



# Adsorption of argon on graphitized carbon black preloaded with methanol, ammonia and water: The role of adsorption regions and adsorbates

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## ABSTRACT

We have carried out an extensive computer simulation study of argon adsorption on graphitized thermal carbon black (*GTCB*) preloaded with associating fluids having different strengths of hydrogen bonding namely: methanol, ammonia and water, in order to identify the different regions for adsorption of simple gases and associating fluids. Adsorption on *GTCB* is governed by the interplay among three interactions: (1) fluid–fluid (*FF*), (2) fluid–functional group (*FFG*) and (3) fluid–basal plane (*FB*). Depending on the relative strength of the interactions, the mechanism of adsorption of the associating fluids shows a diversity of behaviour: (a) for methanol, clustering on the basal plane is favoured, (b) for ammonia, clustering is initiated at the functional groups and molecules spill-over from these onto the basal plane, and (c) for water, clustering occurs around the hydroxyl groups and the water clusters grow without spilling onto the basal plane. These mechanisms are investigated by carrying out grand canonical Monte Carlo simulations of argon adsorption at 87 K on *GTCB*, preloaded with the associating fluid, and we find that the simulation results are in good agreement with the experimental data of Berezkina et al. [1]. Through detailed analyses of the isotherms, the isosteric heats and microscopic configurations, we identify the role of the functional group, the basal plane and the adsorbate on the adsorption mechanism. These have led us to confirm that the mechanism of water adsorption on *GTCB* proceeds by forming an embryo of a *FG*-water complex which grows to form nanoscale water clusters, followed by merging of these clusters, when they are sufficiently close together, to form a bridge and then develop to form mesoscale clusters [2].

## 1. Introduction

Adsorption of gases on graphitized thermal carbon black has been extensively studied experimentally and theoretically with the aim of investigating the intrinsic interaction between an adsorbate molecule and the graphene layers, and to characterize the structure of the first adsorbate layer [3,4]. Graphitized thermal carbon black (*GTCB*) is produced by thermal treatment of carbonaceous precursors at extremely high temperatures, usually greater than 2700 °C, and exposes well-defined flat surfaces of energetically homogeneous basal planes, forming multiple faces of a polycrystallite. Nevertheless, despite careful preparation and thermal treatment at extremely high temperatures, *GTCB* is not solely composed of parallel homogeneous graphene layers, but contains small amounts of very strong adsorption sites at the junctions between the adjacent faces of the poly-crystallites; as evidenced by the strong heat of adsorption at very low loadings [5,6]. These strong sites are either crevices (ultrafine pores) whose the solid-fluid potential energy is strongly negative because of the overlap of the adsorption potentials exerted by the opposite surfaces of a crevice [7],

or functional groups attached at the edges of the graphene layers [8,9]. There is sufficient experimental evidence that functional groups are retained, no matter how high the graphitization temperature is [10–12]. Thus, in terms of the adsorption strength, *GTCB* has two distinct adsorption spaces of different size and affinity: (1) the basal plane of graphene layers which interact with an adsorbate molecule through dispersion forces, and (2) the functional groups, which carry partial charges and whose interaction is primarily electrostatic.

The basal planes comprise most of the adsorbent surface area and, since the C–C separation in graphite is very small (0.142 nm), have a high atom density. There is therefore a strong dispersion interaction between graphite planes and an adsorbate. On the other hand, the smaller space occupied by the functional groups are the primary adsorption sites for polar adsorbates.

Although adsorption may be initiated at crevices for adsorbates that have no electrostatic sites, adsorption on the basal plane is the only mechanism for them to form molecular layers. Rare gas species such as argon are examples of this class of adsorbate. However, for strongly associating fluids, such as water, adsorption occurs primarily at the

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electrostatic sites of the functional groups, and further adsorption proceeds by intermolecular interactions in the growing water clusters, rather than by interactions with the basal plane [8,13–16]. Adsorbates such as methanol and ammonia lie between these two extremes.

For molecules carrying partial charges, both the crevices and the oxygen-containing functional groups can be strong adsorption sites, and clusters can grow from these locations.

The amount adsorbed does not however, depend only on the affinity of a site, but also on the number of sites available for adsorption; for example water clusters form on functional groups, because these are strong sites for further water adsorption, but cover a much smaller area than the area of the basal plane [2,17].

To summarise, the adsorption mechanism of any adsorbate depends on the following:

1. The balance between, the interactions between the adsorbate molecule and the various adsorption spaces (of different affinity) and the fluid-fluid interaction.
2. The number of adsorption sites at the various adsorption spaces.
3. The temperature.

We have cited two extreme adsorption mechanisms for simple gases and water. For adsorbates that have weaker hydrogen bonding (lower electrostatic partial charges), such as ammonia and methanol, coverage of the various adsorption spaces is comparable, and proceeds by a mechanism which we have previously referred to as “spill-over” [3].

An example is methanol adsorption on *GTCB* where cluster formation and growth on the functional groups, initiated by strong electrostatic interactions, is accompanied by adsorption on the basal planes due to dispersion interactions between the methyl group and oxygen with the basal plane. Although the basal plane potential energy is weaker than the electrostatic energy, this is compensated by the much larger surface area of the basal plane compared to that of the functional groups. Because of this, comparable adsorption on these two adsorption spaces, shows a strong increase at around 0.2 reduced pressure [18,19]. The adsorption of ammonia which has a strongly charged nitrogen site, is intermediate between water and methanol and the corresponding increase in adsorption occurs at a relative pressure of 0.5 [20]. The difference in adsorption mechanism between water and methanol was highlighted in the experimental work of Dubinin and co-workers [1,21,22]. These authors showed that the adsorption isotherm for nitrogen (or argon) on *GTCB* preloaded with an “equivalent” monolayer of water is the same as that on pristine *GTCB*, but that the amount of nitrogen adsorbed decreases significantly on *GTCB* preloaded with methanol, which demonstrates that the structures of an adsorbed film of water and of methanol are different.

In a previous study, we proposed a molecular model for *GTCB* as a composite of basal plane graphite surface with micropores and hydroxyl groups at the junction. Simulations of argon at 90 K, using this model, successfully described published experimental data [23], confirming the existence of strong sites on *GTCB*. Here, we have used this model to simulate the experimental data of Dubinin and co-workers [1,21] by studying the adsorption of argon on *GTCB* preloaded with the associating fluids, methanol, ammonia and water, chosen to assess the effects of the different strengths of hydrogen bonding in different adsorption spaces. We have placed particular emphasis on the microscopic configurations and the isosteric heat in order to elucidate the different adsorption mechanisms for these adsorbates.

## 2. Theory

### 2.1. Fluid-Fluid potential energy

The interaction energy between two molecules  $i$  and  $j$ ,  $\varphi_{ij}$ , is given by the sum of the Lennard-Jones (LJ) and Coulombic interactions:

**Table 1**  
Molecular parameters and Cartesian coordinates of adsorbate in this work.

Molecule	Site	$\sigma$ (nm)	$\epsilon/k_B$ (K)	Q (e)	x- (nm)	y- (nm)	z- (nm)
Ar	Ar	0.33952	116.79	0	0	0	0
CH <sub>3</sub> OH	CH <sub>3</sub>	0.375	98.0	0.265	-0.143	0	0
	O	0.302	93.0	-0.7	0	0	0
	H	0	0	0.435	-0.0300	0.0896	0
NH <sub>3</sub>	N	0.3385	170	-1.035	0	0	0
	H	0	0	0.345	-0.0381	-0.0938	0
	H	0	0	0.345	-0.0381	0.0469	-0.0812
	H	0	0	0.345	-0.0381	0.0469	-0.0812
H <sub>2</sub> O	O	0.312	80.51	0	0	0	0
	H	0	0	0.241	0.0757	0.0586	0
	H	0	0	0.241	-0.0757	0.0586	0
	q	0	0	-0.241	0	-0.0404	0.0572
	q	0	0	-0.241	0	-0.0404	-0.0572
	q	0	0	-0.241	0	-0.0404	-0.0572

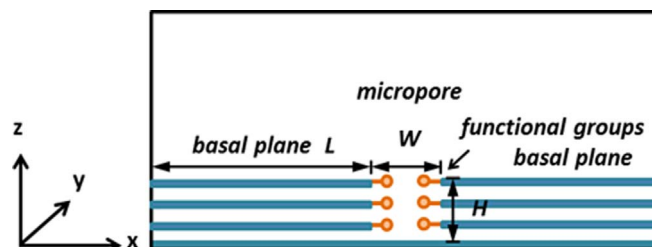
$$\varphi_{ij} = \sum_{c=1}^C \sum_{d=1}^D 4\epsilon_{ij}^{cd} \left[ \left( \frac{\sigma_{ij}^{cd}}{r_{ij}^{cd}} \right)^{12} - \left( \frac{\sigma_{ij}^{cd}}{r_{ij}^{cd}} \right)^6 \right] + \sum_{a=1}^A \sum_{b=1}^B \frac{q_i^a q_j^b}{4\pi\epsilon_0 r_{ij}^{ab}} \quad (1)$$

where  $A$  and  $B$  are the number of partial charges and  $C$  and  $D$  are the numbers of LJ sites on the molecules  $i$  and  $j$ , respectively,  $\epsilon_0$  is the permittivity of the vacuum,  $r_{ij}^{ab}$  is the separation distance between the charge  $a$  on the molecule  $i$  and the charge  $b$  on the molecule  $j$  having charges  $q_i^a$  and  $q_j^b$ , respectively,  $r_{ij}^{cd}$  is the separation between the LJ site  $c$  on the molecule  $i$  and the LJ site  $d$  on the molecule  $j$  with a combined LJ well-depth of  $\epsilon_{ij}^{cd}$  and a combined LJ collision diameter of  $\sigma_{ij}^{cd}$  for the two sites. The potential models for the adsorbates used in this study were taken from the literature: argon from Varbec’s model [24], methanol from the TraPPE model [25], ammonia from Kristof [26] and water was modelled with the TIP5P model [27]. The molecular parameters of these models are presented in Table 1.

### 2.2. Solid-fluid potential model

The model for graphitized carbon black with micropore crevices, grafted with hydroxyl groups, is shown in Fig. 1. There are two distinct adsorption sites: (1) the basal plane and (2) a micropore with the functional groups that are attached to graphene edge sites forming its walls. Each of the two basal planes consists of 3 parallel energetically homogeneous graphene layers, which are finite in the  $x$ -direction and infinite in the  $y$ -direction (perpendicular to the page). The solid-fluid potential energy between an LJ site on an adsorbate molecule and each of these layers was calculated with the Bojan-Steele equation [28–30]. The length of basal plane ( $L$ ) in the  $x$ -direction was 20 nm, and that in the  $y$ -direction was five times the spacing between the two hydroxyl groups. The LJ parameters for a carbon atom in the graphene layer were  $\sigma_{ss} = 0.34$  nm and  $\epsilon_{ss}/k_B = 28$  K. The interlayer distance between two graphene layers was 0.3354 nm, and the carbon atom surface density was  $\rho_s = 38.2$  nm<sup>-2</sup>. The micropore at the junction between two sets of basal planes, had a width ( $W$ ) and height ( $H$ ) both of 1 nm.

The functional groups were represented as hydroxyl groups



**Fig. 1.** Schematic diagram of the model with basal planes, and a micropore crevice with functional groups attached at the junction.

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