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To what extent can mutual shifting of folded carbonaceous walls in slit-like pores affect their adsorption properties?

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Abstract
We have performed systematic Monte Carlo studies on the influence of shifting the walls in slit-like systems constructed from folded graphene sheets on their adsorption properties. Specifically, we have analysed the effect on the mechanism of argon adsorption (T = 87 K) and on adsorption and separation of three binary gas mixtures: CO₂/N₂, CO₂/CH₄ and CH₄/N₂ (T = 298 K). The effects of the changes in interlayer distance were also determined. We show that folding of the walls significantly improves the adsorption and separation properties in comparison to ideal slit-like systems. Moreover, we demonstrate that mutual shift of sheets (for small interlayer distances) causes the appearance of small pores between opposite bulges. This causes an increase in vapour adsorption at low pressures. Due to overlapping of interactions with opposite walls causing an increase in adsorption energy, the mutual shift of sheets is also connected with the rise in efficiency of mixture separation. The effects connected with sheet orientation vanish as the interlayer distance increases.

Keywords: folded graphene, slit-like pores, adsorption, gas mixture separation, Monte Carlo simulations

Online supplementary data available from stacks.iop.org/JPhysCM/16/015002/mmedia

(Some figures may appear in colour only in the online journal)
has been made to predict structures of carbon materials. For example novel carbon allotropes were predicted by Yang et al. [5] by optional substituting carbon atoms in diamond with carbon tetrahedrons. Nicolaï et al. [6] proposed new types of nanopores and membranes built from gyroid surfaces decorated with single-layer carbon materials. Zhou and Zeng [7] classified polymorphic low-energy sp$^3$-hybridized carbon structures into three groups on the basis of different ways of stacking two (or more) out of five types (A–E) of buckled graphene layers. On the other hand, some ‘strange’ carbon models first theoretically proposed, were next synthesized, for example pillared graphene [8–11] or fullerenes distributed between graphene layers [10, 12–14].

In our recent study [15] we reported for the first time a detailed procedure for creating a simulation model of energetically stable, folded graphene-like pores and simulation results of CO$_2$/CH$_4$ and CO$_2$/N$_2$ separation using these structures. It was shown that folding of graphene structures is a very promising method to improve the separation of CO$_2$ from mixtures with CH$_4$ and N$_2$. It is known that finite graphene

![Figure 1.](image-url)
sheets do not possess ideal flat one-layer geometry. There are the possibilities of the deformation of those sheets by external factors (e.g. thermal fluctuation, mechanical forces, capillary pressure, ultrasonication). From the analysis of various reports in the literature one can see that graphene is one of the strongest materials tested, but because of its 2D nature, graphene is strong only under tension and soft under compression [16]. Besides the physical properties of graphene in the pristine form, the behaviour of graphene under strain also 

Table 1. The values of Lennard-Jones (LJ) potential parameters and point charges applied in simulations.

<table>
<thead>
<tr>
<th>Centre</th>
<th>σ [nm]</th>
<th>ε/κ_B (K)</th>
<th>q/ε</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.3405</td>
<td>119.800</td>
<td>—</td>
<td>[60]</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.2824</td>
<td>28.680</td>
<td>+0.664</td>
<td>[61]</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.3026</td>
<td>82.000</td>
<td>−0.332</td>
<td></td>
</tr>
<tr>
<td>C–H⁺</td>
<td>0.3025</td>
<td>30.600</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>0.3310</td>
<td>36.000</td>
<td>−0.482</td>
<td>[62]</td>
</tr>
<tr>
<td>COM⁻</td>
<td>—</td>
<td>—</td>
<td>+0.964</td>
<td></td>
</tr>
<tr>
<td>Graphene</td>
<td>C</td>
<td>0.3400</td>
<td>28.000</td>
<td>[63]</td>
</tr>
</tbody>
</table>

*Cross-interaction parameters.

†Centre of mass.

graphene synthesis or transfer processes. Wang et al [29] created uniform arrays of graphene crumples on the centimetre scale by controlling simple thermal processing parameters without compromising the electrical properties of graphene. Highly crumpled graphene sheets have been prepared by Yan et al [30] by a facile and rapid route through freezing a chemically reduced graphene oxide aqueous suspension with liquid nitrogen. Zhang et al [36] presented a simple and green but very efficient approach using two standard and simple industry steps to make 3D graphene-based porous materials at the bulk scale, with ultrahigh specific surface area (3523 m² g⁻¹) and excellent bulk conductivity. These authors concluded that these materials consist of mainly defected/wrinkled single layer graphene sheets with the dimensions of a few nanometers, with at least some covalent bonds between each other. Moreover, it is well known that the application of so-called two-phase polymerization [37] can lead to the creation of porous carbon containing channel-like pores. In this case one can imagine that the pores are created from folded graphene walls, and now they are not parallel but shifted. One can therefore imagine that intermediate cases of porosity are also possible.

The problem of the deformation of the graphene sheets is also the subject of intensive theoretical investigations [16, 38–48]. Zheng et al [16] studied the mechanical properties of grafold and an architecture of folded graphene nanoribbon via molecular dynamics (MD) simulations. In contrast to graphene, grafold is found to develop large deformations upon both tensile and compressive loading along the longitudinal direction. The mechanical properties of crumpled graphene via MD simulation were studied by Baimova et al [38], Chang et al [39], and Cranford and Buehler [40]. The problem of the formation of corrugated graphene-like surfaces and their stability has been investigated using MD simulation (peeling behaviour of a graphene sheet in adhesive contact with a corrugated copper substrate) [41, 42]. Strain-induced ripples in graphene nanoribbons with clamped edges are also investigated [43]. Graphene nanoribbon folds with single and double closed edges are studies using density functional theory methods [44, 45]. Ju et al [46] theoretically considered thermal conductivity of folded graphene. Neck-Amal and Peeters [47] and Ebrahimi [48] investigated the effect of grain boundary on the buckling of graphene nanoribbons via MD simulations.

C corrugated systems were also studied as nanocontainers [49, 50]. Tozzini and Pellegrini [49] proposed a multilayer graphene-based device in which the storage and release of hydrogen were obtained by exploiting and controlling the corrugation of individual layers of graphene. Dutta et al [50] stated using van der Waals corrected density functional theory calculations that the differential between the adsorption of CO₂ and CH₄ is much higher on folded graphene sheets and at concave curvatures; this could possibly be exploited for CH₄/CO₂ flow separation and gas selective sensors. The discovery of folded graphene shows that the synthesis of carbon membranes containing folded graphene slit-like pores is plausible and it is interesting to investigate the adsorption properties of this type of structure. Using density-functional theory calculations on a variety of model surfaces (folded and rippled
Wood et al. [51] demonstrated that the low theoretical quantum capacitance of graphene-based electrodes can be significantly improved by altering local structural and morphological features.

The boxes constructed from the folded graphene sheets forming slit-like pores considered in our previous work [15] are also a good model representation to study the effects of carbonaceous pore wall folding on the adsorption mechanism.

Figure 2. Comparison of pore size histograms for all the considered systems constructed from folded sheets obtained from the Bhattacharya–Gubbins (BG) method. Subsequent histograms are shifted by 0.7 from the previous ones.
Figure 3. Visualisation of pore sizes detected by the BG method for all the considered systems constructed from folded sheets for the plane $z = 0$. Only the pores with diameters not lower than 0.3 nm are shown. White spaces correspond with the location of carbonaceous structures.
Jagiello et al. [52–54] used pores constructed from corrugated walls during their nonlocal density functional theory (NLDFT) studies on pore size distribution (PSD) determination from experimental adsorption isotherms for real carbons. They showed that due to the use of this approach the typical artefacts of the homogeneous slit pore model were eliminated. Also, the agreement of the new models with experimental data was significantly better than that of the standard slit model. Moreover, one of the available models in interactive SAIEUS software [55] for the analysis of adsorption (PSD calculation data using NLDFT theory) assumed corrugated geometry of pore walls.

In this work, we present the results of systematic Monte Carlo studies on adsorption in model systems constructed from folded graphene sheets. The effects of degree of folding, mutual shifting of the walls and increase in the interlayer spacing are investigated. We consider Ar adsorption at its boiling point and adsorption and separation of model binary gas mixtures (CO2/N2, CO2/CH4 and CH4/N2) at 298 K. Finally we compare obtained results with those calculated previously for nanotubes and porous carbons.

2. Calculation details

2.1. Simulation boxes

We constructed multiplied slit-like systems using folded graphene sheets generated in our previous paper [15]. We used three thermodynamically equilibrated sheets with different amplitudes (A) — see top of figure 1. The following values of A are considered: 0.50, 0.75 and 1.00 nm (we did not use

Figure 4. Ar adsorption isotherms (T = 87 K) for all the considered systems. The dashed lines represent the data for reference systems constructed from flat sheets.
the previously considered sheet with $A = 0.25 \text{ nm}$ since its adsorption properties are not significantly different from the flat graphene sheet [15]). In each simulation box with periodic boundary conditions in all three directions, four sheets were placed in a parallel arrangement. Next, every second sheet was shifted by $1/16$, $2/16$, $3/16$ or $4/16$ of the box length in the $x$ direction—see figure 1. These relative shifts are denoted as RS. RS = $4/16$ is equivalent to antiparallel orientation of sheets. The initial effective distances between sheets ($H_{\text{eff}}$) were selected so that the bulges of opposite carbonaceous structures were osculated for $A = 4/16$ (i.e. the channel-like systems). These interlayer distances were equal to 1.08 nm for $A = 0.50 \text{ nm}$, 1.52 nm for $A = 0.75 \text{ nm}$ and 1.91 nm for $A = 1.00 \text{ nm}$. The series of systems with the smallest initial values of $H_{\text{eff}}$ are named H1. For each series the interlayer distance was next increased by 0.3 nm (obtained series are named H2) and by 0.6 nm (H3). Each system was labelled as Ar$_{x}$xHy,yRS/zz where $x, y$ is the amplitude, $y, y$ is the effective interlayer distance and $zz$ is the relative shift. In addition, for each series (for a given combination of $A$ and $H_{\text{eff}}$ values) we also constructed the reference boxes using ideal flat graphene sheets ($A = 0.00$) placed at an analogous distance. These systems are denoted as A0.00Hy,y. The selected systems together with applied notation are presented in figure 1. Table S1 in the online supplementary data (stacks.iop.org/JPhysCM/16/015002/mmedia) collects the sizes of all the considered simulation boxes.

The porosity of all the studied carbonaceous adsorbents was characterised by a geometrical method proposed by Bhattacharya and Gubbins (BG) [56]. The implementation of the method was described in detail elsewhere [57, 58]. In order to calculate the histogram of pore diameters we applied the uniform grid of test points ($200 \times 200 \times 100$) for each box.

### 2.2. Simulations of argon adsorption isotherms

Argon adsorption isotherms in all the considered systems were simulated using the hyper parallel tempering Monte Carlo method (HPTMC) proposed by Yan and de Pablo [59]. The simulations were performed for Ar boiling temperature ($T = 87 \text{ K}$). For each system, 93 replicas (corresponding to the relative pressures ($p/p_{s}$, where $p$ and $p_{s}$ denote absolute and saturated vapour pressure at the given temperature, respectively) from $1.0 \times 10^{-10}$ to 1.0) were considered. The methodology of computations was described in detail previously [57]. The HPTMC simulations utilized 1 $\times$ 10$^{7}$ cycles (one cycle = 100 attempts of the change of each replica state by (i) creation, (ii) annihilation or (iii) displacement of a randomly chosen atom with equal probabilities, and one attempt of a configuration swap between a pair of randomly chosen replicas). The first 2 $\times$ 10$^{6}$ cycles were discarded to guarantee equilibration. Table 1 collects the values of applied Lennard-Jones (LJ) parameters.

For each simulation point (value of relative pressure) the adsorption amount was calculated from the average number of Ar atoms in each replica ($\langle \text{Ar}\rangle$):

$$
\langle \text{Ar}\rangle = \frac{\sum \text{Ar}}{N_{C} \times M_{C}}
$$

where $N_{C}$ and $M_{C}$ are the number of carbon atoms in the box and the molar mass of carbon, respectively. In addition, for each isotherm the value of Henry’s (or Langmuir) constant ($K_{\text{HL}}$) corresponding with low-pressure region was also determined. The details of these calculations are described in the online supplementary data. Finally, the isosteric enthalpy of adsorption ($q^{\theta}$) was also calculated (from the theory of fluctuations) to study the energetics of the process.

### 2.3. Simulations of gaseous mixtures adsorption

We simulated the adsorption of three binary gas mixtures (important from a practical point of view): CO$_{2}$/CH$_{4}$, CO$_{2}$/N$_{2}$ and CH$_{4}$/N$_{2}$. Their adsorption at $T = 298 \text{ K}$ in the above-described boxes was modelled using the grand canonical Monte Carlo method (GCMC) [64, 65]. Simulations were performed for the total mixture pressure $p_{\text{tot}} = 0.1 \text{ MPa}$ (i.e. atmospheric pressure) and for the following mole fractions of components in the gaseous phase ($y$): 0.0, 0.01, 0.025, 0.05,
0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, 0.975, 0.99 and 1.0. Additionally, in order to check the separation of the mixtures for other pressures, we simulated adsorption of equimolar mixtures ($y = 0.5$) at different total pressure values in the range $1.0 \times 10^{-6}$–1.0 MPa (30 different values). The methodology of calculations was analogous to that described previously [66, 67]. Each GCMC simulation run consisted of $2.5 \times 10^8$ iterations. The first $1.0 \times 10^8$ iterations were discarded to guarantee equilibration. One iteration was an attempt of the system state change by the randomly selected perturbation: (i) displacement and/or rotation of a randomly chosen molecule, (ii) creation of a new molecule, (iii) annihilation of a randomly chosen existing molecule or (iv) swap move with equal probabilities. We used equal probability for each perturbation to guarantee the condition of microscopic reversibility. The values of all the applied interaction parameters are collected in table 1. Other computational details are given elsewhere [12, 66, 68].

From the GCMC simulation results, we determined the average numbers of each kind of adsorbate molecules in the simulation box. These values were used for calculation of mole fractions of components in the adsorbed phase ($x_i$).

Finally, in order to illustrate the efficiency of mixture separation we also computed the values of equilibrium separation factors:

$$S_{1/2} = \frac{x_1/x_0}{y_1/y_2}$$  \hspace{1cm} (2)

The adsorbed phase is enriched in the first component if $S_{1/2} > 1$. Similarly as in the case of Ar adsorption, the isosteric

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**Figure 5.** Isosteric enthalpy of adsorption related to the Ar adsorption isotherms ($T = 87$ K) shown on figure 4. The dashed lines represent the data for reference systems constructed from flat sheets.
enthalpy of adsorption was also calculated from the theory of fluctuations.

3. Results and discussion

3.1. The structure of carbons and its influence on Ar adsorption

Figure 2 collects the pore size histograms calculated using the BG method. Generally, one can observe three important effects. Shifting of the walls increases the pore size; simultaneously very small pores between opposite bulges of carbonaceous structures appear. The effect of the appearance of small pores is especially visible on figure 3 showing the visualization of pore sizes detected by the BG method. Obviously, an increase in interlayer distance causes the rise in pore diameters. Finally, one should notice that for some structures (especially for large RS) the pore diameter reaches the range of mesopores.

Figure 4 collects simulated Ar adsorption isotherms for carbons composed of folded graphene pores, and the isotherms for reference systems (i.e. ideal slit-like graphene pores). It is seen that with the rise in A value maximum adsorption capacity decreases, compared to the reference systems. This is caused by the decrease in pore volumes during the folding of pore walls (see the size of simulation box in x direction ($L_{box,x}$) collected in table S1 in the online supplementary data (stacks.iop.org/JPhysCM/16/015002/mmedia)). On the other hand,
for all the studied cases in the low-pressure limits of adsorption isotherms we observe a rise in adsorption compared to the reference materials. We also observe a rise in pore filling pressure with the rise in RS value for a given series (i.e. for fixed $A$ and $H_{\text{eff}}$) caused by the rise in pore diameters (see figures 2 and 3). A similar effect is observed if the pore diameter increases.

Considering the systems with the smallest interlayer distance between pore walls (i.e. H1 series) one can observe remarkable changes with the change in the RS value. Namely, with the rise in RS value the isotherms become steeper, and this effect is the most clearly visible for $RS = 2/16$. The changes in the series $A0.50H1.08$ and $A0.75H1.52$ have similar qualitative character (figure 4). This can be explained by the analysis of the data collected on figure 3, but it is especially visible on the starting frames of the animations (see animations 1 and 2 in the online supplementary data (stacks.iop.org/JPhysCM/16/015002/mmedia)). One can notice for $RS = 2/16$ the appearance of narrow slit-like pores (remarkably increasing adsorption) vanishing for larger RS values. Additionally, in all the systems adsorption at low pressures also occurs at junctions and on high energy sites of the curved walls. A slightly different situation is observed for the series $A1.00H1.91$. Due to the larger distance between walls, the effect of potential energy overlapping from opposite walls is not as strong as for smaller pores, and adsorption starts simultaneously on curved graphene sheet fragments (present in larger number) and at the junctions (see animation 3 in the online supplementary data).
Due to this effect, the influence of the RS change on adsorption isotherms is in this case small (figure 4).

Since the rise in pore width causes a simultaneous rise in the maximum adsorption capacity one can observe the change in adsorption mechanism (see animations 4–6 in the online supplementary data (stacks.iop.org/JPhysCM/16/015002/mmedia)). In the case of the H2 series (figure 4) for the systems having RS values smaller than 2/16 the differences between isotherms vanish; however they appear for the systems with larger RS values, due to the filling of small pores (~0.3 nm) between opposite bulges. A further rise in the distance between walls (series H3) causes the differences between adsorption isotherms to almost completely disappear. The rise in adsorption, in comparison to the reference system, is caused by the rise in adsorption induced by folding of walls. The appearance of pores (~0.6 nm) between opposite bulges leads to differences in the plots of adsorption isotherms only in the intermediate range of relative pressures (10^{-3}–10^{-2}, see also animations 4–6). With the rise in RS value the swing on adsorption isotherms in this range becomes more pronounced. The differences between isotherms at low pressures are confirmed by the values of Henry’s (or Langmuir) constants which are collected in table 2 and plotted in figure S1 in the online supplementary data. As above the rises in the values of $K_{H/L}$ reflect the regularities observed on figure 4. The fact that the appearance of the narrowest pores and/or of high-energetic places between neighbouring fragments of walls has an important influence on the slope of initial parts of isotherms is

Figure 8. As in figure 6 but for CH$_4$/N$_2$ mixtures.
also confirmed by the values of isosteric enthalpy of adsorption presented in figure 5. The differences in $q_{st}$ values for low adsorption amounts fully correspond to the changes in the shapes of isotherms.

3.2. Adsorption of mixtures

As shown above carbons with folded walls have better adsorption properties towards Ar than ideal slit-like pores. The same can be stated about separation properties. From figures 6–8, collecting the values of equilibrium separation factors for the considered mixtures at the total pressure equal to 0.1 MPa and different compositions, one can see that generally with the rise in $H_{eff}$ the separation factors decrease. The increase in interlayer distance is also connected with reducing (H2 series) or vanishing (H3 series) differences between the systems with different mutual orientation of the walls. The geometry of systems for $RS = 0/16$ is analogous to that in our previous paper [15]. In the case of systems for $A = 0.50$ nm the interlayer distances are similar in the current and in the previous work. So, similar values of equilibrium separation factors are observed. For the other values of $A$ (i.e. 0.75 and 1.00 nm) the higher interlayer distances were necessary to allow unrestricted shift of the walls. Thus, lower values of equilibrium separation factors are observed in this work.

The analysis of separation factors for the H1 series (figures 6–8) leads to the conclusion about similarities in the plots of separation factors for CO$_2$/N$_2$ and CO$_2$/CH$_4$ mixtures.

Figure 9. Isosteric enthalpy of adsorption related to CO$_2$/N$_2$ mixture adsorption at $p_{tot} = 0.1$ MPa and $T = 298$ K in all the considered systems (see figure 6). The dashed lines represent the data for reference systems constructed from flat sheets.
Similarly to the case of Ar adsorption, the best separation properties are recorded for the systems having \( RS = 2/16 \), and just like in the case of Ar adsorption, this is caused by the appearance of small pores preferentially adsorbing CO\(_2\) molecules. The systems having larger RS values (\( RS = 3/16 \) and \( 4/16 \)) show worse separation properties than for \( RS = 2/16 \). In the case of H1 series for \( A = 1.00 \) nm the differences between separation factor values are not large. Here a similar situation as in the case of Ar adsorption is observed, i.e. adsorption properties are determined mainly by the internal parts of curved surfaces (see the solid–fluid potential energy maps collected on figures S2–S4 in the online supplementary data (stacks.iop.org/JPhysCM/16/015002/mmedia)). A different situation is observed for the H1 series if the separation of a CH\(_4\)/N\(_2\) mixture is considered (figure 8). In this case, a significant rise in separation efficiency is observed starting from \( RS = 1/16 \). A further rise in RS values also increases the \( S_{\text{CH}_4/N_2}\) values and the maximum for \( RS = 2/16 \) is not observed for the case of this mixture. Differences observed in comparison to CO\(_2/N_2\) and CO\(_2/\text{CH}_4\) mixtures are caused by the larger diameter of the preferentially adsorbed CH\(_4\) molecule. As a consequence even for small RS values, centres with higher methane adsorption energy are created (see figures S2–S4 in the online supplementary data). The differences described above in the mixture adsorption mechanism at \( p_{\text{tot}} = 0.1 \) MPa connected with mutual shift of walls for the H1 series are also illustrated on animations 7–9 in the online supplementary data.

An increase in interlayer distance by 0.3 nm (series H2) leads to the disappearance of the differences between separation factor values (for all the studied mixtures) for \( S \) values for

![Figure 10](image-url). As in figure 9 but for CO\(_2/\text{CH}_4\) mixture adsorption (data related to figure 7).
RS up to 2/16, and only the systems having larger values of RS (3/16 and 4/16) show better separation efficiency on the similar level as observed for the best H1 systems. As mentioned above, this is a consequence of the presence of small pores between opposite bulges. Figures S5–S7 in the online supplementary data compare the solid–fluid energy maps for adsorption of mixtures’ components in the pores of all the structures in H2 series.

Finally for the H3 series the RS value practically has no influence on separation efficiency. In this case the higher efficiency in comparison to the ideal slit-like systems is determined by the adsorption on surface (higher adsorption energy on folded sheets—see figures S8–S10 in the online supplementary data).

Figure S11 in the online supplementary data compares the values of equilibrium separation factors for equimolar gas mixtures adsorption ($P_{tot} = 0.1$ MPa) in all the considered systems. Figures 9–11 present isosteric enthalpy of all the considered mixture adsorption in all the systems at 0.1 MPa (the data relating to figures 6–8). All the curves are plotted as a function of the mole fraction of preferentially adsorbed component in the bulk phase ($y_{CO2}$, $y_{CO2}^N2$ and $y_{CH4}$, $y_{CH4}^N2$). Since the energy of adsorption of this component is higher than that of the second one, the rise in $y$ causes the increase in the $q^*$ values. The differences in isosteric enthalpy of adsorption between different systems are analogous to those between the equilibrium separation factors shown in figures 6–8. This confirms that the main reason for the changes in...
separation efficiency connected with mutual shift of the walls, and/or increasing interlayer distance, is the appearance or disappearance of the narrowest pores between the neighbouring bulges. In such places the dominant component is adsorbed preferentially with high energy.

Finally, figures 12–14 collect the equilibrium separation factors for the adsorption of equimolar mixtures (all considered) under different total pressure. The rise in the total pressure causes adsorption to take place not only in highly-energetic places but molecules are also bonded on centres having lower adsorption energy. Multilayer adsorption (or even total filling of accessible pores) is also possible especially in the case of CO2 since the considered temperature (298 K) is below the critical value for this gas (304 K). Thus, the rise in total pressure value is usually connected with some increase in the equilibrium separation factors. This is caused by the enhanced disproportion between adsorption of dominant and less adsorbed components. There are some exceptions related to the adsorption of CO2/N2 and CO2/CH4 mixtures in the A0.50H1.08RS2/16 system. In these cases maxima on the curves in the low pressure region are observed. Similar (but less pronounced) behaviour is also observed for A0.75H1.52RS2/16 and A0.50H1.38RS4/16. As was discussed above, high selectivity of mixture adsorption in these structures is connected with the appearance of narrow pores between opposite bulges. The rise in the total pressure means that adsorption takes place not only in these optimal places but also in the remaining pores where selectivity is not as high.

![Figure 12. Equilibrium separation factors for equimolar CO2/N2 mixture adsorption (T = 298 K) at different total pressure (p_{tot}) in all the considered systems. The dashed lines represent the data for reference systems constructed from flat sheets.](image-url)
In consequence, the average value of equilibrium separation factor decreases. Next it slightly increases for \( p_{\text{tot}} \) close to 1 MPa due to multilayer adsorption of CO\(_2\). Comparing the effects of mutual shifting of walls and/or of increase in the interlayer distance for all the systems (figures 12–14) one can see analogous regularities as described above for adsorption of mixtures at \( p_{\text{tot}} = 0.1 \text{ MPa} \) (figures 6–8). However, some differences are observed for adsorption of CO\(_2\)/N\(_2\) and CO\(_2\)/CH\(_4\) mixtures in A0.50H1.08RS0/16, A0.50H1.08RS1/16 and A0.75H1.52RS1/16 systems for the total pressure close to 1 MPa. In this region the values of equilibrium separation factors are similar to those observed for systems with RS = 4/16. This behaviour may be explained by comparison of the pore sizes of these structures (figures 2 and 3). In the case of systems with small RS value the dominant pores have smaller diameter (ca 1 nm for A0.50H1.08RS0/16 and A0.50H1.08RS1/16, ca 1.5 nm for A0.75H1.52RS1/16) than those in systems with high RS (ca 2 nm for A0.50H1.08RS4/16 and ca 2.3 nm for A0.75H1.52RS4/16). In consequence, CO\(_2\) may fully fill pores of the first structures while this is not possible in the case of the second ones. Animations 10–12 in the online supplementary data (stacks.iop.org/JPhysCM/16/015002/mmedia) present the mechanism of equimolar mixtures adsorption at different total pressure values for all the H1 systems.

Summing up, a mutual shift of the folded graphene sheets forming slit-like pores is connected with the formation of small pores. This fact (due to overlapping of interactions with opposite walls) causes a significant increase in adsorption energy and leads to a rise in the efficiency of mixture separation in comparison to ideal slit-like systems. The rise in interlayer

Figure 13. As in figure 12 but for equimolar CO\(_2\)/CH\(_4\) mixture adsorption.
distance is connected with the reduction or disappearance of differences between systems with different shifts. This is caused by the vanishing of effects connected with overlapping interactions with the walls which is demonstrated on solid–fluid energy maps for CO₂, CH₄ and N₂ molecules presented in figures S2–S10 in the online supplementary data.

3.3. Comparison with other systems

To show a comparison with other systems, we chose the CO₂/CH₄ mixture. Figure 15 presents a comparison of equilibrium separation factors for the system having the most promising separation properties (A₀.₅₀H₁.₀₈RS2/16) and for adsorption inside ten single-walled carbon nanotubes ((15,0), (16,0), (17,0), (18,0), (19,0), (20,0), (21,0), (22,0), (23,0) and (24,0)) having diameters in the range 0.826–1.526 nm (the simulated results are taken from our previous study [15]). As one can see, our structure has remarkably larger $S_{CO₂/CH₄}$ values than a (24,0) nanotube with similar pore diameter as the dominant pores in our structure (ca 1.5 nm—see figure 2). Due to the formation of narrow pores between opposite bulges, separation efficiency is comparable with that observed for nanotubes having much smaller diameters. A different situation is observed if we compare the results with those calculated for three virtual porous carbon (VPC, denoted as d₀.₅, d₀.₉, d₁.₃—for their characteristics see [57]) models having very different microporosity (the simulated results for VPCs are taken from our previous study [67]) shown on figure 16. The d₀.₅ carbon has similar diameters of micro pores as the A₀.₅₀H₁.₀₈RS2/16 structure, and two remaining
carbons have smaller micropore diameters. It is seen that A0.50H1.08RS2/16 shows better separation properties than the d0.5 structure and similar to that observed for the d0.9 one. Due to the very much smaller micropores present in d1.3 the separation properties of this structure are the best.

Summing up, our results show that the structures studied in this work containing pores with folded graphene walls should reveal better separation properties than single-walled carbon nanotubes and activated carbon having similar pore diameters.

4. Conclusions

We present the results of systematic Monte Carlo studies on the influence of mutual shift of walls in slit-like systems constructed from folded graphene sheets on the mechanism of argon adsorption (at its boiling point) and on the adsorption and separation of binary gas mixtures (at room temperature). We demonstrate that folding of the walls significantly improves the adsorption and separation properties in comparison to ideal slit-like systems. Moreover, we show that mutual shift of sheets (for small interlayer distances) causes the appearance of small pores between opposite bulges which causes an increase in Ar vapour adsorption at low pressure. Due to the overlapping of interactions with opposite walls causing an increase in adsorption energy the mutual shift of sheets is also connected with the rise in efficiency of mixture separations. The effects connected with sheet orientation vanish as the interlayer distance increases.

The presented results show that the structures studied in this work containing pores with folded graphene walls are very promising since they may display better separation properties than single-walled carbon nanotubes and activated carbon having similar pore diameters.
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