

# Pore wall thickness and interpore influence on adsorption of alkanes in carbons using explicit pore models

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**Abstract** In modeling of activated carbons, the pores are often assumed to be slit-shaped formed of a constant number of graphene layers. X-ray diffraction studies show that micropores are formed between stacks of different numbers of graphene layers. In this study, we investigate, through the grand canonical Monte Carlo method, the influence on the adsorbed alkanes densities of pore walls with different graphene layers thickness and the related interpore adsorbate interaction when the pore wall has only one graphene layer. All studies of thickness and interpore interaction to date were performed using the Steele 10-4-3 potential model. Instead of Steele model, we propose explicit models made up of graphene layers of discrete carbon atoms. We also investigated the sensitivity of the system to the cut-off and solid-fluid parameter. With our explicit model we found that the influence of the number of carbon layers is not significant for  $n > 2$  as previously observed by Steele model—DFT studies. The system was also insensitive to cut-off and well deep parameter variations. A new pore model with an extra dummy graphene wall was proposed to investigate the interpore interaction. The interpore interaction study with the alkanes series C1 to C4 shows that the retention capacity of heavier alkanes is the same whether for activated carbons with few layers (stronger interpore interaction) as for carbons with two or more layers (stronger solid-fluid interaction) assuming negligible surface mediation. The explicit models proposed can be successfully used in the elaboration of virtual porous carbon models to reproduce wall thickness and interpore adsorbate interactions phenomena.

**Keywords** Activated carbon · Explicit models · Monte Carlo Simulation · Alkane adsorption

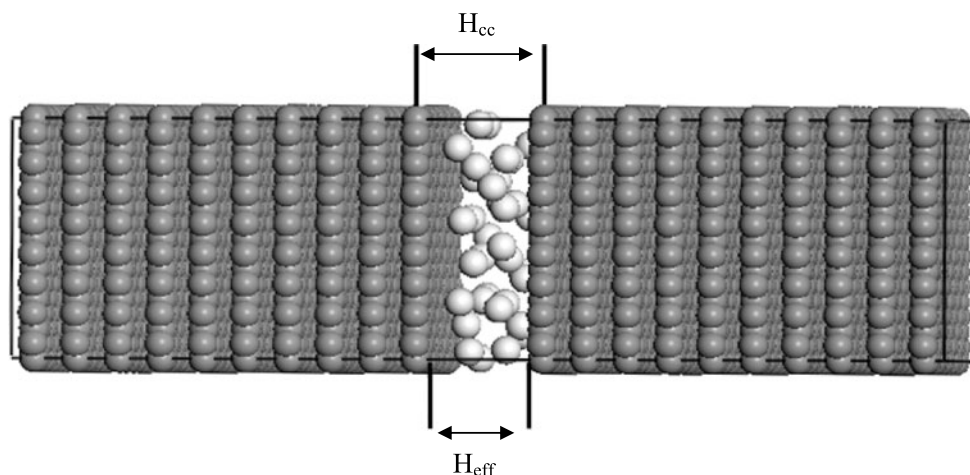
## 1 Introduction

Carbon-based microporous adsorbents, such as activated carbons, carbon molecular sieves, and carbon fibers, comprise a whole family of porous material for which porosity is heterogeneous in size, shape and capacity of adsorption. Such porosity is not easy to visualize, thus modeling the carbon structure is a challenging task. An important feature inherent to most of the local isotherm models refers to the assumption that pore walls are infinitely thick. This assumption is associated with the Steele 10-4-3 potential calculation (Steele 1974). Indirect evidence using high resolution transmission electron microscopy technique shows, however, that most carbons have pore walls with only a few, typically one to three, planes of graphene sheets (Sharma et al. 1999, 2000).

Steele finite wall molecular models to study the influence of different stacks of graphene layers in adsorption were first performed by Mays and co-workers (Mays 1996; Chen et al. 1997). In those studies, the layer stacking was changed from one ( $n = 1$ ) to ten layers ( $n = 10$ ). The authors found that the influence of the number of graphene layers on the adsorbed gas density for N<sub>2</sub> (77 K) and CH<sub>4</sub> (298 K) was not significant for  $n > 5$  and  $n > 2$ , respectively. Bhatia and co-workers (Bhatia 2002; Nguyen and Bhatia 2004) applied a finite wall thickness model in the characterization of activated carbon using N<sub>2</sub> and Argon as probing gases. The authors determined simultaneously pore size distribution and pore wall thickness. Different number of layers incorporated in the model allowed to reproduce heterogeneity attributes of the carbon material.

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**Fig. 1** Explicit pore model with ten graphene sheets layers with main dimensional parameters.  $H_{\text{eff}}$ —effective internal pore size.  $H_{\text{cc}}$ —carbon center-to-center pore size



Since in the finite wall thickness model, the separation between pores may be of just one graphene layer, the impact of interactions between adsorbate molecules in neighboring pores can be significant. Bhatia (2002) also confirmed this possibility performing calculations with an oversimplified butane model at 272 K.

All wall layers thickness and interpore studies to date were performed using Density Functional Theory (DFT) approach and the Steele finite potential approximation (Mays 1996; Chen et al. 1997; Bhatia 2002; Nguyen and Bhatia 2004).

Another approach is to use explicit models of graphene sheets where all the carbon atoms are represented in opposition of Steele integrated potential of the graphene sheet. Instead DFT this approach uses Monte Carlo simulation in the grand canonical ensemble. The explicit model approach is especially useful in the models that go beyond the single slit pore representation (e.g. virtual porous carbons—VPC Biggs and Buts 2000 and reverse Monte Carlo models (Thomson and Gubbins 2000). Explicit model also are more general and have the advantage of giving a direct link between carbon structure and adsorption phenomena (Cai et al. 2007; Do and Do 2006; Lucena et al. 2010a). These are desirable attributes that can help molecular simulation techniques to become a practical and accessible tool for the experimental community (Maginn 2009).

The present study has two main objectives: one is to propose and test explicit models of graphene layers. These models are intended to reproduce the same observed adsorption variations with pore wall thickness and interpore interaction of the Steele based—DFT model. Secondly, we want to use our validated models to investigate the impact of interactions between adsorbate molecules in neighboring pores with realistic models of C1–C4 alkanes at room temperature. As explicit models do not had a Steele infinite wall equivalent, we also included in this study the influence of the cut-off and Lennard Jones well depth parameter.

Alkanes were used in this study because we are interested in storage of natural gas (NG). NG is a mixture of alkanes and one of the activated carbon storage problems is the retention of heavier alkanes during the cycles of charge and discharge. Since the carbons have different pore wall thickness distribution, we want know which wall thickness is better for minimize heavier components retention.

## 2 Simulation model

### 2.1 Carbon and adsorbates models

#### 2.1.1 Finite wall studies

For the finite wall studies the activated carbon model was made up of a slit-shaped simulation cell of  $40 \times 40 \text{ \AA}$  with walls build with stacks of ten graphene sheets layers. This simulation cell with the main dimensional parameters is shown in Fig. 1. The pore model with ten layers of graphene sheets was our equivalent to the infinite pore wall in the Steele model.

For methane, we defined the UA model proposed by the Dreiding force field (Mayo et al. 1990), altering the solid-solid parameter so that it matched the  $\text{CH}_4$  experimental isotherm on Vulcan (Sweetman and Quirke 2001), a reference graphite surface.

#### 2.1.2 Interpore interactions

For the studies on interpore adsorbate interactions the carbon pore walls were modeled with only one layer of graphene sheet and a dummy wall of graphene was added to reduce the effect of interpore interaction (see Sect. 3.2 to details).

The Bhatia (2002) butane model parameters were used for explicit interpore model validation. For the linear alkanes series (C1 to C4), we used the same Dreiding force field

**Table 1** LJ potential parameters for fluid-fluid and solid-solid interactions

	$\sigma_{ff}$ (Å)	$\varepsilon_{ff}$ (kcal mol <sup>-1</sup> )	$\sigma_{ss}$ (Å)	$\varepsilon_{ss}$ (kcal mol <sup>-1</sup> )
Dreiding parameters				
CH <sub>4</sub> (methane)	3.76	0.301	–	–
CH <sub>3</sub>	3.69	0.25	–	–
CH <sub>2</sub>	3.61	0.19	–	–
Graphene	–	–	3.45	0.042 <sup>a</sup>
Butane model validation				
C <sub>4</sub> H <sub>10</sub>	4.897 <sup>b</sup>	0.738 <sup>b</sup>	–	–
Graphene	–	–	3.4 <sup>b</sup>	0.072 <sup>a</sup>

<sup>a</sup> This study

<sup>b</sup> Bhatia (2002)

parameters. The molecular structures of alkanes were considered rigid in the UA model. Molecule flexibility is known to influence adsorption equilibrium but, for a first insight to evaluate the inter pore interaction, a rigid model is a good approximation.

## 2.2 Intermolecular interactions

The fluid-fluid interaction was calculated from the classical 12-6 LJ (Lennard-Jones) potential equation:

$$U(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

where  $\varepsilon_{ij}$  is the well depth,  $\sigma_{ij}$  is the diameter, and  $r_{ij}$  is the distance between interacting atoms  $i$  and  $j$ . All parameters can be seen in Table 1.

Since we used graphene layers made up of discrete atoms of carbon, all the interactions between solid and fluid were also described by LJ potentials (see Table 1). The cross terms were obtained using arithmetic and geometric combination rules.

## 2.3 Effective internal pore size for local isotherm calculations

To correlate Vulcan graphite experimental and simulated isotherms and also to perform wall thickness studies, we defined an effective internal pore size ( $H_{eff}$ ) for our explicit carbon model defined for the equation:

$$H_{eff} = H_{cc} - H_{ex}$$

where  $H_{cc}$  is the carbon center-to-center pore size and  $H_{ex}$  is the excluded pore width. The excluded pore width ( $H_{ex}$ ) was defined empirically by molecular simulation (Gusev et al. 1997; Lucena et al. 2010b). The Monte Carlo simulation

was done down to the smallest pore in which adsorption of methane molecules was possible ( $H_{cc\text{ minimum}}$ ). The excluded pore width  $H_{ex}$  for adsorption of methane was then estimated as  $H_{ex} = H_{cc\text{ minimum}} - \sigma_{ff}$ . For the methane models,  $H_{cc\text{ minimum}} = 6.4$  Å. The effective cell volume was calculated from the product of the surface area and the effective internal pore size ( $H_{eff}$ ). Local isotherms were simulated in pore widths of  $H_{cc} = 7, 10$  and  $30$  Å.

For the study with the alkanes series we took  $H_{ex} = 0$ , thus the effective cell volume was defined as the volume of the simulation cell itself, as previously done by Davies and Seaton (1998).

## 2.4 Simulation details

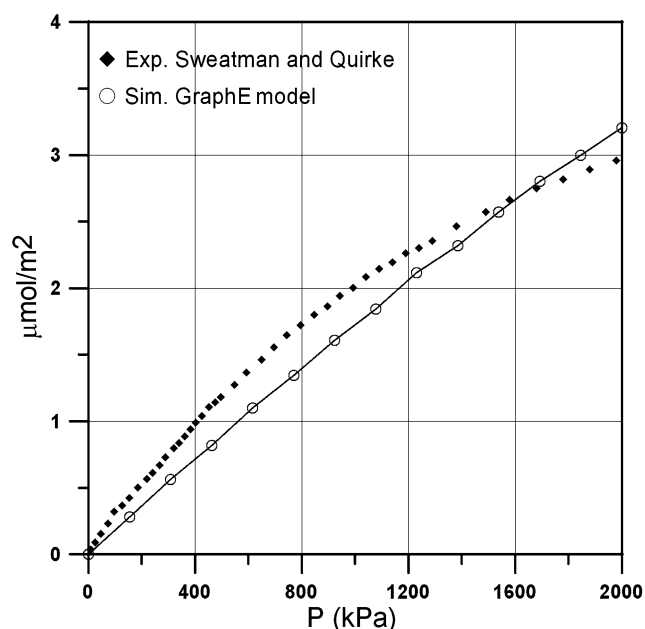
The grand canonical Monte Carlo (GCMC) technique was used in the simulation of adsorption isotherms. The algorithm allows displacements (translations and rotations), creations, and destructions. These simulations consisted of evaluating the average number of adsorbate molecules for which the chemical potential equals that of the bulk phase at a given pressure and temperature. Details of the method can be seen elsewhere (Frenkel and Smit 2002). The output of such a simulation is the absolute adsorbed amount, whereas experimentally the excess adsorbed amount is the property that is measured. The excess amount was calculated by subtracting the simulated absolute amount from the total number of molecules present in the pore effective volume calculated with the Peng-Robinson equation of state. Details of the procedure can be seen in references Gusev et al. (1997) and Davies and Seaton (1998). For conditions in which low densities were expected, extra cells were connected side-by-side to enlarge the simulation cell volume and increase the number of molecules in the simulation.

The GCMC simulations were performed on a PC Dell workstation (Intel dual core, 3.0 GHz processor), using the Material Studio Sorption code (Sorption 2007). Between 2 and  $3 \times 10^6$  Monte Carlo steps were performed in order to calculate mean values. To check the production phase convergence we have tested representative alkane molecules up to  $7 \times 10^6$  Monte Carlo steps, without significant change in the results. The potential cut-off distance was in the range of 12 to 20 Å, with a low cut-off of 0.4 Å.

## 3 Results and discussions

### 3.1 Pore wall thickness studies

Initially, the well depth parameter ( $\varepsilon_{sf}$ ) from Dreiding force field was calibrated to match experimental Vulcan isotherm. A wide slit pore of size  $H_{cc} = 70$  Å was used to obtain the

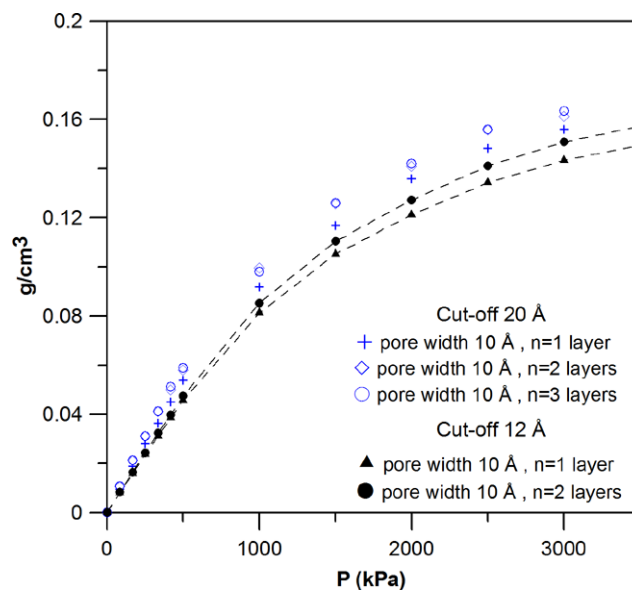


**Fig. 2** Simulated adsorption isotherm of  $\text{CH}_4$  at 298 K in slit carbon pore of  $H_{cc} = 70$  Å and 10 graphene layers used to calibrate the solid-solid parameter. Simulated—line and open circles. Experimental—solid diamonds. Line is drawn as a guide to the eye

independent single surface adsorption behavior. The simulated methane isotherm at 298 K with adjusted parameter calculated by GCMC is shown in Fig. 2. The experimental isotherm for Vulcan (Sweatman and Quirke 2001) is also shown. The estimated value for our adjusted well depth of the solid fluid parameter ( $\epsilon_{sf} = 0.11$  kcal/mol) is practically the same value of the Sweatman and Quirke parameter ( $\epsilon_{sf} = 0.1136$  kcal/mol). Taking into account that those authors used the Steele potential, this small difference in  $\epsilon_{sf}$  indicates that our 70 Å, 10 graphene sheets explicit model yields a good representation of the Steele infinite thick wall model.

After the force field fitting, we deleted successive layers to generate a pore model with only one layer. The one layer pore isotherm calculation was performed for pore widths of 7, 10 and 30 Å. After these calculations, another layer was added and the process repeated until no more variation in the density of adsorbed methane was observed. Isotherms for 1, 2 and 3 graphene layers in the 10 Å pore are shown in Fig. 3. As previously found, the influence of the number of carbon layers is not significant for  $n > 2$  for all pore width tested. This result shows fine equivalence between our explicit model and the Steele finite wall since we found methane density variations of 5 to 8 %, in the same order of magnitude of Chen et al. (1997) study.

Since we may find in the literature diversified cut-offs for finite wall model simulations, we decided to investigate how different cut-offs (20 and 12 Å) affect the density of adsorbed methane. Surprisingly, the difference between one



**Fig. 3** Effect of the pore wall thickness on the methane density at 303 K for pore width  $H_{cc} = 10$  Å and two different cut-offs. Graphene layers ( $n$ ). Cut-off 20:  $n = 1$  (cross),  $n = 2$  (open diamond),  $n = 3$  (open circle). Cut-off 12:  $n = 1$  (solid triangle),  $n = 2$  (solid circle). Dotted lines are drawn as a guide to the eye

and two layers was practically the same for the two cut-offs tested in spite of the decrease in absolute density for smaller cut offs (see solid triangles and circles in Fig. 3 for 12 Å cut-off). These results suggest that different cut-off values will result in similar methane density variations as a function of the wall thickness change. However, absolute densities of methane in explicit systems with different cut-off values can not be properly compared.

Assuming imprecision in the solid-fluid parameter ( $\epsilon_{sf}$ ) we decide to compare a higher well depth ( $\epsilon_{sf} = 0.121$  kcal/mol) representing an increase of 15 % in well deep previously used ( $\epsilon_{sf} = 0.11$  kcal/mol). The simulated isotherms for the 10 Å pore with this new  $\epsilon_{sf}$  parameter are presented in Fig. 4. As expected, the largest  $\epsilon_{sf}$  parameter increases the absolute amount of adsorbed methane but the difference between the adsorbed amounts for one and two graphene layers remains practically the same. Showing analogy with the cut-off, the system is also insensitive to the increase of the  $\epsilon_{sf}$  parameter.

These results suggest that our ten graphene sheets explicit model correctly reproduces methane density between one and two layers and is therefore equivalent to the Steele finite wall model approximation.

### 3.2 Interpore adsorbate interactions

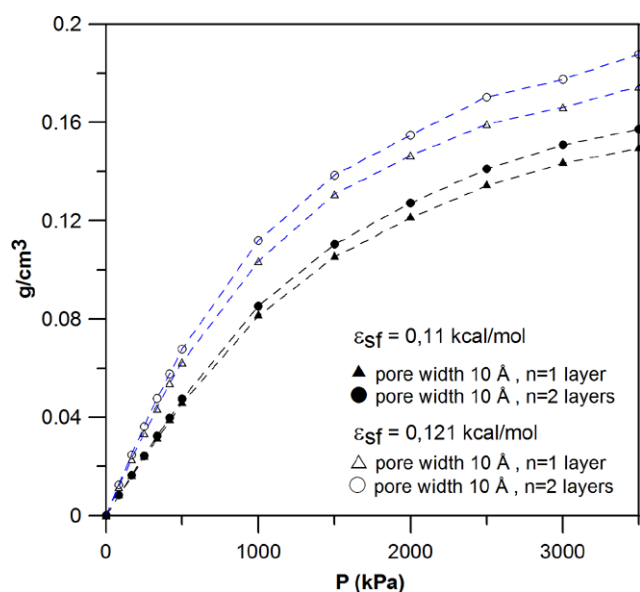
One of the observed factors that increase the interpore adsorbate interactions is the size of the adsorbed molecules. Bhatia (2002) found large filling pressure differences (as high as 25–30 %) when the adsorption of butane molecules was



simulated in subcritical (272 K) conditions in a 10.3 Å pore, in spite of these values being negligible for nitrogen under the same conditions.

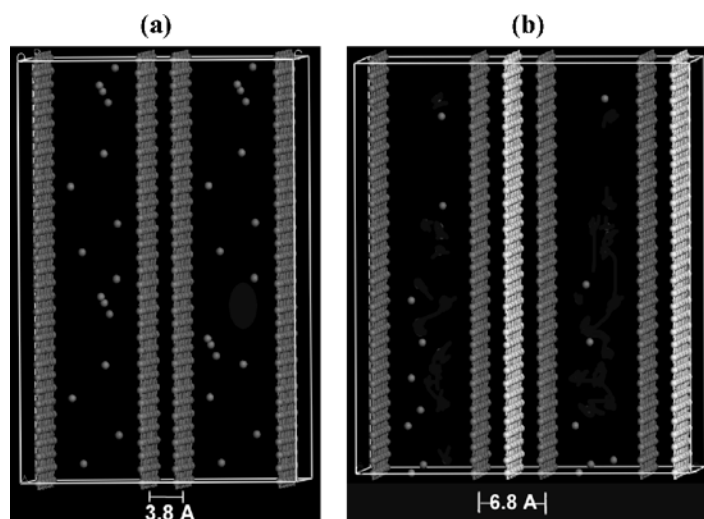
To investigate inter pore interactions, we first develop an explicit pore model and after, tried to reproduce the Bhatia butane simulated isotherms using this model. After this, the explicit model was used to evaluate the impact of the inter pore interaction for linear C1 to C4 alkenes series.

Our explicit model appropriated to investigate inter pore interactions was based in the study of Patrykiewicz et al. (2000). They test a periodic network of pores with width  $H_{cc}$  and distance between neighboring pore wall of  $j$ . Bha-



**Fig. 4** Effect of the  $\varepsilon_{sf}$  parameter and pore wall thickness on the methane density at 303 K: pore width,  $H_{cc} = 10$  Å, Cut-off 20 Å. Graphene layers ( $n$ ).  $\varepsilon_{sf} = 0.11$  kcal/mol:  $n = 1$  (solid triangle),  $n = 2$  (solid circle);  $\varepsilon_{sf} = 0.121$  kcal/mol:  $n = 1$  (open triangle),  $n = 2$  (open circle). Dotted lines only to guide the eye

**Fig. 5** View of the explicit pore models used in the inter pore interaction study. Pore (a) is a one layer graphene wall pore of 10 Å (center to center width). Pore (b) has a dummy wall of graphene (light gray) giving two independent adsorption volumes of 10 Å (center to center width) each. The center to center distance through dummy wall in pore B is 6.8 Å

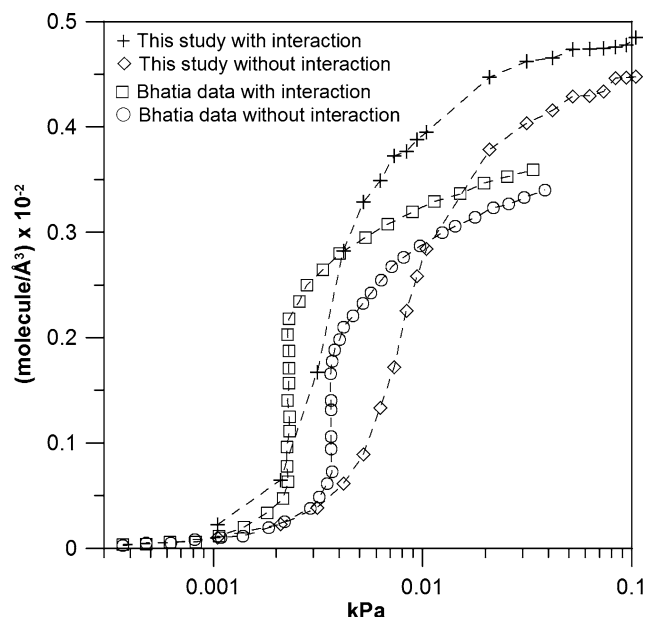


tia uses pores of approximately  $H_{cc} = 10$  Å, with only one Steele finite wall layer with and without inter pore interaction. The simplest manner to eliminate the inter pore interaction in an explicit model scheme, is to add a dummy wall of graphene in one side of the pore (see Fig. 5—pore B). Patrykiewicz has found that for distances  $j$  greater than  $1/2H_{cc}$  the influence of inter pore interaction was insignificant. The inclusion of a dummy wall will give a distance  $j$  between neighboring pores of 6.8 Å that is greater than  $1/2H_{cc} = 5$  Å.

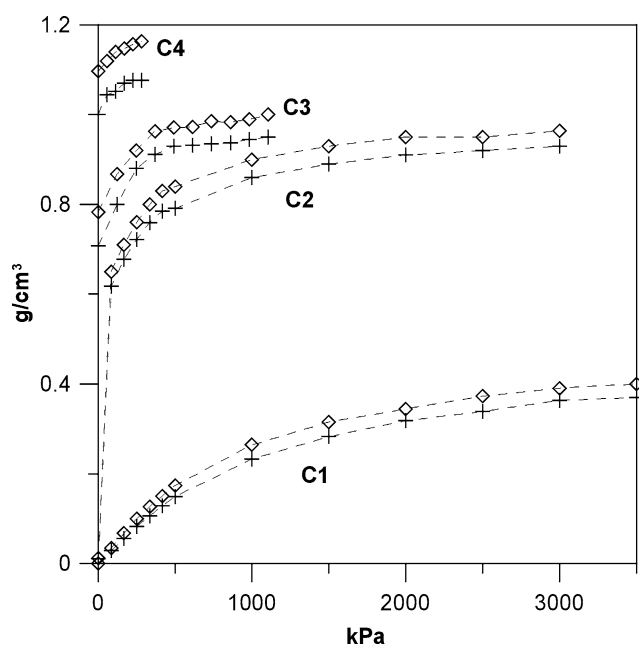
To validate this new explicit model we simulated the adsorption of butane with and without inter pore interaction (cut-off of 20 Å was used), in the same conditions of Bhatia (2002) (pressures from 0.001 to 0.1 kPa and 272 K) and with the same butane model (butane is represented as a sphere of  $\sigma_{ij} = 4.897$  Å and  $\varepsilon_{sf} = 0.738$  kcal/mol). Our simulated results, together with Bhatia's reported results (2002), are plotted in Fig. 6. To better adjust the pressure inflection behavior in our set of isotherms with Bhatia's results, we had to increase the  $\varepsilon_{ss}$  parameter by 20 %. The discrepancies between Bhatia's results (2002) and our isotherms are probably due to the different computational methods (DFT  $\times$  Monte Carlo) as usually reported in previous studies (Ravikovitch et al. 2000; Vishnyakov et al. 1999) and the use of a crude butane sphere model.

Since our explicit model adequately followed the behavior of Bhatia's (2002) results, we proceeded and calculated the adsorption isotherms from C1 to C4 alkanes for the two conditions: with and without inter pore interaction. The results can be seen in Fig. 7. Inter pore interaction increases adsorption from 4 % (C1) until 6 % (C4).

Given our objective of know how to design an activated carbon with a lower retention capacity of heavier alkanes, the inter pore interaction results lead us to an interesting conclusion. While on the one hand, more layers reduce the inter pore interaction, on the other hand increases the overall



**Fig. 6** Validation of the dummy graphene wall pore model through reproduction of the simulated Bhatia (2002) butane isotherms at 272 K. Butane densities in the pores of Figs. 5a (cross) and 5b (diamond)



**Fig. 7** Simulated alkanes adsorption isotherms (C1 to C4) at 303 K in pores with inter pore interaction (diamond) and without inter pore interaction (cross)

solid-fluid interaction. As the magnitude of the two forces are equivalent, the retention capacity of heavier alkanes is the same whether in activated carbons with few layers (stronger inter pore interaction) or with two or more layers (stronger solid-fluid interaction).

It should be stated at this point that our results, as normally done for adsorption simulations, did not take into

account the possibility of surface mediation effects. Fluid molecules close to the surface would be distorted (compared to when they are in the isotropic environment of the bulk phase) and would not interact in the same way as they do in the bulk. Indeed, these effects, if considered in our system, would imply in a reduction of the potential energy between the two adsorbate particles (Birkett and Do 2007), which would reduce the inter pore interactions.

## 4 Conclusions

We simulated alkanes densities through the grand canonical Monte Carlo method in different explicit carbon pore models to investigate the effect of wall thickness and inter pore adsorbate interaction. An explicit pore model with ten layers of graphene sheets was used in the wall thickness study. Cut-off values and solid-fluid parameters were also altered to evaluate the sensibility of the system to such variations. The adsorbed methane densities stay unchanged after  $n > 2$  with methane density variations until 8 % between pore walls with one and two graphene layers. These variations are in the same range of Steele—DFT previous studies. The methane densities of the system did not present significant influence of the cut-off or the solid-fluid parameters.

We also investigated the effect of inter pore adsorbate interactions through the walls of the graphene layers. A new pore model with an extra dummy graphene wall was proposed for blocking the inter pore interaction in the explicit model scheme. The system presented changes in adsorption behavior between blocked and unblocked pores. Inter pore interaction increases adsorption in the range of 4 % to 6 % for C1 and C4 alkanes, respectively. The adsorption improvement has the same magnitude for carbons with few layers (stronger inter pore interaction) as for carbons with two or more layers (stronger solid-fluid interaction). Considering that surface mediation is negligible, we can not reduce the carbon retention capacity of heavier alkanes by changing the number of planes of graphene sheets.

The explicit models proposed can be successfully used in the elaboration of virtual porous carbon models to reproduce wall thickness and inter pore adsorbate interactions phenomena.

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