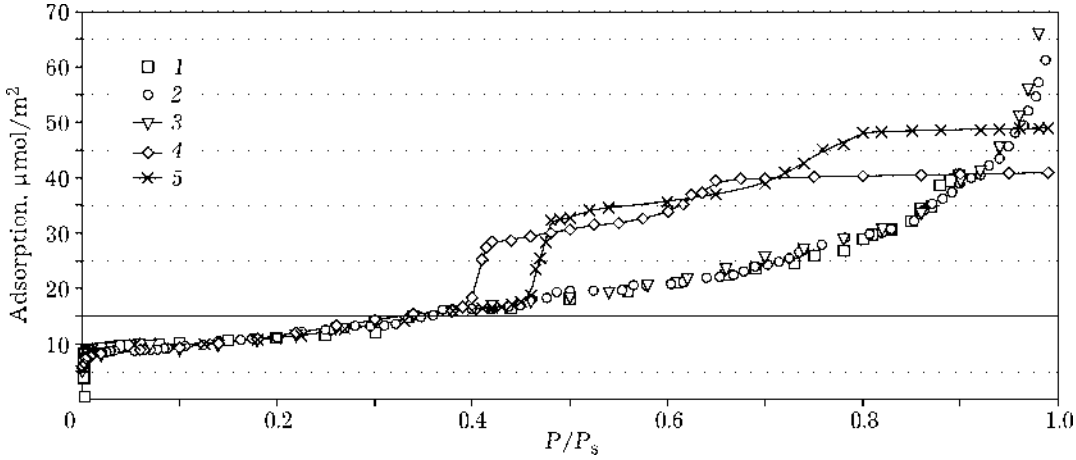

Fig. 1. Experimental and GCMC adsorption N_2 isotherms at 77.4 K: *1* – adsorption data for carbon black Sterling-FTG from [8]; *2* – adsorption data for carbon black TG-10 from this work; *3* – GCMC isotherm on the basal graphitic plane; *4* –GCMC isotherm on the pore with size H_{tr}=10σ_{ff}; *5* – GCMC isotherm on the pore with size H_{tr} = 12σ_{ff}.

by usual way in any case. The interaction potential of a nitrogen molecule with a basal graphitic surface is well described by 10-4-3 potential of Steele [10]. The parameters of potential, *i.e.* density of graphite, $\rho_s = 0.114\ 10^{-3}$ nm^{-3}, distance between layers of graphite, $\Delta = 0.335$ nm, well-depth, $\varepsilon_{sf} = 53.22$ K and effective diameter of N_2/C interaction, $\sigma_{sf} = 0.349$ nm were chosen the same as in [11].

Numerical experiments

The rectangular pores were constructed from semi-infinite 5-layer blocks of graphite just as in [2]. According to this, for the interaction of a nitrogen molecule with pore walls the Bojan–Steele potential [2] having parameters listed above for 10-4-3-potential was used. Only pores with lengths of the smaller side (pore size) from $10\sigma_{ff}$ up to $12\sigma_{ff}$ were investigated. We limited our studies to this interval of pore sizes because, first, it is the most doubtful range of the mesopore sizes for application of the macroscopic adsorption theories on the bases of D-BdB and Kelvin–Cohan [12] equations. As shown below, the filling of pores of such sizes by a capillary condensate occurs along a relative pressure range $P/P_o = 0.4-0.45$. Secondly, GCMC experiments reported here have appeared essentially time consuming even despite the use of the fast GCMC version [13]. For example, good accuracy for relative pressures higher than approximately 0.38 has required in all cases about $4\ 10^4$ Monte Carlo trials per molecule (and $2\ 10^4$ to reach equilibrium). It is necessary to note that all the results reported here are reproduced with the use of well known "slow" GCMC versions [14].

RESULTS AND DISCUSSION

Only adsorption branches of isotherms were generated in all cases. It was established that after the relation of the greater side length to the smaller one became higher than approximately 7 : 1, the value of filling pressure for the given pore size reached the high limit. Below we have restricted an illustration of our results to the consideration of adsorption only for two capillaries having rectangular sections $10\sigma_{ff} \times 80\sigma_{ff}$ and $12\sigma_{ff} \times 96\sigma_{ff}$ and the size of simulation boxes in an axial direction of a capillary equal to $14\sigma_{ff}$. Along this direction, of course, the periodic boundary conditions were applied.

In Fig. 1, the adsorption branches of GCMC isotherms are shown only for adsorption in the central parts of these two capillaries, *i. e.*, for partial volumes – $10 \times 10 \times 14\sigma_{ff}$ and $12 \times 12 \times 14\sigma_{ff}$ take place at the centre of complete volumes – $10 \times 80 \times 14\sigma_{ff}$ and $12 \times 96 \times 14\sigma_{ff}$, correspondingly. Thus, the contribution of a reversible capillary condensation in the corners of the pores is not shown on these GCMC isotherms. We have acted so because we are interested only in rectangular pores having rather large aspect ratio of section sides in which this contribution can be neglected.

It is obvious that these GCMC isotherms can be referred to abstract porous bodies, one of which contains only pores of the size $10\sigma_{ff}$ and the porous space of another one consists only of pores of the size $12\sigma_{ff}$. For definiteness we accepted that both model porous bodies have a specific surface area equal to 500 m^2/g.

In Fig. 2, the apparent volume pore size distributions (PSDs) obtained by NLDFT and D-BdB processing of GCMC isotherms for each of two model porous bodies are shown. The NLDFT calculations were carried out with the use of bimodal lognormal function just as described in [11]. In the same Fig. 2, the "true" and "effective" sizes of pores are marked by means of vertical dot lines. The true size (H_{tr})

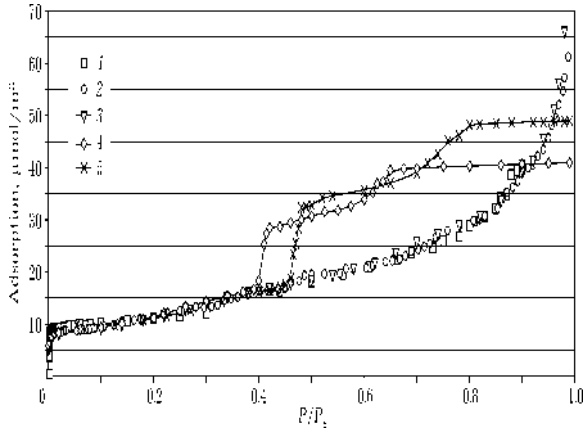

Fig. 2. The apparent volume of the PSDs for $H_{tr} = 10\sigma_{ff}$ and $H_{tr} = 12\sigma_{ff}$ adsorption branches of the N_2 isotherms calculated by D-BdB and NLDFT methods: dashed lines – NLDFT; solid lines – D-BdB.

TABLE 1

Initial and calculated summary characteristics of two model porous solids

Methods	$10\sigma_{ff}$ isotherm				$12\sigma_{ff}$ isotherm			
	S_Σ, m^2/g	V_Σ, cm^3/g	H_{tr}, nm	H_{eff}, nm	S_Σ, m^2/g	V_Σ, cm^3/g	H_{tr}, nm	H_{eff}, nm
GCMC	500.0	0.71	3.945	3.392	500.0	0.85	4.734	4.166
NLDFT	504.9	0.70	2.752	–	497.7	0.79	3.163	–
D-BdB	299.9	1.10	–	3.670	218.9	1.04	–	4.764

means distance between planes passing through the nuclei of carbon atoms on opposite walls of a pore. The effective size (H_{eff}) is connected to that part of volume of a pore, which is accessible to the centres of adsorbate molecules. It is defined by subtraction of some quantity (δ) from the true size of a pore. During GCMC simulations the value $\delta = 1.44s_{ff}$ was established. It is necessary to note that the true size (H_{tr}) is calculated during the NLDFT interpretation [11], while the D-BdB theory operates with effective size (H_{eff}), as the definition of a bulk liquid density contains implicitly the effective pore size representation [6].

NLDFT calculation for the $H_{tr} = 10\sigma_{ff} = 3.945$ nm isotherm has given pore size distributed along the 2.2 nm < H_{tr}^{DFT} < 3.4 nm interval. The average value of this apparent distribution $\overline{H}_{tr}^{DFT}$ = 2.75 nm is less than the size of model pores approximately by 30 %. However, effective size of model pores, H_{eff} = 3.377 nm, is less than the size of model pores only by 18.5 %. Thus, one can hope that if CM materials having size of pores less than 3.0–3.5 nm are studied, the NLDFT calculations should give rather satisfactory information concerning the average effective size of pores. Unfortunately, for wider pores the NLDFT interpretation generates progressing mistakes. Thus, NLDFT calculation for the $H_{tr} = 12\sigma_{ff} = 4.734$ nm isotherm shows a much more extended interval of the apparent pore sizes, 2.2 nm < H_{tr}^{DFT} < 3.5 nm and average size, $\overline{H}_{tr}^{DFT}$ = 3.163 nm which by ~25 % underestimates the effective size of studied pores 4.166 nm (Table 1).

Both specified D-BdB distributions have a very wide distributive interval of apparent size and brightly expressed bimodal form. Such completely wrong information about the size of investigated pores is a consequence of the macroscopic assumption of the D-BdB theory about constancy of density of a capillary condensate in pores at various pressures below 1 atm. The second negative feature of D-BdB interpretation is the very strong underestimation of specific surface area (see Table 1). In the case of pores having the size $H_{tr} = 10\sigma_{ff} = 3.945$ nm, the D-BdB calculation gives a cumulative surface area $S_\Sigma \sim 300\ m^2/g$. This value makes only 60 % of the given specific surface area of 500 m^2/g. For the second model, $H_{tr} = 12s_{ff} = 4.734$ nm, the quantity SS calculated by D-BdB technique makes still smaller fraction of 500 m^2/g, *i.e.*, 44 % of the given specific surface area. However, an average apparent D-BDB size in both cases is rather close to the appropriate true sizes, which is certainly accidental.

CONCLUSION

Thus, concerning CM with the sizes of mesopores less than approximately 5 nm, it is possible to make a conclusion that the macroscopic approaches using the concept of constant density of the capillary condensate at various pressure values are not capable to give the adequate information concerning the PSD, specific surface area and specific pore volume. At the same time, the modern NLDFT method gives satisfactory information about a specific surface area and volume of pores, but this technique can not be considered as the reliable tool concerning the PSD and average pore size calculations, if the porous body contains rather big fraction of large mesopores. The PSD calculations based on model rectangular pores with the infinitely large ratios of side lengths can become a useful addition to already existing methods.

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