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Modeling of high pressure adsorption isotherm using statistical physics approach: lateral interaction of gases adsorption onto metal–organic framework HKUST-1

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Abstract A novel theoretical approach for description of high pressure isotherm is developed in the present study. This approach is based on the grand canonical formalism in statistical physics by taking into account the lateral interaction between the adsorbate molecules. This leads to five parameters equation describing the high pressure adsorption equilibrium. This model is applied to experimental adsorption data of hydrogen, nitrogen, methane and carbon dioxide on metal–organic frameworks HKUST-1. There is a good correlation between experimental data and those calculated by the new model at pressure up to 50 MPa. It was found that hydrogen molecules can be considered as a ideal gas over a wide temperature range and even at high pressures. Lateral interactions were found to be necessary to describe the adsorption of N_2, CH_4 and CO_2 at high pressures. The proposed model allows also prediction of some adsorption thermodynamic functions which govern the adsorption mechanism such as the entropy, the Gibbs free enthalpy and the internal energy.

Keywords Monolayer adsorption · Statistical physics model · Metal–organic framework · Lateral interactions

List of symbols

a	Cohesion pressure (J mL/mol)
A	Adsorbed molecule (s)
b	Covolume (mL/mol)
C	Adsorbate concentration (mol/mL)
E_a	Total adsorption energy (kJ/mol)
E_{int}	Internal energy (kJ/mol)
g	Gibbs free enthalpy for one receptor site (kJ/mol)
G	Gibbs free enthalpy (kJ/mol)
J	Grand potential
k_B	Boltzmann constant ($m^2Kg/(s^2K)$)
n	Fraction or the number of adsorbed gas molecule(s) per site
N_i	Occupation site
N_M	Receptor sites density (mg/g)
N_o	Occupation number
Q_a	Total number of adsorbed molecules (mg/g)
S	Site
s_a	Configurational entropy (J/K)
w	Energetic parameter (J/mol)
w_0	Constant
Z_{gc}	Grand canonical partition function
Z_{gtr}	Translation partition function
β	Boltzman constant
ΔE^a	Adsorption energy (kJ/mol)
$(-\varepsilon)$	Adsorption energy of a receptor site (kJ/mol)
μ	Chemical potential (KJ/mol)
μ_p	Chemical potential for ideal gas (kJ/mol)
μ_a	Chemical potential of adsorbed phase (kJ/mol)

1 Introduction

Adsorption is one of the most widely used techniques to treat industrial waste gas and effluent due to its low cost, high efficiency and easy operation. Particularly, the adsorption process is suitable to separate compounds of low concentration or high toxicity, which are not readily

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treated by biological processes (Xu et al. 2013). The measurement of the amount of gas adsorbed over a range of partial pressures at a constant temperature results in a curve known as an adsorption isotherm. Many different types of isotherms have been observed in the literature. These isotherms have different shapes depending on the type of adsorbent, the type of adsorbate and the intermolecular interactions between the gas and the surface (Balbuena and Gubbins 1993; Czepirski et al. 2000; Wang and Hwang 2000). Over the years, a wide variety of equilibrium isotherm models appeared to describe adsorption data. Among them there is the Langmuir model, which assumes a monolayer adsorption on homogeneous surface without volume interactions between the adsorbed molecules, even on adjacent sites (Hamdaoui and Naffrechoux 2007; Hameed et al. 2008; Desta 2013). Generally, the model is characterized by a steep increase at low pressure followed by a plateau indicating the equilibrium saturation, where no further adsorption takes place. The assumption of Langmuir model is the starting point of the development of many other models such as the BET model. The BET approach is identical to the Langmuir one in all respect, except that it was developed to derive multilayer adsorption systems with relative pressure range from 0.05 to 0.30 corresponding to a monolayer coverage lying between 0.50 and 1.50 (Foo and Hameed 2010). In contrast to the Langmuir isotherm model, the BET isotherm equation occurs no saturation at high relative pressures. These well known empirical models cannot describe excess adsorption of supercritical fluid isotherm at high pressure and they do not take the lateral interactions between the adsorbate molecules into account. In addition, they contain parameters which are not related to the physicochemical variables involved in the adsorption process. For higher pressures the difference between absolute and excess adsorption is important. The absolute amount adsorbed approaches a saturation value but the excess amount adsorbed reaches a maximum and begins to decrease with pressure (Myers and Monson 2002; Senkovska and Kaskel 2008).

The objective of the present work is to propose a theoretical model, based on statistical physics approach to describe precisely the experimental results of adsorption isotherms at high pressure. This model introduces the lateral interactions and gives physical meaningful parameters. The developed model is tested by application to published experimental adsorption data of small gases onto a porous adsorbent published elsewhere by Moellmer et al. (2011).

2 Methodology

The adsorptives used in this study were hydrogen, nitrogen, methane and carbon dioxide. These gases were adsorbed onto metal–organic frameworks HKUST-1 ($Cu_3(BTC)_2$, commercially available product Basolite^{TM} C300 in the temperature range of 303–343 K (Moellmer et al. 2011). HKUST-1 contains Cu^{2+} dimers coordinated to the oxygen atoms of benzene tricarboxylate (BTC) units (Raganati et al. 2014). The positive charges exist on the copper atoms suggest that the adsorption properties of HKUST-1 are given not only by Van der Waals interactions but also by specific interactions due to the Cu^{2+} species (Bordiga et al. 2007). HKUST-1 has a bimodal pore size distribution, the small pore in HKUST-1 has a dimension of approximately 4–5 Å, whereas the large pore is around 9 Å (Wu et al. 2010; Klimakow et al. 2012).

Experimental adsorption isotherms for hydrogen, nitrogen, methane and carbon dioxide on HKUST-1 were measured in the temperature range of 303–343 K (Fig. 1). It can be noted that experimental adsorption isotherms of nitrogen, methane and carbon dioxide for supercritical conditions have the same shape as the already published isotherms (Moellmer et al. 2011). These isotherms exhibit the typical shape for excess sorption isotherms of supercritical fluids on microporous materials up to high pressures (Menon 1968; Herbst and Harting 2002). Indeed, the adsorbed quantity increases with increasing the adsorbate concentration until a maximum is reached. At this point, the difference between the density of the adsorbed phase and the bulk phase is in a maximum. In addition, the adsorbed quantity decreases despite of the rise of the concentration after the maximum in adsorbed quantity. This could be explained by the lateral repulsive interactions between the adsorbate molecules. However, the adsorbed quantity, Q_a, increases by increasing concentration in the case of hydrogen adsorption onto HKUST-1. Depending on the adsorption temperature no excess sorption maximum was found up to 50 MPa with respect to the reduced temperature ($T_{measurement}/T_{critical}$) for hydrogen adsorption such maximum should be observed at higher pressures (Moellmer et al. 2011).

3 Theoretical development

The adsorption process involves an exchange of particles from the free state to the adsorbed one. Thus, the investigation of this phenomenon requires the use of the grand canonical ensemble to take into account the particles number variation through the introduction of the variable chemical potential in the adsorption process. It is assumed that any given receptor site can be empty ($N_i = 0$) or occupied ($N_i = 1$). Such grand canonical partition function is written as follows:

$$z_{gc} = \sum_{N_i=0,1} e^{-\beta(-\varepsilon-\mu)N_i} \qquad (1)$$

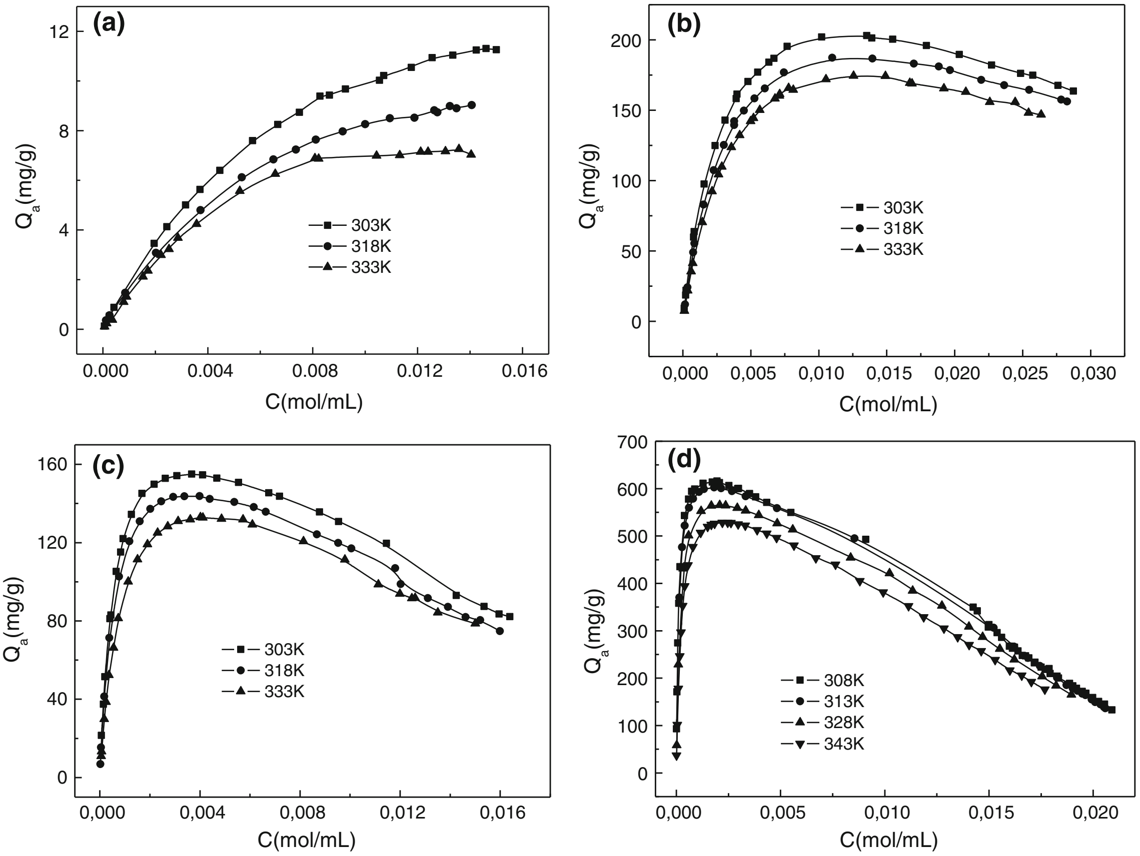

Fig. 1 Experimental adsorption isotherms for **a** hydrogen, **b** nitrogen, **c** methane and **d** carbon dioxide on HKUST-1 (Moellmer et al. 2011) (*lines* are to guide the eyes)

where β is the Boltzman constant, $(-\varepsilon)$ represents the adsorption energy of a receptor site and μ is the chemical potential of the last one.

The ideal law gas describes the macroscopic state of a three-dimensional gas of non-interacting, volume less point particles. It is satisfactory for describing common gases at low pressures and high temperature, but ineffective for real gases over a wide temperature and pressure regime. The change in pressure due to intermolecular forces is taken to be proportional to the square of the molecular density, giving the Van-der-Waals equation of state (Frankenburg et al.1952; Hill 1960; Scott and van Konynenburg 1970):

$$\left(P+\frac{aN^2}{V^2}\right)(V-Nb)=Nk_BT \tag{2}$$

P represents the gas pressure, V the volume, T the temperature, N the number of gas molecules, a and b represent the cohesion pressure and the covolume of the adsorbate molecule, respectively. k_B is the Boltzman constant.

The chemical potential is written then as followed (Diu et al.1989):

$$\mu=\mu_p+k_BT\ln\frac{\mathrm{v}}{\mathrm{v}-Nb}+k_BT\frac{bN}{\mathrm{v}-Nb}-2a\frac{N}{\mathrm{v}} \tag{3}$$

With μ_p as the chemical potential for the ideal gas.

The occupation number of N_M identical receptor sites per unit surface is therefore given as follows (Khalfaoui et al. 2003):

$$N_0=k_BT\frac{\partial\ln\left(z_{gc}\right)^{N_M}}{\partial\mu} \tag{4}$$

Generally, the adsorption reaction should include a stoichiometric coefficient, n, such as:

$$nA+S\Leftrightarrow A_nS \tag{5}$$

where n is the number or fraction of adsorbed molecule(s) A per site S.

If there are n molecule(s) anchored per site, the total number of adsorbed molecules can be described as:

$$Q_a=nN_0 \tag{6}$$

Then we can obtain the monolayer model coupled to the real gas law (MMRG):

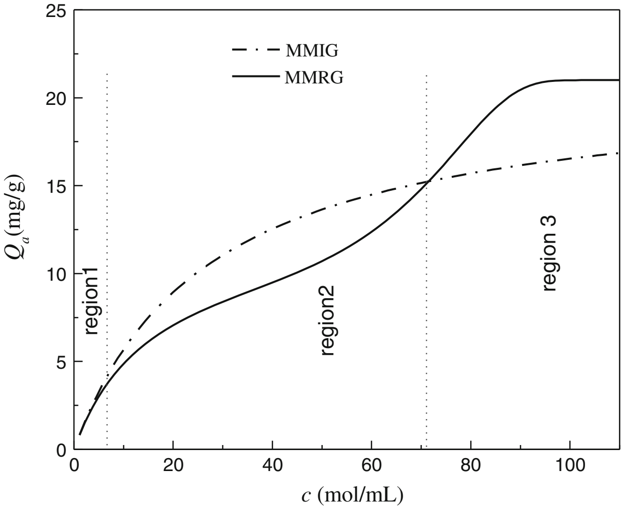

Fig. 2 Comparison between the monolayer model coupled to ideal (MMIG) and real gas (MMRG)

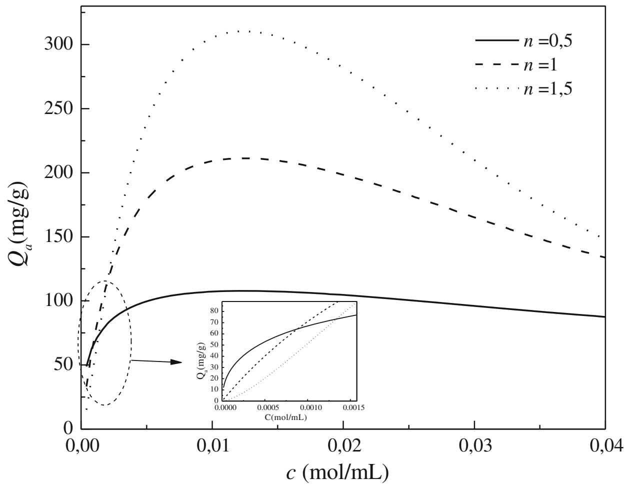

Fig. 3 Effect of the parameter n on the adsorption isotherm in the case of MMRG model ($N_M = 440$ mg/g, $w = 0.00477$ mol/mL, $a = 2.2637 \times 10^{-19}$ J mg/L and $b = 11$ mL/mol)

$$Q_a = \frac{nN_M}{1 + \left(w \frac{1-bc}{c} e^{2\beta ac} e^{-\frac{bc}{1-bc}} \right)^n} \tag{7}$$

where c is the adsorbate concentration and w is an energetic parameter which is written:

$$w = z_{gtr} e^{-\beta\varepsilon} = w_0 e^{-\frac{\Delta E_1^a}{RT}} \tag{8}$$

where z_{gtr} is the translation partition function and w_0 represents a constant.

If one takes $a = b = 0$, Eq. (7) reduced to the following equation for an ideal gas (Khalfaoui et al. 2002, 2003):

$$Q_a = \frac{nN_M}{1 + \left(\frac{w}{c}\right)^n} \tag{9}$$

The model given by Eq. (9) is the well known Hill model which will be denoted MMIG (Foo and Hameed 2010; Shahbeig et al. 2013). Furthermore, if the parameter n takes the value equal to 1, we get the Langmuir model. Therefore, it can be concluded that the presented model (Eq. 7) is a generalized approach taking into account the lateral interactions between adsorbate molecules.

In order to understand the difference between the two models given by Eqs. 7 and 9, we plotted them in the same Figure (Fig. 2). It can be noted that at the beginning of the adsorption, the models are similar (region 1). This could be explained by the fact that the interaction between the adsorbate molecules is neglected at low concentration and the adsorbate molecules are considered as an ideal gas. If we continue to increase the adsorbate concentration, we note that the adsorbed quantity of the monolayer model coupled to the real gas law is lower than the monolayer one coupled to the ideal gas law (region 2). This result can be explained by the fact that for a real gas, the adsorbate–adsorbate interactions are considerable and therefore the adsorbed quantity deceases slightly due to these interactions. A further increase in adsorbate concentration results in the reverse phenomenon (region 3). Indeed, the interactions become more important and a repulsion force appears between the adsorbate molecules and consequently they migrate to the surface, i.e. therefore the adsorbed quantity increases.

4 Physical interpretations of the model parameters

In order to better understand the physical meaning of the MMRG model parameters, in the next sections we will investigate the effect of each parameter on the adsorbed quantity by varying the adsorbate concentration.

The parameter n is a stoichiometric coefficient in the adsorption process. It conveys the anchorage manner of the adsorbate onto the adsorbent and it can be greater or smaller than 1. If n is greater than 1, it represents the number of molecules adsorbed onto one site which allows the formation of a multimolecular adsorption (Knani et al. 2012). If it is less than 1, it represents the fraction of molecule per site and consequently a multianchorage adsorption is obtained (Knani et al. 2012). The effect of such steric parameter on the adsorption process may be understood from Fig. 3, where the relationship between the adsorbed quantity and the adsorbate concentration is plotted for three values of n. At low concentrations, smaller values of n correspond to higher amounts of the adsorbed quantity. However for high concentrations, the reverse phenomenon is applied. This may be easily interpreted by free and energetic attractive receptor sites, which will be

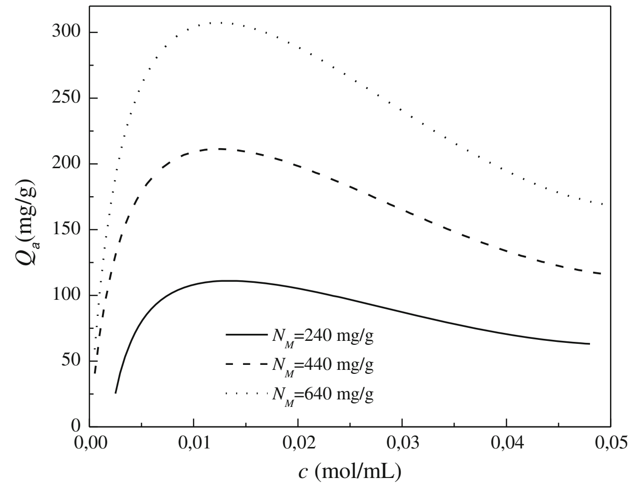

Fig. 4 Effect of the parameter N_M on the adsorption isotherm in the case of MMRG model ($n = 1$, $w = 0.00477$ mol/mL, $a = 2.2637 \times 10^{-19}$ J mg/L and $b = 11$ mL/mol)

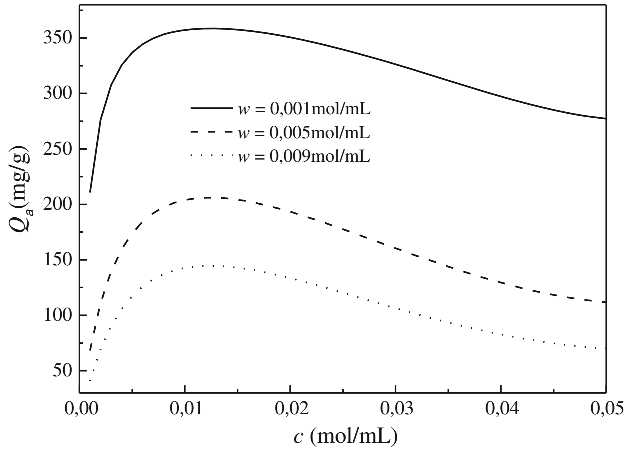

Fig. 5 Effect of the parameter N_M on the adsorption isotherm in the case of MMRG model ($n = 1$, $N_M = 440$ mg/g, $a = 2.2637 \times 10^{-19}$ J mg/L and $b = 11$ mL/mol)

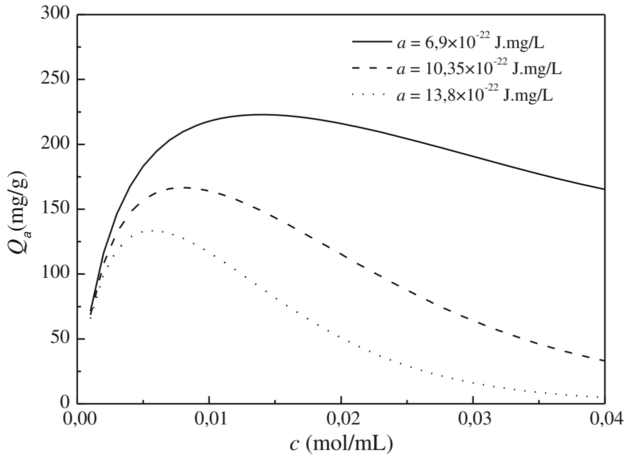

Fig. 6 Effect of the parameter N_M on the adsorption isotherm in the case of MMRG model ($n = 1$, $N_M = 440$ mg/g, $w = 0.00477$ mol/mL and $b = 11$ mL/mol)

preferentially adsorbed in the low coverage region. At high concentrations and especially near the saturation, the inverse phenomenon is observed. This is probably due to the lower probability of finding a sufficient number of empty sites at the same time to be anchored. It can be noted that the adsorbed quantity decreases sharply when the n value is high. Therefore, it can be noted that for the highest n value, the adsorbate–adsorbate interaction becomes stronger than the adsorbent–adsorbate one. As a conclusion, the multianchorage adsorption is favored at low concentrations although the multimolecular adsorption is favored at high coverage. Also the great n value increases the lateral interactions.

The quantity N_M is a parameter associated with the number of receptor sites and, thus, a steric coefficient. We can notice that the increase of the N_M value is followed by the rise of the adsorbed quantity (Fig. 4).

According to Eq. (8), the parameter w is an energetic coefficient which is related to the adsorption energy. The effect of this energetic parameter on the adsorption process is illustrated in Fig. 5 which depicts a plot of the adsorbed quantity versus the adsorbate concentration for three different values of w. The smaller the w value is, the higher the adsorbed quantity for a given concentration is. Indeed, when w decreases, then the adsorption energy increases in absolute value, hence, the receptor sites with a stronger energy will be rapidly occupied.

The parameter a represents the cohesion pressure of the adsorbate molecule. The evolution of the adsorbed amount as a function of the concentration for three values of, a, is shown in Fig. 6. We found that the smaller the a value is, then greater the adsorbed quantity is. This could be explained by the fact that the interaction between adsorbed molecules is weak and so the adsorbent-adsorbate interaction becomes high.

The parameter b is the covolume of the adsorbate molecule. Figure 7 is an illustration of the evolution of adsorbed quantity versus the adsorbate concentration for three values of b. From this figure we can notice that the highest b value is followed by the rise of the adsorbed quantity. Indeed, if the covolume value is higher, the attraction energy between adsorbed molecules becomes weak.

5 Applications: gas adsorption at high pressures

The model parameters n, N_M, w, a and b were determined by fitting procedure using Microcal Origin Lab 8. In the following, the fitting results of experimental data with the

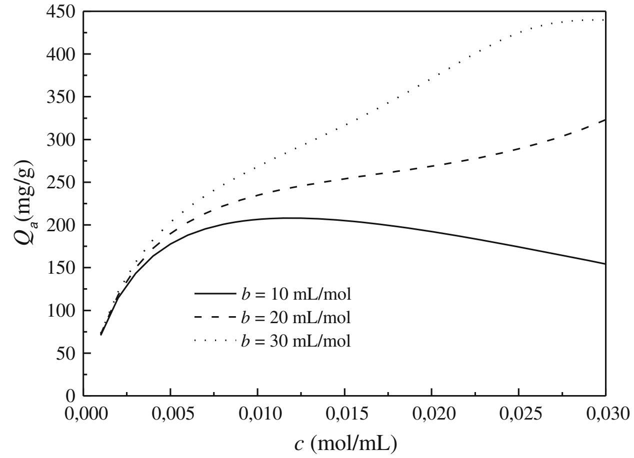

Fig. 7 Effect of the parameter N_M on the adsorption isotherm in the case of MMRG model ($n = 1$, $N_M = 440$ mg/g, $w = 0.00477$ mol/mL and $a = 2.2637 \times 10^{-19}$ J mg/L)

models will be presented and discussed. The monolayer model coupled to the ideal gas was applied to the case of hydrogen sorption. However, the monolayer model coupled to the real gas law was applied in the case of nitrogen, methane and carbon dioxide sorption onto HKUST-1. This choice was done according to the isotherm shape as well as to the fitting criteria.

As an illustration example, Fig. 8 represents the fitting of experimental adsorption isotherm of hydrogen and methane with the two models. The monolayer model coupled to the ideal gas shows a good agreement with the experimental data of hydrogen. Thus, hydrogen can be considered as an ideal gas over a wide temperature range and even at high pressures. The monolayer model coupled to the real gas law is able to describe the methane adsorption onto HKUST-1. All fitting results of studied experimental data are presented in Tables 1 and 2.

5.1 Steric interpretations

In the case of hydrogen adsorption, the evolution of the number or the fraction of adsorbed molecule(s) per site, n, against the temperature shows that this parameter is always higher than unity (Fig. 9a). This indicates that an aggregation phenomenon occurs during the adsorption process where a set of molecules were adsorbed onto one receptor site. Also, these molecules are anchored perpendicularly to the porous adsorbent surface which has a pore diameter 9 Å. This result has been shown by (Georgakis et al. 2007), where in pores larger than 7 Å, hydrogen molecules align in groups and orient themselves perpendicular to the wall surface (Georgakis et al. 2007).

The occupied receptor sites density as a function of temperature is presented in Fig. 4b. It can be noted that N_M values decrease with increasing temperature. This is probably due to the steric hindrance where some sites would become hidden since a set of molecules are adsorbed onto one receptor site. Indeed, the number of hydrogen molecules adsorbed per site, n, increases at high temperature. Furthermore, the increase in temperature has to raise the thermal collisions and then the number of occupied receptor sites decreases. This result can be noticed from the effect of temperature on the adsorbed quantity (Fig. 1).

For nitrogen sorption, all values of n are almost lower to unity $(n \prec 1)$ (Fig. 10a). This indicates that nitrogen molecules can be multianchored on the adsorbent surface, i.e., the adsorbate molecules are adsorbed parallel to the surface (Ganji 2008). Figure 10b shows that the occupied receptor sites density N_m increases with increasing temperature causing a rise of lateral interactions which is presented in Fig. 10c. Furthermore, the covolume, b, decreases at higher temperature since the intermolecular distance decreases (Fig. 10d).

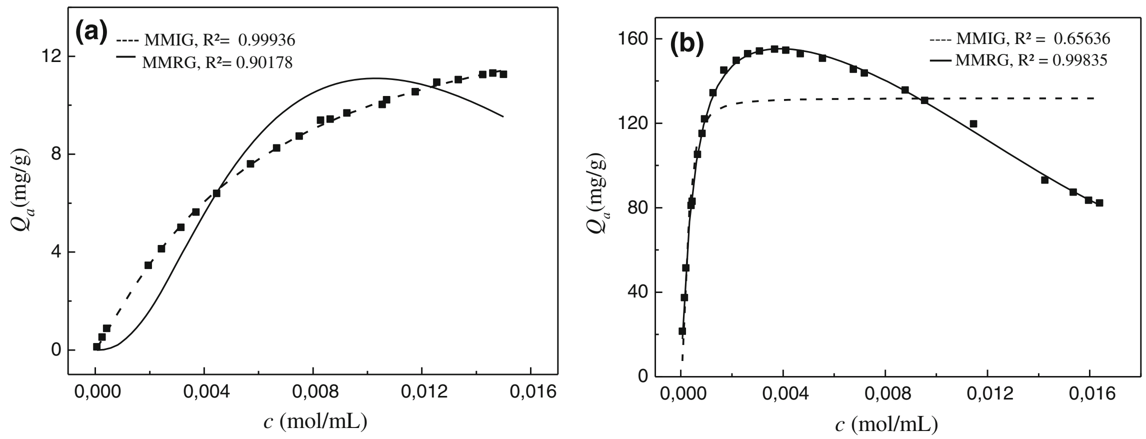

Fig. 8 Fitting example of experimental data of **a** H_2 and **b** CH_4 at 303 K with MMIG and MMRG models

Table 1 Fitting results of experimental data of N_2, CH_4 and CO_2 with the MMRG model

Gas	T (K)	Correlation coefficient	MMRG parameters				
		R^2	*n*	N_M (mg/g)	*W* (mol/mL)	$a \times 10^{-19}$ (J mL/mol)	*b* (mL/mol)
N_2	303	0.99982	0.959	440.400	0.00477	2.263	10.981
	318	0.99972	0.978	429.711	0.00558	2.417	12.253
	333	0.99956	0.981	449.081	0.00693	2.498	11.837
CH_4	303	0.99835	1.052	206.440	0.00058	6.804	28.547
	318	0.99888	1.015	208.685	0.00066	7.149	28.194
	333	0.99937	1.008	234.244	0.00117	7.042	28.894
CO_2	308	0.99555	1.088	593.986	0.00009	9.388	29.686
	313	0.99663	0.933	714.188	0.0001	9.261	27.021
	328	0.99411	1.036	610.891	0.00015	9.673	31.221
	343	0.99505	1.065	586.517	0.00022	10.199	34.250

For methane adsorption, the number of adsorbate molecules is higher than unity (Fig. 10a). This result indicates that the adsorption process is multimolecular. Thus, the adsorbate–adsorbate interaction is weak (Fig. 10c). Also methane molecules are arranged perpendicularly to the surface. More precisely, methane molecule prefers to be adsorbed in the up orientation (Yang et al. 2006; Qiu et al. 2012; Liu et al. 2013). In fact, one H atom is located perpendicular to the surface oriented to the inner cavity (hydrogen tripod directed to the surface). The *n* value decreases when the temperature increases. This is due to the thermal agitation and consequently the cohesion pressure increases. The rise of temperature causes an increase of N_M and *b* parameters (Fig. 10b and d).

Table 2 Fitting results of experimental data of H_2 with the MMIG model

Gas	T (K)	R^2	*n*	N_M (mg/g)	*w* (mol/mL)
Gas	T (K)	R^2	*n*	N_M (mg/g)	*w* (mol/mL)
H_2	303	0.99936	1.134	13.540	0.0058
	318	0.99896	1.110	10.862	0.0051
	333	0.99641	1.465	5.568	0.0031

For carbon dioxide, the *n* values are almost superior to the unity (Fig. 10a) which means that carbon dioxide is anchored perpendicularly to the surface. The receptor sites density, N_M, increases slightly with increasing temperature till a maximum and then decreases (Fig. 10b). This decrease could be attributed to the thermal collisions. The covolume *b* and the cohesion pressure *a* of carbon dioxide can be considered constant (Fig. 10c and d).

As a conclusion, the nitrogen molecule is adsorbed parallel to the surface while hydrogen, methane and carbon dioxide molecules are anchored perpendicularly to the adsorbent surface (Fig. 11). The highest values of *n* are obtained in the case of hydrogen adsorption. This could be explained by the fact that hydrogen molecule is smaller than the other adsorbate molecules. The N_M values for carbon dioxide are the greatest in this row indicating that the carbon dioxide molecule is more anchored than other

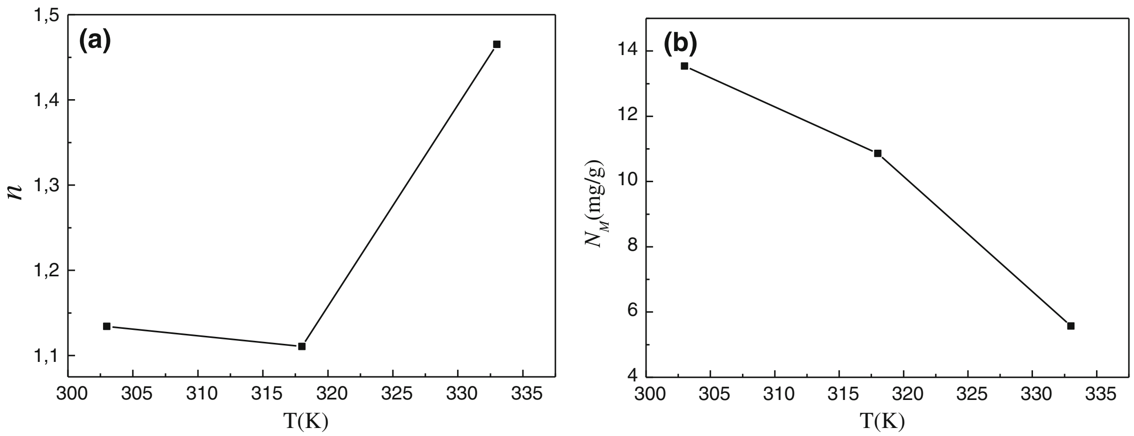

Fig. 9 Behavior of **a** the mean number of adsorbed molecules of H_2 per site and **b** the occupied receptor sites density as a function of temperature

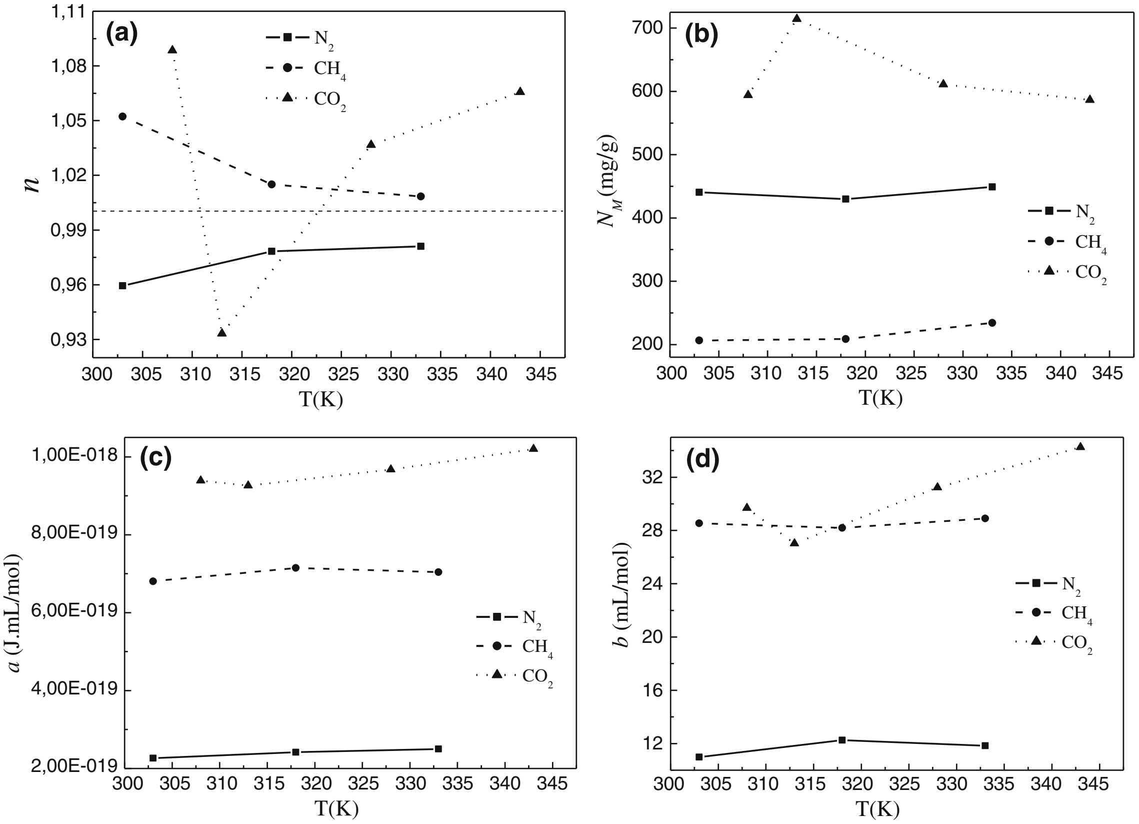

Fig. 10 Behavior of **a** the mean number of adsorbed molecules of N_2, CH_4 and CO_2 per site, **b** the occupied receptor sites density, **c** the cohesion pressure and **d** the covolume as a function of temperature

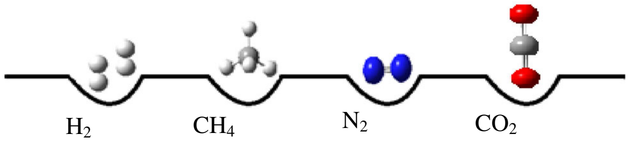

Fig. 11 Schematic illustration of the orientation of gases molecules onto porous adsorbent surface

gases, which is due to its high polarizability. The lateral interactions and the covolume in the case of carbon dioxide are the highest due to its electronic properties; the adsorbed quantity decreases sharply by increasing concentration.

5.2 Energetic interpretations

The theoretical model allows also the investigation of the adsorption process from an energetic point of view. The w parameter is related to the adsorption energies. According to Eq. (8), if w value increases, ΔE^a value decreases. From Table 1 it can be noted that in the case of nitrogen, methane and carbon dioxide, the adsorption energy decreases with the rise of temperature. Indeed, the adsorbed quantity decreases with increasing temperature, therefore, the adsorption is an exothermic process (Ning et al. 2012). However, for hydrogen, the adsorption energy increases with temperature. It can be seen that carbon dioxide adsorption has the highest adsorption energy, hydrogen and nitrogen adsorption have the lowest one. In fact, hydrogen adsorption occurs by physisorption involving weak Van-der-Waals forces (Langmi et al. 2014).

5.3 Thermodynamic study

To deduce the nature of an adsorption process it is necessary to determine thermodynamic parameters such as entropy, internal energy, Gibbs free energy.

5.3.1 Configurational entropy

The entropy is related to the grand potential as well as to the total adsorption energy E_a, to the chemical potential μ_a and to the adsorbed quantity Q_a (Diu et al. 1989) as:

$$J = -k_B T \ln\left(z_{gc}\right) = E_a - \mu_a Q_a - T s_a \tag{10}$$

where Q_a is the adsorbed quantity and E_a is the total energy of the system.

Equation (10) can be rewritten as follows:

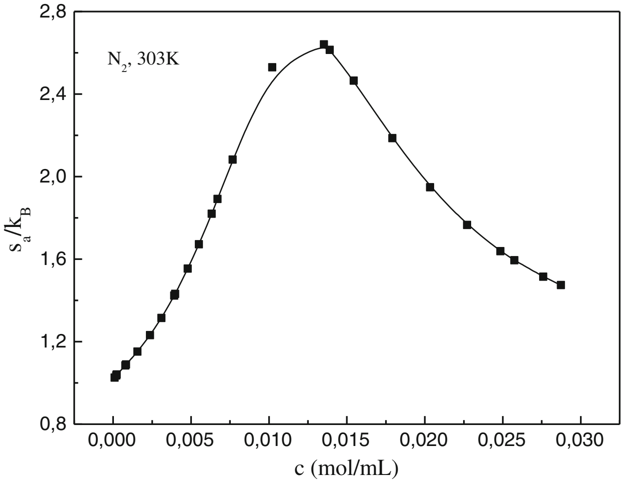

Fig. 12 Behavior of configurational entropy as a function of the nitrogen concentration at 303 K

$$J = -\frac{\partial \ln(z_{gc})}{\partial \beta} - Ts_a \tag{11}$$

Then, the expression of the entropy can be written:

$$s_a/k_B = -\beta\frac{\partial \ln(z_{gc})}{\partial \beta} + \ln(z_{gc}) \tag{12}$$

Finally, the following expression of the entropy for one receptor site in the case of monolayer model coupled to the real gas is obtained:

$$\frac{s_a}{k_B} = \frac{\ln x^n}{x^n + 1} + \ln\left(1 + \frac{1}{x^n}\right) \tag{13}$$

where

$$x = \left(w\frac{1 - bc}{c}e^{-\frac{bc}{1-bc}}e^{2\beta ac}\right)$$

Figure 12 depicts the evolution of the entropy given by Eq. (12) in case of nitrogen adsorption at 303 K. It can be noted that at low concentration, the entropy value increases. However, at the beginning of adsorption the disorder at the adsorbent surface increases where the mobility of gas molecules is important since the adsorbate molecules has many possibilities to find an empty site. Then the entropy reaches a maximum value. The disorder decreases when the saturation is reached.

5.3.2 *Gibbs free enthalpy*

The Gibbs free enthalpy is expressed as (Diu et al. 1989):

$$G = n\mu N_0 \tag{14}$$

It can be written for one receptor site in the following way:

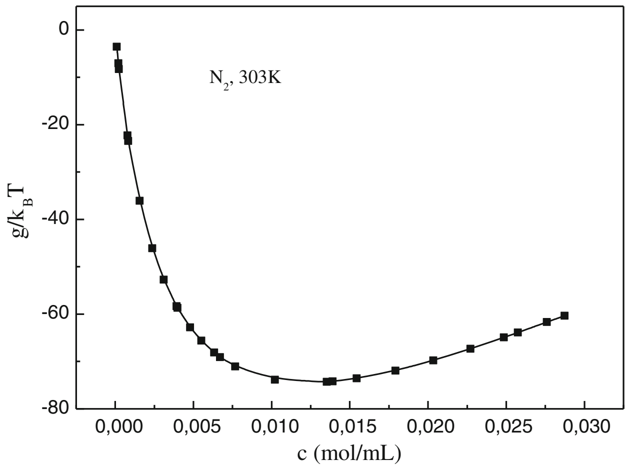

Fig. 13 Behavior of Gibbs free enthalpy as a function of the nitrogen concentration at 303 K

$$\frac{g}{k_BT} = \frac{n\left(\ln\left(\frac{c}{z_{gtr}}\right) + \ln\left(\frac{1}{1-bc}\right) + \frac{bc}{1-bc} - \frac{2a}{k_BT}c\right)}{1 + x^n} \tag{15}$$

Figure 13 shows the evolution of the Gibbs free enthalpy in the case of nitrogen adsorption at 303 K. All values of g are always negative and the adsorption process is spontaneous. Also it can be noted that at low concentrations, the enthalpy value g starts from zero and then decreases algebraically with increasing adsorbate concentration. At the beginning of the adsorption process, the receptor sites are almost empties, which leads to strong interaction between the adsorbed molecule and the surface. The maximum of g values in modulus corresponds to the maximum of adsorbed quantity, while the adsorption process decreases during an increase of *g*.

5.3.3 *Internal energy*

The internal energy is defined as follows:

$$E_{\text{int}} = -\frac{\partial \ln z_{gc}}{\partial \beta} + \frac{\mu}{\beta}\left(\frac{\partial \ln z_{gc}}{\partial \mu}\right) \tag{16}$$

According to grand canonical partition function of the monolayer model coupled to real gas, the internal energy of one receptor site is written as:

$$\frac{E_{\text{int}}}{k_BT} = \frac{\ln\left(\frac{w}{z_{gtr}}\right)}{1 + \left(w\frac{1-bc}{c}e^{\frac{2ac}{k_BT}}e^{-\frac{bc}{1-bc}}\right)^n} \tag{17}$$

The values of the internal adsorption energy are all negative; consequently, the adsorption process is exothermic (Fig. 14). This energy increases with increasing the adsorbate concentration. Indeed, the high internal energy values at low surface coverage are due to the existence of

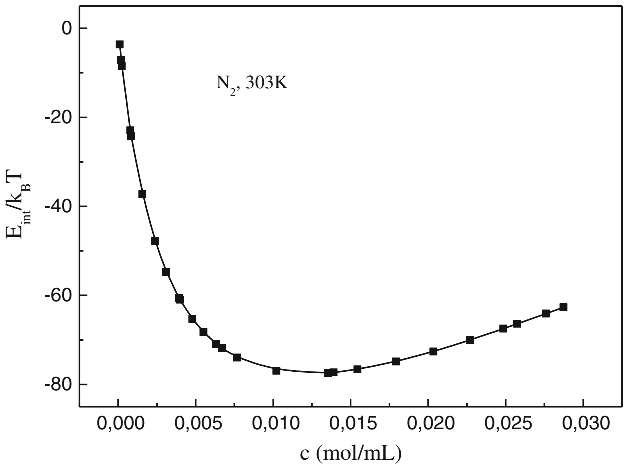

Fig. 14 Behavior of internal energy as a function of the nitrogen concentration at 303 K

highly active sites on the adsorbent surface. Hence, at the beginning of adsorption the adsorbent-adsorbate interactions are strong. The maximum of E_{int} value corresponds to the maximum of the adsorbed quantity. For nitrogen sorption, after reaching a maximum, the internal energy value decreases with increasing in nitrogen concentration, which is due to the weaker adsorbent-adsorbate interactions.

6 Conclusion

This paper presents a theoretical model to describe the adsorption process at the molecular level. This new monolayer model coupled to real gas is established using the grand canonical partition function in statistical physics. All parameters in this model, which are in particular steric and energetic parameters, gave physical meaningful values.

The monolayer model coupled to real gas is applied to experimental adsorption isotherm of hydrogen, nitrogen, methane and carbon dioxide onto HKUST-1. An excellent agreement was found between the monolayer model and the experimental data except for hydrogen which is considered as an ideal gas. The evolution of steric parameters allows us to deduce the adsorbed molecule position, the state of the adsorbent and the lateral interactions between the adsorbate molecules. The energetic parameter w allows us to deduce that carbon dioxide has the greatest adsorption energy when it is anchored to the surface with regard to its high polarizability. The evolution of thermodynamic parameters determined from the monolayer model coupled to real gas such as entropy, Gibbs free energy and internal energy was also studied. The study of the entropy evolution allows deriving information about the order and disorder of the adsorbent surface during the adsorption process. The study of the Gibbs free energy as a function of concentration shows that the adsorption reaction is spontaneous for the entire process. Finally, the evolution of the internal energy tells us about the type of interaction and the nature of adsorption, which is exothermic regarding the considered system.

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