

Heterogeneity on high-resolution α_s plots for carbon nanotubes—GCMC study†

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We present the first study showing the influence of heterogeneity of the internal wall of carbon nanotubes on the shape of high resolution α_s -plots.

The concept of comparative plots was first proposed by Shull in 1948,¹ and from that time it has been developed by different authors.¹ This idea inspired Lippens and deBoer¹ who proposed so called *t*-plot in 1965. Since the term monolayer was controversial for adsorption in carbon micropores, Sing proposed the more general idea of the α_s -plot¹ developed further by Lecloux and Pirard.¹ Today due to experimental possibilities in determination of low-pressure isotherms, usually the high-resolution α_s -plot (called here HRAP) is used, as proposed by Kaneko *et al.*² This method is a standard tool for characterisation of porosity of adsorbents. Due to progress in molecular simulations it was possible to present the general classification of HRAPs and the relation between the shape (and deviations from linearity) and the mechanism of adsorption and pore size distribution of an adsorbent. However, the classifications of this type are usually based on the models of ideal pores, for example slits with homogeneous pore walls. Because there is a progress in developing of new methods of preparation of carbon materials having well defined pore structures (*i.e.* carbon nanotubes, carbons having ordered pores and so on) the HRAP is very simple and fast method of characterisation of new materials. However, problems with the choice of the reference solid often occur. Therefore, the adsorption isotherm on the reference solid obtained from molecular simulations has been suggested, and this is applied by many authors. But another problem with the description of obtained from experimental data HRAP is often observed, *i.e.* an unexpected derivation of this plot from linearity. Inoue *et al.*³ while studying nitrogen adsorption on carbon nanotubes reported the HRAP for obtained data using the reference adsorption isotherm of nonporous carbon black. Since this plot was “wavy” they concluded that if there is an

adsorption process other than layer-by-layer adsorption on a flat surface or there is an energetic difference between the reference and sample surfaces, a deviation from the line passing through the origin can provide such information. The linear region around $\alpha_s = 1$ was extrapolated to the origin. There were three deviations of (A), (B), and (C). The downward deviation (A) at a very low α_s -region stems from the surface energy difference; the surface of the carbon nanotube is more stable than that of the reference carbon black. Both deviations of (B) and (C) can be attributed to an additional adsorption other than layer-by-layer adsorption, that is, capillary condensation. In this study we show, that using the GCMC simulations the mentioned HRAP can be recovered and “an energetic difference between the reference and sample surfaces” can be caused by the heterogeneity of internal surface of carbon nanotubes. To our knowledge, there are no reports showing in what extend HRAP can be disturbed by surface heterogeneity.

Adsorption in single multiwalled carbon nanotubes is studied. We neglect adsorption between nanotubes, however measuring adsorption on nanotubes closed and next opened this can be easily calculated.³ Fig. 1 shows the considered pore geometries and the location of pores in the coordinate system (only the internal walls are shown). They are placed in the same way (and have the same dimension) in the *z* direction and have the ends enabling application of the periodic boundary conditions. The internal wall of each pore is constructed from carbon atoms ($d_{CC} = 0.141$ nm). Three carbon layers separated by 0.335 nm were considered in each wall. In the *x* and *y* directions the dimensions of simulation box were limited by the values of D_{cyl} , (they are tabulated in Fig. 1, str_R denotes the reference isotherm taken for the construction of HRAPs). Those values were selected basing on the diameter of the cylinders given by:

$$D_{cyl} = d_{CC}\{3(n^2 + nm + m^2)\}^{1/2}/\pi \quad (1)$$

They were chosen to obtain similar structures therefore the value of *n* in (*n*, *m*) was changed by 12 (we applied the Nanotube Modeller software⁴). The defecting of walls produces vacancies located at the same place for different nanotubes. The idea of the creation of defects in carbon walls was proposed by Turner and Quirke⁵ who studied by GCMC simulation the influence of defected graphite surface on the adsorption properties of carbon black. This idea was also applied by Do and Do who to introduce the defects proposed the simple numerical procedure⁶ used also in this study. We considered the spheres having the centre located inside the six-membered carbon ring. In this way four defects were created

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† Electronic supplementary information (ESI) available: The movie showing the mechanisms of adsorption in initial and defected nanotubes with relation to the shapes of high resolution α_s plots. See DOI: 10.1039/b806906a

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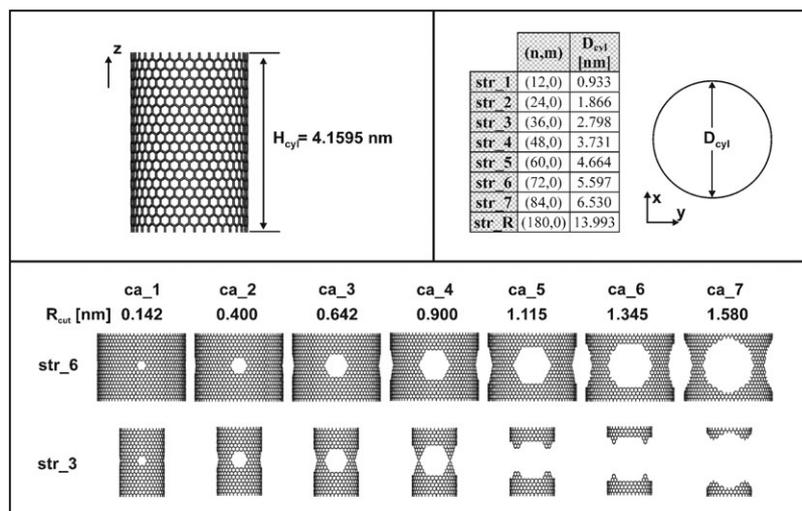


Fig. 1 Simulation box parameters, the geometric parameters of studied nanotubes and introduced defects in internal wall of nanotubes, with applied notification. R_{cut} is the radius of the spheres deleting carbon atoms from the internal layer of the nanotube.

for each tube. Next the values of the radius of the spheres (R_{cut}) deleting carbon atoms from internal layer, were progressively increased (see Fig. 1). In Fig. 1 we show the “holes” created by this procedure. The rise in the value of R_{cut} leads to the rise in the number of deleted carbon atoms and depending on the size of the tube, this can lead to deleting of almost all carbon atoms from inside (str_3, defected in the way ca_7—Fig. 1). In such a case all created “holes” join (this situation occurs for ca_5 and larger). However, this situation does not occur for the case of larger pores and here the independent areas of heterogeneity are still present. For all tubes Ar adsorption isotherms were simulated using the grand canonical Monte Carlo method. The energy of fluid–fluid (ff) interactions was modelled by the classical Lennard-Jones (LJ) potential taking the following values of the parameters: $\sigma_{\text{ff}} = 0.3405$ nm, $\epsilon_{\text{ff}}/k_{\text{B}} = 119.8$ K.⁷ The potential cut-off was at $r_{\text{cut}} = 5\sigma_{\text{ff}}$. The energy of solid–fluid interactions with the internal layer of a carbon pore was calculated from the LJ potential assuming: $\sigma_{\text{sf}} = 0.34025$ nm, $\epsilon_{\text{sf}}/k_{\text{B}} = 57.92$ K.⁷ The solid–fluid interactions with outer carbon layers were calculated using analytical potential model derived by Tanaka *et al.*⁸ using the density of carbon atoms in the wall equal to 38.2 nm⁻², and the respective interlayer spacing value (0.335 nm). The interaction with each layer was calculated by summation. All isotherms were simulated for the temperature of $T = 87$ K. Periodic boundary conditions were applied in one direction (z axis). The probabilities of the change of the state of the systems *via* displacement, creation and/or annihilation of Ar atom were the same and equal to (1/3).

Fig. 2 shows the comparison of HRAPs for the studied nanotubes. The mechanisms of adsorption for ideal and representative nanotubes with defects (and the relation to the shapes of high resolution α_{s} plots) can be observed on the movie provided as ESI† (it was created using the VMD program⁹). For adsorption on ideal structures without defects (ca_0) one can observe two upward deviations for smaller tubes and one for the str_7. As it was pointed out by Ohba and Kaneko¹⁰ this upward deviation (up to α_{s} ca. 0.3) stems from

the enhanced adsorption on monolayer adsorption due to strong molecule–wall interaction. The second deviation(s) for α_{s} larger than ca. 0.35 is due to rearrangement of adsorbed atoms during condensation in a nanotube. For the largest nanotube, the first deviation is absent since the mechanism of adsorption is similar to this observed for the reference tube. As it can be seen in Fig. 2 the heterogeneity has large influence on the recorded HRAPs. This is shown for structure str_2. One can observe the fluttering of the first deviation due to delay in creation of monolayer comparing to the nanotube without defects, while the second deviation is strongly marked. Therefore, there is the relation between the surface area covered by the deviation on the HRAP and the heterogeneity of the internal carbon wall (and this effect needs further studies). Interesting situation is observed for the largest pores having the ca_6 defects. One can see similar effect as observed by Inoue *et al.*³ *i.e.* small deviations from linearity on the α_{s} plots. Therefore, our results show that this type of HRAP can be caused by the heterogeneity of the internal walls of carbon nanotubes. In fact the existence of such defects is possible in nanotubes as for example, bamboo-like closed shells formed along the tube axis instead of well-defined hollow channels running from one end all the way to the other end of the nanotube.¹¹ Those defects are introduced during the procedure of fabrication; however, our results can also mimic the necks or amorphous carbon present inside the nanotubes. The results for defected str_6 confirm the hypothesis that the deviation of α_{s} plots from linearity for large nanotubes is caused by the heterogeneity of the internal walls. As can be observed on the movie in the ESI, the first downward deviation (comparing to the plot for initial structure, where the dashed line is plotted) is caused by “holes” in the monolayer, since adsorbed Ar atoms prefer interactions with walls, and monolayer is irregular because atoms adsorbed in defects have different energy that those covering undefected parts of the walls. The point where all plots coincide reflects the creation of the second layer inside tubes, however the arrangement of molecules in third layer is influenced by heterogeneity in

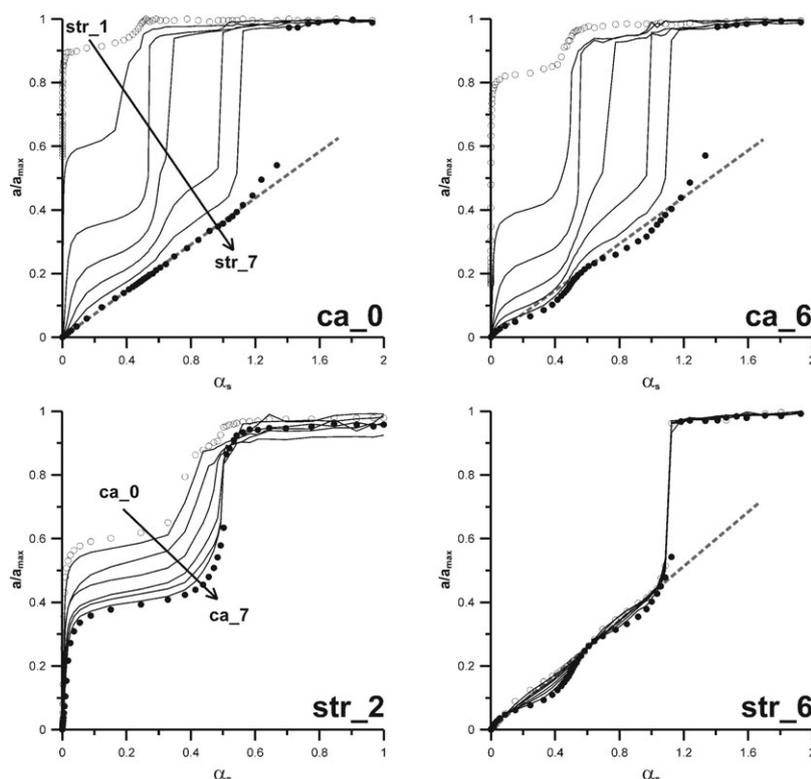


Fig. 2 HRAPs—upper panel—for nanotubes without defects (the diameter increases from str_1 up to str_7—left figure), for the same nanotubes but with defects of ca_6 type (right figure), bottom panel—the change in the shapes of α_s plots for str_2 with progressive defecting (left), the same for larger nanotube (str_6—right).

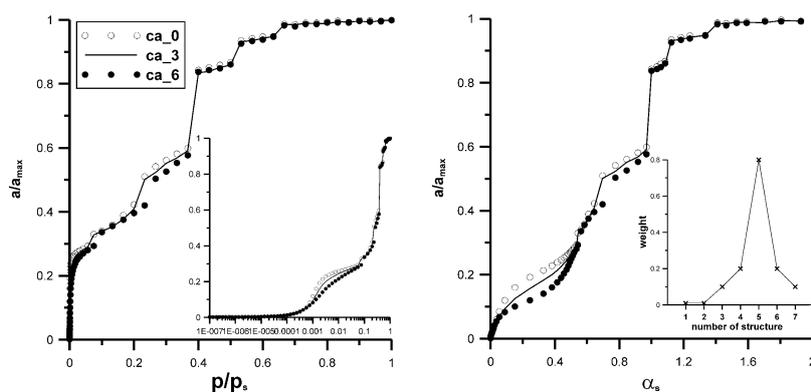


Fig. 3 Global adsorption isotherms generated for ideal and disturbed nanotubes (left) and corresponding HRAPs (right). Inset shows the assumed distribution of nanotubes.

fluid–fluid interactions, what is reflected by the second downward deviation before this observed for condensation (where all curves coincide). Finally, in Fig. 3 we show the influence of heterogeneity on HRAPs for isotherms generated for nanotubes with distributed internal dimension (which is observed in real systems). Using the global adsorption isotherm equation we generated the isotherm for ideal nanotubes and for nanotubes with defects and exactly the same distribution. One can observe that with the rise in defecting, the isotherm becomes more linear (if plotted in the log scale). The differences in obtained α_s plots are clearly visible, showing that this method is very sensitive to heterogeneity. We hope that the presented

results will be interesting from the point of view of characterisation of carbon nanotubes by the α_s plot technique.

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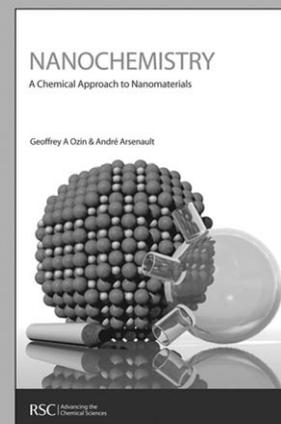
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