

Adsorption mechanisms in a view of DFT and clustering- based models

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Abstract – The paper describes two approaches to mathematical description of adsorption mechanisms aimed at identification of materials porous structure, i.e. the Density Functional Theory (DFT) and the clustering based theory of adsorption (uniBET). Essential assumptions of the both theories, concerning the pore structure description, are compared and application areas are outlined for them.

Key words – adsorption, density functional theory, DFT, isotherms, clustering-based adsorption theory, uniBET, LBET.

I. Introduction

In order to evaluate parameters of porous materials, (specific surface area, pore volume and geometry), measurements of adsorption isotherms are commonly used. Adsorption capacity of small molecules in pores depends mainly on pore amount and size, but a pore geometry (shape) is also of significance, as it affects a strength of solid-fluid energetic interactions and pores availability for adsorptive molecules. Nonetheless, obtaining useful informations on the porous material structure requires mathematical model of adsorption equilibria. A number of models have been already proposed [1-2]. For microporous structure analysis the Dubinin-Radushkevitch, Dubinin-Astachow or BET are commonly used. They are satisfying for surface area evaluation and characterization of adsorption energy.

In order to get more information on the pore size and structure, more advanced description is necessary. Recently the Density Functional Theory (DFT) [3-4] is strongly recommended to this aim. Nevertheless, in our team an alternative approach, employing a clustering-based adsorption mechanisms, was developed and shown to be very useful for analysis the materials of random porous structures (like active carbons). These models are based on different assumptions, but applied to active carbons give adequate picture of their porous structure [3]. This paper shows the application of the both models and may provide insight into adsorption mechanisms.

II. Density Functional Theory

In the DFT method [5] adsorption equilibrium is obtained by minimization the grand potential functional $\Omega[\rho_0(r)]$ of fluid confined in pores by calculation its equilibrium density profile $\rho_0(r)$, describing local density of inhomogeneous adsorbed fluid:

$$\Omega[\rho_0(r)] = F[\rho_0(r)] - \int dr \rho_0(r) [\mu - V_{ext}(r)] \quad (1)$$

where $F[\rho_0(r)]$ is Helmholtz free energy functional, μ is chemical potential and $V_{ext}(r)$ is solid-fluid interaction potential at coordinate r .

Helmholtz free energy functional describes molecular interactions of adsorbate and consists of ideal part, coming from hard-sphere ideal gas contribution, and excess part coming from fluid-fluid interaction pairwise potential. Further this potential is splitted into attractive and repulsive part. Attractive forces between molecules are commonly treated by the mean field approximation including Weeks-Chandler-Andersen (WCA) [6] scheme for fluid-fluid interactions, justifying 12-6 Lennard-Jones (12-6 LJ) potential. The most popular description for repulsive forces is then non-local Tarazona's [7-8] weighted density approximation (WDA).

Solid-fluid potential is commonly described by 10-4-3 Steele potential [9] where the pore structure is also implemented.

NLDFT calculations include separated calculations of sets of isotherms (kernel) for each type of pores of established shape and size. Integration in Eq. (1) is then taken over entire pore volume. Depending on the pore model, calculations for active carbon are provided in one (ideal slit infinite pore, see Fig. 1 [5]) and two dimensions (strip, channel and disk pore, see Fig. 1 [10-12]).

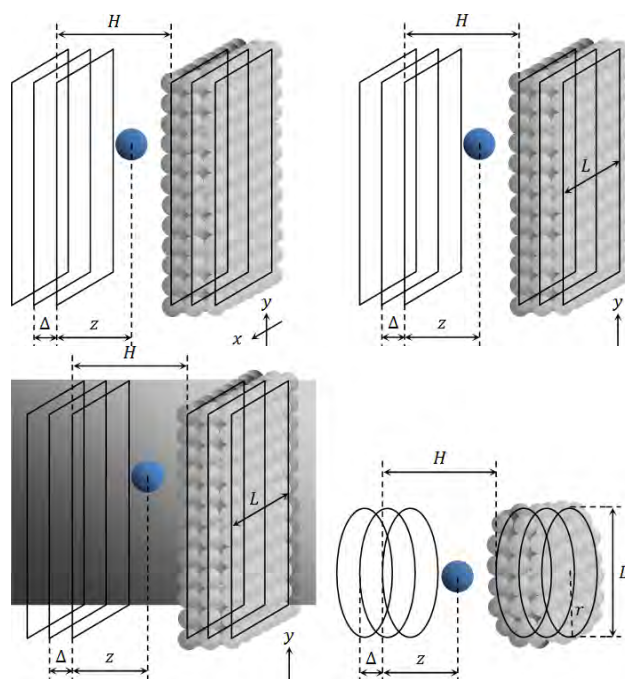


Fig. 1. Examples of commonly used carbon pore models. From top left: ideal slit infinite, strip, channel and disc pore.

DFT is a useful tool to determine the pore size distribution, from adsorption integral equation (AIE) [5]:

$$m(P) = \int_{H_{min}}^{H_{max}} dH \rho(P, H) f(H) \quad (2)$$

where H is pore size parameter, P is adsorption pressure, $\rho(P, H)$ is the sum of local adsorption isotherms for each pore size fitting experimental results and $f(H)$ is pore size distribution. Pore size is most often determined from

gamma distribution, log-normal or combining regularization rules with B-spline distribution function [13].

This calculations requires pore shape assumption, what is hard to accept in view that active carbons are typical microporous adsorbents of irregular structure and pore shape [14]. PSD calculations are more acceptable in this approach for e.g. zeolites [15], which structure is highly regular.

Commonly used NLDFT approach omits energy interactions between adsorbate molecule and adsorbent (however this approach one can find in the newest NLDFT version [16]) and instead nonlocalized adsorption is considered in view of nonlocalized density of adsorbed fluid. Delocalization is introduced via weighting function implemented in WDA, where semi-experimental parameters are included.

III. Generalized BET-like adsorption model

There is important to notice that specific isotherm shape may be explained by different adsorption mechanism. One of the commonly used and reasonable interpretations is localized adsorption mechanism, which is determined by the specific energetic surface properties.

The alternative approach, being elaborated in our team, is by a generalization of the classical BET model, leading to the uniBET description. In this approach [17-23] adsorption is viewed as compressing of the adsorbate molecules to a volume V_s , (a liquid-like reference state [24]), and then, moving them into rigid aggregates of empty cells (each of the same volume V_s) incorporated in the pores.

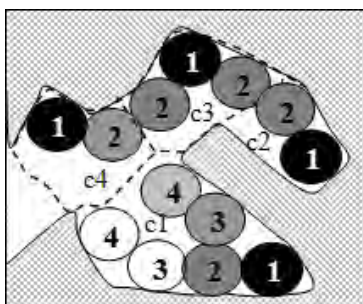


Fig. 2. Pore shape, cells (white circles) and adsorbate clusters (shaded circles) considered in the approach

The aggregates represent total space of pores available for adsorption of considered molecules (see Fig. 2). The filling of the cells starts at a cell (a primary adsorption site), which yields minimal adhesion energy within the aggregate (for nonpolar adsorbates it may be a niche, cavity, corner, ...). In this way the first adsorption layer ($n=1$) is formed due to adhesive interactions only. Further molecules (layers $n>1$) are joined with cohesive and adhesive forces being involved.

Following the Huggins model [24], adsorption energy Q_{Aa} of a -th molecule is expressed as:

$$Q_{Aa} = U_s(1 - 2Z_{aa}) - Z_{Ca} \cdot Q_{sC} \quad (3)$$

where U_s denotes the cohesion energy of adsorptive in its bulk reference state (depending on V_s), Q_{sC} is adhesion energy calculated with Berthelot rule, Z_{aa} is a contact ratio in cohesive interactions (at the first layer $Z_{aa}=0$), and Z_{Ca}

is a correction factor depending on the pore geometry (the pore surface texture parameter) [17].

In contrast to the classical BET model, possible branching of clusters is taken into account (this can significantly affect adsorption isotherms in high pressure range [19]).

The general model (uniBET), being a far generalization of the BET equation [1], describes the local adsorption isotherm on the κ -th type primary sites. It has the form of following algebraic equations written for consecutive layers $n=1, \dots, k$:

$$-\Pi_{\kappa n}^* + (\Pi_{\kappa n}^* + 1) \cdot \theta_{\kappa n} - \theta_{\kappa n} \cdot \theta_{\kappa n+1} = 0 \quad (4)$$

where $\theta_{\kappa n}$ denotes the coverage ratio of $(n-1)$ -th layer in clusters of κ -th class:

$$\theta_{\kappa n} \stackrel{def}{=} \frac{m_{p\kappa n}}{\beta_{\kappa n} \cdot m_{p\kappa n-1}} \quad (5)$$

$\Pi_{\kappa n}^*$ is a transformed pressure depending on the relative pressure/fugacity π , β and on $\theta_{\kappa n}$:

$$\Pi_{\kappa n}^* \stackrel{def}{=} \frac{\pi}{B_{\kappa n}} (1 - \theta_{\kappa n})^{1 - \beta_{\kappa n+1}} = \Pi_{\kappa n} (1 - \theta_{\kappa n+1})^{1 - \beta_{\kappa n+1}},$$

$$B_{\kappa n} \stackrel{def}{=} \exp(Q_{\kappa n} / RT), \quad \Pi_{\kappa n} \stackrel{def}{=} \pi / B_{\kappa n} \quad (6)$$

$B_{\kappa n}$ denotes the energetic parameter of (κn) -th subsystem.

The pore geometry (shape) is represented by the pore length (limiting the cluster length), surface texture parameter $Z_{\kappa n}$ and pore compactness parameter (branching factor) $\beta_{\kappa n}$.

The model (3-6) constitutes the local description of adsorption capacity, which may be incorporated (as the kernel) in an integral adsorption formula, like in eq.(2), assuming arbitrarily the above pore geometry parameters for each subsystem. Also, a particular pore shape and size distribution may be taken and appropriate values for the uniBET model may be calculated by geometrical considerations [23].

To reduce the number of fitting parameters, in our works the following simplifying assumptions were accepted for random microporous structure (like active carbon) [3]:

- Exponential distribution of pore (aggregate) size is accepted and represented by the parameter α .
- For the 2nd and higher layers a constant branching factor β and the same adsorption energy $Q_{Aa}=Q_C$ are taken. The latter produces the energetic parameter:

$$B_C \stackrel{def}{=} \exp(Q_C / RT) \quad (7)$$

depending on a shape of pores. The value found for B_C characterizes generally energetic bounds for adsorbate clusterization.

- The 1st layer adsorption energy is expressed in the following form (see eq.1 and [14, 20]) :

$$Q_{A\kappa} = U_s - Z_A \cdot \zeta_{\kappa} \cdot Q_{sC}, \quad Z_A \stackrel{def}{=} \max_a Z_{Aa} \quad (8)$$

and the random factor ζ_{κ} is uniformly distributed over a range (ζ_{Akb} , ζ_{fk}) enlarging with growing pore size k , while Z_A is the fitting parameter characterizing adhesive

interaction intensity (and so, a surface roughness) in the smallest pores (i.e. for $k=1$, where $\zeta_{A1}=1$ is assumed).

- The parameters characterizing the pore geometry α , β , and roughness Z_A , as well as a volume V_M of a space covering the 1st layer) are the same for any molecule.

The resultant model (LBET formula) involves the adsorbate fugacity f related to that in its reference state f_s , and the energy parameter $B_{Ad} = \exp(Q_{Ad}/RT)$.

For adsorptives at near and super critical temperatures (e.g. CO₂ at 273K, H₂ at 77K) we apply an original equation of state [26] developed for highly compressed fluids. It enables us to calculate the relative fugacity f/f_s and cohesion energy U_s in the bulk reference state at T , for a given V_s .

Properties of the LBET formula were discussed in more detail in our papers [3, 17-23]. The model allows to evaluate the parameters α , β , and V_M characterizing indirectly a pore geometry, as well as the pairs $\{Z_{Ai}, B_{Ci}\}$ for each individual adsorbate i .

IV. Application examples

The comparative study of the above approaches was presented in our paper [3]. It was performed for a microporous carbon (Carbonsieve CS1 [25]) using three adsorption isotherms (Ar at 87 K, H₂ at 77.3K and H₂ at 87K). The isotherms were fitted simultaneously, assuming the same structure of pores. The LBET model operated under MATLAB platform with our own software [3]. As the result it produced the system parameters corresponding to the best fits of the model (α , β – characterizing the cluster size distribution, Z_A – surface texture parameter, and individual molar volumes of adsorbates V_s). The DFT analysis was performed using SAIEUS [13], producing the theoretical isotherms and pore size distribution. The results are shown in Figs. 3, 4 and 5.

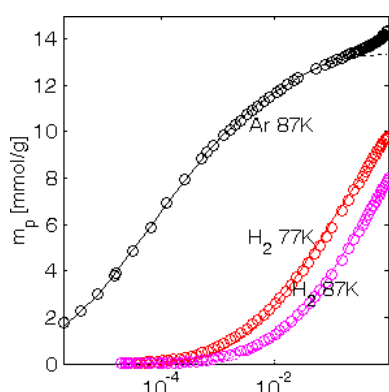


Fig. 3. Adsorption isotherms of Ar and H₂ on Carbonsieve CS1 [3, 25] [mmol/g] v.s. $\log(p/p_0)$, calculated by simultaneous fitting with the LBET model

It may be seen in Figs. 3 and 4 that the both approaches enable for good simultaneous fitting of a number of isotherms on the same material.

Fitting quality is similar despite of different adsorption mechanisms being assumed. Notice that for Ar the simpler pore structure characterization employed in LBET gives a bit better fitting in the lowest pressure range than DFT (it suggests an overparametrization of DFT). Also

the porous structure characterization compared in Fig. 5 for the both models is similar.

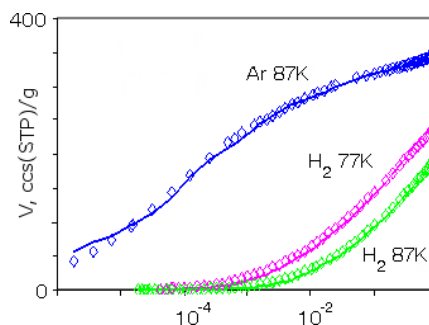


Fig. 4. Results of fitting of Ar and H₂ adsorption on Carbonsieve CS1 [3, 13, 25] with the DFT calculations. Adsorption isotherms expressed in $V[\text{cc}(\text{STP})/\text{g}]$ v.s. $\log(p/p_0)$

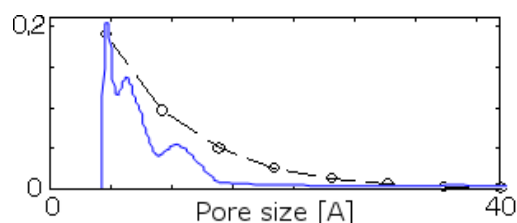


Fig. 5. PSD found with DFT fittings (bold line) and the exponential pore size (length) distribution assumed in LBET fittings (circles-dotted-line)

V. Conclusion

The paper shows that adsorption process may be modeled in different ways, based on different assumptions on main factors affecting the fluid-solid interactions. In the DFT formalism the adsorbate molecules are treated as a fluid encountering the solid surface, its density depends on the averaged solid-fluid potential. Hence, in order to evaluate the adsorption capacity, a strict model of the pore shape has to be assumed, with the pore size distribution adjusted up to fit empirical data.

The uniBET formalism stresses the role of local niches in the pores, viewed as the active sites on the pore surface, where adsorption can be started due to adhesive forces, and then continued by joining further molecules (2nd and higher layers) due to cohesive and adhesive interactions. A pore texture parameter (affecting the adsorption energy) and clusters branching factor are used to characterize generally a shape of pores, while the pore size/length is treated as the factor limiting the cluster length.

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