

TWO-DIMENSIONAL FINITE CARBON PORE MODELS. EFFECTS OF PORE WALL SHAPE AND LENGTH ON NLDFT ADSORPTION ISOTHERMS

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Introduction

The most commonly used carbon pore model is a slit shape pore infinitely extended in two dimensions. This model allows describing gas adsorption isotherms as a function of temperature, pressure and pore width. A set of such isotherms (kernel) calculated using tools such as the non-local density functional theory (NLDFT) or Monte Carlo simulations can be used for the characterization of carbon pore structure in terms of its pore size distribution (PSD).

Recently, we have proposed using a finite pore model for the carbon PSD analysis [1]. In that model, we assumed the simplest possible finite slit pore having parallel circular walls. Such a pore is finite in all directions but due to its circular symmetry it can be described using only two dimensions; r and z . Due to finite dimensions of pore walls the adsorption potential varies in the direction parallel to the wall, which leads to variations of adsorbate density in two or three dimensions. The effects of finite pore length are most strongly pronounced near the pore edges. We found that this more realistic model agrees better with the adsorptions isotherms measured for microporous carbons than the classical infinite pore model

Results and Discussion

In present work, we consider two models with slit pore geometries. (i) Two dimensional semi-finite slit pore having parallel strip walls composed by graphene sheets. The walls are finite in x and infinite in y directions. This pore is open on both sides of the strip walls and may represent carbon structures consisting of locally parallel graphite-like crystallites observed in graphitizing and non-graphitizing carbons [2]. (ii) The partially closed pore model obtained from model (i) by closing on one side of the pore with a perpendicularly oriented graphene sheet. Such pores may occur as a result of crossing between the graphite-like crystallites.

To describe adsorption for these models we apply the Tarazona's version of NLDFT [3,4]. The solid-fluid interaction potential is calculated by the numerical integration of the LJ potential over featureless graphene sheets that constitute the pore walls.

To illustrate effects of pore geometry on adsorption properties of these model pores we show adsorbate density contours (Figure 1) calculated for N_2 equilibrium adsorption ($T = 77$ K, $p/p_0 = 0.2$) in both model pores having width of 27.5 Å. The observed dramatic difference in density profiles in these pores is clearly due to the difference in adsorption

potentials. The additional wall in pore (ii) contributes to the effective adsorption potential and thus causes the increase in adsorbate density in this pore.

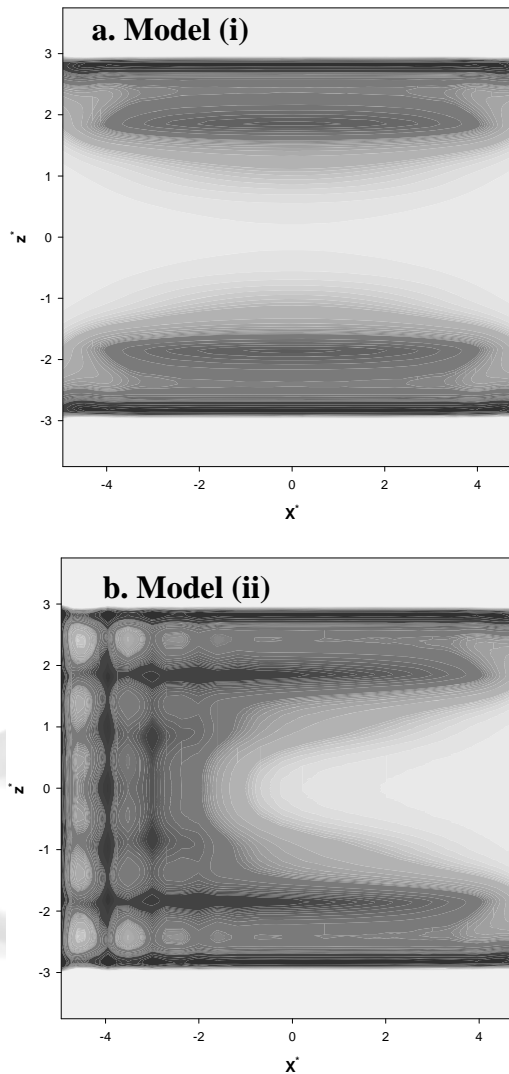


Fig. 1 Calculated cross-sectional contours of N_2 densities at 77K and $p/p_0=0.2$ for pore models (i) and (ii). Pore width = 27.5 Å; pore length 36 Å. The reduced variables used here are: $x^*=x/\sigma_{ff}$ and $z^*=z/\sigma_{ff}$. Darker areas represent higher fluid density.

It is interesting to note that model (i) shows adsorbed layers development similar to that known for infinite slit models. However, with the introduction of an additional wall we observe the highly structured density profile shown for model (ii). This profile exhibits both horizontal and vertical order of adsorbed molecules. The way the molecules are ordered is due to the geometry of the pore model. Lower degree of molecular order shown in model (i) is due to the fact that this model is less confined than model (ii).

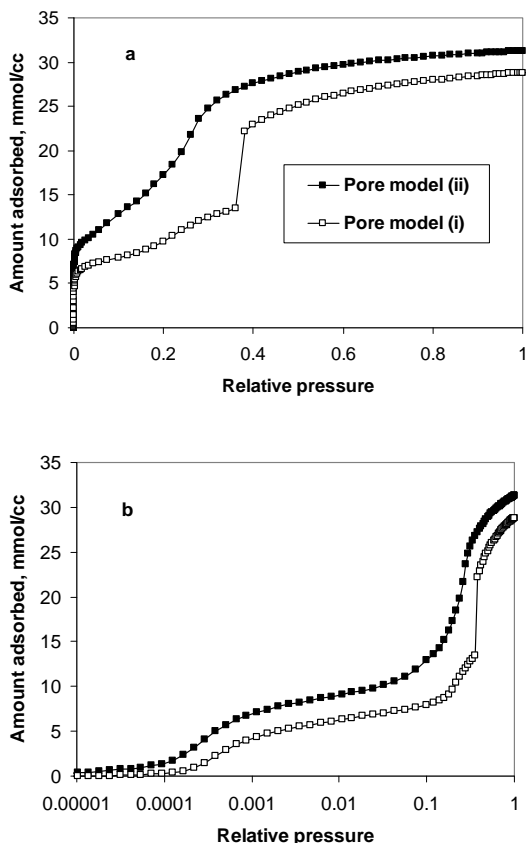


Fig. 2 Calculated equilibrium adsorption isotherms of nitrogen at 77 K for pore models (i) and (ii) shown in linear (a) and logarithmic scale. Pore width = 27.5 Å; pore length 36 Å.

As a consequence of the increased fluid density in pore model (ii) the calculated adsorption isotherm for this model show higher adsorption values than those for model (i) (Figure 2). The adsorption mechanism for model (ii) does not show a capillary condensation step which is clearly visible on the adsorption isotherm of model (i). This is a significant qualitative difference between the two models. In this case, lack of a condensation step for model (ii) is related to the fact that the adsorption mechanism of this model does not exhibit a capillary condensation loop.

Conclusions

The two-dimensional finite pore models for porous carbons presented here are more realistic than the widely applied one-dimensional slit model that assumes infinitely extended graphite-like walls. Assumption of finite pore length introduces more options to the carbon slit like model. The introduced variables of pore length and shape allow for the input of information from independent analytical techniques to the modelling process of carbon structure and its adsorption properties. The two examples of slit models shown here demonstrate how significant differences in adsorption properties of porous carbons may arise as effects of pore lengths and shapes. We think that recognizing these effects may improve our understanding of adsorption in porous carbons and lead to the development of more accurate characterization methods.

References

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