Approximate analytical overall isotherms: lateral interactions of adsorbate species and patchwise topology

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ABSTRACT

Approximate analytical solutions for the overall adsorption functions based on the Fowler-Guggenheim local isotherm with a patchwise topology of adsorption centres location and four different adsorption heat distribution functions have been obtained. The Gaussian, constant, linear (as a particular case of power distribution), and exponential distribution functions have been applied. Overall adsorption functions have been analytically obtained, studied and commented. The Gaussian-related adsorption function reproduces the classic computational result nearly perfectly.

1. Introduction

Lateral interactions of adsorbed particles are known to have been the subject of modelling in numerous studies during the last eighty years. Nevertheless, solving the direct problem analytically, i.e. obtaining a closed expression for surface coverage \( \theta \) in Eq. (1)

\[
\theta = \int_{-\infty}^{\infty} K(e, p) g(e) \, de,
\]

where \( g(e) \) stands for an adsorption heat distribution function, kernel \( K(e, p) \) is a local isotherm valid on homotattic patches of the surface and \( p \) means pressure in the gas phase, ionic activity in a solution or concentration provided the solution had a constant ionic power, has had just a limited progress. Most advanced approach has appeared to be a system with \( K(e, p) \) as a Langmuirian that is without lateral interactions. Its analytical solutions, exact or approximate, have been known just in a few cases [1a, 2, 3]. A much more complicated situation arises when \( K(e, p) \) has to incorporate lateral interactions between adsorbate species and turns out to have a non-Langmuirian form. Ross and Olivier characterized in the 60es the state of the problem as intractable [4a]. They developed the Hill-de Boer local isotherm in series for \( \theta \), found divergence of the expansion at the 13th term and extended their judgement to the Fowler-Guggenheim local isotherm as well. This well-known problem has the mathematical concern, i.e. the local isotherm \( y = K(e, p) \) is represented by an inverse function even in one of the simplest cases taking into account lateral interactions, Fowler-Guggenheim isotherm

\[
p = K^{-1}(e, y(p)) = \frac{1}{a(e)} \frac{y(e, p)}{1 - y(e, p)} \exp[-\alpha \cdot y(e, p)],
\]

and does not enable one to analytically retrieve a direct function. This conditioned mainly the two directions of studies which are (i) analytical approaches restricted to models with random distribution of adsorption centres over the surface when \( y(e, p) \) in the exponent in Eq. (2) is to be replaced with overall coverage, and the intractability fortunately disappears [1b], and (ii) purely numerical investigations of models with both random and patchwise (as Eq. 2) distributions of adsorption centres over the surface [1c]. Solving the integral in Eq. (1) perfectly analytically is complicated by the well-known fact that with \( a \geq 4 \) (\( a \) incorporates here both specific interaction energy, positive for attraction and negative for repulsion, and the number of neighboring particles) the local isotherm in Eq. (2) produces a classic phase transition in the system with a 2D-gas, -liquid and -solid phases as well as stable, meta-stable and unstable states. Therefore, the direct dependence \( y = K(e, p) \) turns then out to be a multiple-valued function [5].

From the other side, there are a huge number of contemporary studies ([6, 7, 8, 9, 10] are just some of those) where the properties and consequences of existing lateral interactions remain latent, and the macroscopic results of adsorption measurements are interpreted in terms of well-known overall adsorption functions based mainly on the local...
Langmuir isotherm. Among them are the Langmuir isotherm itself (\textit{de facto} as a must to be considered), Freundlich, Temkin and Dubinin-Radushkevich (introduced first empirically for porous surfaces and found later to belong to a family of adsorption functions based on the exponential distribution of adsorption centres on adsorption heat) isotherms. Such a choice is likely to be conditioned by the three principal factors otherwise, first, cumbersome mathematics or directly less interpretable numerical results, and/or second, rather complex systems (e.g., related to catalytic or corrosion processes with inhibitors what means involvement of multiple active participants), and third, that the heterogeneity of a surface is well-known to be a factor typically prevailing over lateral interactions in the adsorption bed, i.e. the sharper the energetic heterogeneity of the surface is, the less significant the lateral interactions become. Nevertheless, the importance of an opportunity to have in a closed form an approximate analytical adsorption function in the case with lateral interactions can scarcely be overestimated as well as those advantages analytical solutions bring, typically compared to numerical ones.

The goal of the present study is to outline and mathematically substantiate an approximate purely analytical approach to solving the integral in Eq. (3) based on the Fowler-Guggenheim local adsorption function (2) as well as to study its limitations and to apply it to four distribution functions of adsorption centres on adsorption heat. Among those are the Gaussian, constant, linear and exponential distributions. The constant distribution describing an even surface heterogeneity, together with the Langmuirian kernel in Eq. (1) is well-known to result in the Temkin adsorption function. Besides that, both Langmuir and Temkin adsorption functions were shown to be related to the Gaussian distribution function as its limiting or degenerative ancestors [3, 11]. The linear distribution functions were shown to be related to the Gaussian distribution function as its limiting or degenerative ancestors [3, 11]. The linear distribution function that occupies a conditionally intermediate place between the Temkin and Freundlich adsorption functions in the case without lateral interactions of adsorbate species [2].

2. Constructing a direct local adsorption function

We start with Eq. (2) that upon introducing a dimensionless variable \( x = \alpha(\varepsilon)p \) that stands for pressure, ionic activity or concentration depending on the nature of a medium and is further referred to as pressure just for the sake of brevity, takes the form

\[
y(\varepsilon, p) = \frac{x}{x + \exp(-\alpha \cdot y(\varepsilon, p))}
\] (3)

The basic idea isn’t new and consists in constructing such an expansion that the resulting power series will be converging. Since we use a relatively simple mathematical apparatus of continuous and continuously differentiable functions, the resulting direct local isotherm will be a single-valued function and therefore won’t be able to reproduce phase transitions for corresponding magnitudes of interaction parameter \( \alpha \). A discussion of phase transitions will follow further. The procedure is first related to (i) construction of the direct local isotherm in the low- and high-pressure areas in the framework of the method of successive approximation and (ii) a linkage of these solutions at some intermediate point.

2.1. Convergent expansions

Thus, we have to distinguish between the two cases, \( x \gg 1 \) and \( 1 < x \ll 1 \) (high- and low-pressure areas respectively).

For \( x \gg 1 \) we build the functional sequence \( \{y^{(n)}\}, n = 1, +\infty \), like that: we neglect first the exponent in Eq. (3) and obtain the zero-th sequence member

\[
y^{(0)}_H = 1
\]

Substitution of \( y^{(0)}_H \) into the exponent in Eq. (3) gives the 1st sequence member

\[
y^{(1)}_H = \frac{x}{x + \exp(-\alpha)}
\]

At each successive i-th step we substitute \( y^{(i-1)}_H \) into the exponent in Eq. (3) and get \( y^{(i)}_H \). For example, the 3rd sequence member reads

\[
y^{(3)}_H = \frac{x}{x + e^{-\alpha} + e^{-2\alpha} + \ldots}
\]

The analysis of relationships between terms in the multi-storey denominator enables us to conclude that the following relations obviously take place:

\[
0 < \ldots < y^{(m)}_H(x) < y^{(m-1)}_H(x) < \ldots < y^{(0)}_H(x) = 1
\] (4a)

Functional analysis says that since the functional sequence \( \{y^{(n)}_H(x)\} \) in Eq. (4a) is monotonously decreasing for any \( x \) within a segment and bounded, it converges. The limit of this sequence finds itself between 0 and 1 (Figure 1) and has to be pre-determined by Eq. (3).

It’s important to make a lower estimate for \( y^{(n)}_H(x) \). For these purposes we consider \( y^{(2)}_H(x) \) as an example:

\[
y^{(2)}_H = \frac{x}{x + e^{-\alpha} + e^{-2\alpha} + \ldots} < \frac{x}{x + e^{-1} + e^{-2} + \ldots} = y_H + O\left(\frac{1}{x}\right)
\] (4b)

We’ll consider an estimate of this kind at \( n \to \infty \) as the upper bound of the sequence \( \{y^{(n)}_H(x)\} \) and with particular \( n \) as the corresponding approximation. We perform necessary transformations and estimation for \( y^{(3)}_H \) because it’s worth providing a sufficient number of expansion terms for our solution. Doing as in Eq. (4b), we obtain:

\[
y^{(1)}_H = \frac{x}{x + \exp(-\alpha)} = \frac{x}{x + e^{-\alpha} + e^{-2\alpha} + \ldots} = y_H + O\left(\frac{1}{x}\right)
\]

where we are to explicitly retain the first terms up to \( O\left(\frac{1}{x^2}\right) \) only, so that the \( y^{(0)}_H \)-approximation of local coverage \( y_H \) reads in the high-pressure limit

\[
y_H = 1 - \frac{e^{-\alpha}}{x} + \left(1 - \alpha\right) e^{-2\alpha} x^2 - \left(1 - 3\alpha + \frac{3}{2} \alpha^2\right) e^{-3\alpha} x^3 - \ldots
\] (5)

Letting \( \alpha = 0 \) in the equations above, we obtain the pure Langmuir adsorption function for \( y^{(0)}_H \) and the approximate one for \( y^{(3)}_H \)

\[
y^{(3)}_H = 1 - \frac{1}{x} + \frac{1}{x^2} - \frac{1}{x^3} + \ldots = \frac{1}{1 + 1/x}
\]

\[
y_H = 1 - \frac{1}{x} + \frac{1}{x^2} - \frac{1}{x^3} + \ldots \approx \frac{1}{1 + 1/x}
\]

We consider now the low-pressure limit \( x \ll 1 \). The principal approach remains unchanged whereas its technical realisation is a bit different. We construct the functional sequence \( \{y^{(n)}_L\}, n = 1, +\infty \), for Eq. (3) transformed into the form
y(x, p) = 1 - \frac{1}{1 + x \exp[\alpha \cdot y(x, p)]} \quad (7)

as follows: by letting \( x = 0 \), we obtain in this limit

\[ y_L^{(0)} = 0 \]

for the zero-th sequence member. By substituting \( y_L^{(0)} \) into the exponent in Eq. (7), we have for the 1\textsuperscript{st} sequence member

\[ y_L^{(1)} = 1 - \frac{1}{1 + x} \]

Every time we substitute \( y_L^{(j-1)} \) into the exponent in Eq. (7) we get \( y_L^{(j)} \). For example, the 3\textsuperscript{rd} sequence member reads

\[ y_L^{(3)} = 1 - \frac{1}{1 + x} \left( 1 - \frac{1}{1 + x} \left( 1 - \frac{1}{1 + x} \right) \right) \]

By analogy with Eq. (4), we get the monotonously increasing within the segment, bounded and therefore convergent sequence \( \{y_L^{(n)}(x)\} \) (Figure 1)

\[ 0 = y_L^{(1)}(x) \ldots < y_L^{(n-1)}(x) < y_L^{(n)}(x) \ldots < 1 \]

Although we can build an upper estimate for \( y_L^{(n)} \), we don’t actually need it and therefore proceed with \( y_L^{(3)} \) in the following example because of the same reasons as above:

\[ y_L^{(3)} = 1 - \frac{1}{1 + x} \left( 1 - \frac{1}{1 + x} \left( 1 - \frac{1}{1 + x} \right) \right) = 1 - \frac{1}{1 + x} \left( 1 - \frac{1}{1 + x} \left( 1 - \frac{1}{1 + x} \right) \right)

\]

\[ = 1 - \frac{1}{1 + x} \left( 1 - \frac{1}{1 + x} \left( 1 - \frac{1}{1 + x} \right) \right)

\]

\[ = \sum_{n=0}^{\infty} (-1)^n \frac{x^n}{(n+1)!} \]

Upon expanding all the exponents into the Taylor series what leads to a bit more cumbersome than before and therefore omitted here intermediate expressions, and collecting coefficients at the items with similar powers of \( x \) up to the 3\textsuperscript{rd} power, we get finally

\[ \ldots = y_L + O(x^4) \]

where the \( y_L^{(3)} \)-approximation \( y_L \) of local coverage in the low-pressure limit reads

\[ y_L = x - (1 - a)x^2 + \left( 1 - 3a + 3a^2 \right)x^3 \quad (8) \]

The Langmuir limiting case with \( a = 0 \) is to be retrieved exactly as in the high-pressure limit:

\[ y_H^{(3)} = x - x^2 + x^3 - \ldots \approx \left\{ \frac{x}{1 + x} \right\} \quad (9) \]

Noticeable is that the \( a \)-dependent coefficients in brackets in Eqs. (5) and (8) are exactly the same in their modulus. Thus, the convergent expansions generating solutions with desired accuracy in terms of orders of infinitesimal residues \( \sim \frac{x}{1 + x} \) and \( -x^4 \) appear to have been built in Eqs. (5) and (8) at the high- and low-pressure limits respectively for \( n = 3 \).

### 2.2. Linkage of solutions \( y_H \) and \( y_L \) for local coverage in the intermediate area

A linkage procedure consists in this case of three successive steps. First, we need to upgrade Eqs. (5) and (8) so that there appears some freedom to adjust them to one another in the intermediate pressure area, second, a linkage point has to be determined, and third, linkage conditions should be defined based on physical principles. We perform these steps one by one.

1. We will look for the functional upgrade of solutions (5) and (8) in the form

\[ y = y_{H,L} + \delta y_{H,L} \quad (10) \]

where

\[ \delta y_H = - \frac{\exp(-2a)}{x^2} C_1(a) - \frac{\exp(-3a)}{x^3} C_2(a) \quad (11a) \]

\[ \delta y_L = x^2 C_1(a) - x^3 C_2(a) \quad (11b) \]

Such a representation of the upgrading functions isn't sporadic. Polynomial functions of this kind bring flexibility and keep the Langmuir-like behaviour of solutions (6) and (9) at low and high pressures where the linear terms dominate. Furthermore, as it will be seen beneath, there appears an opportunity to keep the Langmuir-like behaviour in Eqs. (6), (9), and (10) altogether with the quadratic terms as well. The resemblance of \( a \)-dependent coefficients noted above evokes an idea to keep this property further what is foreseen in Eq. (11).

2. To determine a linkage point, the following heuristic considerations are to be taken into account. The basic idea remains the same i.e. keeping the internal symmetry of the local adsorption function relative to the future linkage point. To proceed with it, we consider the main terms of the power representations (5) and (8):

\[ \tilde{y}_H = 1 - \frac{e^x}{x} \quad (12a) \]

\[ \tilde{y}_L = x \quad (12b) \]

Depending on value of \( a \), they have either two intersection points (Figure 2a) or one tangent point (Figure 2b) or no common points at all (Figure 2c).

The points of extremum of the metric function are to be determined by letting its value be zero.
and define either local minima or maxima (up to three in total). Existence of the two solutions on \( \mathbb{R} \)
\[
x_{1,2} = \frac{1}{2} \left( 1 \pm \sqrt{1 - 4\exp(-\alpha)} \right)
\]
is subject to \( \alpha \), typically corresponds to the case of the two intersection points and emerges at \( \alpha = \log 2 \) when \( x_{1,2} \) degenerate to a single tangent point \( x_1 = x_2 = 0.5 \). At least one solution of Eq. (12) exists always and reads
\[
x_3 = \sqrt{\exp(-\alpha)},
\]
is greater than 1 at repulsion, less than 1 at attraction, equal to 1 at \( \alpha = 0 \), always equidistant from \( x_{1,2} \) on \( \mathbb{R} \) for any \( \alpha \) and coincides with the tangent point provided the latter existed: \( x_3 \mid_{\alpha = \log 2} = x_{1,2} \mid_{\alpha = \log 4} \). In such a situation \( \tilde{y}_3 = \tilde{y}_1 = \frac{1}{2} \). Thus, all the three solutions are the points of the maximal approach of \( \tilde{y}_3(x) \) and \( \tilde{y}_1(x) \) equal to zero at \( x_{1,2} \) in the case of intersection or osculation and non-zero at \( x_3 \) otherwise. The present consideration has us to lean toward \( x^* \equiv x_3 \) as a linkage point due to some additional internal symmetry to be introduced into the configuration of the optimal solution.

Such a choice appears to have conditioned the continuity of the first derivative of the solution in the form (10), (11) for any \( C_1 \) and \( C_2 \) (easy to check!)
\[
\frac{dy_0(x)}{dx} \bigg|_{x=x^*} = \frac{dy_0(x)}{dx} \bigg|_{x=x^*} \equiv \mu
\]
and truly enables us to call solution Eqs. (10) and (11) a function-vigilante.

3. One of the obvious linking conditions to determine coefficients \( C_1 \) and \( C_2 \) is a continuity of the whole solution at the linkage point:
\[
y_0(x = x^*) = y_0(x = x^*)
\]
We define another necessary condition in a flexible way by means of letting \( \mu \) in Eq. (15a) be some particular function of \( \alpha \) depending on physical circumstances in every particular case. Thus, the expressions for the coefficients read
\[
C_1(\alpha) = \frac{3}{2}e^{2\alpha} - (\mu + 2\alpha - 1)
\]
\[
C_2(\alpha) = (\mu + 1)e^\alpha - e^{\alpha^2} - \left( 1 - 3\alpha + \frac{3}{2}\alpha^2 \right)
\]
and letting \( \mu = \mu(\alpha) = \frac{3}{2}\sqrt{\alpha^2 + (1 - \alpha)e^{-\alpha} - 2} \) results in \( C_1 = 0 \) and \( C_2 = -0.5 \) at \( \alpha = 0 \) and thereby enables us to provide the Langmuir-like behaviour of Eqs. (10) and (11) incl. the quadratic terms. As we’ll see later, for small values of \( \alpha \) it may be worth choosing \( \mu \) close to 0.5 to reproduce the Langmuir case whereas at big \( \alpha \) (a 2D-condensation) one has to choose a greater \( \mu \).

Finally, we write down now the constructed solution:
\[
y(x) = \begin{cases} 
  r_1 x - r_2 x^2 + r_3 x^3, & x < e^{-\alpha} \\
  1 - r_1 \frac{e^{-\alpha}}{\alpha} + r_2 \frac{e^{2\alpha}}{\alpha} - r_3 \frac{e^{-3\alpha}}{\alpha}, & x \geq e^{-\alpha} 
\end{cases}
\]
where
\[
r_1 = 1, \quad r_2(\alpha) = (\mu + 2)e^{\alpha^2} - \frac{3}{2} \alpha, \quad r_3(\alpha) = (\mu + 1)e^\alpha - e^{\alpha^2},
\]
Coefficient \( r_1 \) is introduced for the sake of compactness of future equations.

It's important to note that whereas solution (17) for the direct local adsorption function is polynomial it doesn't incorporate any built-in self-control mechanism for a physical meaning. This means that with wrong \( \alpha \), too big or too small \( \mu \), the solution can suffer nonphysical local minima and maxima. Besides that, there arises a question of the solution domain with respect to \( \alpha \).

2.3. Properties of the direct local adsorption function constructed

Figure 3 demonstrates how the direct local adsorption function (17) looks like for some values of \( \alpha \) compared to its generating, inverse with
We have discussed above some ideas about a possible choice of the derivative $\mu$ at the linkage point. A more substantial approach is related to minimizing a mean-square distance between $y(x)$ and $y_{FG}(x)$ by varying $\mu$. To do that, we first introduce the partitioning of the coverage segment as $[y_0 = 0, \ldots, y_i, \ldots, y_I = 0.999]$ in view of forthcoming trial computations. That the rightmost point is equal to 0.999 is related to the circumstance that the value of coverage $y = 1$ is mathematically reached at $x = \infty$ what represents an idealisation inadmissible in computations. We do not employ now the formulated in detail [12] more correct and recommended approach for the sake of clarity only. We can numerically calculate now the true values of $\mu$ at $\alpha_i$ due to Eq. (18). For these $\alpha_i$ we have discussed above some ideas about a possible choice of the numerical method to be used.

We introduce the norm $N1$ for the mean-square distance between the adsorption functions $y(x)$ and $y_{FG}(x)$ as

$$\|y(x), y_{FG}(x)\|_{N1} = \sqrt{\sum_{i=0}^{I} [y(x_i) - y_i]^2}$$

(19a)

The nodes can be multiple in the phase transition area, this is foreseen by Eq. (19a). Minimizing by $\mu$ is provided on account of the equation

$$\frac{dy(x)}{d\mu} = \left[ \frac{e^{\alpha x_0}}{x_0^{2\alpha}} - \frac{1}{x^{2\alpha}} \right]$$

(19b)

with

$$\frac{dy(x)}{d\mu} = \left[ \frac{e^{\alpha x_0}}{x_0^{2\alpha}} - \frac{1}{x^{2\alpha}} \right], x < e^{-\alpha}$$

(19c)

Eqs. (19b) and (19c) have been solved numerically. The true values of $\mu$ have been calculated (the derivative in the area $x > e^{-\alpha}$ can in infinity one (at $\alpha = 4$) or two (at $\alpha > 4$) points. Therefore, expression $|y(x_i) - y_i|^2$ in Eq. (19a) can become rather big in such points what belongs to demerits of the norm $N1$.

An alternative approach is related to a different definition of the norm for the distance between the adsorption functions $y(x)$ and $y_{FG}(x)$. We introduce the alternative norm $N2$ for the grid functions as

$$\|y(x), y_{FG}(x)\|_{N2} = \sum_{i=0}^{I} \inf_{\mu \in J} \left[ \frac{[y(x_i) - y_i]^2} + (y_{FG}(x_j) - y_j)^2 \right]$$

(20)

This means that for every node $x_i$ identified for the respective value of $y_i$, $i = 1, \ldots, I$, a $j$-th point, $j = 1, \ldots, J$, is being sought for which the distance between the points $(x_i, y_i) and (x_j, y_j)$ is minimal, and the norm (20) is to be minimized by $\mu$ similar to the norm $N1$ (further calculations are to be carried out for norm $N2$ purely numerically):

$$\|y(x), y_{FG}(x)\|_{N2} = 0$$

(21)

The optimal in the sense of the N2 norm $\mu$-values are given in Table 1 as well. At $\alpha > 3$ they appear to be greater than the respective $\mu$-values in the sense of norm $N1$ and grow further relatively fast resulting in solutions with minima and maxima. In order to prevent going into the area of nonphysical solutions the critical values $\mu$-values have been calculated under which solution (17) remains monotonous. They should be used for the best fits where the $\mu$-values optimal in the sense of norms $N1$ and $N2$ are missing in Table 1. To identify the critical $\mu$-values the derivatives of Eq. (17) have been calculated (the derivative in the area $a > e^{-\alpha}$ can be obtained also by means of replacement $\alpha \to 2e^{-\alpha}$ in the derivative in the area $x < e^{-\alpha}$). By letting them be equal to zero what corresponds to the boundary points where minima and maxima emerge the quadratic equation with respect to $\mu$ arises. Letting its discriminant be equal to zero has enabled us to obtain the critical $\mu$-values. Noticeable is that for these $\mu$-values another quadratic equation emerges whose coefficients are $\alpha$-dependant. Letting the discriminant of this equation in its turn be equal to zero corresponds to the $\alpha$-boundary critical with respect to existence of $\mu \in \mathbb{R}$. This $\alpha$-area where such $\mu$ do not exist is related to nonphysical solutions in the form of Eq. (17) possessing always minima and maxima. The relevant boundary value of $\alpha$ appears to have been calculated and equal to $\alpha_2 = 2 \log 5 \approx -1.39$ (attractive lateral interactions). This is why the optimal $\mu$-values in the sense of norm $N1$ could not be found and are missing in Table 1 for $\alpha < -1$.

Summarizing the analysis proposed above we are to notice that the use of norm $N1$ can be more appropriate for systems without a phase transition.
transitions (a single-value local true adsorption function). In the area close to emerging or related to the existing phase transition the norm N1 is less suitable in the area of multiple-valuedness of the adsorption function where the use of norm N2 provides a closer positioning of the local adsorption function (17) to the Fowler-Guggenheim local adsorption function and can be preferable. A simple statistical correlative evaluation here doesn't seem to be reasonable because the standard mathematical statistics operates institutionally in terms of the norm N1 (values of functions are to be evaluated referring to common nodes or absissa values) which therefore will always have an advantage with formal evaluations of this kind. Therefore, the best judgement could be done rather on the basis of analysis of overall adsorption functions.

3. Calculations of an overall adsorption function

The local adsorption function (17) is formulated in terms of dimensionless pressure $a$ that incorporates an energetic dependence of coefficient $a = a_0 \exp(\varepsilon/\mu)$ [13]. We need to further process it explicitly while integrating according to Eq. (1) and therefore introduce the new variables, i.e., dimensionless pressure $e$ and a dimensionless pressure $s$ at $e = 0$:

$$e = \frac{\varepsilon}{\mu T} \quad \text{and} \quad s = s \exp(-e) = a_0 p$$ (21)

The local adsorption function (17) takes then the form

$$y(s, e) = \left\{ \begin{array}{ll}
\sum_{n=1}^{n_1} (-1)^{n-1} r_n e^{\omega s} e^{\omega n s}, & s < e^{-\omega s} \\
1 - \sum_{n=1}^{n_1} (-1)^{n-1} r_n e^{\omega s} e^{\omega n s}, & s \geq e^{-\omega s} 
\end{array} \right.$$ (22)

It will be used hereinafter instead of the kernel $K(e, p)$ in Eq. (1). The linkage point with respect to adsorption heat is now defined as $e_\alpha = -\frac{\mu}{\omega} + \log s$.

We introduce also a modified dimensionless pressure $q = s \exp(e_0)$ to be involved in final representations of overall adsorption functions and note that in every case the value of $e_0$ is to be defined particularly. Similar is that in all the cases $e_0$ represents a midpoint of the adsorption heat distribution functions. The linkage point reads thereby in terms of $q$: $e_\alpha = e_0 - \frac{\mu}{\omega} + \log q$.

3.1. Gauss-Fowler-Guggenheim (G-FG) adsorption model: the Gaussian distribution on adsorption heat

Integration of the local adsorption function (22) with the Gaussian distribution

$$g(e) = \frac{1}{\sqrt{2\pi} \sigma} \exp \left[ -\frac{(e - e_0)^2}{2\sigma^2} \right]$$ (23)

where $\omega \equiv \frac{\varepsilon}{\mu T}$ is dimensionless adsorption heat dispersion and $e_0 \equiv \frac{\varepsilon}{\mu T}$ is a dimensionless distribution peak position, according to Eq. (1) results in the following overall Gauss adsorption function with lateral interactions in the Fowler-Guggenheim model:

$$\theta(q) = \frac{1}{2} \left\{ \sum_{n=1}^{n_1} (-1)^{n-1} r_n e^{\omega s} e^{\omega n s} \left( 1 - \Phi \left[ \frac{1}{\sqrt{2} \sigma} \log q + m \sigma \right] \right) q^n + 1 \right\}$$

$$+ \Phi \left[ \frac{1}{\sqrt{2} \sigma} \log q \right]$$

$$- \sum_{n=1}^{n_1} (-1)^{n-1} r_n e^{-\omega s} e^{-\omega n s} \left( 1 + \Phi \left[ \frac{1}{\sqrt{2} \sigma} \log q - m \sigma \right] \right) \frac{1}{q^n}$$ (24)

where $\Phi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{x} \exp(-t^2)dt$ is the error function integral [14]. In the Langmuir case ($\alpha = 0, \mu = 0.5$) Eq. (24) reproduces the result obtained earlier in [3] up to the 2nd power of pressure (the coefficient of the 3rd power of pressure is different because of the linkage condition other than that in [3]):

$$\theta(q \to 0) \mid_{\alpha = 0} = q e^{\omega s} - q^2 e^{2\omega s}$$

$$\mu = 0.5$$

In the high-pressure limit the first three and the last three terms become infinitesimal and $\theta(q \to +\infty) = \frac{1}{2} \left[ 1 + \Phi[\alpha \mu t + \infty] \right] \to 1$.

Figure 4 presents the Gauss adsorption function (24) for various values of parameters compared to that with the classic Fowler-Guggenheim local adsorption function in Eq. (2).

The curves have been calculated for $\alpha = 2.57$ what, according to [4], corresponds to a localised argon adsorption film on a hexagonal substrate as graphitized carbon or boron nitride at 77.5 K. While computing in [4a] one had to use a curtailed Gaussian distribution within the range $e_\alpha \approx 16.25 \pm 16.25 \times 10^{-3}$ kT with re-normalization to unity and to calculate with it the partial coverages for 50 values of adsorption heat each for its local surface fraction, with a successive summation. Just a little discrepancy with those classic results numerically computed for the same system is observed in Figure 4.

3.2. Temkin-Fowler-Guggenheim (T-FG) adsorption model: an even distribution on adsorption heat

This is the Temkin-like case of energetically evenly heterogeneous surfaces. The adsorption heat distribution has in this case the form

$$g(e) = \frac{1}{2\pi} \left[ 1 - H(e - e_0 - c) \right]$$ (25)

where $2c$ is the width of the non-zero adsorption heat range $e \in [e_0 - c, \ e_0 + c]$ where $g(e) = \frac{1}{2\pi}$ is the Heaviside step function. Out of this interval $g(e) = 0$. Upon integrating according to Eq. (1) we have

$$\theta(s) = \frac{1}{2\pi} \int_{e_0-c}^{e_0+c} g(s, e)de$$ (26)

and have to distinguish between the three configurations.

A. The linkage point is located on the left from the non-zero adsorption heat range: $e_\alpha < e_0 - c$ (a higher-pressure area $q > \exp(-\frac{\mu}{\omega} + c)$). In
this configuration, only the right-handed branch of the local adsorption function (22) is in use, and the overall adsorption function (26) reads

\[ \vartheta(q) = 1 - \frac{1}{c} \sum_{m=1}^{\infty} (-1)^{m-1} r_m e^{-\mu m} \sinh(mc) \frac{m q^m}{m!} \]  

(27a)

At \( \alpha \to 0 \), Eq. (27a) reproduces the result obtained earlier for the local Langmuir case (\( \mu = 0.5 \)) up to the 2nd power of pressure (why the coefficient at the 3rd power of pressure is different has the same reason as with the Gaussian distribution) [15]:

\[ \vartheta(q \to 0)_{=0} = 1 - \frac{1}{c} \left[ \sinh(c) - \frac{1}{q} \sinh(2c) - \frac{1}{2q^2} + \sinh(3c) \frac{\mu}{3q^3} \right] \left| \alpha = 0 \right. \]

\[ \left. - \frac{1}{6q^4} \right] \]

(27b)

In this configuration we consider the linkage point on the right from the non-zero adsorption heat range: \( c_+ > c_0 - c \) (a lower-pressure area \( q < \exp(-\gamma/\alpha + c) \)). The left-handed branch of the local adsorption function (22) is then to be involved in integration in (26) according to that we obtain

\[ \vartheta(q) = 1 - \frac{1}{c} \sum_{n=1}^{\infty} (-1)^n r_n e^{-\mu n} \sinh(nc) \frac{n q^n}{n!} \]  

(27b)

Similar to configuration A, this equation reproduces the Langmuir case with the same accuracy [15]:

\[ \vartheta(q \to 0)_{=0} = \frac{1}{c} \left[ \sinh(c) q - \sinh(2c) \frac{\mu + 0.5}{q^2} + \sinh(3c) \frac{\mu}{3q^3} \right] \left| \alpha = 0 \right. \]

\[ \left. - \frac{1}{6q^4} \right] \left| \mu = 0.5 \right. \]

(27c)

C. In this configuration, the linkage point is located within the non-zero adsorption heat range: \( c_0 - c \leq c_+ \leq c_0 + c \). The relevant pressure area is determined here as \( q \in [\exp(-\gamma/\alpha + c), \exp(-\gamma/\alpha + c)] \).

Integration of Eq. (26) results in

\[ \vartheta(q) = 1 - \frac{1}{c} \left[ \frac{1}{2} (q \log q) - \left( -1 \right)^{m-1} \sinh(m \frac{\mu}{2} + m \log q) \right] \]  

(27d)

In the limiting Langmuir case, Eq. (27c) is being transformed into

\[ \vartheta(q \to 0)_{=0} = \frac{1}{c} \left[ \frac{1}{2} (q \log q) - \left( -1 \right)^{m-1} \sinh(m \frac{\mu}{2} + m \log q) \right] \]  

(27e)

Figure 5 presents the adsorption function (27) for various values of parameters.

The isotherms have a sigmoidal form similar to that with even surface heterogeneity without lateral interactions. Figure 5B shows the nearly-Temkin case with \( \alpha = 0 \), the difference is hardly noticeable and conditioned by the three reasons, among them are a different coefficient 1/6 in the 3rd expansion term (instead of 1/3 in the Temkin adsorption model), the absence of further expansion terms in the limits \( q \to 0 \) and \( q \to \infty \), and the linkage in the area of intermediate pressures.

3.3. The "polylogarithmic" Fowler-Guggenheim (P-FG) adsorption model: a linear distribution on adsorption heat

This is a particular case \( \beta = 1 \) of the power distribution within the adsorption heat range \( \phi \in [c_0 - c, c_0 + c] \)

\[ g(c) = g^d c^d \]  

(28a)

where \( \beta > 0 \) and \( \gamma \) are the heterogeneity factors, \( d \) is constant determined due to the normalization condition \( \int_{c_0-c}^{c_0+c} g(c) dc = 1 \):

![Figure 5](image-url)

Figure 5. Dependence of coverage on dimensionless pressure according to the T-FG adsorption model. a: \( \alpha = -1 \), \( q_{0.5} \approx 1.64 \); b: \( \alpha = 0 \) (a nearly-Temkin case), \( q_{0.5} \approx 0.99 \); c: \( \alpha = 2.5 \), \( q_{0.5} \approx 0.28 \); d: \( \alpha = 5 \), \( q_{0.5} \approx 0.08 \). Curves: green \( c = 1 \), blue \( c = 5 \), orange \( c = 10 \). Fitting parameters \( \mu \) correspond to those in Table 1.
\[ d = \frac{1}{2c} \{ 1 - \frac{\gamma}{\beta + 1} \left[ (e_0 + c)^{\beta+1} - (e_0 - c)^{\beta+1} \right] \} \]  

(28b)

From the non-negativity condition for the distribution function, a requirement to \( \gamma \) arises: \( |\gamma| \leq \frac{a}{(\gamma_0 + \varepsilon_1)} \) at \( \gamma \leq 0 \) and \( |\gamma| \geq -\frac{a}{(\gamma_0 - \varepsilon_1)} \) at \( \gamma \geq 0 \). One has to consider exactly those three intervals as in the even distribution case.

Here we consider in detail the case \( \beta = 1 \) i.e. the probability to meet an adsorption centre with adsorption heat \( |e, e + \varepsilon| \) is a linear function of \( e \), increasing or decreasing depending on the sign of energy gradient \( \gamma \). While integrating with the Langmuir local adsorption function, it results in the overall polylogarithmic adsorption function [2]:

\[ \theta = \gamma [\Lambda_2(-a_p) - \Lambda_2(-a.p)] + \frac{1}{c} \log \frac{1 + a_p}{1 + a.p} + \frac{c}{2} \log ((1 + a.p)(1 + a.p)) \]

where coefficients \( a_\pm = a_0 \exp \left( \frac{\pm}{2c} \right) \) and \( a_- = a_0 \exp \left( -\frac{\pm}{2c} \right) \) correspond to the strongly and weakly adsorbing surface areas respectively, \( e_0 \) is the middle of the adsorption heat range considered and \( \Lambda_2 \) is polylogarithmic function of the 2nd order whose name the adsorption function was assigned with.

In our simpler case with \( \beta = 1 \), the distribution function reads

\[ g_1(e) = \gamma(e - e_0) + \frac{1}{2c} \]

(29)

where \( |\gamma| \leq \frac{1}{2c} \) has to be met.

A. This is a higher-pressure area. The positions of the linkage points are not affected by the transition from distribution function in Eq. (25) to that in Eq. (29). The coverage reads

\[ \theta(q) = 1 - 2 \times \sum_{n=1}^{3} \frac{(-1)^n r_n \exp(-m \eta)}{m} \left[ \left( \frac{1}{2c} + \frac{\gamma}{m} \right) \sinh(mc) - \gamma \cosh(mc) \right] \frac{1}{q^n} \]  

(30a)

B. In the lower-pressure area the coverage is equal to

\[ \theta(q) = 2 \times \sum_{n=1}^{3} \frac{(-1)^n r_n \exp(-m \eta)}{m} \left[ \left( \frac{1}{2c} + \frac{\gamma}{m} \right) \sinh(mc) + \gamma \cosh(mc) \right] q^n \]  

(30b)

C. In the intermediate pressure area the coverage is represented by the expression

\[ \theta(q) = \frac{1}{2} \left\{ q \left[ c^2 - \left( \frac{a}{\beta} + \log q \right) \right] + \frac{1}{c} \log q + 1 \right\} \]

\[ + \frac{1}{c} \sum_{n=1}^{3} \frac{(-1)^n r_n \exp(-m \eta)}{m} \left\{ \frac{2q}{m} e^{-\eta} \left[ 2\gamma \left( \frac{c}{m} + 1 \right) \cos \left( m \frac{\beta}{2} + \log q \right) - \sin \left( m \frac{\beta}{2} + \log q \right) \right] \right\} \]

(30c)

All the basic limiting cases are being reproduced similar to those for the even distribution on adsorption heat.

Figure 6 presents the adsorption function (30) for various values of parameters.

The curves of this kind do not have any inflection in normal coordinates and have an inflection point in semilogarithmic coordinates similar to the Temkin adsorption function. The greater the heterogeneity gradient and the weaker the lateral interactions are, the slower the coverage increases depending on pressure.

Coverage for the general case of function in Eq. (28) can be expressed with employment of the incomplete \( \Gamma \)-function.

\[ \text{Figure 6. Dependence of coverage on dimensionless pressure according to the P-FG adsorption model. Orange curves: } \alpha = -1; \text{ blue: } \alpha = 2.5; \text{ green } \alpha = 5.0. \text{ Solid curves: } \eta = 1.0, \text{ dashed } \eta = 5.0, \text{ a value close to the limit allowed. Fitting parameters } \mu \text{ correspond to those in Table 1.} \]

\[ \text{Figure 7. Dependence of coverage on dimensionless pressure according to the } ]

Integration of the local adsorption function in Eq. (22) with the distribution function (28) leads to the following general expressions for the surface coverage:

A. A higher-pressure area: \( q > \exp(-\frac{1}{2}a + c) \):

\[ \theta(q) = 1 - \sum_{n=1}^{3} \frac{(-1)^n r_n \exp(-m \eta)}{m} \left[ \left( \frac{1}{2c} + \frac{\gamma}{m} \right) \sinh(mc) - \gamma \cosh(mc) \right] \frac{1}{q^n} \]  

(31a)

where \( \Gamma(\beta, \chi) = \int_0^\chi t^\beta e^{-t} dt \) is the incomplete \( \Gamma \)-function [14].

B. A lower-pressure area: \( q < \exp(-\frac{1}{2}a + c) \):

\[ \theta(q) = \sum_{n=1}^{3} \frac{(-1)^n r_n \exp(-m \eta)}{m} \left[ \left( \frac{1}{2c} - \frac{\gamma}{m} \right) \sinh(mc) + \gamma \cosh(mc) \right] q^n \]  

(31b)

C. An intermediate pressure area: \( \exp(-\frac{1}{2}a - c) \leq q \leq \exp(-\frac{1}{2}a + c) \):

\[ \theta(q) = \frac{1}{2} \left\{ q \left[ c^2 - \left( \frac{a}{\beta} + \log q \right) \right] + \frac{1}{c} \log q + 1 \right\} \]

\[ + \frac{1}{c} \sum_{n=1}^{3} \frac{(-1)^n r_n \exp(-m \eta)}{m} \left\{ \frac{2q}{m} e^{-\eta} \left[ 2\gamma \left( \frac{c}{m} + 1 \right) \cos \left( m \frac{\beta}{2} + \log q \right) - \sin \left( m \frac{\beta}{2} + \log q \right) \right] \right\} \]  

(30c)
\[ \theta(q) = -\frac{\eta}{\beta+1} \left\{ (e_0 + \alpha \frac{\eta}{\beta+1} - (e_0 - \alpha \frac{\eta}{\beta+1} - \log q)^{\beta+1} \right\} + d \left( \frac{\alpha}{2} - c + \log q \right) \\
+ \gamma \sum_{n=1}^{\infty} \frac{r_n}{\eta^{\alpha-n}} \left\{ \frac{(-1)^n \eta^{\alpha-n}}{e^{\eta^{\alpha-n}} q^n} \Gamma\left( \beta, 1, \frac{\alpha}{2} - e_0 + \log q \right) \right\} - \Gamma(\beta) \\
+ 1, n(m_e - \alpha) \right\} + \frac{(-1)^n \alpha n e^{-\frac{\alpha}{2} + \log q}}{m_e - \alpha} \right\} \right\} + 2d \\
\times \sum_{n=1}^{\infty} \frac{(-1)^n r_n}{m_e - \alpha} \left\{ \frac{(-1)^n \alpha n e^{-\frac{\alpha}{2} + \log q}}{m_e - \alpha} \right\} \sinh\left( \frac{\alpha}{2} - \log q \right) \right\} \\
(31c) \]

For integer \( \beta > 0 \), general solutions are being transformed into polynomials with exponential factors that can also be directly obtained by means of integrating the Eq. (1) by parts.

It is interesting to compare the structure of solution (31) with that in Eqs. (27) and (30). Now the adsorption heat \( \theta_0 \) that plays the role of a reference point is explicitly present in the solution whereas earlier (even and linear distributions on adsorption heat) \( \theta_0 \) was present within dimensionless pressure only.

An answer to the question whether the reference point \( \theta_0 \) actually important physically since it refers to the position of the adsorption heat range should be explicitly present in the general solution (31) is not an obvious consequence of properties of the incomplete \( \Gamma \)-function. Based on some general physical considerations one could assume that \( \theta_0 \) were likely to affect the coverage within the dimensionless pressure only. Should it be so, the following lemma would expect to be proved once.

**Lemma about incomplete \( \Gamma \)-function's integration limits.** The following equality takes place

\[ \left[ \Gamma(\beta + 1, e_0 - \alpha) - \Gamma(\beta + 1, e_0 + \alpha) \right] = \frac{\alpha}{\eta} \left[ e^{-\frac{\alpha}{2}} \mathfrak{R}(a, c, \beta) \right] \\
- d \int_{\frac{\alpha}{2}}^{\frac{\alpha}{2} + c} e^{-\frac{\alpha}{2} + \beta} \, dt \right\}, \]

where \( \mathfrak{R}(a, c, \beta) \) is some real-valued continuously differentiable function of four parameters, \( d \) is given by Eq. (28b).

### 3.4. Freundlich-Fowler-Guggenheim (F-FG) adsorption model: an exponential distribution on adsorption heat

We consider the distribution function normalized to unity as

\[ g(e) = \frac{1}{\eta} e^{-\frac{\alpha}{\eta} e} \]

where \( \eta > 0 \) is typically called a distribution modulus, \( 0 \leq \theta_0 < e \).

Although negative values do not generally have to be out of considerations, we introduce here such a restriction in order to consider a half-infinite range of adsorption heats. This is likely to introduce more distinctions compared to a previous finite range case.

Due to less segmented range of adsorption heats, the two possibilities for pressures have to be considered separately.

**A.** A higher-pressure area: \( q \geq \exp(-\frac{\alpha}{\eta} a) \). The coverage reads

\[ \theta(q) = 1 - \sum_{n=1}^{\infty} \left\{ \frac{(-1)^n r_n e^{-\frac{\alpha}{\eta} n}}{\eta m + 1} \right\} \frac{1}{q^n} \]

**B.** A lower-pressure area: \( q < \exp(-\frac{\alpha}{\eta} a) \). Coverage is equal to

\[ \theta(q) = \exp(\frac{\alpha}{\eta} q) + \sum_{n=1}^{\infty} (-1)^n r_n \left\{ \frac{1}{\eta m + 1} \right\} e^{-\frac{\alpha}{\eta} n} \]

In that physically less probable case when \( 1/\eta \) is equal to either of \( m \), the first term in the curly-squaredbrackets is singular but this singularity is removable. For such an \( m_0 \) the corresponding term in the sum reads

\[ \left\{ \frac{1}{\eta m + 1} \right\} e^{-\frac{\alpha}{\eta} n} \]

A general character of these curves (see Figure 7) is similar to that in the previous case. They experience no inflection in normal coordinates whereas in semilogarithmic they have one inflection point. The greater the heterogeneity gradient is and the weaker the lateral interactions are, the slower the coverage increases depending on pressure. The greater the distribution modulus and the lateral interactions are, the faster the coverage increases depending on pressure.

### 4. Conclusions

In this paper, an approximate purely analytical solution for the overall adsorption function taking the lateral interactions of adsorbate particles into account is presented. To achieve this, a converging sequence of solutions in the local Fowler-Guggenheim adsorption model with the patchwise topology of adsorption centres was built in the form of a power expansion. Based on deep functional properties of these solutions, an explicit continuously differentiable and single-valued function \( \theta = \theta(p) \) was built. It was than integrated with local energy distribution functions such as (i) the Gaussian, (ii) constant (even distribution), (iii) linear (an overall polylogarithmic adsorption function in the Langmuir case) as a particular case of power distribution, and (iv) exponential distribution. Properties of the resulting overall adsorption functions obtained approximately in a closed analytical form, among which are Gauss-, Temkin-, “polylogarithmic” and Freundlich-Fowler-Guggenheim isotherms, have been studied and commented. The Gaussian-Fowler-Guggenheim isotherm reproduced the classic computational result nearly perfectly.

The results presented in this study appear to be applicable to the adsorption processes proceeding at surfaces approached by a gas or liquid phase. The adsorption functions represent dependencies of coverage on pressure for the former and on ionic activity or concentration (for solutions with constant ionic power) for the latter. The last case seems promising, in particular, for modeling of the corrosive environment where there exists a competition between aggressive surface-active ions (as, e.g., Cl-ions whose adsorption is sure to be considered involving lateral interactions) and inhibitor’s molecules for the surface’s active centres at which intermediate adsorption complexes are being formed [16, 17, 18].

### Declarations

**Author contribution statement**

Michael Vigdorowitsch: Conceived and designed the analysis; Analyzed and interpreted the data; Wrote the paper.

Liudmila Tsygankova: Conceived and designed the analysis; Analyzed and interpreted the data.

Elena Tanygina: Analyzed and interpreted the data; Contributed analysis tools or data.
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