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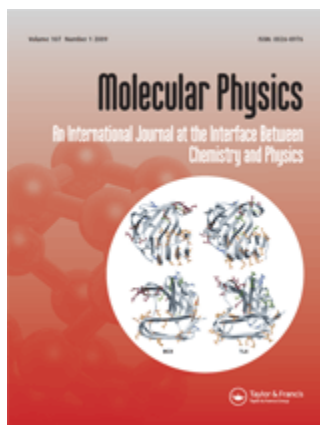
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**Pore geometry and isosteric heat : an analysis for the carbon dioxide adsorption on activated carbon.**

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RESEARCH ARTICLE

**Pore geometry and isosteric heat : an analysis for the carbon dioxide adsorption on activated carbon**

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The isosteric heat of the carbon dioxide adsorption on activated carbon is determined by grand canonical Monte Carlo simulations. The results, obtained at room temperature and low pressures for an adsorbent model with a slit type porosity, show that the isosteric heat depends strongly on the slit width. The maximum of the isosteric heat is reached for a pore with a width such as cooperative effects between the adsorbed molecules enhance the adsorption. The possibility to estimate the isosteric heat of a macroscopic sample, from adsorption isotherms computed for a distribution of slit pores with given sizes, is discussed.

**Introduction**

The isosteric heat is a very important characteristic of the adsorption phenomena. Its value is relevant, in particular for the first stages of the adsorption process, since the released heat increases the delay to achieve an equilibrium state between the adsorbed phase and bulk phase in contact with the porous material. In addition, a large isosteric heat induced by a strong interaction between adsorbed molecules and adsorbing surface can slow the gas desorption. Hence, the determination of the isosteric heat has been studied in many theoretical and experimental works for various adsorbent materials (activated carbons, zeolites, silicalites, ... ) and adsorbed gases (cf., for example, some recent publications [1–11]). For a theoretical computation of the isosteric heat, the adsorbents divide into two main categories. The porous materials, as the zeolites, with a crystalline structure have identical pores at the microscopic scale. For these adsorbents, to estimate the isosteric heat for one or few unit cells of the porous crystal is sufficient to have a reliable value of that of the bulk material. For the porous materials with complex pore networks, as the activated carbons, the whole isosteric heat of a material sample depends on the isosteric heat value associated to each pore type. So, the theoretical calculation of the isosteric heat requires to know the pore size distribution which defines the material porosity and the set of isosteric heats which vary with the pore properties.

The changes of the isosteric heat value with the pore size and shape have been studied mainly by numerical simulations or theoretical methods, as the density functional theory [12–14]. Using a theoretical approximate scheme, Schindler and LeVan [15] have shown that the isosteric heat of simple gases Ar, N<sub>2</sub>, CO<sub>2</sub> or CH<sub>4</sub> adsorbed in graphite slit pores has a maximal value when the slit width, defined

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1 as the distance between the carbon atoms located inside the slit walls, is of the  
 2 order of  $\sim 0.7$  nm. In this work, we present the results of a similar calculation  
 3 for  $\text{CO}_2$  performed by using grand canonical Monte-Carlo (GCMC) simulations  
 4 which allow to take into account the contribution to the adsorption process from  
 5 important cooperative effects between the  $\text{CO}_2$  adsorbed molecules. These effects,  
 6 combined with the modification of the molecule-adsorbent interaction when the  
 7 slit width varies, lead to large differences between the pore isosteric heats. Such  
 8 differences imply that an adequate method must be used to determine the isosteric  
 9 heat of activated carbon samples with various pore size distributions from those  
 10 computed for a set of slit pores with a given width [16].

11 In the first part of this work, is described the model considered for studying the  
 12  $\text{CO}_2$  adsorption in graphitic slit pores. The results of GCMC simulations of this  
 13 process are presented in the second section. The third section is devoted to the  
 14 discussion of the simulation results and to their possible use for a comparison with  
 15 experimental data.  
 16  
 17

### 18 Model Description

19 The  $\text{CO}_2$  molecule is modeled as a linear rigid molecule of length equal to 0.232  
 20 nm and its molecular interactions are described by Lennard-Jones (LJ) pair po-  
 21 tential centers of generic equation  $v_{\text{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ . Two of these  
 22 potentials correspond to oxygen atoms and are located to the molecule ends. The  
 23 third potential corresponds to the carbon atom and is located to the middle of the  
 24 molecule. The LJ parameters of oxygen and carbon potentials are  $\epsilon_0 = 79.0$  K,  
 25  $\sigma_0 = 0.305$  nm, and  $\epsilon_C = 27.0$  K,  $\sigma_C = 0.28$  nm, respectively. In addition, the lin-  
 26 ear quadrupole of the  $\text{CO}_2$  molecule is described by a neutral distribution of three  
 27 charges located at the LJ center positions. The charges on the O atom positions are  
 28 equal to  $-0.35 e$ , that on the C atom position is  $0.70 e$  ( $e$  electronic charge). This  
 29 model of  $\text{CO}_2$  interaction has been tested successfully in the literature [17, 18]. The  
 30 interaction of the carbon atom in a graphite plane is a LJ potential with parameters  
 31  $\epsilon_G = 28.0$  K and  $\sigma_G = 0.340$  nm. The cross-interaction between  $\text{CO}_2$  molecules  
 32 and between  $\text{CO}_2$  molecules and carbon atoms of the pore walls are derived by  
 33 using the Berthelot's rule, expressed by the relations:  $\sigma_{\alpha\beta} = 0.5(\sigma_\alpha + \sigma_\beta)$  and  
 34  $\epsilon_{\alpha\beta} = \sqrt{\epsilon_\alpha\epsilon_\beta}$  where the indices  $\alpha$  and  $\beta$  refer to the indices O, C or G of the LJ  
 35 parameters of a  $\text{CO}_2$  molecule and carbon atom. Such an effective potential for the  
 36 graphite carbon atoms and the rule used to compute the gas-graphite interactions  
 37 have been justified by many studies, cf., for instance, the work on the graphite  
 38 cohesion energy [19], the text-book [20] and the recent comparison with ab-initio  
 39 calculations [21].  
 40

41 The activated carbon model supposes that the material pores are mainly slits  
 42 with different widths [22]. The pore walls are made from a stack of three graphite  
 43 basal planes. Inside the stack, the distance between the planes is equal to 0.34  
 44 nm. The slit width  $h$  is defined as the distance between carbon atoms located in  
 45 the external planes of pore opposite walls. With these characteristics, the specific  
 46 surface of the material model is  $\sim 1030$  m<sup>2</sup>/gr.  
 47

48 The potential energy of one single  $\text{CO}_2$  molecule inside slit pores of the model  
 49 material is presented in Fig. 1. The energy potential varies strongly with increasing  
 50  $h$  and molecule orientation. Fig. 1(a) gives the potential energy for a molecule the  
 51 axis of which is parallel to the pore walls and Fig. 1(b) for a molecule the axis  
 52 of which is perpendicular. For a given  $h$  value, the potential energy of a molecule  
 53 parallel to the walls is larger than that of a molecule perpendicular to the walls. For  
 54  $h \leq 0.5$  nm, the simulations show that in the considered range of pressure at room  
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1 temperature no CO<sub>2</sub> molecule can be adsorbed in pores with such a width. For 0.6  
 2 nm ≤ *h* ≤ 0.8 nm, the potential energy for a molecule with its axis perpendicular  
 3 to the walls is strongly positive and is not plotted. For *h* ≥ 0.8 nm, for both  
 4 molecular axis orientations, the potential has two minima which are located in the  
 5 wall vicinity.  
 6

7  
 8  
 9 **Simulation Results**

10  
 11 The GCMC simulations are realized following the procedure described in the lit-  
 12 erature [23–25]. The GCMC code developed by us and used in previous works,  
 13 for instance [26], implement the Metropolis algorithm adapted to the configuration  
 14 sampling of a GC ensemble in a standard way. Specifically, an initial configura-  
 15 tion of adsorbed molecules in the volume filled with the adsorbent is generated.  
 16 From this initial configuration the new configurations are sampled by iteratively  
 17 attempting to insert a new molecule at random in the volume, to delete or to dis-  
 18 place randomly one of molecules present in the volume chosen at random. These  
 19 changes are accepted or refused accordingly to the GC Boltzmann weight ratio of  
 20 the previous and trial configurations. The set of generated configurations allows to  
 21 compute the average values of quantities as the energy and molecule number.  
 22

23 The simulation cell is parallelepipedic with periodic boundary conditions in the  
 24 *x*, *y* and *z* directions. It contains two stacks of graphite basal planes. These stacks,  
 25 constituted of three planes, are positioned perpendicularly to the *z* axis. The *x* and  
 26 *y* dimensions of planes are chosen identical to those of the simulation cell in order  
 27 that the hexagonal arrangement of C atoms and the cell boundary conditions are  
 28 compatible. The two stacks form the pore walls and are placed in such a way to  
 29 define two slits with same width *h* taking into account the boundary conditions.  
 30 The cell size is equal to 8.116 and 4.257 nm in the *x* and *y* directions, respectively,  
 31 and, in the *z* direction, it varies between 2.537 and 6.339 nm when *h* varies between  
 32 0.6 nm and 2.5 nm. The cell contains 7920 C atoms. For an efficient computation  
 33 of the molecule energy, a cell linked list algorithm [24] is used by partitioning the  
 34 simulation volume in parallelepipedic sub-volumes with edge equal to or larger  
 35 than the interaction range.  
 36

37 For a given pressure *P*, temperature *T* and chemical potential *μ*, the total ad-  
 38 sorption *m<sub>a</sub>*, expressed in mol per gram of adsorbent, is given by  
 39

40  
 41 
$$m_a = \frac{\langle N_a \rangle}{N_C M_C} \tag{1}$$
  
 42

43 where  $\langle N_a \rangle = \bar{N}_a$  is the average value of the adsorbed molecule number. *N<sub>C</sub>* is  
 44 the number of C atoms in the simulation cell and *M<sub>C</sub>* the carbon molar mass. The  
 45 excess adsorption *m<sub>e</sub>*, obtained in removing the contribution of compression effects  
 46 to *m<sub>a</sub>*, is defined by *m<sub>e</sub>* = *m<sub>a</sub>* − *ρ<sub>b</sub>* *V<sub>f</sub>*. *ρ<sub>b</sub>* is the density of the gas in the bulk phase  
 47 in mmol per volume unit and *V<sub>f</sub>* the free volume accessible to the adsorbed gas per  
 48 gram of adsorbent. The *V<sub>f</sub>* values have been computed from the amount of Helium  
 49 adsorbed *m<sub>a</sub><sup>He</sup>* in the slit pores by GCMC simulation at 653 K and 0.1 MPa. In  
 50 agreement with the experimental Helium displacement method [27], *V<sub>f</sub>* is given  
 51 by *V<sub>f</sub>* = *m<sub>a</sub><sup>He</sup>* / *ρ<sub>b</sub><sup>He</sup>* where *ρ<sub>b</sub><sup>He</sup>* is the Helium bulk density at 653 K and 0.1 MPa.  
 52 The bulk pressure and density associated to the *μ* value used in a simulation run  
 53 at given *T* were determined from GCMC simulations performed with a simulation  
 54 cell containing no adsorbent.  
 55

56 The isosteric heat *q<sub>i</sub>*, following the definition quoted from refs. [23, 28], is “the  
 57 differential entropy change in a reversible process where fluid is transferred from  
 58  
 59  
 60

the porous material at fixed volume and temperature to the bulk phase at fixed temperature and bulk pressure". It is given by

$$q_i = T \left\{ \left( \frac{\partial S_b}{\partial \bar{N}_b} \right)_{T,P} - \left( \frac{\partial S_a}{\partial \bar{N}_a} \right)_{T,V_f} \right\} \quad (2)$$

where  $S_b$  and  $S_a$  are the entropies and  $\bar{N}_b$  and  $\bar{N}_a$  the molecule numbers of the bulk and adsorbed phases. This expression can be rewritten as

$$q_i = H_b - \left( \frac{\partial \bar{U}_a}{\partial \bar{N}_a} \right)_{T,V_f} \quad (3)$$

where  $H_b$  is the enthalpy per molecule of the bulk phase and  $\bar{U}_a$  the energy of the adsorbed phase. When  $\partial \bar{U}_a / \partial \bar{N}_a$  is expressed in terms of fluctuations of  $\bar{U}_a$  and  $\bar{N}_a$  in the GC ensemble,  $q_i$  writes

$$q_i = H_b - \frac{\langle U_a N_a \rangle - \langle U_a \rangle \langle N_a \rangle}{\langle N_a^2 \rangle - \langle N_a \rangle^2}, \quad (4)$$

a formula adapted to the  $q_i$  computation by GCMC simulations. Taking into account the expression of  $H_b$  in terms of the pressure and energy at a fixed temperature, we can write:

$$q_i = P/\rho_b + U_b^c + U_b^i - U_a^c - \frac{\langle U_a^i N_a \rangle - \langle U_a^i \rangle \langle N_a \rangle}{\langle N_a^2 \rangle - \langle N_a \rangle^2} \quad (5)$$

where  $U_b^c$  and  $U_a^c$ , the average kinetic energies per molecule of the bulk and adsorbed phases, are equal obviously to  $5k_B T/2$  for  $\text{CO}_2$  ( $k_B$  Boltzmann constant).  $U_b^i$  is the internal energy per molecule of the bulk phase and  $U_a^i$  that of the adsorbed phase. The hypothesis that the bulk phase is a perfect gas, leads to the approximate formula often used in the literature :

$$q_i = k_B T - \frac{\langle U_a^i N_a \rangle - \langle U_a^i \rangle \langle N_a \rangle}{\langle N_a^2 \rangle - \langle N_a \rangle^2}. \quad (6)$$

$m_a$  and  $q_i$  have been estimated from GCMC runs comprising, at least,  $12 \times 10^6$  MC steps to achieve the equilibrium state of adsorbed phases followed by  $48 \times 10^6$  MC steps to compute the average quantities. These numbers of MC steps were sufficient for slit pores with  $h \geq 0.9$  nm to determine  $m_a$  and  $q_i$  with a statistical uncertainty  $\sim 1-2\%$ . For the pores with  $h \leq 0.8$  nm, the statistical error on  $m_a$  is similar but the values of  $\langle N_a \rangle^2$  and  $\langle N_a^2 \rangle$  being close,  $\langle N_a^2 \rangle - \langle N_a \rangle^2$  is difficult to estimate accurately and the uncertainty on the  $q_i$  values is of the order of  $\sim 5\%$  for  $h = 0.6$  and  $0.7$  nm and  $\sim 10\%$  for  $h = 0.8$  nm.

The excess adsorption isotherms and  $q_i$  values at  $T = 293$  K between 0.01 and 0.20 MPa for slit pores with increasing widths are presented in Fig. 2 and 3. For pores with  $h \geq 0.9$  nm, the excess adsorption  $m_e$  varies monotonically and this variation is almost proportional to that of the pressure. By contrast, for  $h = 0.8$  nm,  $m_e$  remains quasi constant between 0.02 and 0.2 MPa, a behavior which results from the tight stack of the adsorbed molecules for this pore size. A snapshot of the molecule arrangement is given in Fig. 5 ; it shows that molecules are in average slightly tilted with respect to the orientation where they would be perpendicular to the the pore walls. In such configurations, where the contribution to  $U_a$  and  $q_i$  from the molecule-molecule interaction  $U_a^m$  and molecule-adsorbent interaction



1  $U_a^G$  are almost equal, the cooperative effects between molecules have an important  
 2 role in the adsorption process. For  $h = 0.7$  nm, these effects remain important  
 3 since  $U_a^G/5 < U_a^m < U_a^G/2$  in the pressure range 0.01-0.2 MPa. At  $h = 0.6$  nm, the  
 4 confinement involves that the molecules are parallel to the pore walls and from the  
 5 disorder of the bidimensional molecular arrangement inside the slit (cf. snapshot  
 6 in Fig. 5), it results that  $U_a^m$  is of the order of  $U_a^G/15$  at 0.01 MPa and  $U_a^G/7$  at  
 7 0.2 MPa. For the size  $h = 2.5$  nm,  $U_a^m$  varies from  $\sim 0.0$  at 0.01 MPa to  $U_a^G/15$  at  
 8 0.2 MPa.

10 These data and the modification of the molecule-adsorbent interactions when  $h$   
 11 increases (cf. Fig. 1) help to the interpretation of the variation of  $q_i$  with those  
 12 of  $P$  and  $h$ . When the interaction between molecules is negligible or weak in the  
 13 adsorbed phase, to a good approximation  $q_i$  has a value determined by the only  
 14 interaction of one molecule with the adsorbent surface implying that  $\langle U_a^i N_a \rangle$   
 15  $- \langle U_a^i \rangle \langle N_a \rangle$  is almost proportional to  $\langle N_a^2 \rangle - \langle N_a \rangle^2$ . In this case  
 16 and when, for  $h$  sufficiently large, the molecule-adsorbent interaction has no more  
 17 variation with  $h$ ,  $q_i$  depends little on  $P$  and  $h$ , as it is found by simulation for  
 18 the adsorption in pores with  $h > 1.2$  nm. For  $h$  between 0.9 nm and 1.2 nm, to  
 19 the strong increase of  $m_e$  with the pressure corresponds an increase of the  $U_a^m$   
 20 contribution to  $U_a$  from 2% up to 30% while the  $U_a^G$  contribution per molecule  
 21 remains constant. As a consequence of the variation of  $U_a^m$  and  $\langle N_a^2 \rangle - \langle N_a \rangle^2$   
 22 when the molecule density in the pores increases,  $q_i$  varies by 30 % in the considered  
 23 pressure range. In the narrow pores, in particular for 0.8 nm,  $m_e$  is close to  $m_a$   
 24 and varies only by 10-20% between 0.01 and 0.2 MPa. Due to the packing of the  
 25 molecules  $\langle N_a^2 \rangle - \langle N_a \rangle^2$ , which has a value much smaller than its perfect gas  
 26 value equal to  $\langle N \rangle$ ,  $U_a$  and  $\langle U_a N_a \rangle - \langle U_a \rangle \langle N_a \rangle$  vary little and  $q_i$  remains  
 27 quasi constant between 0.01 and 0.2 MPa.

30 Similarly to the results obtained in [15],  $m_e$  and  $q_i$  present a maximum for a  
 31 pore with a width of  $h \simeq 0.8$  nm. But the maximum values of  $q_i$  are larger by  
 32 a factor of  $\sim 2$  as a consequence of the strong contribution of the intermolecular  
 33 interactions in the adsorbed phase and  $m_e$  and  $q_i$  have almost achieved at 0.1 MPa  
 34 their maximal values.

### 37 Discussions and Conclusions

40 For the considered temperature and pressure domain, the strong variations of  $m_e$   
 41 and  $q_i$  with the pore size give a typical example of the difficulty to compare the  
 42 simulation results with experimental data for CO<sub>2</sub> adsorbed on activated carbons.  
 43 Only, in the cases where the material porosity is very homogeneous or corresponds  
 44 to slit widths larger than 1.6 nm, such a comparison can be easily performed, since  
 45 all pores contribute almost similarly to the excess adsorption. When the activated  
 46 carbon pore network comprises slits with widths smaller than 1.0 nm, the excess  
 47 adsorption of the material need to be estimated from an average where the excess  
 48 adsorptions computed for each slit type is weighted in agreement with the pore  
 49 size distribution [6, 16, 29]. Supposing that the pores differ only in width,  $m_e$  the  
 50 excess adsorption per gram of adsorbent is given by

$$52 \quad m_e = \int m_a^h v(h) dh - \rho_b V_f \quad (7)$$

56 where  $m_a^h$  is the total amount of adsorbed gas in a slit pore with width  $h$  and free  
 57 volume unity.  $v(h)dh$  ( $V_f = \int v(h)dh$ ) is the contribution to  $V_f$  from pores with  
 58 width between  $h$  and  $h + dh$ .

For the  $q_i$  computation of activated carbons, Birkett and Do [16] have shown that a formula, similar to Eq. 7, expressing  $q_i$  as a weighed average on the isosteric heats  $q_i^h$  of the slits with width  $h$  is incorrect and should be replaced by

$$q_i = H_b + \frac{\int q(h)_i (\partial \bar{N}_a^h / \partial \bar{P})_{T, V_h} v(h) dh}{(\partial \bar{N}_a / \partial \bar{P})_{T, V_f}} \quad (8)$$

where  $\bar{N}_a^h$  is the molecule number adsorbed in a slit with a width  $h$  and free volume unity and  $q(h)_i = q_i^h - H_b$ . In practice the use of Eq. 7 and 8 with simulation results, supposes that the pore size distribution  $v(h)$  is experimentally known and partial derivatives are estimated from discrete approximations.

Experimental estimates of  $q_i$  are often obtained from adsorption isotherms determined at close temperature intervals by using the formula [28],

$$q_i = \frac{T}{\rho_b} \left[ \frac{dP}{dT} \right]_{eq, m_a} \quad (9)$$

where the subscript  $eq, m_a$  indicates that the pressure derivative with respect to temperature is computed at equilibrium between bulk and adsorbed phases and constant value of  $m_a$ . The possibility that a correct estimate of  $q_i$  for adsorbents, such as active carbons, can be obtained from Eq. 9 depends on its compatibility with Eq. 8 which has to be established and, obviously on its validity when it is used for a single pore with a given width. By computing adsorption isotherms at temperatures 298 K and 288 K,  $[dP/dT]_{eq, m_a}$  can be calculated at 293 K from

$$\left[ \frac{dP}{dT} \right]_{eq, m_a} = \frac{P(T + dT, m_a) - P(T - dT, m_a)}{2dT} \quad (10)$$

where  $P(T + dT, m_a)$  and  $P(T - dT, m_a)$  are the pressures on isotherms at temperatures  $T + dT$  and  $T - dT$  where the total adsorption is equal to the value  $m_a$  obtained at a given pressure  $P$  on the isotherm at temperature  $T$ . Such a verification of the agreement between the Eqs. 4 and 9 is successful when the slit pores have widths  $h \geq 1.6$  nm. For instance, for  $h = 2.5$  nm from Eq. 4,  $q_i$  is equal to 14.1 and 14.7 kJ/mol at  $P = 0.02$  and 0.1 MPa, respectively, and, from Eq. 9, equal to 14.5 and 15.2 kJ/mol. The differences of few percents between the estimates of  $q_i$  are compatible with the statistical error on simulations results and uncertainty which results from the discrete approximation of the pressure derivative. For  $h \leq 1.2$  nm the discrepancy between the two estimates of  $q_i$  increases when  $h$  decreases and at  $h = 0.6$  nm and  $P = 0.02$  and 0.10 MPa,  $q_i$  values obtained from Eq. 4 are, respectively equal to 33.1 and 37.3 kJ/mol and, from Eq. 9, equal to 37.1 and 46.7 kJ/mol. The explanation of such differences is the large numerical error on the  $dP/dT$  estimate from isotherms at temperatures differing by 10 K in the pressure domain where,  $m_a$  varies quite slowly. In fact, a precise estimate of  $(dP/dT)_{eq, m_a}$  for  $h = 0.6$  nm at 293 K, can be only obtained from very accurate computations of the adsorption isotherms at 295 and 291 K. Using the results of such computations, Eq. 10 give, for  $h = 0.6$ ,  $q_i$  equal to 33.3 and 37.7 kJ/mol at  $P = 0.02$  and 0.10 in close agreement with the simulation data obtained from Eq. 4. So, it seems possible to determine  $q_i$  from Eq. 9 for the mesopores  $h \simeq 1.5 - 2.0$  nm and micropores  $h \leq 0.9$  nm when, in the latter case, adsorption isotherms, differing in temperature only by few degrees are determined with an accuracy of  $\simeq 0.2\%$  in the domain of pressures where  $m_a$  is almost constant.

In summary, our calculations of the CO<sub>2</sub> adsorption and isosteric heat in graphitic



1 slit pores of various widths are compatible with experiments, (cf., for instance, [8])  
2 and show that, at room temperature and low pressures, an unambiguous com-  
3 parison between simulation data and adsorption experiments on activated carbon  
4 seems only possible when the pore size distribution of the material is known or if,  
5 in the pore network, the pores have mainly a width larger than 1.5 nm. They also  
6 show that in narrow pores ( $h \simeq 0.8$  nm), the excess weight percent is of the order  
7 of 20 %, a value obviously favorable for the CO<sub>2</sub> capture.  
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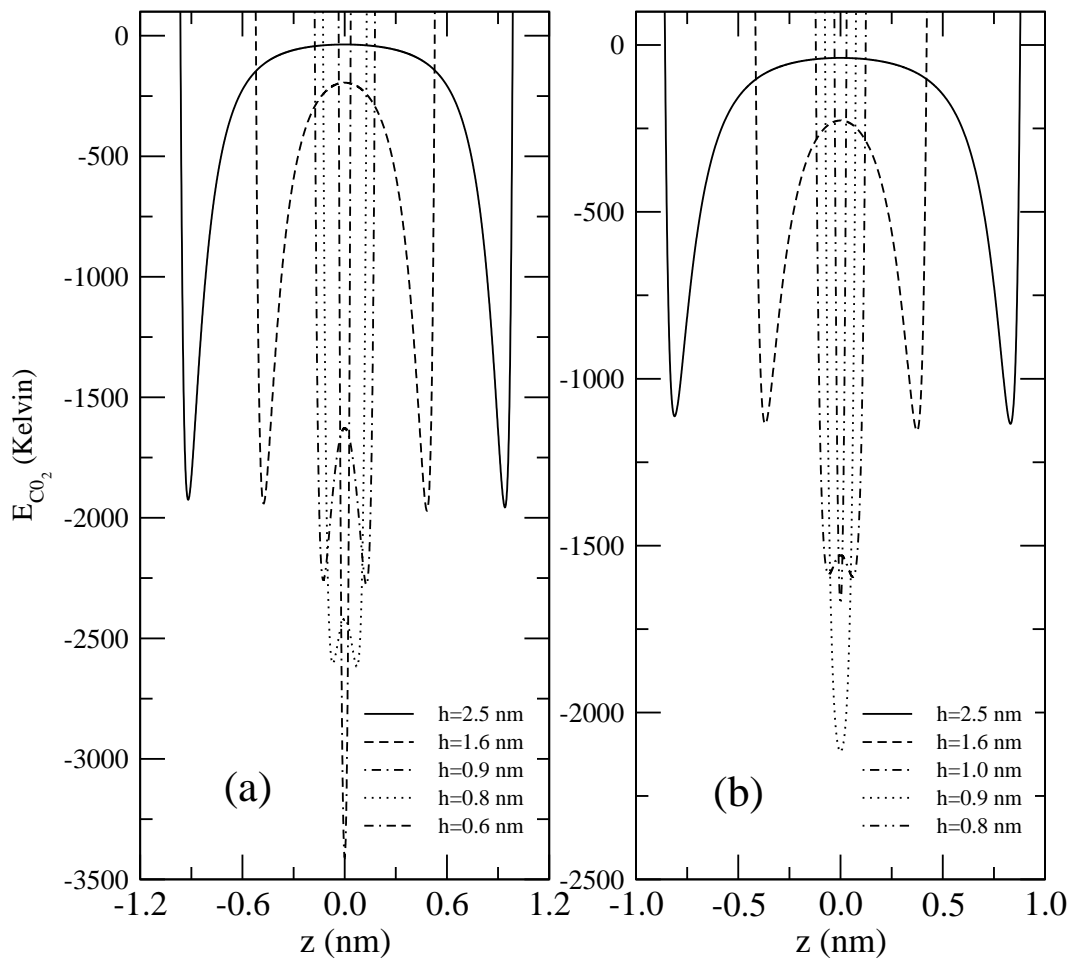


Figure 1. Potential energy (Kelvin degree) of one  $CO_2$  molecule in graphitic slit pores with widths increasing from 0.6 nm to 2.5 nm. Fig. 1(a) : axis of the molecule parallel to the pore walls, Fig. 1 (b) : axis of the molecule perpendicular to the pore walls. The middle of the slit is the coordinate origin of the  $z$  axis.

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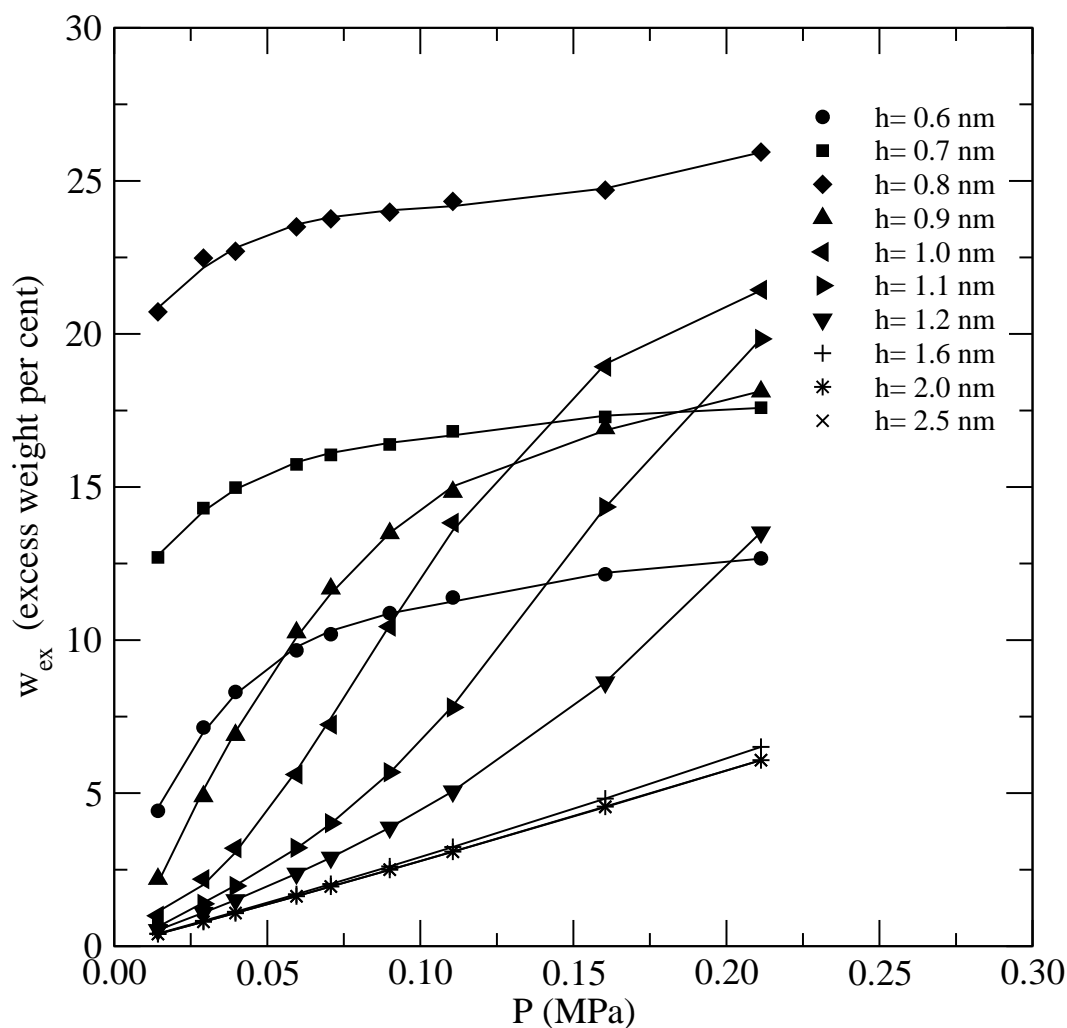


Figure 2. Excess adsorption ( $w_{ex} = 100 m_e M_{CO_2}$ ,  $M_{CO_2}$  molar mass of  $CO_2$ ) for graphitic slit pores with widths increasing from 0.6 nm to 2.5 nm at  $T = 293$  K.

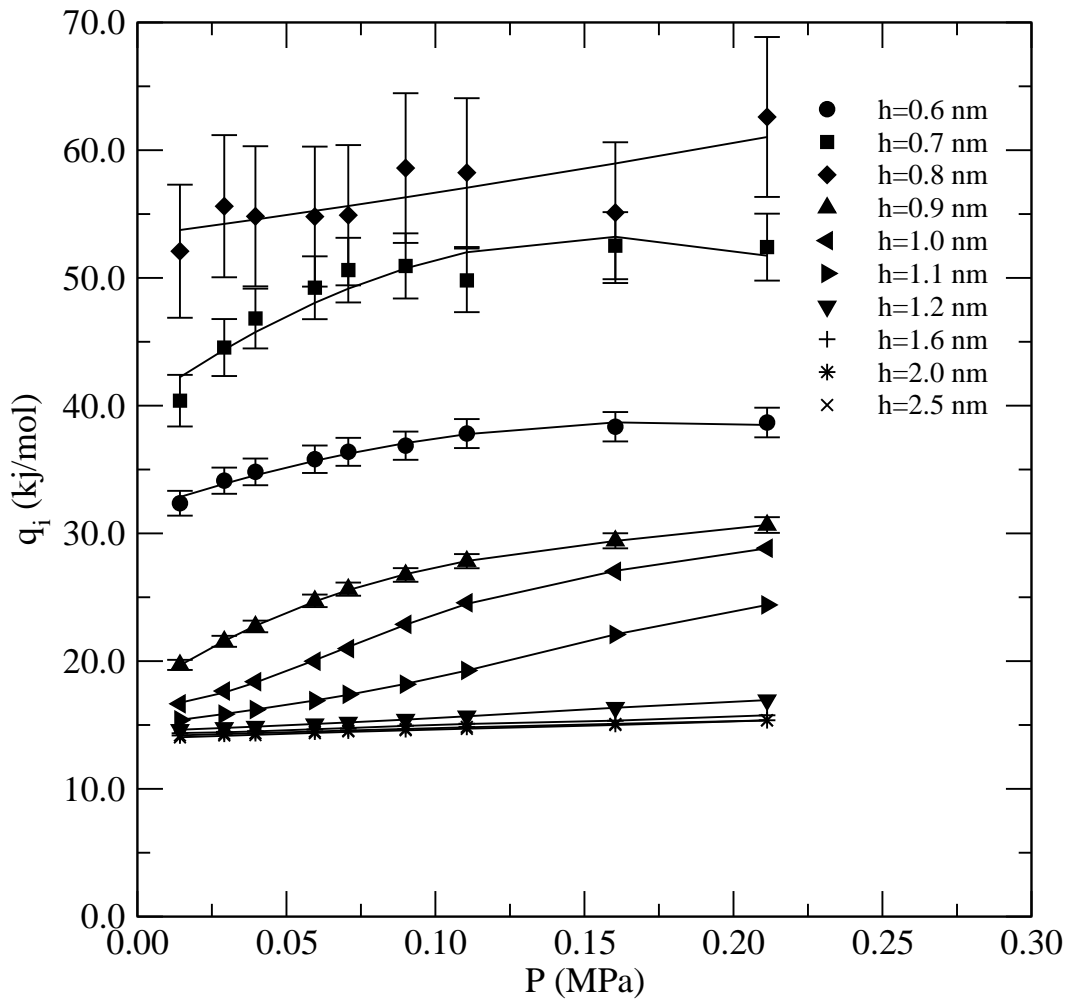


Figure 3. Isosteric heat (kJ/mol) for graphitic slit pores with widths increasing from 0.6 nm to 2.5 nm at  $T = 293$  K.

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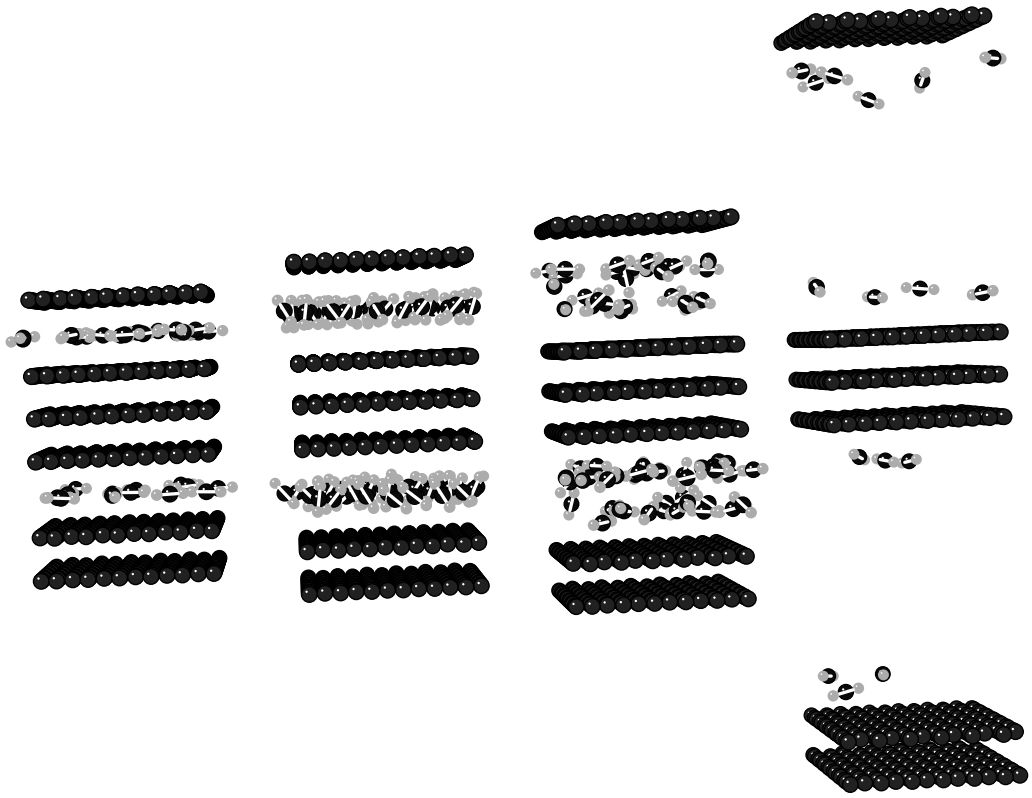
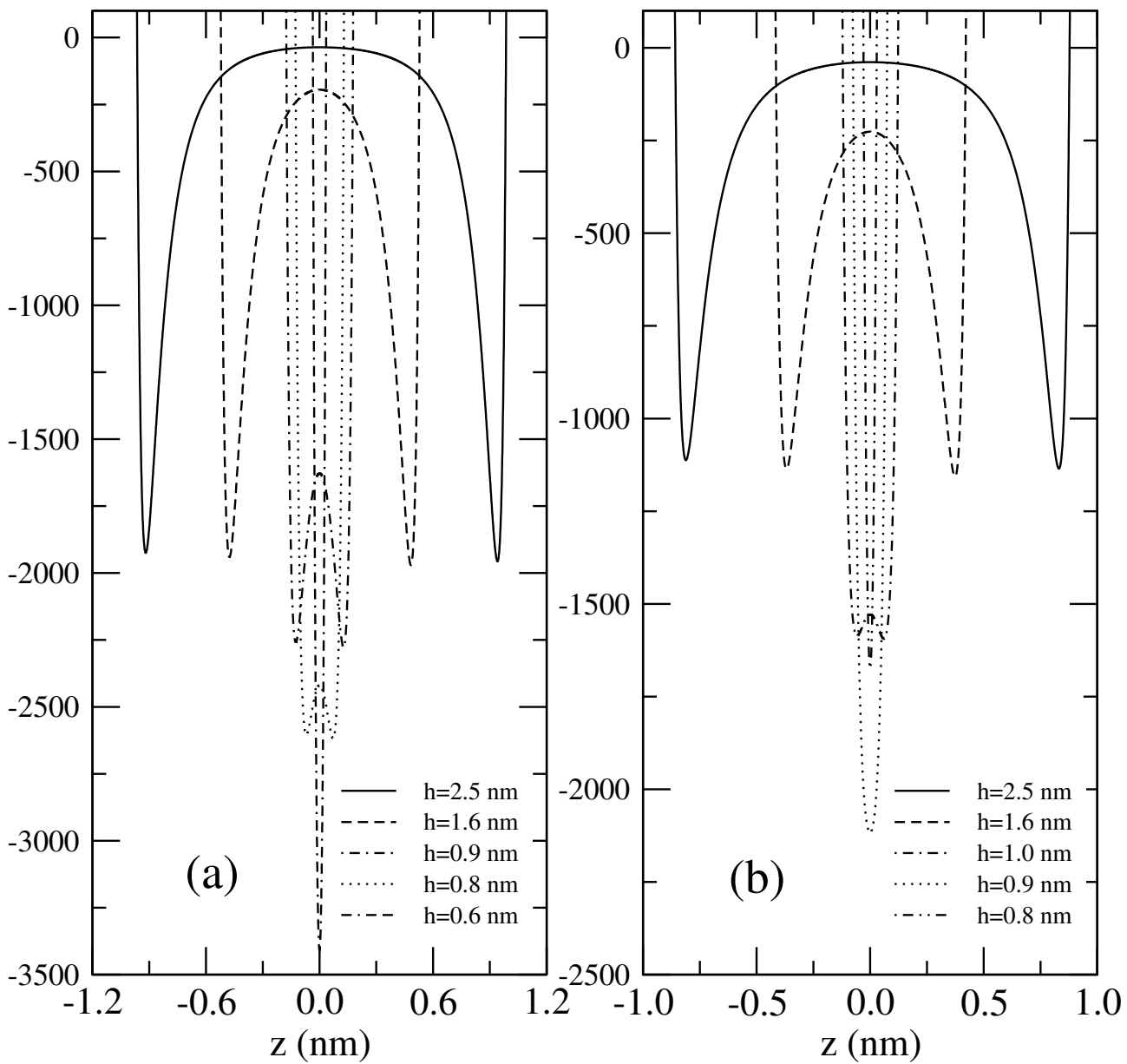


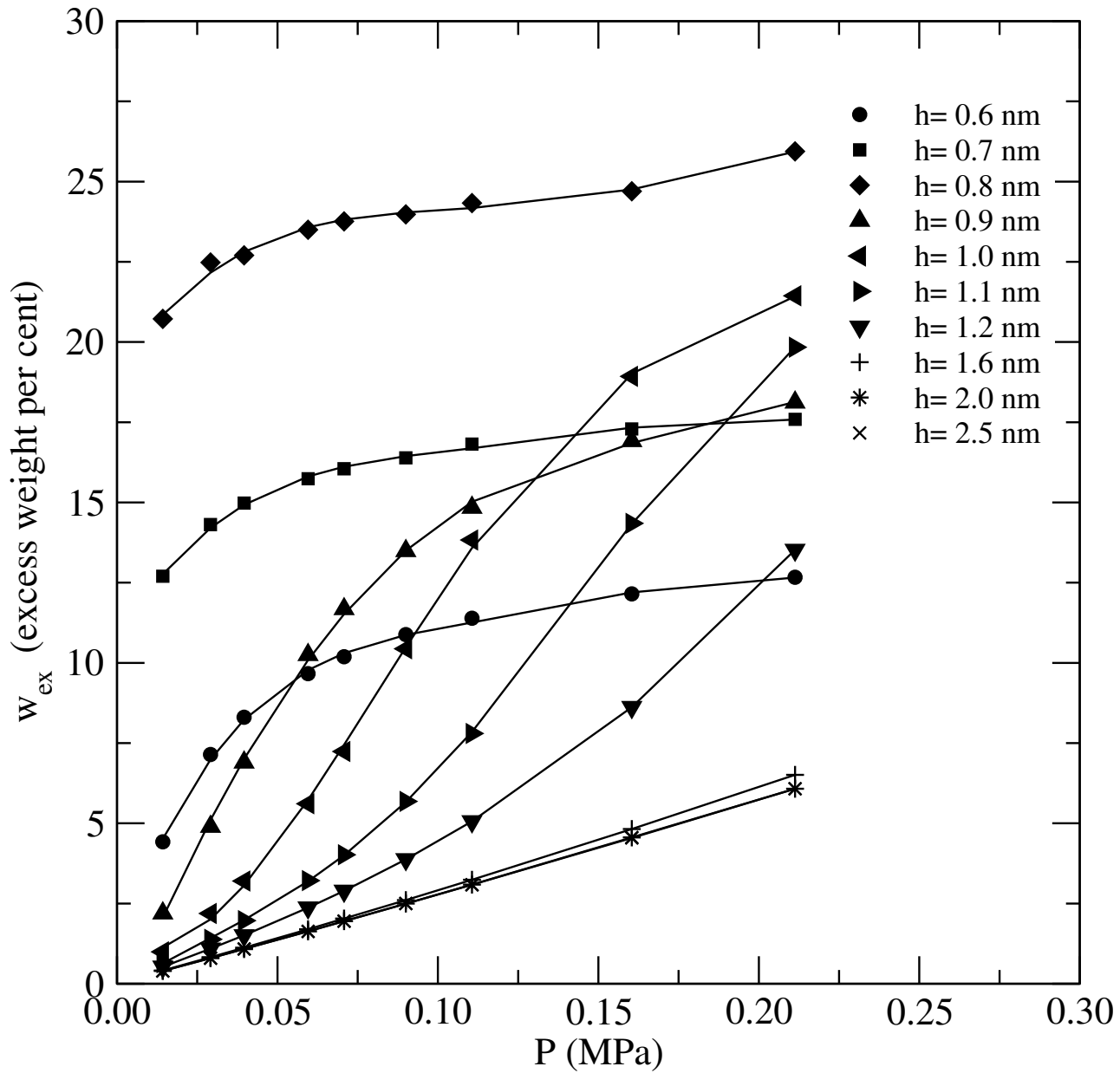
Figure 4. From left to right, snapshots of the local arrangements of CO<sub>2</sub> molecules in slits of width equal to 0.6 nm, 0.8 nm, 1.0 nm and 2.5 nm at  $P = 0.1$  MPa and  $T = 293$  K.

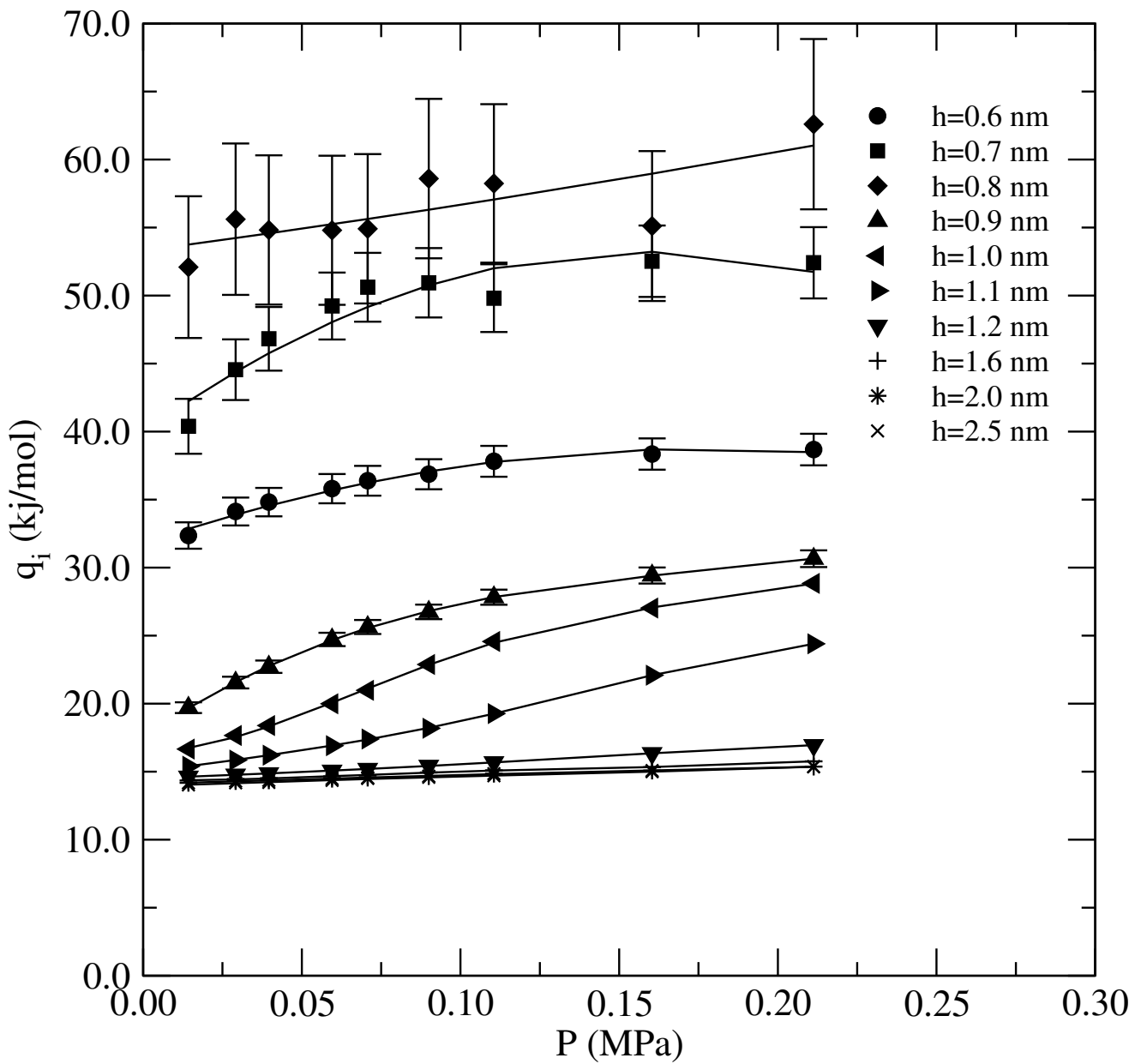
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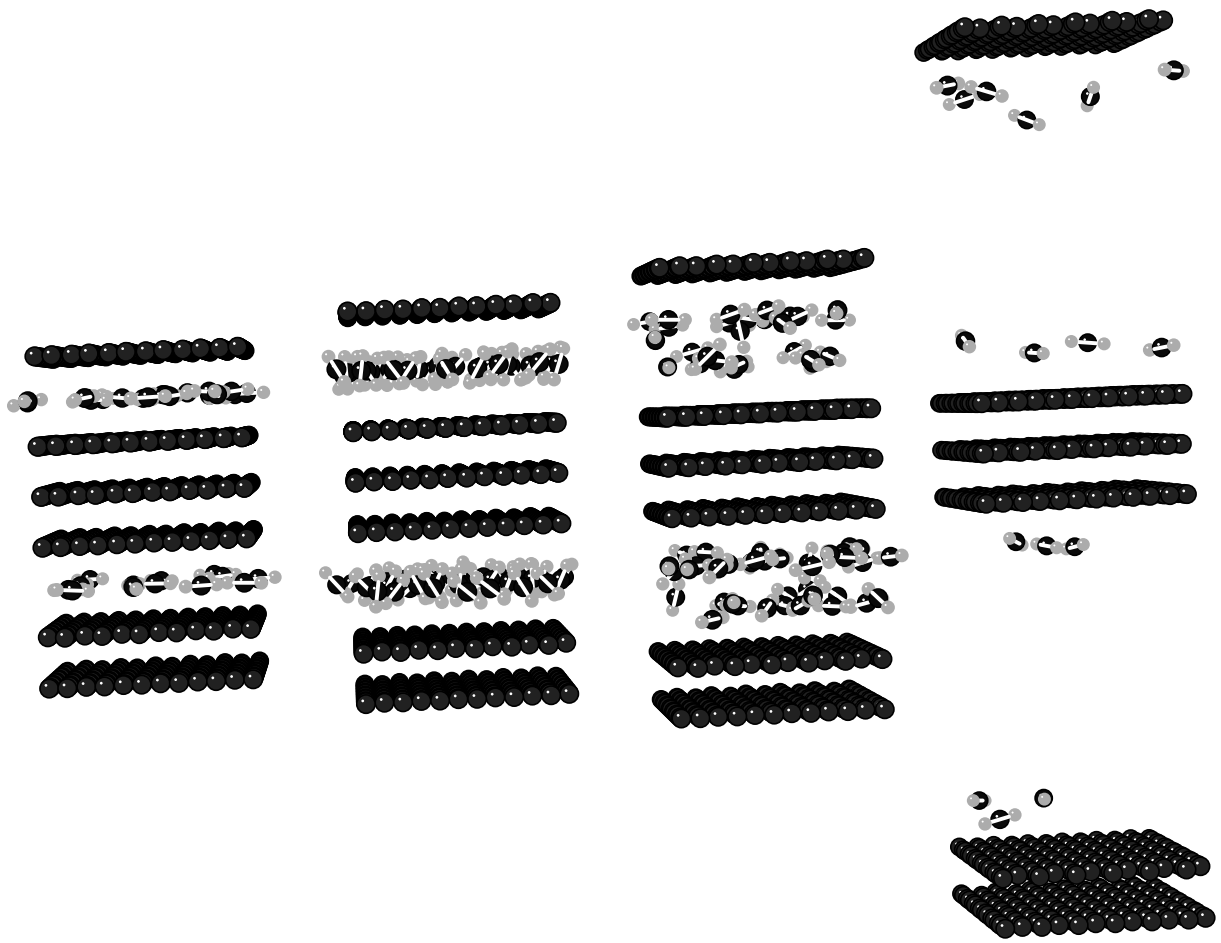
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