

Supporting Information

General Theory of Absorption in Porous Materials: The Restricted Multilayer Theory

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I. ADSORPTION THEORY

In this subsection we firstly derive the Langmuir or monolayer theory of adsorption. Following this, we consider Brunauer-Emmett-Teller (BET) or multilayer theory. Finally, we derive a more general Restricted Multilayer Theory (RMT). Langmuir and BET theories are RMT's special cases, when the number of possible adsorption layers equal 1 and ∞ respectively. Finally, we will see that we are able to overcome the unphysical restrictions imposed by Langmuir and BET theories, i.e. the requirement of a monolayer for the Langmuir theory and infinite layers for the BET case.

We make the following definition and assumptions based on the postulates above. In the system, there are B equivalent sites, there are N molecules distributed in B sites, there are no interactions between molecules and the lattice may be one-, two-,three-periodic.

A. Derivations of the different absorption theories

Monolayer theory. Using the the Gibbs ensemble (also known as Grand Canonical distribution), we have

$$\begin{aligned}\Xi(\mu, \tau) &= \sum_{N=0}^{\infty} \sum_{S(N)} \exp[(N\mu - \epsilon_{S(N)})/\tau] \\ &= \sum_{[S(N), N]} \exp[(N\mu - \epsilon_{S(N)})/\tau],\end{aligned}$$

where,

- $[S(N), N]$ is for all states of the system for all number of particles

- $\epsilon_{S(N)}$ defines that each ϵ_S depends on the number of particles. $\epsilon_{S(N)}$ is the energy of the state $S(N)$ of the exact N -particle Hamiltonian.

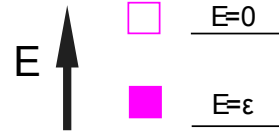


FIG. 1: Assumption from Langmuir theory

Now we can calculate the thermal average number of particles by

$$\bar{N} = \frac{\sum_{S,N} N \exp[(N\mu - \epsilon_{S(N)})/\tau]}{\Xi}.$$

Combining that with

$$\frac{\partial \Xi}{\partial \mu} = \frac{1}{\tau} \sum_{S,N} N \exp[(N\mu - \epsilon_{S(N)})/\tau]$$

we obtain:

$$\bar{N} = \frac{\tau}{\Xi} \frac{\partial \Xi}{\partial \mu} = \tau \frac{\partial \ln \Xi}{\partial \mu}.$$

Here we considered only one adsorption site. Let B be the number of adsorption sites. From the definition of $\lambda = \exp(\mu/\tau)$, we have

$$\frac{\bar{N}}{B} = \lambda \frac{\partial \ln \Xi}{\partial \lambda} \quad (1)$$

Now we take into account the assumption from the Langmuir theory as two energy states for each particle, as

shown in the figure 1. We consider adsorption as favorable process. Therefore, the lower energy corresponds to the adsorbed state, and thus $\epsilon < 0$. Given this, we can derive the partition function as

$$\Xi = 1 + \lambda \exp\left(\frac{-\epsilon}{\tau}\right)$$

Substituting this result into eq. (1), we have

$$\begin{aligned} \frac{\bar{N}}{B} &= \frac{\lambda \exp(-\epsilon/\tau)}{1 + \lambda \exp(-\epsilon/\tau)} \\ \frac{\bar{N}}{B} &= \frac{1}{\lambda^{-1} \exp(\epsilon/\tau) + 1} \end{aligned} \quad (2)$$

Multilayer theory. It is postulated that a gas molecule can be absorbed on each site B , with partition function j_1 , which is denoted as the “first layer”. This first molecule can then be used as a site for another “second layer” molecule, and so on. The partition function for the second and subsequent molecules is given as j_∞ . If given N total number of molecules, of which N_1 are in the first layer, then $N^* = N - N_1$ are in higher layers (more details can be found elsewhere [1], [2]).

Using the grand canonical partition function, we have

$$\begin{aligned} \Xi(B, \mu, T) &= \sum_{N \geq 0} \exp[(N\mu)/k\tau] Q(N, B, T) \\ &= 1 + \sum_{N_1=1}^B \frac{B!(j_1 \exp(\mu/(kT)))^{N_1}}{N_1!(B - N_1)!(N_1 - 1)!} \\ &\quad \times \sum_{N^*=0}^{\infty} \frac{(N_1 + N^* - 1)!(j_\infty \exp(\mu/(kT)))^{N^*}}{N^*!} \end{aligned}$$

Furthermore,

$$\Xi(B, \mu, T) = \sum_{N_1=0}^B \frac{B!(y)^{N_1}}{N_1!(B - N_1)!} = (1 + y)^B \quad (3)$$

where we have defined,

$$y = \frac{j_1 \exp(\mu/kT)}{1 - j_\infty \exp(\mu/kT)}$$

Again using

$$\bar{N} = kT \left(\frac{\partial \log \Xi}{\partial \mu} \right)_{T,B} \quad (4)$$

and applying it to equation 3, we have

$$\frac{\bar{N}}{B} = \frac{cx}{(1 - x + cx)(1 - x)} \quad (5)$$

where $c = \frac{j_1}{j_\infty}$ and $x = j_\infty \exp(\mu/kT)$. This is also known as the BET adsorption isotherm equation [3].

Restricted Multilayer theory (RMT) A more realistic approach is that the adsorption is restricted to n layers. We assume that there are only three types of interactions in this system, which are

1. Those between the surface ($n = 0$) and the first layer molecules ($n = 1$), with partition function j_1
2. Those between first layer molecules ($n = 1$) and second layer molecules ($n = 2$), with partition function j_2 , and
3. Those between n^{th} ($n > 1$) layer molecules and $n^{\text{th}} + 1$ layer molecules, with partition function j_∞ .

This creates a columnar structure of bound molecules. Additionally, we assume that there are no interactions between molecules of neighboring columns and the partition function j_2 is equal to j_∞ . Given the total number of molecules, N , then N_1 of them are in the first layer and $N_n = N - N_1$ are in higher layers. From these set of assumptions, we can derive the adsorption behavior for a restricted number of multilayer.

Using the grand canonical partition function, we have

$$\begin{aligned} \Xi(B, \mu, T) &= \sum_{N \geq 0} \exp[(N\mu)/kT] Q(N, B, T) \\ &= \sum_{N_1=0}^B \sum_{N_2=0}^{N_1} \sum_{N_3=0}^{N_2} \cdots \sum_{N_n=0}^{N_{n-1}} \frac{B!}{(B - N_1)!N_1!} \\ &\quad \times \frac{N_1!}{(N_1 - N_2)!N_2!} \cdots \\ &\quad \times \frac{N_{n-1}!(cx)^{N_1}x^{N_2+\dots+N_n}}{(N_{n-1} - N_n)!N_n!}. \end{aligned}$$

In the preceding equations, μ is chemical potential, T is temperature and k is the Boltzmann constant.

Summing in turn over $N_n, N_{n-1}, \dots, N_1$ we find

$$\begin{aligned} \Xi &= [1 + cx(1 + x + x^2 + \dots + x^{n-1})]^B \\ &= \left[1 + cx \left(\frac{1 - x^n}{1 - x} \right) \right]^B \end{aligned}$$

where we have defined,

$$c = j_1/j_\infty, \quad x = j_\infty \exp(\mu/kT).$$

Using this equation in conjunction with the identity,

$$\bar{N} = kT \left(\frac{\partial \log \Xi}{\partial \mu} \right)_{T,B},$$

we find the equation for the *adsorption of a restricted number of multilayers*:

$$\frac{\bar{N}}{B} = \frac{cx[1 - (n+1)x^n + nx^{n+1}]}{(1-x)(1-x+cx-cx^{n+1})}. \quad (6)$$

Source Code for the calculation of the Occupancy Ratio is found in Section IX Code 1.

This equation is more general, since assumptions on the number of layers $n = 1$ or $n = \infty$ give the Langmuir and BET equations, respectively. The substitution,

$$\frac{\bar{N}}{B} \xrightarrow{n=\infty} \frac{cx}{(1-x+cx)(1-x)}$$

gives the BET equation (Eq. 5), and

$$\frac{\bar{N}}{B} \xrightarrow{n=1} \frac{j_1 \exp(\mu/kT)}{1 + j_1 \exp(\mu/kT)}$$

gives the Langmuir equation (Eq. 2).

B. Applications of these formulas to H₂ in porous materials

In this subsection we assume ideal behavior for molecular hydrogen gas and consider no interaction between its molecules. At this point, we neglect rotations, however consideration of rotations will be reported in the following sections. Changes in chemical potential, μ , arising from rotations are fully derived later. Nevertheless, we should note that for $T = 77$ K rotations are not very significant, as the rotational activation temperature is 85.4 K for molecular hydrogen. Moreover, in order to consider rotations at such a temperature, one must separately consider orthohydrogen and parahydrogen because, at this temperature, their rotational partition functions differ significantly. Thus in this section we consider only translational part of entropy and free energy, which is exact for monoatomic gases, and is quite a good approximation for the hydrogen molecule at such a low temperature. In order to obtain consistent results for room temperature, we consider rotations later in this text. There is no issue with orthohydrogen and parahydrogen for room temperature as partition functions for both of them differ only slightly.

In this subsection we begin by applying our assumptions to the Langmuir or monolayer theory of adsorption. Following that, we consider the BET or multilayer theory. Finally, we employ the more general Restricted Multilayer Theory (RMT). Langmuir and BET theories are special cases of RMT, when the number of adsorption layers equals 1 and ∞ , respectively.

According to prior assumptions, we get

$$\lambda = \frac{n}{n_q} = \frac{p}{\tau n_q} = \frac{p}{kT n_q}$$

and

$$n_q = \left(\frac{M\tau}{2\pi\hbar^2} \right)^{3/2} = \left(\frac{MkT}{2\pi\hbar^2} \right)^{3/2}$$

Monolayer theory in molecular hydrogen. If we apply these assumptions to equation 2 we get the Langmuir equation for H₂

$$\begin{aligned} \frac{\bar{N}}{B} &= \frac{1}{(n_q\tau/p) \exp(\epsilon/\tau) + 1} \\ \frac{\bar{N}}{B} &= \frac{p}{(n_q\tau) \exp(\epsilon/\tau) + p} \\ &= \frac{p/p_0}{(n_q\tau) \exp(\epsilon/\tau)/p_0 + p/p_0} \end{aligned} \quad (7)$$

where $p_0 = 1$ bar.

Multilayer theory in molecular hydrogen. In order to obtain j_1 and j_∞ , the procedure illustrated in Figure 2 was used. We consider adsorption as a favorable process and therefore the energies ϵ_1 and ϵ_∞ are negative relative to the energy of a free molecule. Figure 2 illustrates the common situation when adsorption on higher levels is less favorable than adsorption on the first one and therefore $\epsilon_\infty > \epsilon_1$.

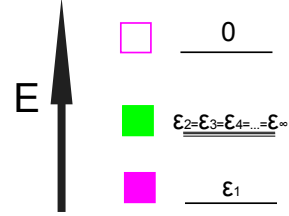


FIG. 2: Assumption for the multilayer theory

Thus for partition functions j_1 and j_∞ , for molecules adsorbed on first and higher levels, respectively, we get

$$\begin{aligned} j_1 &= e^{-\epsilon_1/kT} = e^{\Delta H_{ads}/RT} \\ j_2 = j_3 = j_4 = \dots = j_\infty &= e^{-\epsilon_\infty/kT} = e^{\Delta H_{ads}^*/RT} \end{aligned}$$

$$\begin{aligned} \Delta H_{ads}/RT &= \text{Surface} \cdots \text{H}_2 \\ \Delta H_{ads}^*/RT &= \text{H}_2 \cdots \text{H}_2 \end{aligned}$$

Figure 3 illustrates the adsorption process. Filled squares represent adsorbed molecules, and empty squares represent free sites. First layer molecules (colored in magenta) are bonding sites for higher level molecules (colored in green).

If we set $\epsilon_2 = 0$, then we will nearly have the monolayer case. There will be some effect due to the existence of higher levels, but it will not be significant in the studied range of pressure (0 to 100 bar). Consider

$$\alpha = \frac{P_0}{kT} \left(\frac{MkT}{2\pi\hbar^2} \right)^{-3/2},$$

where $P_0 = 1$ bar. For $T = 77$ K, $\alpha \approx 2.6 \cdot 10^{-4}$ which is a relatively small value. In the multilayer case for H₂

$$\begin{aligned} \frac{\langle N \rangle}{B} &= \frac{\alpha \frac{P}{P_0} e^{\Delta H_{ads}/RT}}{1 + (e^{\Delta H_{ads}/RT} - e^{\Delta H_{ads}^*/RT}) \alpha \frac{P}{P_0}} \times \\ &\quad \frac{1}{1 - \alpha \frac{P}{P_0} e^{\Delta H_{ads}^*/RT}}, \end{aligned} \quad (8)$$

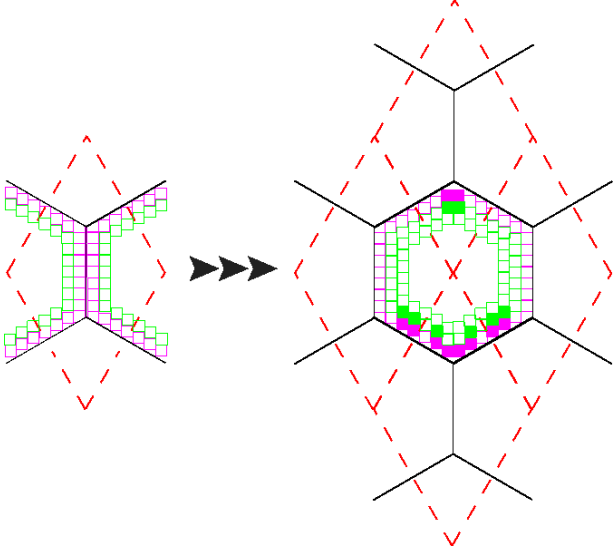


FIG. 3: Assumption for the multilayer theory

where $R = kN_A = 8.314 \text{ J}/(\text{mol} \times \text{K})$. For hydrogen,

$$x = \alpha \frac{P}{P_0} \exp\left(\frac{\epsilon_2}{k_B T}\right),$$

and

$$c = \exp\left(\frac{\epsilon_1 - \epsilon_2}{k_B T}\right).$$

If we set $\Delta H_{ads}^* = 0$, then for the considered pressures

$$1 \geq 1 - \alpha \frac{P}{P_0} e^{\Delta H_{ads}^*/RT} \geq 1 - 2.6 \cdot 10^{-4} \times 100 \approx 1.$$

If $e^{\Delta H_{ads}/RT} \gg 1$, then

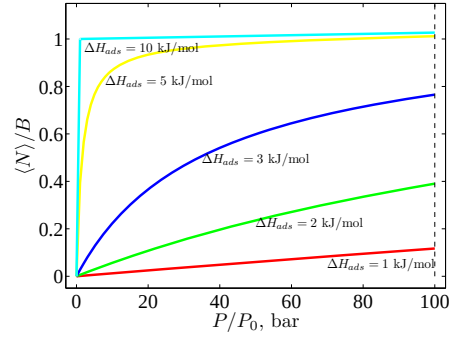
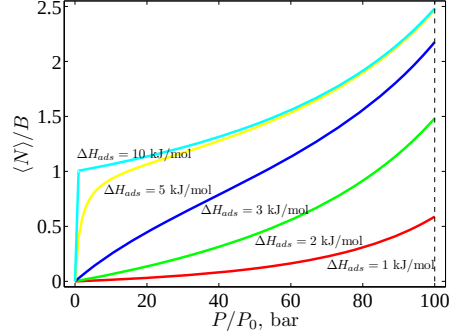
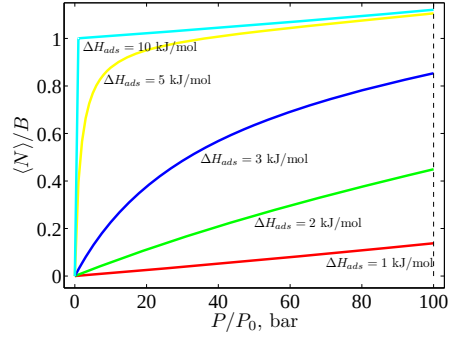
$$\frac{\langle N \rangle}{B} \approx \frac{1}{1 + \frac{1}{\alpha} \frac{P_0}{P} e^{-\Delta H_{ads}/RT}},$$

which is exactly the same as equation (7). When increasing ΔH_{ads}^* , the effect from higher layers becomes more noticeable (compare Figure 4a and Figure 4b). Due to the limitation arising from $1 - x > 0$ in eq. (5), we get

$$\frac{\Delta H_{ads}^*}{RT} < -\log\left[\alpha \frac{P}{P_0}\right].$$

ΔH_{ads}^* is treated as equal to the heat of hydrogen liquefaction and therefore equals 0.904 kJ/mol.

The isotherm for the hydrogen molecule in the multilayer case for calculated ΔH_{ads}^* at $T = 77 \text{ K}$ is plotted (see Figure 4c). However, if ΔH_{ads}^* changes, the shape of the isotherm changes. For example, $\Delta H_{ads}^* = 0$ gives a similar plot to Figure 4c while $\Delta H_{ads}^* = 2 \text{ kJ/mol}$ is very different (see Figure 4b vs Figure 4c).

(a) $\Delta H_{ads}^* = 0 \text{ kJ/mol}$ (b) $\Delta H_{ads}^* = 2 \text{ kJ/mol}$ (c) Real case, $\Delta H_{ads}^* = 0.904 \text{ kJ/mol}$ FIG. 4: Isotherms for H_2 in the multilayer case for $T = 77 \text{ K}$

Restricted Multilayer theory with molecular hydrogen. Now we analyze molecular hydrogen through an application of RMT with n layers. For $\epsilon_2 = 0$ (or $\Delta H_{ads}^* = 0$), we obtain that $x = \alpha P/P_0 \leq 2.6 \times 10^{-2}$. Moreover if $\Delta H_{ads} \leq 3 \text{ kJ/mol}$, then $cx = \exp(\Delta H_{ads}/(RT))x \leq 2.83$ for $T = 77 \text{ K}$. That is why, in this case, cx^n has a small value for $n > 1$. But for $n = 1$ we have the monolayer case, which has already been considered. Furthermore, if we let $n \geq 2$, as $x \leq 2.6 \cdot 10^{-2}$ and $cx \leq 2.83$, we exclude from equation (6) all powers of x higher than the first power and obtain

$$\frac{\langle N \rangle}{B} = \frac{cx}{1 + cx} \times \left(1 + \frac{2x}{1 + (c - 2)x}\right).$$

This relation shows that the difference between monolayer theory and restricted multilayer is not very significant if $\Delta H_{ads} \leq 3$ kJ/mol, because the multiplying factor is the sum of 1 and a function raised to the first power of x . Now we consider isotherms of molecular hydrogen for different numbers of layers n , and different values of ΔH_{ads} , depending on the relative pressure P/P_0 .

For small values of ΔH_{ads}^* , there is no significant dependence of $\langle N \rangle/B$ on the number of layers, whereas for high ΔH_{ads}^* , this dependency is noticeable.

C. Derivation for General Uptake Formula.

We first derive a general equation for the uptake, m , defined as the total mass of gas that can be incorporated per unit volume of a porous framework (in units of g/L). This equation applies for any framework based on the geometric constraints of the framework. Given that the molar mass of hydrogen $M = 2.018$ g/mol, the uptake per $V = 1$ L = 10^{27} Å³ equals

$$m = M \frac{N}{N_A},$$

where N is the number of adsorbed molecules per unit of material volume, N_A is the Avogadro constant. Let B be the number of first layer sites per pore, then

$$m = M \frac{N}{N_A} = M \frac{BN/B(\tilde{n})n_p}{N_A}, \quad (9)$$

where n_p is the number of pores per unit of volume V , $N/B(\tilde{n})$ is the occupancy ratio defined by RMT theory with effective number of layers $\tilde{n}$ (6). Number of pores per unit of material volume V is given by

$$n_p = \frac{\gamma V}{V_p}, \quad (10)$$

where γ is the fraction of void volume of the considered porous material, while V_p is pore volume. Let r_w be effective radius of adsorbed gas molecule meaning that one molecule occupies πr_w^2 of pore surface (see Section V for derivation of r_w for molecular hydrogen), then neglecting edge effects it is possible to estimate the number of adsorption sites B as the ratio of the pore surface area to the cross sectional area of a hydrogen molecule (πr_w^2)

$$B = \frac{S_p}{\pi r_w^2}, \quad (11)$$

where S_p is the pore surface area. Using (11) and (10) in (9) we get the following formula for uptake m

$$m = \frac{\gamma \mu V}{N_A \pi r_w^2} \frac{S_p}{V_p} N/B(\tilde{n}). \quad (12)$$

We may generalize our derivation to M types of conventional unit cells with volumes and surface areas V_p^i and S_p^i , respectively. We also introduce factors

$\gamma_1, \dots, \gamma_M$ for the fraction of volume occupied by every type of the cell,

$$\gamma = \sum_{i=1}^M \gamma_i. \quad (13)$$

Applying equation (12) to every type of cell separately, we get the total uptake for the most general configuration given different types of cells,

$$m = \sum_{i=1}^M \frac{\gamma_i \mu V}{N_A \pi r_w^2} \frac{S_p^i}{V_p^i} \frac{N}{B}(\tilde{n}_i). \quad (14)$$

This final general equation can be used for the different porous materials reported in literature that serves as hosts for many chemical compounds to form energy storage materials.

D. Derivation for Optimal Framework Parameters for the maximized gas delivery amount such as molecular hydrogen.

Optimal enthalpy of absorption. We find optimal values of ΔH_{ads} in a low-temperature region (for instance, for $T = 77$ K). We choose to investigate where rotational degrees of freedom are not significantly activated. We also pursue high temperatures (for instance, for $T = 298$ K) just by considering the full chemical potential later.

According to our theory, geometric properties of a framework only define some factors to the uptake. The shape of the isotherm is defined by the factor $\nu = N/B(\tilde{n})$ from the RMT. Thus to get the highest delivery amount for fixed number of layers (fixed geometry), one must derive the enthalpy ΔH_{ads} that leads to the highest possible difference in the factor ν between pressure P_0 and P .

$$\Delta \nu = [\nu(P) - \nu(P_0)] \rightarrow \text{Maximize } \Delta \nu.$$

The function $\nu(P)$ is smooth, thus the necessary condition to obtain the maximum is

$$\frac{\partial \Delta \nu}{\partial \Delta H_{ads}} (\Delta H_{ads}^{opt}) = 0. \quad (15)$$

For convenience, we introduce the multiplier m defined as $P = m P_0$

We also define

$$\beta_1 = \exp\{\Delta H_{ads}/(RT)\}, \beta_2 = \exp\{\Delta H_{ads}^*/(RT)\},$$

$$\tilde{\beta}_1 = \alpha \beta_1, \tilde{\beta}_2 = \alpha \beta_2,$$

$$c = \beta_1/\beta_2, x = \alpha P/P_0 \beta_2.$$

Here, H_{ads}^* is the interaction of first layer with the second layer of adsorbed molecules.

$$\alpha = \frac{P_0}{P} \exp(\mu/kT)$$

is a function of temperature. For the low temperature region chemical potential is defined by a translational part ($\mu \approx \mu_{tr}$) and

$$\alpha = \frac{P_0}{kT} \left(\frac{\mu kT}{2\pi N_A \hbar^2} \right)^{-3/2}.$$

For the high temperature region, when rotational degrees of freedom are fully activated,

$$\alpha = \frac{P_0}{kT} \left(\frac{\mu kT}{2\pi N_A \hbar^2} \right)^{-3/2} \left(\frac{2T_r}{T} \right). \quad (16)$$

Here μ is molar mass of gas, T_r is the activation temperature for rotational degrees of freedom, and $P_0 = 1$ bar.

Deriving $\partial\Delta\nu/\partial\Delta H_{ads}$ for the RMT gives the values for optimal enthalpy ΔH_{ads}^{opt} . Thus, the optimal enthalpy for the restricted multilayer case is given by eq. (17).

$$\Delta H_{ads}^{opt} = RT \ln \beta_1 = RT \ln \tilde{\beta}_1/\alpha, \quad (17)$$

where

$$\tilde{\beta}_1 = \frac{a(1 - m\tilde{\beta}_2) - b\sqrt{m}(1 - \tilde{\beta}_2)}{b\sqrt{m}(1 - \tilde{\beta}_2^n) - am(1 - m^n\tilde{\beta}_2^n)},$$

$$a = \sqrt{1 - (n+1)\tilde{\beta}_2^n + n\tilde{\beta}_2^{n+1}},$$

$$b = \sqrt{1 - (n+1)m^n\tilde{\beta}_2^n + nm^{n+1}\tilde{\beta}_2^{n+1}}.$$

Particularly for the high-temperature region, (e.g. $T=298$ K), and the associated value of α (16) we get

$$\Delta H_{ads}^{opt} = RT \ln \beta_1 = RT \ln \left(\tilde{\beta}_1 T^{7/2} / \left(\alpha_0 T_0^{7/2} \right) \right), \quad (18)$$

where $\alpha_0 = 5.1 \cdot 10^{-6}$, $T_0 = 298$ K and

$$\tilde{\beta}_1 = \alpha_0 (T_0/T)^{7/2} \beta_1.$$

Source Code for the computation of the enthalpy of adsorption under RMT for high and low temperatures can be found in Section IX Codes 3 and 2 respectively.

Optimal Linker Length and void volume We derive an approach to define optimal linker length for a series of frameworks. The linker length influences the asymptotic value of the isotherm (when $P \rightarrow \infty$). This is because the pore volume V_p , surface area S_p and fraction of void volume γ depend on the linker length.

To get the optimal linker length we consider the general equation for uptake (Eq. (14)) and, using one type of cell ($M = 1$), we obtain (Eq. (12)),

$$m = \frac{\gamma \mu V}{N_A \pi r_w^2} \frac{S_p}{V_p} \frac{N}{B} (\tilde{n}).$$

We've considered the factor $(N/B)(\tilde{n})$ in a previous section. Now we consider the second one

$$\gamma \frac{S_p}{V_p}$$

since all the other terms are constant and do not depend on the geometrical characteristics of the framework. We assume that the framework has one characteristic length a , which is the length of the linker. We assume that the net can be expanded based on a reduced unit cell. Total volume is given as $V \sim a^3$, but for the volume of the framework itself we suggest $V_{net} \sim a^{1+\xi}$, where ξ indicates how the volume of the net grows with the growth of a . For instance, if $\xi = 0$, it means that the volume of the net grows only with linker length, whereas the cross section of linkers is constant.

We get

$$\gamma = 1 - \frac{V_{net}}{V} = 1 - \frac{\kappa}{a^{2-\xi}}, \quad (19)$$

where κ is some constant depending on the framework. We also get $S_p/V_p = c/a$, where c is constant for every framework not changing when enlarging the linkers. Thus,

$$f(a) = \gamma \frac{S_p}{V_p} = \left(1 - \frac{\kappa}{a^{2-\xi}} \right) \frac{c}{a} \rightarrow \text{Maximize } f(a).$$

This gives

$$a^{2-\xi} = (3 - \xi)\kappa$$

and therefore

$$a = ((3 - \xi)\kappa)^{\frac{1}{2-\xi}}. \quad (20)$$

The factor κ can be defined from experimental data if γ is known. Therefore, we obtain the universal recipe of best linker length under these assumptions.

For the high temperature region (for instance, for $T = 298$ K), we should consider not only translational part of the chemical potential for hydrogen, but also its rotational part (as the rotational activation temperature for hydrogen molecule is $T_r = 85.4$ K). The appropriate considerations (see section VI and VII) show that considerations of the full chemical potential in our theory only alter α as follows (see eq. (21))

$$\alpha \rightarrow \alpha(2T_r)/T, \quad (21)$$

which for $T = 298$ K gives $\alpha = 5.1 \cdot 10^{-6}$ for full chemical potential. This can be compared with the value obtained at 77 K, $\alpha = 2.6 \cdot 10^{-4}$. Thus, all the equations from previous sections are valid for the high temperature region where the appropriate substitution of α is made.

II. ISOTHERMS FOR DIFFERENT ΔH_{ads}^* IN THE RESTRICTED MULTILAYER CASE

Let us plot isotherms for values of ΔH_{ads}^* different from 0.904 kJ/mol. Isotherms for $\Delta H_{ads}^* = 0$ and $\Delta H_{ads}^* = 0.5$ kJ/mol are similar (see Figure 6 and Figure 7) whereas the ones for $H_{ads}^* = 2$ kJ/mol (see Figure 8) are different due to the significant impact of higher levels.

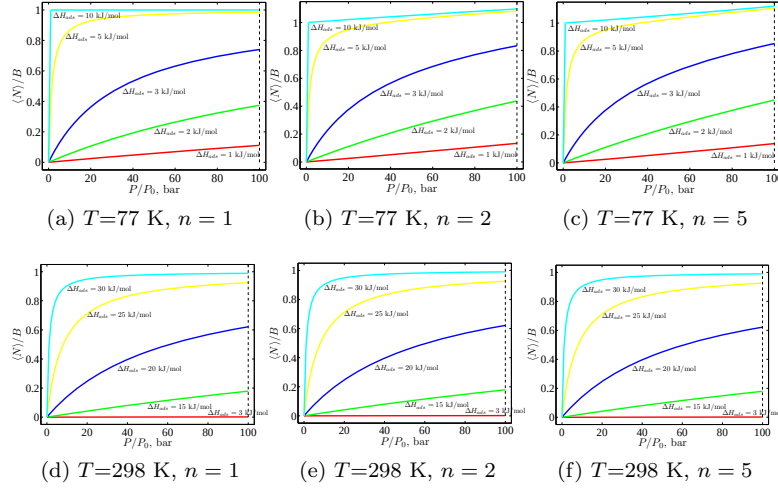


FIG. 5: Isotherms for H_2 in the restricted multilayer case when $\Delta H_{ads}^* = 0.904$ kJ/mol at $T=77$ K and $T=298$ K.

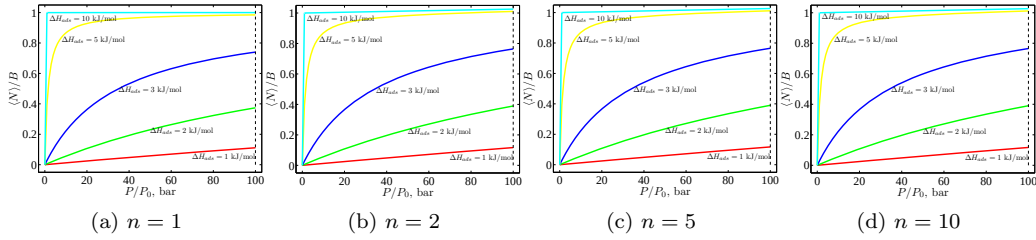


FIG. 6: Isotherms for H_2 in restricted multilayer case ($n = 1, 2, 5, 10$) when $\Delta H_{ads}^* = 0$ kJ/mol for $T=77$ K.

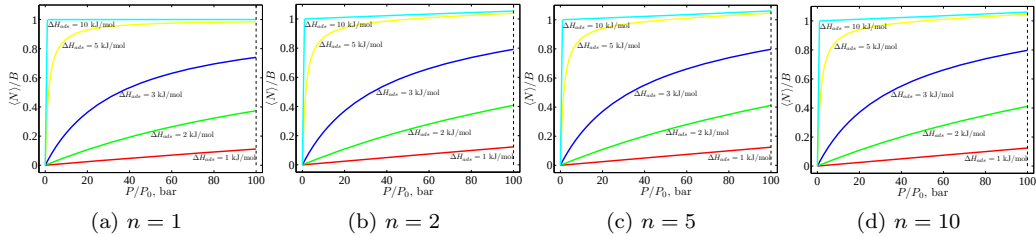


FIG. 7: Isotherms for H_2 in restricted multilayer case ($n = 1, 2, 5, 10$) when $\Delta H_{ads}^* = 0.5$ kJ/mol for $T=77$ K.

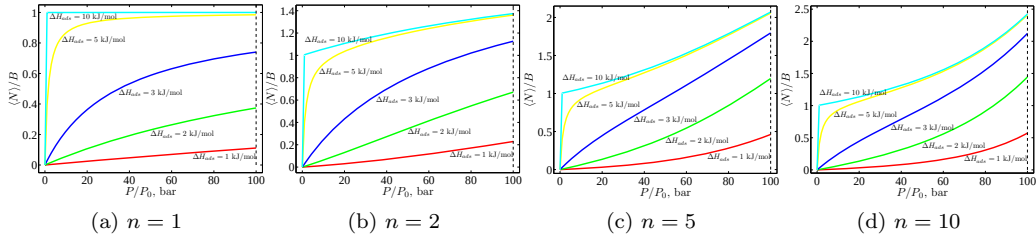


FIG. 8: Isotherms for H_2 in restricted multilayer case ($n = 1, 2, 5, 10$) when $\Delta H_{ads}^* = 2$ kJ/mol for $T=77$ K.

A. Optimal parameters of the framework for the highest gas delivery using the Langmuir and BET theory

Enthalpy of adsorption ΔH_{ads} . We define

$$\beta_1 = \exp\{\Delta H_{ads}/(RT)\}, \beta_2 = \exp\{\Delta H_{ads}^*/(RT)\},$$

$$\tilde{\beta}_1 = \alpha\beta_1, \tilde{\beta}_2 = \alpha\beta_2,$$

$$c = \beta_1/\beta_2, x = \alpha P/P_0\beta_2,$$

where α is a function of temperature that was defined previously. Deriving $\partial\Delta\nu/\partial\Delta H_{ads}$ for monolayer and multilayer theories gives the following values for optimal enthalpy ΔH_{ads}^{opt} .

For the monolayer case, we get the optimal value of adsorption enthalpy ΔH_{ads} as follows.

$$\Delta H_{ads}^{opt} = RT \ln \frac{1}{\alpha\sqrt{m}} = RT \ln \left(\frac{T^{5/2}}{\alpha_0 T_0^{5/2}} \sqrt{\frac{P_0}{P}} \right) \quad (22)$$

where $\alpha_0 = 2.6$, and $\cdot 10^{-4}$, $T_0 = 77$ K. For instance, for pressure $P=100$ bar and $T=77$ K we get $\Delta H_{ads} = 3.75$ kJ/mol.

To obtain the optimal enthalpy in the monolayer case for the high-temperature region (for instance, for $T=298$ K) we make the appropriate change of α (see eq. (21)) and get

$$\Delta H_{ads}^{opt} = RT \ln \frac{1}{\alpha\sqrt{m}} = RT \ln \left(\frac{T^{7/2}}{\alpha_0 T_0^{7/2}} \sqrt{\frac{P_0}{P}} \right), \quad (23)$$

where $\alpha_0 = 5.1 \cdot 10^{-6}$ and $T_0 = 298$ K. Evaluating (23) for pressure $P=100$ bar and $T=298$ K, we get $\Delta H_{ads} = 24.5$ kJ/mol.

To calculate $\Delta\nu$ in the monolayer case using the calculated optimal adsorption enthalpy, ΔH_{ads}^{opt} , we obtain,

$$\Delta\nu = \frac{\sqrt{m} - 1}{\sqrt{m} + 1}. \quad (24)$$

Substituting $P=100$ bar into (24), we get

$$\Delta\nu = 9/11 = 81.8\%.$$

The optimal adsorption enthalpy in **multilayer case** is given by eq. (25), given as

$$\Delta H_{ads}^{opt} = RT \ln \frac{1}{\alpha\sqrt{m}} + \beta_2 = RT \ln \left(\frac{T^{5/2}}{\alpha_0 T_0^{5/2}} \sqrt{\frac{P_0}{P}} + \exp \frac{\Delta H_{ads}^*}{RT} \right). \quad (25)$$

Comparing (22) and (25) indicates that as $T \rightarrow \infty$ (and even at relatively high temperature), there is nearly no

difference in the optimal enthalpy of adsorption between the monolayer and multilayer cases. For instance, for $P=100$ bar and $T=77$ K, this difference is only 8 J/mol. But when $T \rightarrow 0$ in the monolayer case, $\Delta H_{ads}^{opt} \rightarrow 0$, whereas in the multilayer case, $\Delta H_{ads}^{opt} \rightarrow \Delta H_{ads}^*$.

To obtain the optimal enthalpy in the multilayer case for high-temperature regions (for instance, $T=298$ K), we make the appropriate change of α (see eq. (21)) and get

$$\Delta H_{ads}^{opt} = RT \ln \frac{1}{\alpha\sqrt{m}} + \beta_2 = RT \ln \left(\frac{T^{7/2}}{\alpha_0 T_0^{7/2}} \sqrt{\frac{P_0}{P}} + \exp \frac{\Delta H_{ads}^*}{RT} \right), \quad (26)$$

where $\alpha_0 = 5.1 \cdot 10^{-6}$ and $T_0 = 298$ K.

Source code for the computation of the enthalpy of adsorption for monolayer (Langmuir) and multilayer (BET) theory at low and high temperatures is found in Section IX Codes 4 and 5 respectively.

To determine the difference in the factor ν between pressures P_0 and P , we get, in the multilayer case,

$$\Delta\nu = \frac{1 + \alpha\beta_2\sqrt{m}}{1 + \sqrt{m}} \left[\frac{\sqrt{m}}{1 - \alpha m\beta_2} - \frac{1}{1 - \alpha\beta_2} \right]. \quad (27)$$

As the assumption of an infinite number of layers is not realistic, from (27), we obtain a restriction on the range of pressures. This theory works if

$$m < \frac{1}{\alpha\beta_2}. \quad (28)$$

For $T=298$ K, the upper border according to (28) equals 137,200 bar, which is far more than the value of 100 bar considered previously. For $T=77$ K, the upper bound is also far more than that of 100 bar, and equals 955 bar. At 45.5 K the upper bound reaches $P=100$ bar and hence the multilayer theory is not applicable for this range of pressures and temperatures below 45.5 K.

From equations (22), (25) and (17) we determine that optimal enthalpy increases with temperature.

We plot in color the dependence of the optimal enthalpy on temperature, T , and pressure, P , in all three cases for low and high temperatures: monolayer (see Figure 9a, d), multilayer (see Figure 9b, e) and restricted multilayer for 3 layers (see Figure 9c, f). For molecular hydrogen, ΔH_{ads}^* is relatively low. Hence the graphs shown in Figure 9d,e,f for different number of layers are identical. Discrepancies are significant only at very low temperatures.

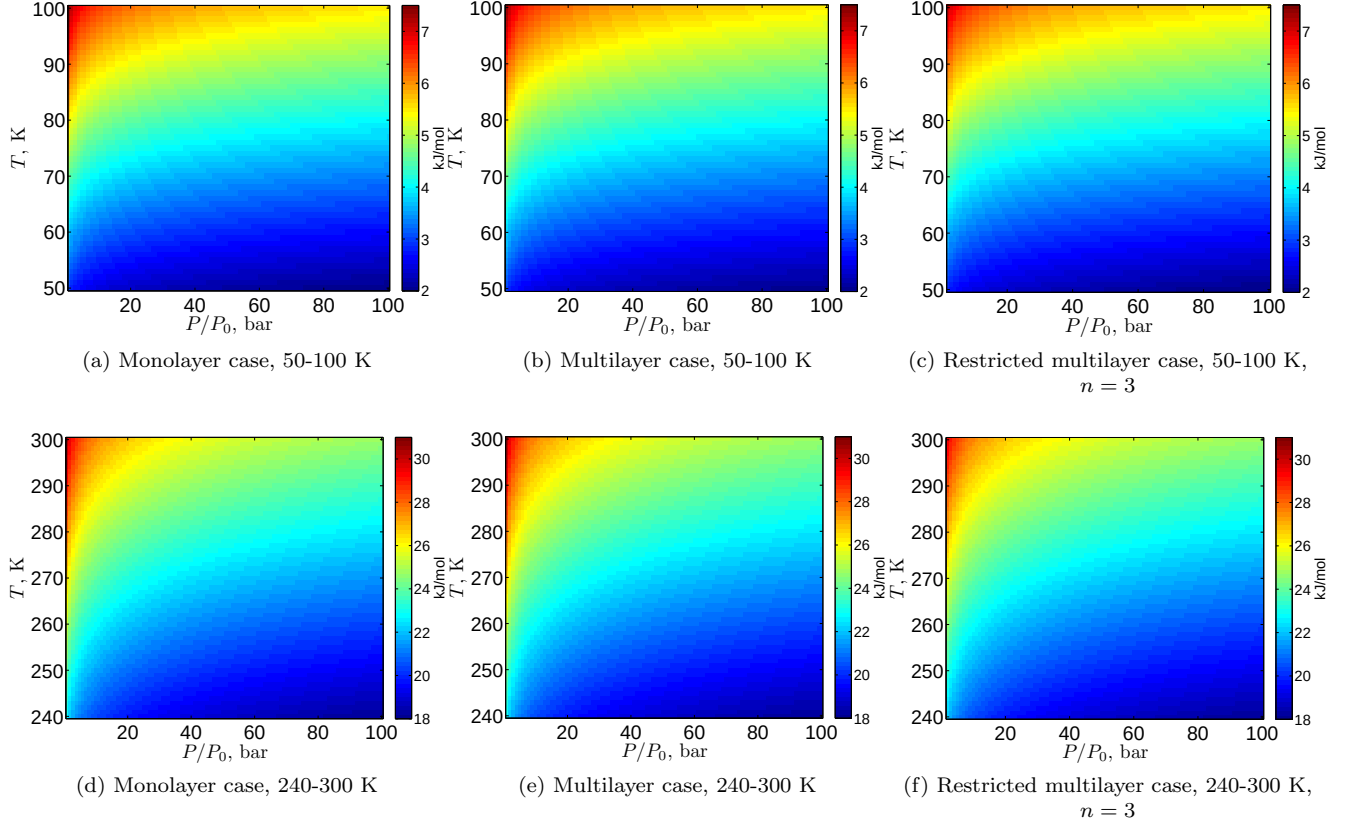


FIG. 9: Temperature and pressure dependence of optimal enthalpy ΔH_{ads}^{opt} for low and high temperature region

III. CUBIC FRAMEWORK WITH INTERPENETRATION.

Another framework explored in this work is one where there is interpenetration present, where frameworks of the same kind are catenated starting with a two-fold degree and eventually reaching a maximum limited by the space inside the pores.

We consider the framework of q interpenetrated cubic nets with linkers that are cylinders of length l and base radii r , and SBU-nodes that we treat as spheres with diameter d . If the volume of the porous material is V , then we get

$$\frac{V}{(d+l)^3}$$

cells and therefore the uptake in number of hydrogen molecules would be

$$N = \frac{V}{(d+l)^3} B \frac{N}{B}(\tilde{n}),$$

where $\tilde{n}$ is an effective number of layers, B is a number of sites and $\frac{N}{B}(\tilde{n})$ is $\frac{N}{B}$ for restricted multilayer case with $\tilde{n}$ layers. In order to estimate the effective number of layers one can consider the longest distance in a cubic

cell, which is its main diagonal, and thus get the effective number of layers in the following equation,

$$\tilde{n} = \frac{\sqrt{3}(d+l)}{D+\delta},$$

where, D is the diameter of a hydrogen molecule and δ is the characteristic distance between them. Another approach takes into account the symmetry of adsorption in a cubic cell and therefore the effective number of layers is smaller. In this approach the effective longest distance is not the diagonal but is instead the edge of a cube. Therefore, we get

$$\tilde{n} = \frac{d+l}{D+\delta}. \quad (29)$$

Thus we use eq. (29) for estimating the effective number of layers. We should also note that if eq. (29) gives fractional number of layers e.g. 1.54, one can pick up either 1 or 2 layers. In this article we use the biggest integer number not higher than $\tilde{n}$.

Let us consider the case of cubic frameworks with an interpenetration of degree q . In this case, the length of the linker is l , the diameter of the SBU-node, which is considered to be a sphere, is d , and the radius of the linker is r . The factor γ , which, in this case, defines the

share of the free volume, equals

$$\gamma = 1 - q \frac{\pi/6d^3 + 3\pi r^2 l}{(d+l)^3}.$$

The surface area of a pore is equal to

$$S_p = 6(d+l)^2 - 6\pi d^2/4 = 6[(d+l)^2 - \pi d^2/4].$$

Given that the degree of interpenetration is q , we can say that

$$S = qS_p,$$

and therefore

$$B = \frac{qS_p}{\pi r_{H_2}^2}.$$

Now let us apply this equation to determining the adsorption in MOF-9, which is a cubic interpenetrated framework of degree two. For this MOF, $d = 9.65 \text{ \AA}$, $l = 11.88 \text{ \AA}$ and $2r = 5 \text{ \AA}$. Thus we get

$$\gamma = 1 - 2 \cdot 0.119 = 0.762.$$

This agrees well with experimental measurements of $\gamma = 0.71$ that were carried out by Eddaoudi et al. [4]. According to (30), $S_p = 2340 \text{ \AA}^2$, and therefore the number of sorption sites is $B = 194.16 \approx 194$, and the number of layers is $\tilde{n} = 3.9 \approx 4$. The uptake (Eq. 12) gives

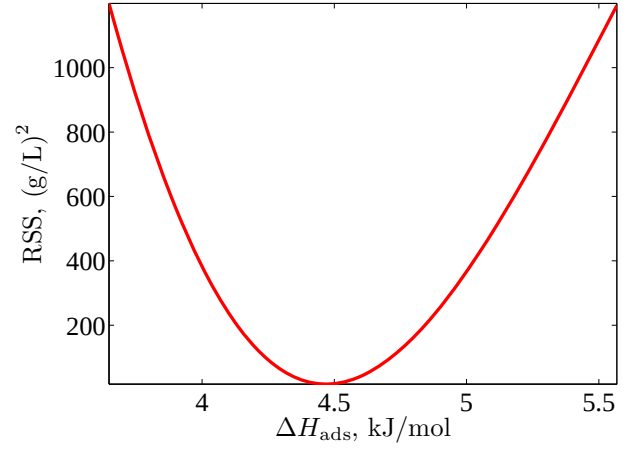
$$m = 45.9 \frac{N}{B}(4) \text{ g/L}.$$

IV. COMPARISON TO EXPERIMENTS

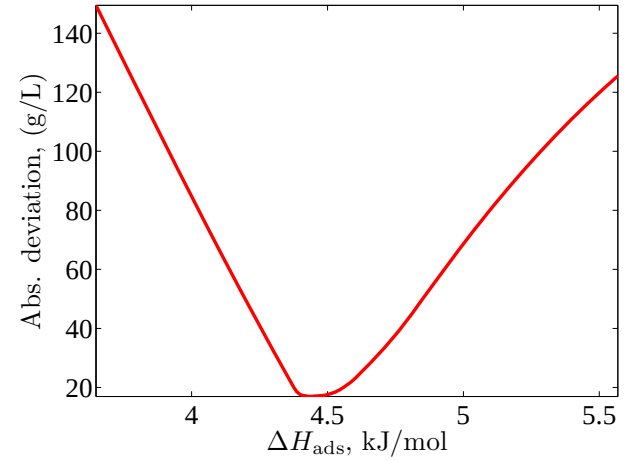
A. MOF-5

We assume that the discrepancy in the low-pressure region can also be caused by a slight decrease of the adsorption enthalpy reported in [5]. This assumption is further supported by the fact that excess uptake in the region of high pressures and low temperatures is mainly sensitive not to changes in adsorption enthalpy, but to changes in pore properties [6]. We will use two optimized enthalpy estimations. The first is the sum of squares of deviations of uptake. The second is the sum of the absolute values of deviations. The dependency of these parameters on enthalpy of adsorption can be seen in Figure 10a and Figure 10b.

The optimal values of ΔH_{ads} are very close: 4.47 kJ/mol and 4.43 kJ/mol, respectively. Isotherms with these enthalpies of adsorption are plotted on the Figure 11a and Figure 11b. The square root of the average square deviation and absolute deviation are, respectively, 0.81 (g/L) and 0.65 g/L.



(a) Sum squares of deviations



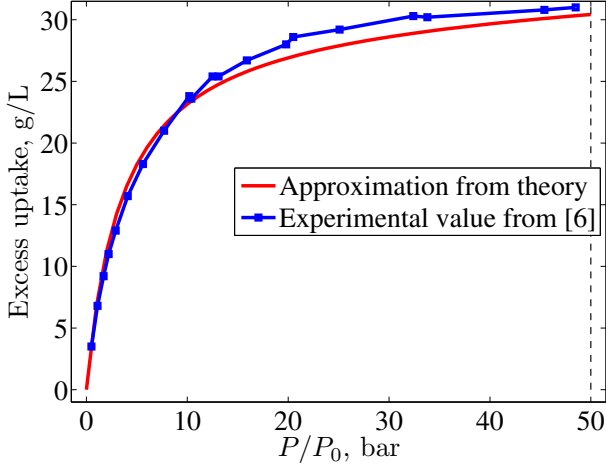
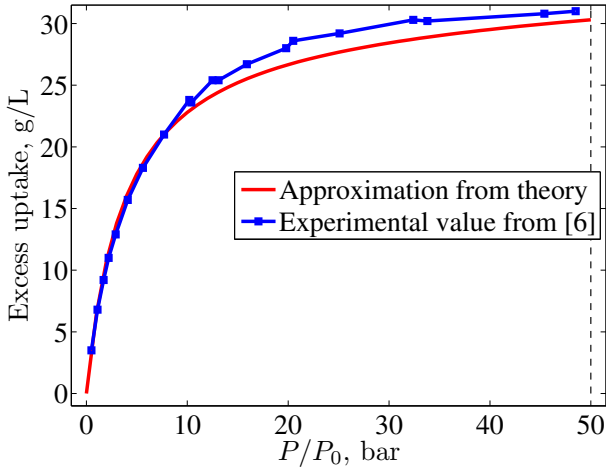
(b) Sum absolute values of deviations

FIG. 10: Two measures of fit for MOF-5

B. MOF-177

We assume that it is caused by the slight decrease of adsorption enthalpy reported in [5] which can also be supported by the fact that excess uptake in region of high pressures and low temperatures is mainly sensitive not to changes in adsorption enthalpy, but to changes in pore properties [6]. We will use the same two optimized enthalpy estimations as was done in the previous section. The dependency of these parameters on enthalpy of adsorption can be seen in Figure 12 a and Figure 12b.

The optimal values of ΔH_{ads} are very close: 4.07 kJ/mol and 4.05 kJ/mol, respectively. Isotherms for these enthalpies of adsorption are displayed in Figure 13a and Figure 13b. The square root of the average square deviation and the absolute deviation are, respectively, 0.64 (g/L) and 0.51 g/L.

(a) $\Delta H_{ads} = 4.470$ kJ/mol(b) $\Delta H_{ads} = 4.431$ kJ/molFIG. 11: Isotherm for MOF-5 for two obtained optimal enthalpies ΔH_{ads}^*

V. EFFECTIVE RADIUS OF HYDROGEN

Now we calculate the effective radius of hydrogen necessary for the number of sites calculations. Let the relation between the number of available sites and the surface area be

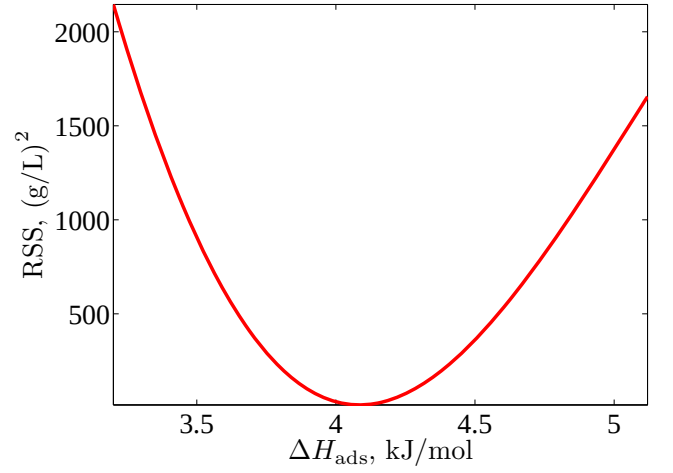
$$B = \theta_0 S.$$

A. T=77 K

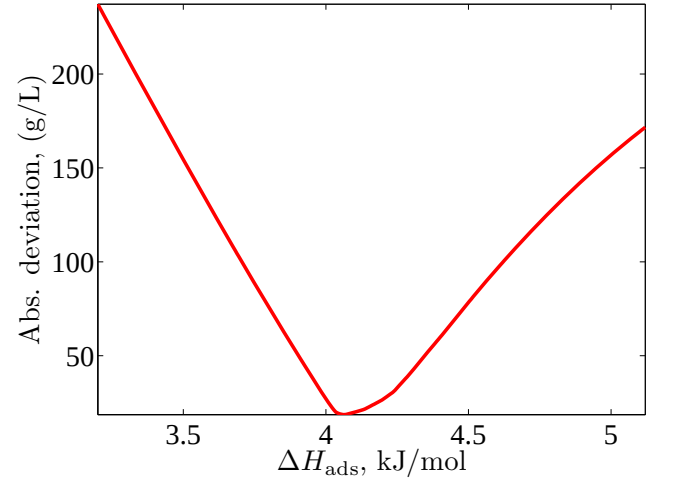
To obtain the coefficient we use the data from [5],

$$N = \frac{S}{S_0} = B \frac{N}{B} (\tilde{n}) = \theta_0 S \frac{N}{B} (\tilde{n}),$$

where S_0 is the characteristic surface area occupied by one adsorbed molecule of hydrogen and S is a surface



(a) Sum squares of deviations



(b) Sum absolute values of deviations

FIG. 12: Two measures of fit for MOF-177

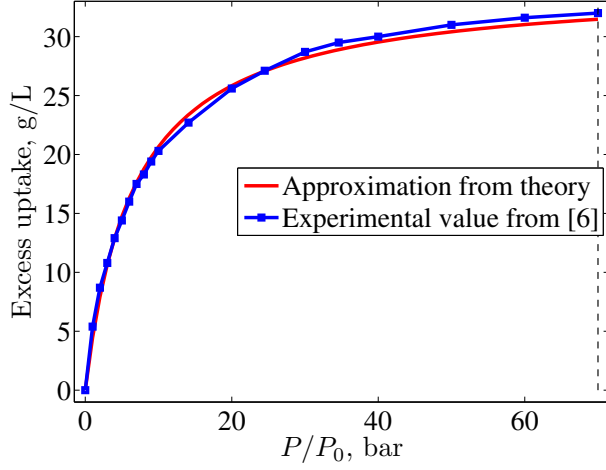
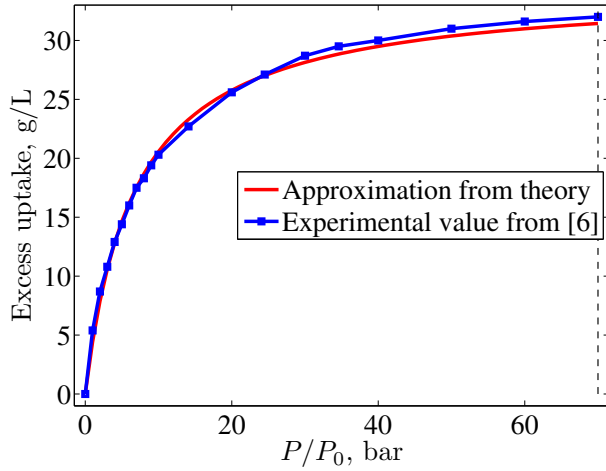
TABLE I: Surface area and excess uptake for different MOFs

Surface area, m ² /g	Uptake, mg/g	MOF
1100	22	MOF-74
2300	34	HKUST-1
2400	37	IRMOF-11
3300	50	IRMOF-6
4200	53	IRMOF-1
4700	68	IRMOF-20
5700	75	MOF-177

area. We will make the assumption that

$$\frac{N}{B}(\tilde{n})$$

does not depend on MOF, which is based on the insignificant impact of slight changes in the enthalpy of adsorption at such a low temperature. The other way to count

(a) $\Delta H_{ads} = 4.067$ kJ/mol(b) $\Delta H_{ads} = 4.054$ kJ/molFIG. 13: Isotherm for MOF-177 for two obtained optimal enthalpies ΔH_{ads}^*

the excess uptake is as follows,

$$\theta = \frac{m}{S} = \frac{N\mu}{N_A S} = \frac{2}{N_A S_0} \text{g/m}^2.$$

When fitting a linear model for data from table SII, we obtain

$$\theta = 0.0139 \text{mg/m}^2.$$

Therefore, we get

$$S_0 = 10^{20} \text{\AA}^2 \frac{2 \text{g/mol}}{0.0139 \cdot 10^{-3} \text{g} \cdot 6.02 \cdot 10^{23} \text{mol}^{-1}} = 23.9 \text{\AA}^2.$$

And thus the effective radius of hydrogen equals

$$r_{H_2} = \sqrt{\frac{S_0}{\pi}} = 2.76 \text{\AA}.$$

B. T=298 K

To obtain the coefficient we use the data from [7],

TABLE II: Surface area and excess uptake for different Li-MOFs

Surface area, m ² /g	Uptake, mg/g	MOF
3047	50.86	IRMOF-1-4Li
3620	58.97	IRMOF-8-6Li
4135	72.77	MOF-177-15Li
5558	87.34	MOF-200-27Li

$$N = \frac{S}{S_0} = B \frac{N}{B} (\tilde{n}) = \theta_0 S \frac{N}{B} (\tilde{n}),$$

where S_0 is characteristic surface area occupied by one adsorbed molecule of hydrogen and S is a surface area. We will make the assumption that

$$\frac{N}{B} (\tilde{n})$$

does not depend on MOF because, at such a pressure and such a high enthalpy of adsorption, the saturation of the first layer is nearly reached, whereas the second and subsequent layers are not as attracted to one another, since $\Delta H_{ads}^* < RT$. The other way to count the excess uptake is the following

$$\theta = \frac{m}{S} = \frac{N\mu}{N_A S} = \frac{2}{N_A S_0} \text{g/m}^2.$$

After fitting a linear model for the data from table SII, we obtain

$$\theta = 0.0164 \text{mg/m}^2.$$

Therefore we get

$$S_0 = 10^{20} \text{\AA}^2 \frac{2 \text{g/mol}}{0.0139 \cdot 10^{-3} \text{g} \cdot 6.02 \cdot 10^{23} \text{mol}^{-1}} = 20.3 \text{\AA}^2.$$

And thus the effective radius of hydrogen equals

$$r_{H_2} = \sqrt{\frac{S_0}{\pi}} = 2.54 \text{\AA}.$$

We will also use this effective radius of hydrogen for temperatures which are close to 298 K, for 243 and 273 K.

VI. CHEMICAL POTENTIAL FOR HIGH TEMPERATURES

For low temperatures (e.g., for 77 K), rotations in molecular hydrogen are not significant, because the rotation activation temperature is 85.4 K and therefore we only used the translational part of chemical potential. Here we derive the rotational chemical potential for high

temperatures. Consideration of both high temperature and low temperature cases can be found in [8]. As the vibration activation temperature is 6,100 K, we do not consider the vibrational part of chemical potential.

Due to nuclear symmetry, the normal term of a hydrogen molecule has different degree of degeneration for rotational levels with odd and even orbital moment K . The molecules with an even total spin ($S = 0$ for hydrogen) must have an even orbital moment (0, 2, ...), whereas molecules with an odd total spin ($S = 1$ for hydrogen) must have an odd orbital moment (1, 3, ...). The energy corresponding to the orbital movement with moment K is

$$\frac{\hbar^2 K(K+1)}{2I},$$

where $I = m/2 r_0^2$, where m is a mass of hydrogen atom and r_0 is the equilibrium distance between atoms in molecule. We introduce the designation

$$kT_r = \hbar^2/2I,$$

where T_r is the rotation activation temperature. For molecular hydrogen, $T_r = 85.4$ K. Further hydrogen modification with odd spin is called ortho- or u-hydrogen, whereas hydrogen modification with even spin is called para- or g-hydrogen. Relative degenerations of these two modifications are $g_u = 3/4$ and $g_g = 1/4$, respectively. Thus the partition functions for the modifications are

$$Z_u = \sum_{K=1,3,\dots} (2K+1) \exp(-T_r/TK(K+1)), \quad (30)$$

and

$$Z_g = \sum_{K=0,2,\dots} (2K+1) \exp(-T_r/TK(K+1)). \quad (31)$$

Therefore the full partition function is

$$Z = g_u Z_u + g_g Z_g = \frac{Z_g + 3Z_u}{4}. \quad (32)$$

For high temperatures,

$$Z_u \approx Z_g \approx 1/2 \sum_{K=0,1,2,\dots} (2K+1) \exp(-T_r/TK(K+1))$$

which we approximate by an integral

$$\begin{aligned} \sum_{K=0,1,2,\dots} (2K+1) \exp(-T_r/TK(K+1)) &\approx \\ \sum_{K=0,1,2,\dots} 2K \exp(-T_r/TK^2) &\approx \\ \int_0^\infty \exp(-T_r/TK^2) dK^2 &= T/T_r. \end{aligned}$$

Thus $Z \approx T/(2T_r)$ and the corresponding free energy

$$F_{rot} = -NkT \log \frac{T}{2T_r}.$$

Finally we get the equation for rotational part of chemical potential for high temperatures

$$\mu_{rot} = -kT \log \frac{T}{2T_r}. \quad (33)$$

VII. THEORY WHEN CONSIDERING FULL CHEMICAL POTENTIAL

In this section we show how it is necessary to alter the calculations which were previously presented for the translational part of chemical potential in order to consider the rotational part of the chemical potential. We use $\lambda = \exp(\mu/RT)$.

$$\lambda = \exp(\mu/kT) = \exp(\mu_{tr}/kT) \times \exp(\mu_{rot}/kT) = \alpha P/P_0 \exp(\mu_{rot}/kT), \quad (34)$$

where μ_{tr} and μ_{rot} are the translational and rotational parts of chemical potential, respectively. As the enthalpy of adsorption is relatively high, we can still consider adsorption as localized. Therefore, from eq. (34) and eq. (33), we get

$$\lambda = \alpha \frac{2T_r}{T} P/P_0. \quad (35)$$

From equation (35), we obtain that the consideration of full chemical potential results only in an appropriate change of α

$$\alpha_{new} = \alpha \frac{2T_r}{T}. \quad (36)$$

VIII. DEPENDENCE OF ENTHALPY OF ADSORPTION ON PRESSURE

For Li-metalated frameworks with high enthalpy of adsorption that face high uptake at room temperature, there is a significant dependence of the enthalpy of adsorption on uptake and therefore on pressure. Here we illustrate how this dependence was calculated for MOF-200-27Li at room temperature. At the end of this section we provide tables for calculated enthalpies for MOF200-27Li and MOF-177-15Li at 243, 273 and 298 K.

From [7], we get the dependence of adsorption enthalpy on total weight uptake, for which we use the following linear approximation

$$\Delta H_{ads} = Q_{st} = (29 - u) \text{ kJ/mol},$$

where u is the weight total uptake in units of percent. As $\Delta H_{ads}^* \ll RT \ll \Delta H_{ads}$, we use monolayer theory. We also make an assumption that reaching 10% of total uptake is nearly the same as total uptake at saturation. We also apply our theoretical approximation of excess uptake to total uptake, and therefore we obtain

$$u = \frac{10}{1 + 1/\alpha \cdot P_0/P \exp(-\Delta H_{ads}/RT)}.$$

Thus we get the following equation

$$29 - \Delta H_{ads}/1000 = \frac{10}{1 + 1/\alpha \cdot P_0/P \exp(-\Delta H_{ads}/RT)}. \quad (37)$$

For $T = 298$ K, equation (37) gives

$$29 - 2.4764x = \frac{10}{1 + 1.954 \cdot 10^5/m \cdot e^{-x}},$$

where $x = \Delta H_{ads}/RT$ and $m = P/P_0$. Solving the last equation at different pressures P , we obtain the data for enthalpy at $T = 298$ K at different pressures (see tab. III). Using the same approach we obtain the enthalpies for other temperatures.

TABLE III: Enthalpy of adsorption of MOF-200-27Li for different pressures for T=243, 273 and 298 K

P , bar	$\Delta H_{ads}/RT$ for $T=298$ K	$\Delta H_{ads}/RT$ for $T=273$ K	$\Delta H_{ads}/RT$ for $T=243$ K
1	10.8607	11.2894	11.7611
5	10.1310	10.4301	10.8103
10	9.7863	10.0511	10.4133
20	9.4388	9.6790	10.0346
30	9.2383	9.4681	9.8251
40	9.0988	9.3228	9.6831
50	8.9927	9.2131	9.5774
60	8.9078	9.1258	9.4942
70	8.8372	9.0536	9.4261
80	8.7772	8.9925	9.3690
90	8.7252	8.9397	9.3201
100	8.6795	8.8934	9.2776

TABLE IV: Enthalpy of adsorption of MOF-177-15Li for different pressures for T=243, 273 and 298 K

P , bar	$\Delta H_{ads}/RT$ for $T=298$ K	$\Delta H_{ads}/RT$ for $T=273$ K	$\Delta H_{ads}/RT$ for $T=243$ K
1	10.4573	10.9922	11.5831
5	9.9044	10.2709	10.7403
10	9.6198	9.9404	10.3879
20	9.3265	9.6143	10.0561
30	9.1562	9.4303	9.8760
40	9.0378	9.3044	9.7560
50	8.9481	9.2100	9.6680
60	8.8765	9.1354	9.5997
70	8.8174	9.0742	9.5445
80	8.7674	9.0227	9.4988
90	8.7242	8.9785	9.4601
100	8.6864	8.9400	9.4268

IX. SOURCE CODES FOR MATLAB

Code 1: Occupancy Ratio Calculation

```

1 % Calculates occupancy ratio (N / B) given a temperature, number of layers.
2 % Enthalpy of adsorption for higher layers is set to that of hydrogen.
3 % The equation holds for low temperature. To make calculation for high
4 % temperature one should make a proper adjustment for alpha (see Supp. Info)
5
6 T=77;
7 T_0=298;
8 R=8.31;
9 H_star=904;
10
11 alpha=8.9e-6*power(T_0/T,2.5);
12 beta=H_star/R/T;
13
14 n=3;
15
16 H_ads=4400;
17 par=H_ads/R/T;
18 p=70;
19 x=alpha*exp(beta)*p;
20
21 c=exp(par-beta);
22 n_total=(c*x*(1-(n+1)*power(x,n)+n*power(x,n+1))/(1-x+c*x-c*power(x,n+1)))/(1-x)

```

Code 2: Optimal Enthalpy Calculation for Restricted Multilayer Theory at High Temperatures

```

1 % Plots the optimal enthalpy in given range of temperatures for restricted
2 % multilayer case for specified number of layers for low
3 % temperature region. Since the optimal enthalpy varies only slightly for
4 % different number of layers the results are very exact for any restricted
5 % multilayer case as well.
6
7 n=6;
8
9 T_min=50;
10 T_max=100;
11 T=linspace(T_min,T_max,T_max-T_min+1);
12 T_0=298;
13 R=8.31;
14 alpha_0=8.9e-6;
15 H_star=904;
16
17 m=linspace(2,100,99);
18 H_opt_restr_multi=zeros(size(T,2),size(m,2));
19
20 for t=1:size(T,2)
21     for mul=1:size(m,2)
22         alpha=alpha_0*power(T_0/T(1,t),2.5);
23         beta2=exp(H_star/R/T(1,t));
24
25         beta2_tilde=alpha+beta2;
26
27         a=sqrt(1-(n+1)*power(beta2_tilde,n)+n*power(beta2_tilde,n+1));
28         b=sqrt(1-(n+1)*power(m(1,mul)*beta2_tilde,n)+n*power(m(1,mul)*beta2_tilde,n+1));
29
30         beta1_tilde=(a*(1-m(1,mul)*beta2_tilde)-(1-beta2_tilde)*b*sqrt(m(1,mul)))/...
31         (b*sqrt(m(1,mul))*(1-power(beta2_tilde,n))-n(1,mul)*a*(1-power(m(1,mul)*beta2_tilde,n)));
32
33         beta1=beta1_tilde/alpha;
34
35         H_opt_restr_multi(t,mul)=R*T(1,t)*log(beta1);
36     end
37 end
38
39 h=figure;
40
41 mu=imagesc(m,T,H_opt_restr_multi/1000);
42
43 xlabel('$P/P_0$, bar','Interpreter','latex','FontSize',24);
44 ylabel('$T$, K','Interpreter','latex','FontSize',24);
45
46
47 set(gca,'FontSize',24);
48 set(gca,'Position',[.12 .15 .8 .8]);
49 set(gca,'YDir','normal');
50 g=colorbar('location','eastoutside','FontSize',18);
51 %caxis([18 31]);
52 caxis([2 7.5]);
53 ylabel(g,'kJ/mol');
54
55
56 str=strcat('H_opt_restr_multilayer ',int2str(T_min),'_',int2str(T_max),'_',int2str(n));
57
58 saveas(h,strcat(str,'.png'),'png');
59 saveas(h,strcat(str,'.eps'),'eps');

```

Code 3: Optimal Enthalpy Calculation for Restricted Multilayer Theory at Low Temperatures

```

1  % Plots the optimal enthalpy in given range of temperatures for restricted
2  % multilayer case for specified number of layers for low
3  % temperature region. Since the optimal enthalpy varies only slightly for
4  % different number of layers the results are very exact for any restricted
5  % multilayer case as well.
6
7  n=6;
8
9  T_min=50;
10 T_max=100;
11 T=linspace(T_min,T_max,T_max-T_min+1);
12 T_0=298;
13 R=8.31;
14 alpha_0=8.9e-6;
15 H_star=904;
16
17 m=linspace(2,100,99);
18 H_opt_restr_multi=zeros(size(T,2),size(m,2));
19
20 for t=1:size(T,2)
21     for mul=1:size(m,2)
22         alpha=alpha_0*power(T_0/T(1,t),2.5);
23         beta2=exp(H_star/R/T(1,t));
24
25         beta2_tilde=alpha*beta2;
26
27         a=sqrt(1-(n+1)*power(beta2_tilde,n)+n*power(beta2_tilde,n+1));
28         b=sqrt(1-(n+1)*power(m(1,mul)*beta2_tilde,n)+n*power(m(1,mul)*beta2_tilde,n+1));
29
30         beta1_tilde=(a*(1-m(1,mul)*beta2_tilde)-(1-beta2_tilde)*b*sqrt(m(1,mul)))/...
31         (b*sqrt(m(1,mul))*(1-power(beta2_tilde,n))-m(1,mul)*a*(1-power(m(1,mul)*beta2_tilde,n)));
32
33         beta1=beta1_tilde/alpha;
34         H_opt_restr_multi(t,mul)=R*T(1,t)*log(beta1);
35     end
36 end
37
38 h=figure;
39
40 mu=imagesc(m,T,H_opt_restr_multi/1000);
41
42 xlabel('$P/P_0$', 'bar', 'Interpreter', 'latex', 'FontSize', 24);
43 ylabel('$T$, K', 'Interpreter', 'latex', 'FontSize', 24);
44
45
46
47 set(gca, 'FontSize', 24);
48 set(gca, 'Position', [.12 .15 .8 .8]);
49 set(gca, 'YDir', 'normal');
50 g=colorbar('location','eastoutside', 'FontSize', 18);
51 %caxis([18 31]);
52 caxis([2 7.5]);
53 ylabel(g, 'kJ/mol');
54
55
56 str=strcat('H_opt_restr_multilayer ', int2str(T_min), '_', int2str(T_max), '_', int2str(n));
57
58 saveas(h, strcat(str, '.png'), 'png');
59 saveas(h, strcat(str, '.eps'), 'ps2');

```

Code 4: Optimal Enthalpy Calculation for Langmuir and BET Theories at Low Temperatures

```

1 % Plots the optimal enthalpy in given range of temperatures for both
2 % monolayer case (par = 0) and multilayer case (par = 1) for low
3 % temperature region. Since the optimal enthalpy varies only slightly for
4 % different number of layers the results are very exact for any restricted
5 % multilayer case as well.
6
7 T_0=298;
8 T_min=50;
9 T_max=100;
10 T=linspace(T_min,T_max,T_max-T_min+1);
11 R=8.31;
12 alpha_0=8.9e-6;
13 par=0; %equals 1 when it's multilayer case
14 H_star=904;
15
16 m=linspace(1,100,100);
17 H_opt_mono=zeros(size(T,2),size(m,2));
18 H_opt_multi=zeros(size(T,2),size(m,2));
19
20 for t=1:size(T,2)
21     for mul=1:size(m,2)
22         H_opt_mono(t,mul)=R*T(1,t)*log(power(T(1,t)/T_0,2.5)...
23             /sqrt(m(1,mul))/alpha_0);
24         H_opt_multi(t,mul)=R*T(1,t)*log(power(T(1,t)/T_0,2.5)...
25             /sqrt(m(1,mul))/alpha_0+exp(H_star/R/T(1,t)));
26     end
27 end
28 h=figure;
29
30 if (par==0)
31     mu=imagesc(m',T',H_opt_mono/1000);
32 else
33     mu=imagesc(m',T',H_opt_multi/1000);
34 end
35 xlabel('$P/P_0$', 'bar', 'Interpreter', 'latex', 'FontSize', 24);
36 ylabel('$T$, K', 'Interpreter', 'latex', 'FontSize', 24);
37
38 set(gca, 'Position', [.12 .15 .8 .8])
39 set(gca, 'FontSize', 24);
40 set(gca, 'YDir', 'normal');
41 g=colorbar('location', 'eastoutside', 'FontSize', 18);
42 %caxis([20,29])
43 caxis([2 7.5])
44
45 ylabel(g, 'kJ/mol');
46
47 if (par==0)
48     str=strcat('H_opt_monolayer_', int2str(T_min), '_', int2str(T_max));
49 else
50     str=strcat('H_opt_multilayer_', int2str(T_min), '_', int2str(T_max));
51 end
52 saveas(h, strcat(str, '.png'), 'png');
53 saveas(h, strcat(str, '.eps'), 'psc2');
54
55
56 P_req=[2 10 30 100];
57
58 g=figure;
59
60 hold 'on'
61 plot(T, H_opt_mono(:, P_req(1,1))/1000, 'g-', 'LineWidth', 3);
62 plot(T, H_opt_mono(:, P_req(1,2))/1000, 'r-', 'LineWidth', 3);
63 plot(T, H_opt_mono(:, P_req(1,3))/1000, 'b-', 'LineWidth', 3);
64 plot(T, H_opt_mono(:, P_req(1,4))/1000, 'c-', 'LineWidth', 3);
65
66 %plot(T, H_opt_multi(:, P_req)/1000, 'r-', 'LineWidth', 2);
67
68 xlabel('T, K', 'Interpreter', 'latex', 'FontSize', 24);
69 ylabel('$\Delta H_{\mathrm{ads}}^{\mathrm{opt}}$, kJ/mol', 'Interpreter', 'latex', 'FontSize', 24);
70
71 legend('P=2 bar', 'P=10 bar', 'P=30 bar', 'P=100 bar');
72 set(legend, 'FontSize', 16, 'FontName', 'Times', 'Location', 'Southeast');
73 set(gca, 'FontSize', 24);
74 set(gca, 'Position', [.12 .15 .8 .8])
75 axis 'tight'
76 str=strcat('H_opt_diff_pressures');
77
78 saveas(g, strcat(str, '.png'), 'png');
79 saveas(g, strcat(str, '.eps'), 'psc2');

```

Code 5: Optimal Enthalpy Calculation for Langmuir and BET Theories at High Temperatures

```

1 % Plots the optimal enthalpy in given range of temperatures for both
2 % monolayer case (par = 0) and multilayer case (par = 1) for high
3 % temperature region. Since the optimal enthalpy varies only slightly for
4 % different number of layers the results are very exact for any restricted
5 % multilayer case as well.
6
7 T_0=298;
8 T_min=240;
9 T_max=300;
10 T=linspace(T_min,T_max,T_max-T_min+1);
11 R=8.31;
12 alpha_0=5.1e-6;
13 par=0; %equals 1 when it's multilayer case
14 H_star=904;
15
16 m=linspace(1,100,100);
17 H_opt_mono=zeros(size(T,2),size(m,2));
18 H_opt_multi=zeros(size(T,2),size(m,2));
19
20 for t=1:size(T,2)
21     for mul=1:size(m,2)
22         H_opt_mono(t,mul)=R*T(1,t)*log(power(T(1,t)/T_0,3.5)...
23             /sqrt(m(1,mul))/alpha_0);
24         H_opt_multi(t,mul)=R*T(1,t)*log(power(T(1,t)/T_0,3.5)...
25             /sqrt(m(1,mul))/alpha_0+exp(H_star/R/T(1,t)));
26     end
27 end
28 h=figure;
29
30 if (par==0)
31     mu=imagesc(m,T,H_opt_mono/1000);
32 else
33     mu=imagesc(m,T,H_opt_multi/1000);
34 end
35 xlabel('$P/P_0$', 'bar', 'Interpreter', 'latex', 'FontSize', 24);
36 ylabel('$T$, K', 'Interpreter', 'latex', 'FontSize', 24);
37
38 set(gca, 'Position', [.12 .15 .8 .8])
39 set(gca, 'FontSize', 24);
40 set(gca, 'YDir', 'normal');
41 g=colorbar('location', 'eastoutside', 'FontSize', 18);
42 caxis([18,31])
43
44 ylabel(g, 'kJ/mol');
45
46 if (par==0)
47     str=strcat('H_opt_monolayer_high_temp', int2str(T_min), '_', int2str(T_max));
48 else
49     str=strcat('H_opt_multilayer_high_temp', int2str(T_min), '_', int2str(T_max));
50 end
51 saveas(h, strcat(str, '.png'), 'png');
52 saveas(h, strcat(str, '.eps'), 'psc2');
53
54
55 P_req=[2 10 30 100];
56
57 g=figure;
58
59 hold 'on'
60 plot(T, H_opt_mono(:, P_req(1,1))/1000, 'g-', 'LineWidth', 3);
61 plot(T, H_opt_mono(:, P_req(1,2))/1000, 'r-', 'LineWidth', 3);
62 plot(T, H_opt_mono(:, P_req(1,3))/1000, 'b-', 'LineWidth', 3);
63 plot(T, H_opt_mono(:, P_req(1,4))/1000, 'c-', 'LineWidth', 3);
64
65 %plot(T, H_opt_multi(:, P_req)/1000, 'r-', 'LineWidth', 2);
66
67 xlabel('T, K', 'Interpreter', 'latex', 'FontSize', 24);
68 ylabel('$\Delta H_{\mathrm{ads}}^{\mathrm{opt}}$, kJ/mol', 'Interpreter', 'latex', 'FontSize', 24);
69
70 legend('P=2 bar', 'P=10 bar', 'P=30 bar', 'P=100 bar');
71 set(legend, 'FontSize', 16, 'FontName', 'Times', 'Location', 'Southeast');
72 set(gca, 'FontSize', 24);
73 set(gca, 'Position', [.12 .15 .8 .8])
74 axis 'tight'
75 str=strcat('H_opt_diff_pressures_high_temp');
76
77 saveas(g, strcat(str, '.png'), 'png');
78 saveas(g, strcat(str, '.eps'), 'psc2');

```

Code 6: Optimal Parameters Calculation from Linker Length and Void Volume

```

1 % Calculates optimal parameters (see the model from the paper) of a
2 % framework given the linker lengths and void volumes for the series of
3 % equivalent frameworks. R_squared is linear regression determination
4 % coefficient. The closer it is to 1 the better the model fits experimental
5 % data.
6
7 function [kappa_opt xi_opt R_squared]=count_opt_par(gamma, a_approx)
8
9 x=log(a_approx);
10 y=log(1-gamma);
11 x=[ones(size(x,1),1) x];
12 res=inv(x'*x)*x'*y;
13 kappa_opt=exp(res(1,1));
14 xi_opt=2+res(2,1);
15
16
17 y_hat = x * res;
18 R_squared = 1 - (y - y_hat)' * (y - y_hat) / ((y - mean(y))' * (y - mean(y)));
19
20 return

```

Code 7: Translational Chemical Potential Calculation

```

1 % Function implements calculation of translational chemical potential given
2 % temperature, n_q which is the function of gas molar mass and
3 % temperature and concentration (N / V)
4
5 function mu=count_mu(N, T, V, n_q)
6
7 k=1.38e-23;
8 hbar=1.05e-34;
9 mu=-k*T*log(2*V/N*n_q);
10
11 return

```

Code 8: Calculation of Maximum Pressure where Restricted Multilayer Theory still holds

```

1 % Calculates and plots border pressure depending on temperature.
2 % The border pressure is a maximum pressure where the theory still holds.
3
4 T=linspace(40,300,261);
5 alpha0=8.9e-6;
6 Delta_H=886;
7 R=8.31;
8 T0=298;
9
10 beta2=exp(Delta_H/R./T);
11 alpha=alpha0*power(T0./T,2.5);
12
13 max_m=1./(alpha.*beta2);
14
15 h=figure;
16 hold('on');
17 box 'on'
18
19 plot(T,max_m,'r-','LineWidth',3);
20
21
22 set(gca, 'FontSize', 24, 'FontName', 'Times');
23 axis('tight');
24 set(gca,'Position',[.12 .15 .8 .75])
25 xlabel('$T$, K','FontSize',24,'Interpreter','latex');
26 ylabel('$P/P_0$, bar','FontSize',24,'Interpreter','latex');
27
28 str='max_pressure_multilayer';
29 saveas(h, strcat(str, '.png'), 'png');
30 saveas(h, strcat(str, '.eps'), 'ps2');

```

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