ADSORPTION ON HETEROGENEOUS SURFACES: NUMERICAL ANALYSIS OF MODELS FOR THE DUBININ-RADUSHKEVICH EQUATION

Miloš SMUTEK and Arnošt ZUKAL

J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2

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A numerical method, based on the integral equation of the adsorption on energy heterogeneous surfaces, is suggested for the evaluation of overall isotherms. It is shown that for the distribution of adsorption energies given by Eq. (*1.11*) and different models of the adsorption behaviour, the overall isotherms obey approximately the Dubinin–Radushkevich equation. The strong energy heterogeneity smears effectively the differences between the localized and mobile adsorption and leads to the same character of the overall isotherm with only a slightly changed heterogeneity parameter.

Among the empirical correlations used to express the experimental data for the isothermic adsorption on a heterogeneous surface, the Dubinin–Radushkevich (DR) isotherm

$$\Theta(p, T) = a/a_\mathrm{m} = \exp\left\{-\left[\frac{RT}{E}\ln\left(p_\mathrm{m}/p\right)\right]^2\right\}; \quad p < p_\mathrm{m} \qquad (1.1)$$

is very important. The observable quantity is here the adsorbed amount a at a partial pressure p of the adsorbing species, and at a temperature T. Moreover, Eq, (*1.1*) contains three adjustable parameters E, p_m, and a_m which can be estimated easily from a quadratic regression of $\ln a$ *vs* $\ln p$. In the original derivation[1], based on the Polanyi theory of the adsorption potential ε, the expression (*1.1*) has been suggested to correlate adsorption data for porous materials, provided that the integral distribution function for the volume W of micropores is given by

$$W/W_0 = a/a_\mathrm{m} = \exp\left(-k\varepsilon^2\right). \qquad (1.2)$$

In this theory, the pressure parameter p_m has been identified with the equilibrium vapour pressure p_s of the adsorbing species, requiring thus a subcritical temperature during the adsorption. To the quantity $a_\mathrm{m} = W$ a meaning was given of the volume of all the micropores in the adsorbent (accessible for the gaseous species).

It has been shown, that the correlation (*1.1*) is also applicable to some nonporous surfaces and the supercritical temperatures. In such cases the parameter p_m loses its original physical meaning (for a review, see[2]). As a consequence of this extension of the applicability, several authors tried to obtain a distribution $f(q)$ of adsorption energies q on an energy heterogeneous (but nonporous) surface, consistent with the overall adsorption isotherm given by Eq. (*1.1*). Generally, the starting point has been the integral equation

$$\Theta(\mathrm{p}, T) = a(p, T)/a_{\mathrm{m}}(T) = \int_{q_0}^{\infty} \vartheta(p, T, q)\, f(q)\, \mathrm{d}q\,. \tag{1.3}$$

Here, q_0 is the lowest adsorption energy, $f(q)$ is normalized to unity, and hence the kernel $\vartheta(p, T, q) \leqq 1$ expresses the coverage of adsorption sites or regions with the adsorption energy q, at the pressure p and the temperature T. In the simplest case the kernel is given by the Langmuir isotherm

$$\vartheta(p, T, q) = \frac{p}{p + a(T)\exp\left[-(q - q_0)/RT\right]}\,. \tag{1.4}$$

This means a restriction of the problem to submonolayer coverages only, with localized adsorption without any interaction between admolecules. Yet it is so far the only case claimed to be solved exactly for $f(q)$. The authors[3] used the Wiener–Hopf method for the solution of integral equations and arrived at the expression

$$f(x) = \frac{\exp(A^2)}{A}\exp(-x^2)\sin(2Ax) \tag{1.5}$$

with

$$A = \frac{\pi RT}{E}\,; \quad x = \frac{q - q_0 + BRT}{E} \quad \text{and} \quad B = \ln p_{\mathrm{m}}/a(T)\,. \tag{1.6}$$

The parameters E and p_m have the same meaning as in Eq. (*1.1*). The lower integration limit in Eq. (*1.3*) becomes $x_0 = BRT/E$, the upper one is infinity and $\mathrm{d}q = E\,\mathrm{d}x$. Unfortunately, the claim of the correctness of solution (*1.5*) is unsubstantiated. First, $f(q)$, and also $f(x)$, should be normalized to unity according to the initial definitions. But (see[4])

$$\frac{\exp(A^2)}{a}\int_0^{\infty}\exp(-x^2)\sin(2Ax)\,\mathrm{d}x = \frac{1}{A}\int_0^{A}\exp(x^2)\,\mathrm{d}x =$$

$$= \exp(A^2)\sum_{k=1}^{\infty}\frac{(-2A^2)^{k-1}}{(2k-1)!!} > 1 \tag{1.7}$$

for $A > 0$. The substitution of zero by $x_0 = BRT/E = AB/\pi$ in the lower integration limit of (*1.7*) leads generally to values of the integral different from unity.

An even more serious objection may be raised against the distribution function (*1.5*). The distribution function in this form is unacceptable since its term $\sin(2Ax)$ leads to nonphysical negative values of the distribution function $f(x)$. Thus, Eq. (*1.5*) can provide at best an approximate solution to the integral equation (*1.3*), with the kernel (*1.4*) and the left-hand side given by Eq. (*1.1*). Assuming next that B is nonnegative, *i.e.*, that $p_m \geqq a(T)$, the physically meaningful part of $f(x)$ runs from $x_0 = AB/\pi = BRT/E$ to $x_{max} = \pi/2A = E/2RT$. Thus, good approximation to the observed isotherm (*1.1*) can only be obtained for large values of E/RT (low values of A), except for the estimate of a_m which is uncertain because of the above mentioned lack of normalization of $f(x)$.

In an earlier paper[5], the integral equation (*1.3*) with the Langmuir kernel (*1.4*) has been solved for the left-hand side given by

$$\Theta(p, T) = \exp\left\{-\left[\frac{RT}{E}\ln(1 + p_m/p)\right]^2\right\}; \quad p < p_m . \tag{1.8}$$

This expression differs only slightly from the DR-equation (*1.1*) for $p \ll p_m$. The modification (*1.8*) has been necessary owing to the use of the Stieltjes' method[6] for the solution of the integral equation. The result is formally identical with the solution (*1.5*), only $x = (q - q_0)/E$, *i.e.*, $B = 0$ in this case. Unfortunately, the last step of calculations involved an error. The correct expression for x is

$$x = \frac{RT}{E}\ln\{\exp[(q - q_0)/RT] - 1\} . \tag{1.9}$$

Consequently, we obtain $x_0 = -\infty$ at the lower integration limit, q_0, of Eq. (*1.3*), so that $\sin(2Ax)$ in (*1.5*) oscillates strongly between positive and negative values near $q = q_0$ and the distribution function $f(x)$ lacks any physical meaning.

In this way it is seen that attempts to assign experimental isotherms obeying the DR-equation (*1.1*) to some continuous distribution function $f(q)$ in adsorption energies have met with limited success so far, even when using the simplest kernel (*1.4*) of the Langmuir form.

An approximate solution of Eq. (*1.3*) is given by the so called condensation method[7]. Here the local isotherm is represented by a step function (0; 1), where the jump from unoccupied to fully occupied sites occurs for a value $q(p)$ which is a monotonously decreasing function of the pressure. Then the approximate energy distribution function leading to Eq. (*1.1*) becomes

$$f(q) = \frac{2(q - q_0)}{E^2}\exp\{-[(q - q_0)/E]^2\} . \tag{1.10}$$

Formally, it is the same differential distribution function as that obtained from the integral distribution function (*1.2*). Indeed, the Dubinin procedure, which assumes subsequent filling of pores according to their size (with the corresponding adsorption potential ε), matches closely the condensation method for continuously heterogeneous surfaces. It is seen that the parameter E^2 in Eq. (*1.10*) has the meaning of the variance s^2 of the distribution, *i.e.*, it characterizes its energy width and its mean adsorption energy $\bar{q} - q_0 = \sqrt{(\pi)}/2E$.

In this paper, we have tried to tackle the problem from another side: by numerical solution of the integral (*1.3*) for the normalized distribution function

$$f(q) = \frac{2(q - q_0)}{s^2} \exp \{- [(q - q_0)/s]^2\} \tag{1.11}$$

for different kernels $\vartheta(p, T, q)$, *i.e.*, for different assumptions for the local adsorption probabilities. The values of $-\ln \Theta$ obtained in this way are further correlated with a power function in $\ln p$. At last, we study in which range of coverages a truncation at the quadratic term in $\ln p$ will reproduce the input of $-\ln \Theta$ data with sufficient accuracy. With this truncation, the correlation is of the form (*1.1*) of the DR-isotherm.

METHOD

Numerical solution of the problem with the Langmuir isotherm for the kernel in Eq. (*1.3*) has been already published[8]. However, the results were presented only graphically and also the goal of that paper was different from the ours. We assumed the following simple isotherms for the kernel in Eq. (*1.3*):

1) The Fowler isotherm

$$pK_H = \frac{\vartheta}{1 - \vartheta} \exp(-K_i\vartheta) . \tag{2.1}$$

2) The Hill–deBoer isotherm

$$pK_H = \frac{\vartheta}{1 - \vartheta} \exp\left(\frac{\vartheta}{1 - \vartheta} - K_i\vartheta\right) . \tag{2.2}$$

Here

$$\vartheta = \vartheta(p, T, q) , \tag{2.3}$$

$$K_H = K_H(q, T) = K_H^0 \exp(q/RT) , \tag{2.4}$$

and

$$K_i = K_i^0/RT \tag{2.5}$$

represents a rough approximation of lateral interactions between admolecules.

3) Further, a few calculations have been performed for the "scaled particles" variant of the perfectly mobile adsorption[9]

$$pK_H = \frac{\vartheta}{1-\vartheta} \exp\left[\frac{\vartheta(3-2\vartheta)}{\vartheta(1-\vartheta)^2} - K_i\vartheta\right]. \tag{2.6}$$

The above isotherms can be easily extended to a multilayer adsorption of the BET type, *i.e.*, starting with the second layer, the heat of adsorption is equal to the heat of condensation. It is sufficient to write

$$\vartheta^1 = \vartheta(1-h)\,; \quad h = p/p_s \tag{2.7}$$

instead of ϑ in the right-hand sides of Eqs (*2.1*), (*2.2*) and (*2.6*), and the left-hand sides become

$$pK_H/(1-h)\,. \tag{2.8}$$

Here, p_s is the saturation pressure of adsorbing vapours and it is meaningful only for subcritical temperatures.

In order to simplify the calculations, the following substitutions have been introduced:

$$t = [(q-q_0)/s]^2\,, \tag{2.9}$$

$$c = s/RT\,, \tag{2.10}$$

and

$$u = q_0/RT + \ln(pK_H^0)\,. \tag{2.11}$$

These substitutions transform Eq. (*1.3*) into

$$\Theta(u, c, K_i) = \int_0^\infty \vartheta(t, u, c, K_i)\, e^{-t}\, dt \tag{2.12}$$

and the kernels (*2.1*), (*2.2*) and (*2.6*), respectively, are defined by

$$c\sqrt{(t)} + u = \ln\frac{\vartheta}{1-\vartheta} - K_i\vartheta\,, \tag{2.13}$$

$$c \surd(t) + u = \ln \frac{\vartheta}{1 - \vartheta} + \frac{\vartheta}{1 - \vartheta} - K_{\mathrm{i}}\vartheta \,, \tag{2.14}$$

and

$$c \surd(t) + u = \ln \frac{\vartheta}{1 - \vartheta} + 3\,\frac{\vartheta}{1 - \vartheta} + \left(\frac{\vartheta}{1 - \vartheta}\right)^2 - K_{\mathrm{i}}\vartheta \,. \tag{2.15}$$

These forms are suitable for iterative search for the values of $\vartheta(t, u, c, K_{\mathrm{i}})$ corresponding to the given sets of $(t, u, c, K_{\mathrm{i}})$. The form of the integral (*2.12*) suggests its numerical integration by means of the Gauss–Laguerre method[10]. But even for the highest available number of terms, $n = 32$, the results of numerical integration agree only poorly with the exact values. This is caused by a steep increase of $\vartheta(t)$ in a narrow range of t-values. Therefore, a set of Gauss–Legendre integrations has to precede the Gauss–Laguerre integration. For a given number of terms in the integration formula, the number of ranges and their widths have been changed in order to obtain the accuracy of Θ better than 10^{-5} for the Fowler isotherm, and better than 10^{-4} for the Hill–deBoer isotherm. The accuracy has been checked either directly by increasing the network of t_{i} in the critical region of the steepest changes in $\vartheta(t)$, or indirectly by following improvement of the fit of the correlation of $-\ln \Theta$ in powers of u with the increase in the highest power of u applied.

The values of $\Theta(u, c, K_{\mathrm{i}})$ were evaluated for the following parameters:

1) Fowler isotherm: $K_{\mathrm{i}} = 0; 0{\cdot}5; 1{\cdot}0; 1{\cdot}5; c = 3; (1); 10;$ *2*) Hill–deBoer isotherm: $K_{\mathrm{i}} = 0; (1); 5; 1{\cdot}5; 2{\cdot}5; c = 6\,(1); 11;$ *3*) Scaled particles: $c = 8; K_{\mathrm{i}} = 0; 2; 4; 6$, and $c = 7; K_{\mathrm{i}} = 2$. Separation of the adsorbate into two adsorbed phases in these models begins for $K_{\mathrm{i}} > 4; 6{\cdot}25$, and $11{\cdot}6823$, respectively. Therefore, the parameters K_{i} used above correspond to moderate lateral interactions when only one adsorbed phase is defined.

Values of $\Theta > 0{\cdot}9$ were obtained in the case of Fowler isotherms, the range decreasing below 0·8 for the Hill–deBoer isotherms for low K_{i} and c-values; still lower coverages were reached for the "scaled particles" model. The step in u (corresponding to the same step in $\ln p$) for the individual isotherms was usually $\Delta u = 1$, only for the most compact isotherms (low c, high K_{i}) it was decreased to $\Delta u = 1/2$.

The correlations of $-\ln \Theta$ in powers of u have been examined up to u^6. Of primary interest, however, were the quadratic correlations

$$-\ln \Theta = a_0 + a_1 u + a_2 u^2 = \ln b_0 + b_2(u_{\mathrm{m}} - u)^2 \,, \tag{2.16}$$

where

$$\ln b_0 = a_0 - a_1^2/2a_2 \,, \quad b_2 = a_2 \,, \quad \text{and} \quad u_{\mathrm{m}} = -a_1/2a_2 \,. \tag{2.17}$$

According to the definition (*2.11*) one obtains

$$u_m - u = \ln (p_m K_H^0) - \ln (p K_H^0) = \ln (p_m/p) . \qquad (2.18)$$

Comparison with the DR equation (*1.1*) shows the formal equivalence of the two expressions. As far as the correlation (*2.16*) is satisfactory, the adsorption data fit formally the correlation (*1.1*), but with $\Theta' = \Theta b_0$, *i.e.*, the parameter a_m in the DR-isotherm (giving $\Theta = 1$ for $p = p_m$) goes over to $a'_m = a_m/b_0$, giving $\Theta = 1/b_0$ for $p = p_m$.

The fit has been considered satisfactory if the overall standard deviation in $\ln \Theta$ did not exceed $2 \cdot 10^{-3}$, which is a value lower than the experimental error in most cases.

RESULTS AND DISCUSSION

The most important result achieved is the satisfactory fit of adsorption data by means of the quadratic equation (*2.16*) over a wide range of pressure for most of the cases treated. This implies directly that the surface heterogeneity of the type (*1.10*) smears out (at least for higher values of the heterogeneity parameter c) any effect of lateral interactions (provided they are not too strong) and even of the mobility character of admolecules. Clearly, this implication can be extended to other types of strong surface heterogeneity.

In all the cases studied, the pressure range for a satisfactory fit of $-\ln \Theta$ *vs* powers of u, as well as its standard deviation, remain almost unaffected by lateral interactions, provided the latter are moderate. An increase in the surface heterogeneity, *i.e.*, the increase in c, improves the quadratic fit (as well as any higher polynomial fit).

In the quadratic correlation (*2.16*), the parameter b_2 reflects the adsorption heterogeneity of the surface, whereas the parameter $\ln b_0$ represents a correction of the true value of a_m, and u_m can be interpreted as a measure of the adsorption energy, according to the definition (*2.11*) of u. Comparison of expressions (*1.10*) and (*1.11*) with the definition (*2.10*) suggests the equality $b_2 = 1/c^2$ should hold, provided the condensation approximation is valid. This is, however, not the case, as will be shown below.

The quadratic fit (*2.16*) becomes poor for too high and too low coverages Θ. With high coverages, *i.e.*, for high pressure, a rather sudden deterioration is met. This occurs in the region of little interest, where, most probably a multilayer adsorption is developed to a considerable extent. For coverages $\Theta < 0{\cdot}07$, the misfit increases more gradually and leaves Θ well within experimental error. Thus the quadratic fit appears to express very satisfactorily the experimental data over the whole significant range of adsorption.

In the following, details for the individual types of adsorption isotherms $\vartheta(p, T, q)$ are discussed.

The Fowler Isotherm

The kernel (*2.1*) corresponding to the Fowler isotherm gives the best fit of the integral (*1.3*) with the overall isotherm (*1.1*) for the heterogeneity parameter $c \geqq 6$. A satisfactory correlation of $b_2(c, K_i)$ is then

$$b_2 = 1/c^2 - (6{\cdot}41 - 1{\cdot}56K_i)/c^4 \qquad (3.1)$$

instead of expected form $b_2 = 1/c^2$.

Using this correlation, the parameters $\ln b_0$ and u_m of the fit (*2.16*) have been reevaluated. The fit thus obtained was not appreciably inferior to the original regressions in which all three parameters were optimized. The range of u values has been limited by the condition that the standard deviation of the fit must not increase significantly by the incorporation of a new u value and that it must be lower than $2 \,.\, 10^{-3}$ in any case. The attempts to construct simple correlation for $u_m(c, K_i)$ and $\ln b_0(c, K_i)$ have failed. The coefficients are given in the Table I, together with the corresponding ranges of u values, the standard deviations of the fit, and the values of c', defined by the relationship

$$b_2(c, K_i) = b_2(c', 0)\,. \qquad (3.2)$$

The value of c' characterizes the apparent heterogeneity, if the adsorption with lateral interactions, defined by K_i, is dealt with as if no interactions occurred.

The data of Table I show that moderate lateral interactions, when neglected, distort only insignificantly the type (*1.11*) of the heterogeneity distribution. Moreover, this neglect of interactions causes only small decrease in the apparent heterogeneity, the latter becoming more marked as the heterogeneity parameter c is decreased. The increase in K_i is accompanied by a decrease in $u_m = q_0/\boldsymbol{R}\boldsymbol{T} + \ln\,(p_m K_H^0)$. This can be interpreted as an apparently stronger overall adsorption, since for a given value of c it holds

$$\begin{aligned} u_m(K_i) - u &= u_m(0) - [u_m(0) - u_m(K_i) + u] = \\ &= u_m(0) - u'\,, \end{aligned} \qquad (3.3)$$

where

$$u' = u_m(0) - u_m(K_i) + u = u_m(0) - u_m(K_i) + q_0/\boldsymbol{R}\boldsymbol{T} + \ln K_H^0 + \ln p\,. \qquad (3.4)$$

Since the difference $[u_m(0) - u_m(K_i)]$ is positive, it gives rise to an apparent increase in the sum $(q_0/\boldsymbol{R}\boldsymbol{T} + \ln K_H^0)$, which means a stronger adsorption.

Further, it can be shown that the parameter p_m in Eq. (*2.18*) has not a meaning of the saturation pressure p_s. Indeed, to the first approximation one obtains

$$\ln p_s \approx A - q_L/RT\,, \tag{3.5}$$

where q_L is the heat of condensation. This would give

$$u_m = u_s = q_0/RT + \ln K_H^0 + A - q_L/RT = A' + (q_0 - q_L)\,c/s = A' + B'c\,. \tag{3.6}$$

Thus, u_m should increase roughly linearly with c, as for as the lowest heat of adsorption q_0 is higher than the heat of condensation q_L of the adsorbing vapour. An inspection of the u_m data in the Table I reveals, however, that for a given K_i value

TABLE I

Quadratic correlation (*2·16*) for Eq. (*1·3*) with the kernel (*2·1*) and b_2 given by Eq. (*3·1*)

c	K_i	Range of $-u$	$10^4 s$	$10^2 b_2$	$\ln b_0$	u_m	c'
6	0·0	1—12	14·200	2·28318	0·05425	0·21224	6·0000
6	0·5	1—12	14·638	2·34336	0·04644	−0·06389	5·9006
6	1·0	2—12	11·841	2·4035$\bar{5}$	0·04117	−0·34773	5·8042
6	1·5	2—11	6·280	2·46274	0·03514	−0·62958	5·7106
7	0·0	2—13	5·080	1·77384	0·04822	0·1221$\bar{5}$	7·0000
7	0·5	2—13	5·313	1·80633	0·04064	−0·13573	6·925$\bar{5}$
7	1·0	2—13	5·036	1·83882	0·03427	−0·40001	6·8527
7	1·5	2—12	4·089	1·87130	0·02880	−0·66899	6·7816
8	0·0	3—14	2·394	1·40601	0·04099	0·07499	8·0000
8	0·5	3—14	2·943	1·4250$\bar{5}$	0·03419	−0·17429	7·9396
8	1·0	3—14	2·895	1·44409	0·02859	−0·43720	7·8803
8	1·5	3—14	2·148	1·46314	0·02416	−0·69130	7·8222
9	0·0	3—15	1·302	1·13687	0·03446	0·04874	9·0000
9	0·5	3—17	1·889	1·14876	0·02875	−0·1977$\bar{5}$	8·9489
9	1·0	3—17	2·542	1·1606$\bar{5}$	0·02421	−0·45161	8·8986
9	1·5	3—16	1·716	1·17253	0·02010	−0·70823	8·8489
10	0·0	3—16	1·122	0·93590	0·02906	0·03212	10·0000
10	0·5	3—17	1·218	0·94370	0·02416	−0·21169	9·9555
10	1·0	3—18	1·532	0·95150	0·02007	−0·46224	9·9116
10	1·5	3—18	1·114	0·95930	0·01672	−0·71777	9·8682

u_m decreases as c is increased and this variation is strongly nonlinear. Thus, for $K_i = 0$ (Langmuir isotherm), the simplest fair approximation,

$$u_m(c, 0) \approx 0{\cdot}01004 - \frac{0{\cdot}48657}{c - 1{\cdot}9} + \frac{5{\cdot}39421}{(c - 1{\cdot}9)^2} \tag{3.7}$$

involves four parameters for five degrees of freedom.

Finally, if a_m is identified with the full monolayer coverage, the quadratic correlation (*2.16*) gives its estimate a few per cent too low. The error rises up to 5·5 per cent at $c = 6$ and $K_i = 0$ and decreases with the increase in both c and K_i. For lower heterogeneity (or for higher temperatures) with $c < 6$, a quadratic fit of $-\ln \Theta$ *vs* u (or $\ln p$) with a sufficiently small standard deviation can be achieved over a restricted range of Θ values only, although inclusion of higher terms in u^i (or $\ln {}^ip$) extends this range markedly. The coefficients of these higher-order polynomials behave reasonably and change regularly with the increase in K_i and with the order of the polynomials used. It is only the case of $c = 3$ and $K_i = 1{\cdot}5$ in which the presence of lateral interactions may be inferred from experimental data. This is evidenced by the impossibility to express the Θ data as a series of the Langmuir isotherms

$$\Theta \approx \sum_i \frac{b_i p}{p + a_i}$$

with only positive coefficients a_i and b_i.

The Hill–deBoer Isotherm

For the kernel (*2.2*), the quadratic fit has been satisfactory over the significant range of u (or $\ln p$) values for the heterogeneity parameters $c \geqq 6$, as for the Fowler isotherm. The dependence of the parameter b_2 in Eq. (*2.16*) on c, however, deviates from the expected one somewhat more than in the Fowler case, and satisfies the correlation

$$b_2 = (0{\cdot}955 + 0{\cdot}004K_i)/c^2 - (6{\cdot}65 - 9{\cdot}84K_i)/c^4\,. \tag{3.8}$$

With b_2 fixed by Eq. (*3.8*), the best parameters $\ln b_0$ and u_m in the correlation (*2.16*) have been reevaluated. These are summarized in Table II. Therein, again, the apparent heterogeneity parameters c', defined by Eq. (*3.2*), are listed, together with the parameters c'' for the substitution of the kernel (*2.2*) by the Langmuir isotherm, *i.e.*, from the equality

$$(0{\cdot}955 + 0{\cdot}004K_i)/c^2 - (6{\cdot}65 - 0{\cdot}84K_i)/c^4 = 1/(c'')^2 - 6{\cdot}41/(c'')^4\,. \tag{3.9}$$

TABLE II

Quadratic correlation (*2·16*) for Eq. (*1·3*) with the kernel (*2·2*) and b_2 given by Eq. (*3·8*)

c	K_i	Range of $-u$	$10^4 s$	$10^2 b_2$	$\ln b_2$	u_m	c'	c''
6	0	2–14	15·494	2·13966	0·30248	0·57679	6·0000	6·2605
6	1	2–14	13·417	2·21559	0·27504	0·22144	5·8627	6·1155
6	2	2–14	13·997	2·29151	0·24871	−0·14358	5·7305	5·9861
6	3	2–14	15·58$\bar{5}$	2·36744	0·22480	−0·52318	5·6027	5·8617
6	4	3–13	6·399	2·44336	0·20580	−0·92520	5·4790	5·7420
6	5	3–13	6·186	2·51929	0·18972	−1·34618	5·3587	5·6264
7	0	3–15	8·729	1·67301	0·27387	0·57712	7·0000	7·2461
7	1	3–15	7·867	1·71516	0·24742	0·23940	6·8936	7·1394
7	2	3–15	8·438	1·75831	0·22330	−0·11487	6·7905	7·0363
7	3	3–15	8·806	1·80146	0·20258	−0·48928	6·6908	6·9365
7	4	3–15	7·615	1·84461	0·18462	−0·88384	6·5940	6·8399
7	5	3–15	8·867	1·88776	0·17044	−1·30086	6·5001	6·7462
8	0	3–15	8·626	1·32983	0·24487	0·63259	8·0000	8·2536
8	1	3–15	8·390	1·35660	0·22136	0·29573	7·9096	8·1622
8	2	3–15	8·563	1·38335	0·20053	−0·06072	7·8216	8·0734
8	3	3–15	8·935	1·41011	0·18240	−0·43673	7·7359	7·9868
8	4	3–16	9·152	1·43567	0·16685	−0·83133	7·6525	7·9027
8	5	3–18	8·927	1·46362	0·15424	−1·24724	7·5712	7·8207
9	0	3–15	8·793	1·07766	0·21908	0·71166	9·0000	9·2664
9	1	3–15	7·796	1·09540	0·19892	0·36765	8·9192	9·1845
9	2	3–15	7·851	1·11314	0·18110	0·00475	8·8402	9·1043
9	3	3–15	8·935	1·13088	0·16597	−0·3794$\bar{5}$	8·7630	9·0260
9	4	4–17	9·330	1·14862	0·15275	−0·77689	8·6875	8·9495
9	5	4–19	8·197	1·16636	0·14151	−1·19393	8·6136	8·8746
10	0	3–15	8·457	0·88850	0·19697	0·80049	10·0000	10·2823
10	1	3–15	7·125	0·90090	0·17983	0·44629	9·9253	10·2064
10	2	3–15	6·613	0·91330	0·16462	0·07480	9·8521	10·1319
10	3	3–15	6·643	0·92570	0·15137	−0·31402	9·7803	10·0590
10	4	4–18	7·500	0·93810	0·13910	−0·71654	9·7099	9·9874
10	5	4–19	7·104	0·95050	0·13048	−1·14049	9·6408	9·9172
11	0	3–19	8·739	0·74384	0·17740	0·8988$\bar{5}$	11·0000	11·3000
11	1	4–19	8·864	0·75288	0·16288	0·53458	10·9294	11·2281

From the inspection of Table II it is seen that also here the moderate lateral interactions cause only a small decrease in the apparent heterogeneity. Treating the mobile adsorption as if it were localized leads, however, to an apparent increase in heterogeneity (the parameter c'').

The parameter $\ln b_0$ decreases with the increase in both c and K_i as before, but it is substantially higher; the true value of the full monolayer is 14 – 35 per cent higher than its estimate given by the correlation (*2.16*) and uncorrected for $\ln b_0$. This complies with the fact that the quadratic correlation fails for high coverages if $d\Theta/dp$ is very low.

The parameter u_m decreases strongly with the increase of weak lateral interactions, which again can be interpreted as an overall strengthening of the adsorption according to the relationship (*3.3*). Contrary to the Fowler case, however, u_m increases slowly with c, but in general in a strongly nonlinear way. This is at variance with Eq. (*3.6*) in which u_m was interpreted in terms of the saturation pressure.

"Scaled Particles" Isotherm

Test calculations have been undertaken for the kernel (*2.6*). The parameters obtained for $-u$ between 3 and 13 are listed in Table III.

The behaviour of the parameters is analogous to that for the Hill–deBoer case. According to the relationship (*2.6*), the increase of the pressure with the coverage starts to be very steep already for lower coverage relative to the Hill–deBoer model of mobile adsorption. Therefore the parameter $u = -3$ corresponds only to about half a coverage and the parameter $\ln b_0$ is large, giving a substantial correction for the true value of the monolayer coverage. The parameter u_m behaves as before but its increase with the heterogeneity parameter c is higher than in the Hill–deBoer model.

TABLE III

Quadratic correlation (*2·16*) for Eq. (*1·3*) with the kernel (*2·6*)

c	K_i	Range of $-u$	$10^4 s$	$10^2 b_2$	$\ln b_0$	u_m
7	2	3–15	17·261	1·66284	0·60016	0·26466
8	0	3–15	18·445	1·27498	0·59842	0·85847
8	2	3–15	16·982	1·31044	0·55464	0·43562
8	4	3–15	16·245	1·34679	0·51464	−0·02687
8	6	3–15	16·191	1·38224	0·47826	−0·52207

CONCLUSIONS

The performed calculations show that on a strongly energy heterogeneous surface the differences between localized and mobile adsorptions are effectively smeared out and that the lateral interactions between adsorbed species manifest themselves on adsorption isotherm only as an overall strengthening of adsorption. Not only the type of the distribution of adsorption energies remains unaffected, but also its heterogeneity parameters change only little for different models of the adsorption behaviour. Approximate irrelevancy of the adsorbing mode for the resulting adsorption isotherm on heterogeneous surface has already been assumed by Cerofolini[11], who noted that at sufficiently low temperatures (which is equivalent to a well developed heterogeneity) the local isotherms can be approximated successfully by a step function. Although the arguments given in that paper were plausible, they were not properly justified. Our numerical results allow to specify the range of approximate validity of this behaviour and also to extend the general features to other shapes of distributions in adsorption energies.

Furthermore, the results show that the Dubinin–Radushkevich isotherm (*1.1*) can be formally applied with a reasonable accuracy to pressure range of about five orders of magnitude, even for nonporous materials provided the energy distribution function is of the type (*1.11*). In this case, however, the isotherms for different temperatures will be correlated with parameters c and u_m, defined by Eqs (*2.10*) and (*2.11*), respectively, the temperature dependence of which is different from that given by the Dubinin–Radushkevich model for porous materials.

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