

The evaluation of the surface heterogeneity of carbon blacks from the lattice density functional theory

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Abstract

Recently developed two lattice density functional theory (DFT) models are verified experimentally. For this purpose the experimental nitrogen isotherms on carbon blacks at 77 K (M4040 and M32B) were carefully measured by the volumetric apparatus. Moreover, the additional nitrogen data on Sterling FT and SAO carbon blacks were taken from the literature and analyzed. The main goal of this study is the evaluation of the adsorption energy distribution function (and differential adsorption enthalpy at zero coverage) by the new powerful tool based on the lattice DFT formalism proposed by Do and Do and Aranovich and Donohue. New algorithms are proposed for this purpose. The quantitative agreement between these two independent approaches is recognized. The presented in this study new heterogeneous lattice DFT model seems to be very promising one in the investigation of flat surfaces heterogeneity effects.

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1. Introduction

There is no doubt that the solid surfaces are never ideally regular that is, geometrically and energetically homogenous [1–4]. It seems rather obvious that real solid surfaces consist of structural and chemical irregularities (i.e. defects of molecular dimensions, cracks, dislocations, and surface contaminations). Therefore, the real solid surfaces are in more or less extent heterogeneous [1–4]. It is reasonable to assume that the heterogeneity effect for carbonaceous adsorbent surfaces (i.e. activated carbons, activated carbon fibers, etc.) is really pronounced due to existence of pores of different dimensions, various surface chemical groups, mineral impurities like ash, and so on [5]. Different experiments confirmed the existence of surface heterogeneity—for example the measured heat of adsorption was usually, the decreasing function of the surface coverage [6,7] also

the observed kinetics of adsorption results did not follow the behavior predicted by Langmuir's kinetic equations [8] assuming homogeneity of a surface.

It is believed that carbon blacks have well defined “flat-surfaces” [9]. However, many researchers showed that even carbon blacks possess very small amounts of pores comparing to porous materials like, for example, activated carbons [9,10]. A new adsorption measurement from an ultrahigh vacuum evidenced clearly the presence of ultramicropores in carbon black [11]. Calorimetric studies showed that the surface of well-known Sterling NT carbon black is, in fact, heterogeneous [12]. Other authors also postulated that on graphite surface different voids between crystalline regions can be found and they play an important role in the surface energy calculations [13]. It is also possible that during the preparation of carbon blacks by high temperature treatment some microcrystallites may break up into their primary crystallites producing pores.

Obviously, the question how the surface of carbon black is far from the homogeneity, is particularly important. The answer to this question is not simple.

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However, adsorption measurements with proper mathematical approaches can be used to the assessment of the heterogeneity effect of carbon black surfaces on adsorption.

In the present study the high accurate volumetric adsorption measurements with the lattice density functional theory (LDFT) formalism are used for the investigation of energetic heterogeneity of carbon blacks. We show that the reliable information about the heterogeneity effect can be obtained from the adsorption measurements and the novel mathematical treatment based on the LDFT method [14,15].

2. Theory and models

Realistic treatment of adsorption on heterogeneous solid surfaces came with the introduction of the integral approach at the beginning of the 1940s. According to this classical approach, the observed (i.e. total) adsorption isotherm $\theta_t(p)$ is formulated as the following integral of local adsorption isotherms $\theta(\varepsilon, p)$ [1–4]:

$$\theta_t(p) = \int_{\Omega(\varepsilon)} \theta(\varepsilon, p) \chi(\varepsilon) d\varepsilon \quad \text{for } T = \text{const}, \quad (1)$$

where p is the equilibrium bulk pressure, T is the absolute temperature, ε is the local adsorption energy on a certain part of solid surface, and $\Omega(\varepsilon)$ is the physical integration region. $\theta(\varepsilon, p)$ and it is chosen from the optimum classical adsorption isotherm, which was developed for energetically homogenous surfaces. $\chi(\varepsilon)$ is the normalized differential energy distribution function, which describes the distribution of surface areas among the corresponding values of the adsorption energy. Hence, $\chi(\varepsilon)$ describes the global heterogeneity effects originating from the different factors mentioned above [4].

Mathematically speaking, Eq. (1) is a linear Fredholm integral equation of the first kind and it is commonly known, that the solution is not trivial [16]. Jaroniec and Madey [4] pointed out the importance of the condensation approximation (CA) method and Rudziński and et al. [17] suggested that simplified (CA) method is the only one which can be applied for the extraction of stable $\chi(\varepsilon)$ by inversion. It is important to point out, that in the CA true continuous kernel is replaced by another unrealistic step-wise one. As a result the mathematical problem is redefined since Eq. (1) is replaced by the Volterra type integral equation easily solved by the differentiation [1–3]. Nowadays, it is generally accepted that “ill-posed” problems, opposed to the classical Hadamard opinion, are fully solvable by the new class of advanced numerical algorithms [16]. Here we want to point out that the knowledge obtained by means of the CA method can be incorporated into hybrid regularization method. In other words the CA

adsorption energy distribution can be applied as an initial approximation of the real one.

The detailed characterization of the “ill-posed” theory is beyond the scope of this study (the details can be found elsewhere [16,18]). Here we only show the essence of the ill-posed theory on the basis of the illustrative example given below.

The difficulties with the integral equation (1) are connected with the compactness of the operator which is associated with $\theta(\varepsilon, p)$. In the physical terms, the integration with $\theta(\varepsilon, p)$ in Eq. (1) has a “smoothing” effect on $\chi(\varepsilon)$ in the sense that the high-frequency components, cusps, and edges in $\chi(\varepsilon)$ are “smoothed out” by the integration. To illustrate this damping of the high-frequency components we can write:

$$\chi(\varepsilon) = \sin(2\pi\zeta\varepsilon), \quad \zeta = 1, 2, \dots \quad \text{and} \quad \Omega(\varepsilon) \in [0, 1]. \quad (2)$$

Subsequently, the corresponding right-hand size $\theta_t(p)$ is given by:

$$\theta_t(p) = \int_0^1 \theta(\varepsilon, p) \sin(2\pi\zeta\varepsilon) d\varepsilon, \quad \zeta = 1, 2, \dots \quad (3)$$

and the Riemann–Lebesgue lemma states that $\theta_t \rightarrow 0$ as $\zeta \rightarrow \infty$. We can therefore expect that the reverse process, i.e. that of computing $\chi(\varepsilon)$ from the incomplete $\theta_t(p)$, will tend to amplify any high-frequency components in $\theta_t(p)$.

As mentioned above, the kernel in Eq. (1) is the physical model of adsorption process on the homogeneous surfaces, and it is selected arbitrarily [1–4]. Let us assume that the adsorption of nitrogen at 77 K is of localized type (i.e. the molecules are adsorbed on the localized sites and cannot diffuse freely on the surface due to high activation energy barrier which is larger than $k_B T$). Additionally, we assume that all adsorption sites are grouped into none-interacting “patches” (i.e. the “patch-wise” model of solid surface is assumed) [2,19]. Following such assumptions the kernel in Eq. (1) is usually represented by the Langmuir or the Fowler–Guggenheim local isotherms [1–4]. However, as was proved by Aranovich and Donohue such local isotherms are the special cases of the statistical lattice gas approach firstly introduced by Ono and Kondo [20]. So, it is reasonable to represent $\theta(\varepsilon, p)$ in Eq. (1) by the more general local monolayer adsorption isotherm developed by Aranovich and Donohue and given by the following formula [21]:

$$\ln \left[\frac{x_1(1 - x_\infty)}{x_\infty(1 - x_1)} \right] + \alpha(4x_1 - 5x_\infty) + \beta = 0, \quad (4)$$

where x_∞ is the concentration of the adsorbate in the bulk fluid, x_1 denotes concentration of the adsorbate in the monolayer, α is the dimensionless energy of adsorbate–adsorbate interactions, and β is the dimensionless

energy of adsorbate–surface atoms interactions. Eq. (4) is the well-known adsorption equation being the solution of cubic lattice gas model restricted to the first layer of adsorbed molecules.

Due to the heterogeneity effects the total Gibbs excess can be treated as the superposition of the Gibbs excess from the each homotatic patch of surface. Mathematically we can write it as follows [22]:

$$\theta(x_\infty, \beta) \equiv x_1(\beta) - x_\infty. \quad (5)$$

Finally, combining Eqs. (4) and (5) we obtain the final integral equation which can be used for the estimation of the adsorption energy distribution from a single adsorption isotherm [22]:

$$\theta_1(x_\infty) = \int_a^b [x_1(\beta) - x_\infty] f(\beta) d\beta, \quad c \leq x_\infty \leq d$$

(for $T = \text{const}, \alpha = \text{const}$). (6)

Eq. (6) is equivalent to Eq. (1) (i.e. the pressure, p , is substituted by the dimensionless density, x_1 , and the adsorption energy, ε , is treated in the dimensionless form, β). Eq. (6) represents very hard numerical problem, as well as others linear Fredholm integral equations. Kowalczyk et al. [22] recently described the new method of solving Eq. (6), it was shown that transformation from dimensionless adsorption energy distribution $f(\beta)$ to $\chi(\varepsilon)$ is very simple task [22].

Until now we have incorporated the integral theory of adsorption for the description of solid surfaces heterogeneity. It seems to be reasonable to assume, that the heterogeneity effects are different from one carbon black surface to another [22,23]. Furthermore, other studies proved that carbon blacks can be divided into two main classes of weak and strong heterogeneities. Following the experimental as well as theoretical studies another question appears: should the integral theory of adsorption be incorporated for the proper analysis of the adsorption process on carbon blacks? To answer this question we used the method recently proposed by Do and Do [24].

According to Do and Do [24] the adsorption process on homogenous flat surface can be modeled by the lat-

tice gas theory and, the adsorbed concentration in each layer, x_i , can be obtained from the following system of non-linear finite equations (see Fig. 1):

$$\ln \left[\frac{x_1(1-x_\infty)}{x_\infty(1-x_1)} \right] - \ln(\beta) + \frac{\varepsilon_{s,1}}{k_B T} + \frac{\varepsilon}{k_B T} (\alpha z_2 x_1 + z_1 x_2 - z_0 x_\infty) = 0, \quad (7)$$

$$\ln \left[\frac{x_i(1-x_\infty)}{x_\infty(1-x_i)} \right] + \frac{\varepsilon_{s,i}}{k_B T} + \frac{\varepsilon}{k_B T} (z_1 x_{i-1} + z_2 x_i + z_1 x_{i+1} - z_0 x_\infty) = 0 \quad \text{for } i = 2, 3, \dots, \quad (8)$$

where x_∞ is the adsorbate bulk concentration, x_i is the adsorbate concentration in the i th adsorbed layer, $\alpha = \varepsilon_1/\varepsilon$ is the ratio of the adsorbate–adsorbate interaction energy in the first layer, ε_1 , to the other layers ε , $\beta = q_1/q$ is the relation between the partition function for the vibrational energy in the first layer, q_1 , and the other layers q , z_1 is the coordination number between two adjacent layers, z_2 is the coordination number within the same layer, $z_0 = 2z_1 + z_2$, k_B is the Boltzmann constant, and T is the temperature.

The interactions between a molecule in the layer i and the surface at the vertical distance z_i are given by Steele 10-4-3 potential energy equation [25]:

$$\varepsilon_{s,i} = \varphi_w \left[\frac{1}{5} \left(\frac{\sigma_{sf}}{z_i} \right)^{10} - \frac{1}{2} \left(\frac{\sigma_{sf}}{z_i} \right)^4 - \frac{\sigma_{sf}^4}{6\Delta(z_i + 0.61\Delta)^3} \right], \quad (9)$$

where $\varphi_w = 4\pi\rho_s\sigma_{sf}^2\Delta\varepsilon_{sf}$. Here $\rho_s = 114 \text{ nm}^{-3}$ is the number density of carbon atoms, $\Delta = 0.335 \text{ nm}$ is the interlayer spacing in graphite, σ_{sf} and ε_{sf} is the solid–fluid collision diameter and interaction energy, respectively.

Additionally Do and Do developed, from the lattice gas theory, the simple relation between measured relative pressure and the bulk density [24]:

$$\ln \left(\frac{p}{p_0} \right) = \frac{z_0 \varepsilon}{k_B T} \left(x_\infty - \frac{1}{2} \right) + \ln \left(\frac{x_\infty}{1-x_\infty} \right). \quad (10)$$

In the lattice gas adsorption-type theory knowing the lattice concentration, the surface excess is given by:

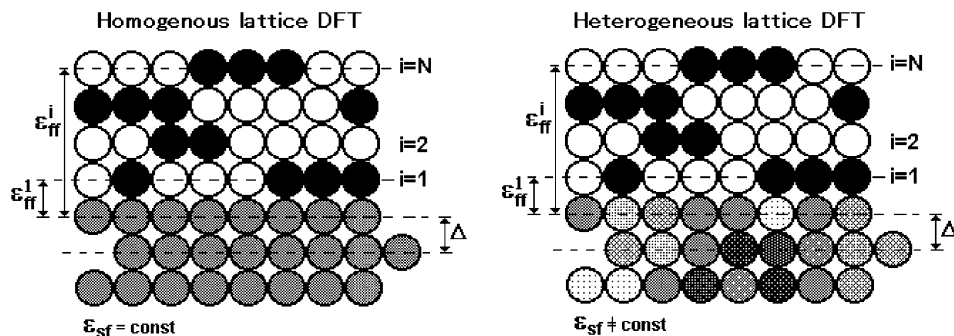


Fig. 1. The schematic representation of the lattice DFT model according multilayer homogenous and heterogeneous adsorption; ε_{ff} denotes the adsorbate–adsorbate interaction energy, and ε_{sf} is the adsorbent–adsorbate interaction energy (other details are discussed in Section 2).

$$\Gamma = \Gamma_m \sum_i (x_i - x_\infty), \quad (11)$$

where Γ_m is the monolayer coverage concentration.

There is one fundamental assumption introduced by Do and Do, i.e. behavior of the first adsorbed layer is different from that of the second and higher layers. In other words, the adsorbate–adsorbate interaction energy and the partition function of the first adsorbed layer are different from those for the higher layers (Fig. 1). This statement is reasonable if we take into account that the influence of solid surface on the first adsorbed layer is the largest. It is commonly known from the continuous DFT theory [26] or molecular layer structure theory (MLST) [27] that the external potential generated by a solid surface is rapidly decreasing function (i.e. the density in 3–4 adsorbed layers, in comparison to the bulk fluid, is strongly increased due to the external potential).

As was shown by Do and Do, besides introduced simplifications, Eqs. (7)–(11) can describe the adsorption isotherms of different adsorbates on different carbon blacks [24]. It is important to realize, that in Eqs. (7)–(11) the surface heterogeneity effect is absent, since ε_{sf} is constant for all adsorption sites distributed on the surface. Therefore, this simplification seems to be realistic only for the carbon blacks characterized by the weak heterogeneity effect (i.e. for the first group mentioned above). Recently, Olivier has proposed the approach leading for the adsorption energy distribution basing on the density functional theory (DFT) [28–30]. In this method Olivier assumed the distribution of ε_{sf} due to heterogeneity effect. However, we must mention that the classical non-local DFT cannot describe the adsorption isotherm on carbon black in the full range of relative pressure without some empirical assumptions [31].

The approach of Olivier is particularly interesting since it leads to the well-known thermodynamic quantities such as the isosteric enthalpy of adsorption extrapolated to the zero surface coverage [28–30], giving a separated physical quantity other than adsorption. Then, we are incorporating the Olivier's formalism into the LDFT approach via the Do and Do method (Fig. 1).

In the next part of this study we use the Aranovich–Donohue (heterogeneous introduced by Kowalczyk et al. [22]) and Do–Do lattice formalism (homogenous and introduced here heterogeneous) for the investigation of the energetic heterogeneity of selected carbon blacks. We try to answer the questions mentioned above. For this purpose we described some experimental data measured recently with high accuracy by introduced lattice type theories. We pay special attention to the adsorption of nitrogen at 77 K since this adsorbate is used as the standard one for the evaluation of the basic properties of adsorbents (i.e. the BET apparent surface area, pore size distribution, adsorption potential distribution curves, and so on).

3. Experimental

The nitrogen adsorption isotherm (at 77 K) on M4040 (Mitsubishi, Japan) sample was measured by super-wide pressure range adsorption technique (SWPA) introduced by Sunaga et al. [11]. Here we performed the measurements on two samples of M4040 carbon black. The first sample was preevacuated at $p < 10^{-7}$ Pa and at 393 K for 2 h. Next the nitrogen isotherm was carefully measured by gravimetric SWPA equipment covering the wide range pressure $5.0 \times 10^{-8} < p/p_0 < 1.0$. The nitrogen adsorption isotherms on M32B sample (Mitsubishi, Japan) and the second sample of M4040 were measured using the volumetric equipment (Quantachrome AS-1-MP) after preevacuation at $p < 10^{-4}$ Pa at 423 K for 2 h.

4. Results and discussion

4.1. The heterogeneity of carbon blacks from the heterogeneous lattice DFT

Four isotherms, usually used as the standard ones, determined on samples of different non-porous carbon blacks are the object of the current study (Figs. 2 and 3). The first two isotherms on Mitsubishi carbon blacks were measured under procedures described in the Experimental part (see Fig. 3). The remaining data were taken from the literature (the adsorption data on the SAO was tabulated by Choma and Jaroniec [32], the data on Sterling FT are taken from the paper of Isirikyan and Kiselev [33]).

At the first step heterogeneous lattice model via the Aranovich and Donohue description was used for evaluation of the adsorption energy distribution from the monolayer part of nitrogen adsorption isotherm by inverting Eq. (6). Here we applied zero order Tikhonov regularization method with and without non-negativity constrain. The regularization parameter was selected by the L-curve criterion introduced by Lawson and Hanson [34]. The final results are displayed in Fig. 2. The M4040 and Sterling FT carbon blacks seem to be much more homogenous than the two remaining studied materials. All obtained adsorption energy distributions are characterized by the well-defined smoothed single peak and the fitting of the theoretical model to the experimental data is good. The inversion with or without non-negativity constrain leads to almost the same results. The mean interaction energy of the considered adsorption system, i.e. nitrogen-surface carbon atom of carbon black, can be estimated as being equal to 7–8 kJ mol⁻¹. It is worth to emphasis that up till now we assume that the integral formalism should be used for proper description of experimental data on the selected carbon blacks.

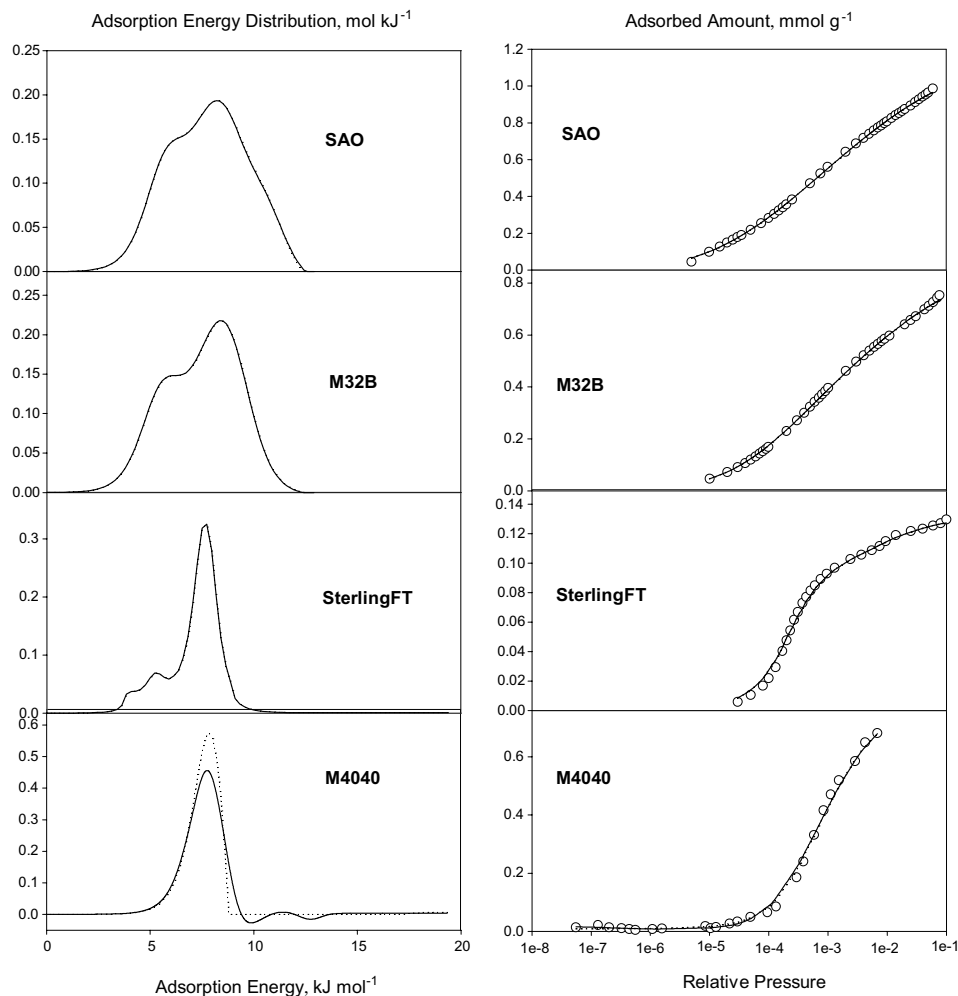


Fig. 2. The distributions of adsorption energy for carbon blacks obtained from the Aranovich and Donohue lattice DFT monolayer adsorption isotherm (dots and solid lines represent the solution of Eq. (6) obtained by the Tikhonov's zero order regularization method with non-negativity constraint and without this constraint, respectively; open circles denotes the low-pressure experimental data).

4.2. The heterogeneity of carbon blacks from the homogeneous lattice DFT

At the second step we were tried to describe all experimental data on carbon blacks by the homogenous Do and Do LDFT (Fig. 1). Eqs. (7)–(11) were solved by the proposed algorithm, being combination of successive substitution, bisection, and Newton–Ralston procedures [35]. Such a powerful combination of the mentioned numerical algorithms gives us the possibility to obtain the final solution with assumed accuracy. The obtained results are displayed in Fig. 3 and in Table 1. It is seen that homogenous model proposed by Do and Do can describe properly the data for the M4040 and Sterling FT in the whole relative pressure range. On the other side, this model cannot describe the adsorption isotherms on two remaining samples of carbon blacks. It seems clear since we have found recently, applying the lattice Aranovich and Donohue theory, that the SAO

and M32B surfaces are characterized by the strong energetic heterogeneity (Fig. 2).

4.3. The new development of the homogenous lattice DFT

For the proper description of experimental data on heterogeneous carbon black surfaces the LDFT theory developed by Do and Do should be modified by incorporation of displacement in solid–fluid interaction parameter ε_{sf} (Fig. 1). For the clarity, following Olivier, in all equations we assume that $\varepsilon_{sf} \equiv \varepsilon_{sf}/k_B$ [28–30]. In the current study we apply the main Olivier's ideas for the case of the LDFT formulated by Do and Do.

Firstly, the so-called “reference isotherm” on homogenous carbon black should be selected [28–30]. This is the basic crux of the method. From the information obtained so far we can conclude that the data measured on two carbon blacks, i.e. M4040 and Sterling FT, can be accepted as the “reference isotherms”.

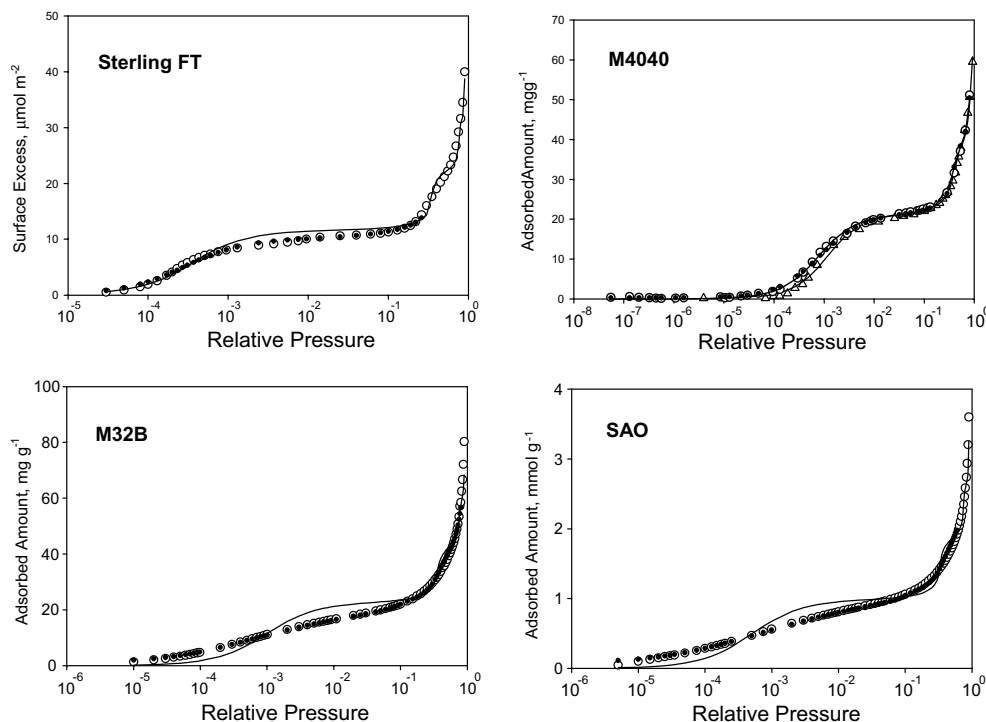


Fig. 3. The fitting of experimental nitrogen adsorption isotherms determined at 77 K (open circles and triangles) by the homogenous lattice DFT model developed by Do and Do (solid line) and introduced heterogeneous one (black circles). The maximum number of adsorbed layers was assumed $N = 10$, and the range of the relative pressure is bounded by $p/p_0 \leq 0.9$.

Table 1

The comparison of the parameters obtained from the homogenous Do and Do lattice density functional method

Carbon black	Γ_m (mmol g ⁻¹)	ε_{sf}/k_B (K)	ε_{fl}/k_B (K)	α	β
Sterling FT	0.13	41.93	72.58	0.26	0.25
M4040 (triangles)	0.77	36.32	56.54	0.28	0.21
M4040 (circles)	0.76	38.13	59.78	0.20	0.24
M32B	0.81	40.45	67.44	0.15	0.14
SAO	0.99	43.39	70.96	0.13	0.14

However, we choose the data for M4040 since they were measured recently by the very accurate apparatus and in wide relative pressure range.

The information concerning the energetic heterogeneity of the SAO and M32B, basing on the Do and Do heterogeneous LDFT, can be obtained applying the following discrete form of the integral equation [28–30]:

$$Q_t(p) = \sum_i Q_i(\varepsilon_{sf}, p) f_i(\varepsilon_{sf}) \quad \text{for } T = \text{const.} \quad (12)$$

As above (Eq. (1)) $Q_t(p)$ is the “global” experimental adsorption isotherm interpolated onto vector p of pressure points, $Q_i(\varepsilon_{sf}, p)$ is a matrix consist of local isotherms generated from homogenous Do and Do LDFT, and $f_i(\varepsilon_{sf})$ is a vector of positive or null values describing the contribution of the i th patch to the total adsorbed amount.

To solve Eq. (12), we generated 94 local adsorption isotherms applying the homogenous Do and Do LDFT

model (i.e. twice more then Olivier [29] applying the DFT). For this purpose, all parameters, besides ε_{sf} , obtained from M4040 fitting were applied. Solid–fluid interaction energy (ε_{sf}) was gradually changed from 6 K up to 100 K by step equal to 1 K. Fig. 4 displays the selected local isotherms used for construction of the base. Obviously, an increase in the adsorbate–adsorbent interaction energy causes a sharper increase in the uptake. It is very important to realize that ε_{sf} influences mainly the monolayer region and as a result the multi-layer parts of the local isotherms are very similar. This phenomenon makes it possible to solve the “ill-posed” problem, i.e. to estimate the distribution of ε_{sf} among different patches.

A significant progress was made during the past decade in utilizing the most advanced numerical algorithms (such as the regularization) for solving different types of the linear Fredholm integral equation of the first kind formed on the ground of adsorption science [36,37].

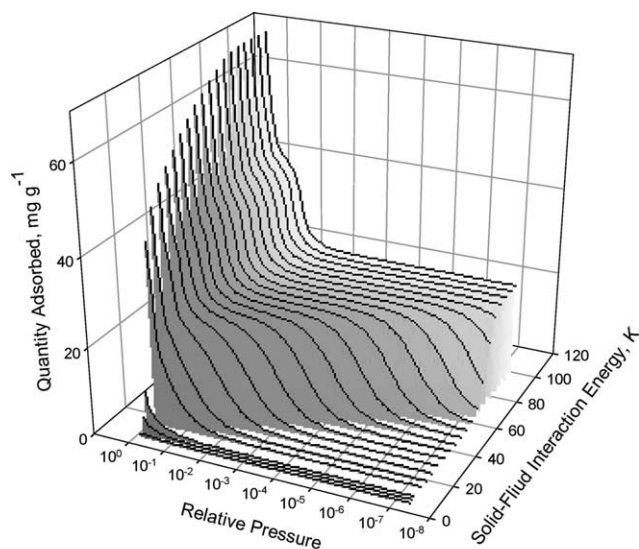


Fig. 4. The selected local nitrogen isotherms (77 K) generated from the homogenous Do and Do lattice DFT model. Solid–fluid interaction energy varies from 6 to 100 K by step equal to 1 K.

However, we want to point out that each type of the integral equations should be very carefully and separately considered, due to different smoothing properties of the integral equation kernel. For the proper solution of Eq. (12) we propose in this study the new regularization type algorithm with the well-known L-curve criterion of regularization parameter selection [34]. Moreover, we propose the original procedure for creation of the regularization matrix from the base of local isotherms. For this purpose, at the first step, the number of local isotherms used for inversion of Eq. (12) is selected randomly. Next, the integration range (here the portion of local isotherms) is divided uniformly. Obtained in this way the representative matrix of the local isotherms is used for the proper inversion of Eq. (12). The question arises what is the reason to take different number of the local isotherms used for the inversion of Eq. (12)? This is strictly related to the “ill-posed” character of this equation. The mathematical theories indicate that if the number of the local isotherms increases, the obtained matrix used for the inversion is more near-singular (i.e. the matrix condition number is increasing and the problem is more complicated). This phenomenon was reported on the ground of the adsorption science by Papenhuijzen and Koopal [38]. This is the reason why several computations were performed for each data and the final results comes from the careful analysis of the all obtained ones. Additionally, our method gives the possibility of the selection of the relative pressure range used for the estimation of $f(\varepsilon_{sf})$ from Eq. (12). It can be easily shown that the extension of the relative pressure range to multilayer region greatly influences on the stability of obtained $f(\varepsilon_{sf})$. To explain this fact let us split off the Eq. (12) as follows:

$$Q_t(p_j) = \sum_{j=1}^k Q(\varepsilon_{sf,i}, p_j) f_i(\varepsilon_{sf,i}) + \sum_{j=k}^N Q_i(\varepsilon_{sf,i}, p_j) f_i(\varepsilon_{sf,i})$$

for $T = \text{const.}$ (13)

Let us assume that k separates the monolayer and multilayer regions of the experimental adsorption isotherm. It seems clear that the matrix singularity is increasing due to attachments of the multilayer region of the measured adsorption isotherm (due to the similarity between all local isotherms in this region). In other words the columns of attached matrix in Eq. (13) are linearly dependent, and as results the condition number of final inversion matrix given by Eq. (13) rapidly increases. Obviously, we can extend the analyzed relative pressure range in Eq. (13) but with the attention. In the proposed algorithm we also attach the option of the non-negativity performed by the most powerful algorithm proposed so far by Lawson and Hanson [34]. This option is particularly important for the samples characterized by a small heterogeneity since classical regularization scheme in such cases always produces more broadened peaks, usually characterized by small negative value of the adsorption energy distribution (as an example see the analysis of adsorption data on the Sterling carbon black sample performed by von Szombathely et al. [36]).

The software described above was applied for the analysis of $f(\varepsilon_{sf})$ of all investigated carbon black samples by the inversion of Eq. (12). Obviously, for the case of the M4040 carbon black (used as the reference isotherm in our method) we suspect the recovering of the mono-modal $f(\varepsilon_{sf})$ by the deconvolution algorithm.

Following the method developed by Olivier it is possible to convert the of $f(\varepsilon_{sf})$ to the distribution of the adsorption energy, $f(U_0)$ and next, to calculate the experimentally measured quantities such as the isosteric and the differential heats of adsorption extrapolated to surface zero coverage [28–30].

It is well known that each adsorption isotherm must converge to the Henry’s law at very low pressure [1–6]:

$$p = K\theta, \quad (14)$$

where $\theta = a/a_m$, a_m is the monolayer capacity, and a is the adsorbed amount at low pressure. Evidently the following condition $a \ll a_m$ must be hold. However, the Henry’s region is not the same for all local adsorption isotherms and changes significantly. For the proper detection of the Henry’s range we used classical least-squares method with statistical correlation analysis. The proposed algorithm automatically detects the Henry’s region for each local adsorption isotherm.

From the basic theory of adsorption it is known that the Langmuir constant K is defined as follows [1–6]:

$$K = A_0 \exp(-U_0/RT), \quad (15)$$

where A_0 is the preexponential factor, U_0 is the adsorptive potential and R is the universal gas constant.

Basing on the results of all generated by the LDFT (Fig. 4) local adsorption isotherms, and combining Eqs. (14) and (15), we obtain the following basic relation (Fig. 5):

$$U_0 = 0.2782RT(\varepsilon_{sf}). \quad (16)$$

On the other hand, it is known that the values of the both isosteric and differential enthalpy of adsorption at the zero surface coverage can be obtained from the following relations (assuming the localized adsorption) [1,4,6]:

$$q^{st} = U_0 + (3/2)RT, \quad (17)$$

$$q^{diff} = q^{st} - RT. \quad (18)$$

Knowing the function $f(\varepsilon_{sf})$ and using the relation given by Eq. (16) we can easily calculate $f(U_0)$ by the following transformation:

$$f(U_0) \equiv \frac{d\theta}{dU_0} = \frac{d\varepsilon_{sf}}{dU_0} \cdot \frac{d\theta}{d\varepsilon_{sf}} = \frac{d\varepsilon_{sf}}{dU_0} f(\varepsilon_{sf}). \quad (19)$$

Clearly the value of U_0 for the real heterogeneous systems should be calculated as a weighted mean from all patches of the surface [30]:

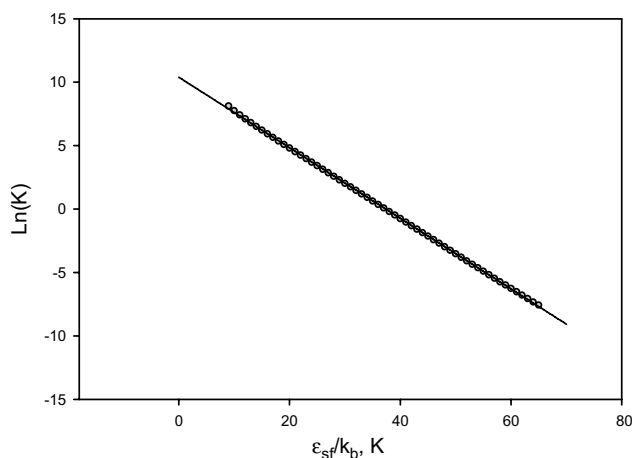


Fig. 5. The dependence of Langmuir constant on the solid–fluid interaction energy of 10-4-3 Steele potential function. The relation was obtained from the low part of local isotherms of nitrogen at 77 K generated from homogenous Do and Do lattice DFT model.

$$U_0 = \frac{\sum_i U_0^i f(U_0^i)}{\sum_i f(U_0^i)}. \quad (20)$$

For a homogenous surface Eq. (20) reduces to the single value of U_0 corresponding to the one patch of surface. The final results are shown in Table 2. The most interesting are the values of the adsorption heats calculated for the zero coverage. They can be compared with those determined calorimetrically. Thus, Kiselev and co-workers [39] compared the values of zero coverage adsorption heats determined for adsorption on different carbon blacks. The comparison of the results obtained by him with those reported by Beebe et al. [40] and Ross and Winkler [41] leads to the range of initial adsorption enthalpy between 11.3 and 9.17 kJ mol⁻¹. This is in the reasonable agreement with the results reported in Table 2, especially taking into account that the results of the reported measurements were performed 50 years ago, and that the enthalpy of adsorption at zero coverage was determined with large error (the error due to low precision of the determination of pressure was high).

Finally, basing on Eqs. (16)–(20) we can describe the monolayer parts of all investigated adsorption isotherms on carbon blacks (Fig. 6). As we suspected, the mono-energetically surface of the reference material (M4040) is reproduced very well by the regularization procedure with the non-negativity constrain. For the Sterling FT carbon black we obtain also the spectrum suggesting very high homogeneity of the surface however, the main peak is slightly shifted to the higher value of the adsorptive potential. For the two remaining carbon blacks the heterogeneity effect is very well pronounced. They are characterized by the broader peaks covering the range from 2 up to 10 kJ mol⁻¹. Since we use the LDFT formalism we can extend the relative pressure range including multilayer formation on carbon black surfaces. The obtained results are presented in Fig. 7. It is obvious that the intensity of the peaks becomes smaller when the relative pressure range increases. Additionally, the inversion problem is numerically more difficult (i.e. the stability of the obtained solution rapidly decreases). From our studies arises that the expanding of the relative pressure range for the inverting of Eq. (12) is possible, but it becomes very difficult. In other words, the obtained knowledge about surface energetic heterogeneity of investigated sample from low part of adsorption isotherm can be lost. It is worth to emphasize

Table 2
The comparison of the parameters obtained from the heterogeneous Do and Do lattice density functional method

Carbon black	a_m (mg g ⁻¹)	A_s (m ² g ⁻¹)	U_0 (kJ mol ⁻¹)	q^{st} (kJ mol ⁻¹)	q^{diff} (kJ mol ⁻¹)
Sterling FT	3.65	12.7	7.09	8.06	7.42
M4040 (triangles)	20.71	72.12	6.98	7.94	7.30
M32B	24.48	85.16	6.29	7.26	6.61
SAO	31.90	111.10	6.48	7.45	6.81

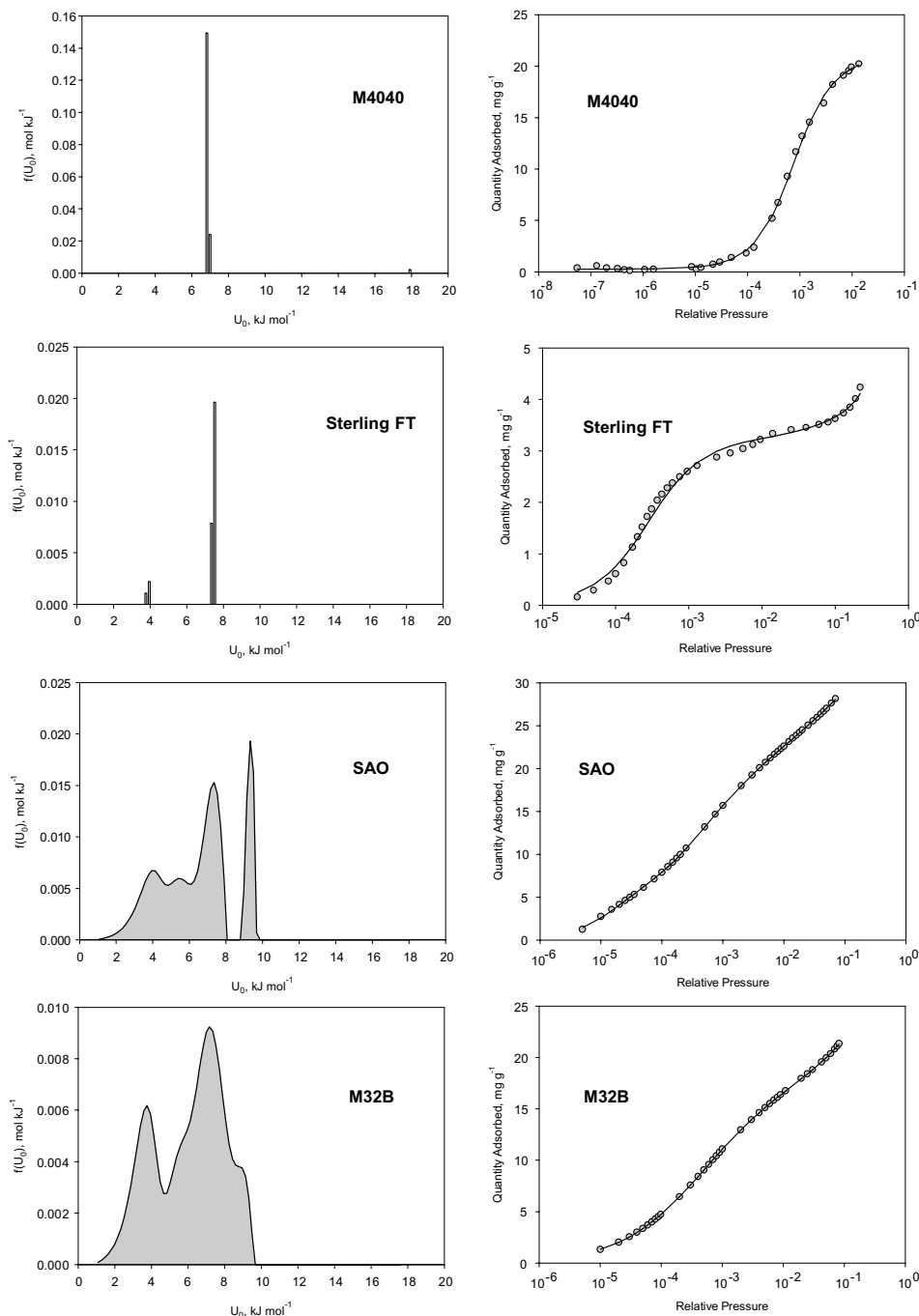


Fig. 6. Adsorption energy distributions for systems carbon black-nitrogen at 77 K obtained from heterogeneous Do and Do lattice DFT model.

that contour plots displayed in Fig. 7 clearly show the heterogeneity effect for both homogenous and heterogeneous surfaces.

5. Conclusions

Taking under consideration all obtained results we can state that the lattice DFT theories seem to be very promising tool for the investigation of the solid surface

energetic heterogeneity. The computer effort of lattice DFT is much more less than the other most sophisticated techniques such as continuous DFT or Grand Canonical Monte Carlo Simulation. Here we use two different lattice DFT formulations. The first one is very close to the classical approaches, whereas the second represents the new insights into the problem of determination of the surface energetic heterogeneity. The quantitative agreement between these two approaches is observed however, further progress is still needed. This

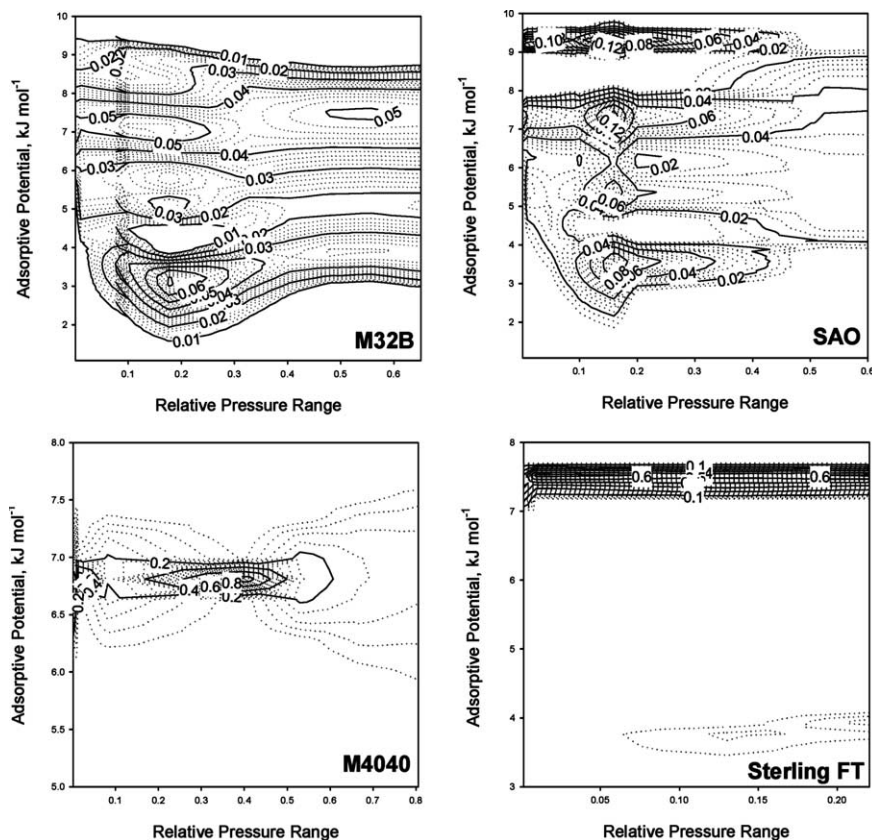


Fig. 7. Adsorption energy distributions for the studied systems obtained from heterogeneous Do and Do lattice DFT model. The effect of different relative pressure range is shown.

will be the subject of our further studies dealing with the problems of energetic heterogeneity of adsorbents.

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