

A Fractal Approach to Adsorption on Heterogeneous Solid Surfaces. 1. The Relationship between Geometric and Energetic Surface Heterogeneities

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Solid surfaces are never ideally regular, that is, geometrically and energetically homogeneous, nor are they fully irregular or fractal. Instead, real solid surfaces exhibit a limited degree of organization quantified by the fractal dimension D . We find that there is a functional relationship between the differential distribution of adsorption energies and the differential distribution of pore sizes on such “*partially correlated*” surfaces. We also show that the differential pore size distribution reduces to the classical fractal pore size distribution in the limit of very small pore sizes, or when the fractal dimension D approaches 3. To do this, analytical expressions are developed describing pore size correlations, and correlations between adsorption energies. These correlation functions are then used to develop a general form of the interaction term in the equations for adsorption isotherms. Finally, using our theoretical approach, existing equations describing adsorption on heterogeneous surfaces are reexamined. It is shown that some of these equations have to be revised whereas others can be generalized to take into account both energetic and geometric heterogeneity.

Introduction

The main goal of surface science is to find fundamental features which are common to many different adsorption systems. The existence of such fundamental features was suggested by early adsorption experiments carried out at the end of the 19th century and at the beginning of the 20th.

As early as 1906 Freundlich showed¹ that all the then-known adsorption isotherms can be described by a simple formula, now called the “Freundlich isotherm”. However, the fundamental physical property lying behind the common applicability of Freundlich’s *empirical* equation remained unexplained for the next 30 years.

In 1916 Langmuir² published the first *theoretical* isotherm. This explained the “plateau” found in experimental adsorption isotherms. The related physical model assumed adsorption on a flat surface with energetically equivalent adsorption sites, one molecule per adsorption site.

During the next 2 decades this model was elaborated, mainly to take into account possible interactions between adsorbed molecules. A similar model of mobile adsorption on a flat, energetically homogeneous surface, was also considered, but this and similar models all led to similar predictions.^{3–6}

A general prediction was that one should observe first-order and other kinds of phase transitions in the adsorbed phase. One should observe, for instance, a discontinuity (a sudden jump) in experimental adsorption isotherms, corresponding to the first-order transition at a certain surface coverage. Heats of adsorption should either be increasing functions of surface coverage or be

constant in a region of surface coverage preceding the first-order transition. One should also observe discontinuities in the heat capacities of the adsorbed phases. These are only three examples of the predicted phenomena which, however, were not observed in the behavior of real adsorption systems. Instead, experimental isotherms sometimes showed a rapid increase in some region of surface coverage but were always continuous. Moreover, contrary to theoretical predictions the measured heats of adsorption were, as a rule, *decreasing* functions of surface coverage. Finally, instead of discontinuities, rounded *peaks* were sometimes observed in heat capacities.⁶ More worryingly, the observed kinetics of adsorption did not follow the behavior predicted by Langmuir’s kinetic equations. Instead, the empirical Elovich equation was found to be generally applicable to adsorption kinetics.⁷

All this suggested that a fundamental feature of adsorption systems had not been taken into consideration. Finally, at the beginning of the 1940s, a series of papers were published showing that this missing fundamental property is the energetic heterogeneity of solid surfaces. Most commonly that energetic heterogeneity was formulated as a dispersion of adsorption energy values on the available adsorption sites.

By adding the factor of surface energetic heterogeneity one might expect a large variety of the adsorption behaviors to be made possible. Surprisingly, it appears that almost all the reported experimental isotherms can be well correlated using three simple empirical isotherm equations. In the case of nonporous solids Freundlich’s empirical equation applies at low pressures (i.e., low surface coverages). At higher surface coverages its empirically generalized form, the Langmuir–Freundlich isotherm,⁶ can be used. Finally, the empirical Dubinin–Radushkevich equation describes adsorption in porous materials very well. Of course, a number of other isotherms was proposed to describe adsorption in specific adsorption systems in order to account for their individual features.

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However, to describe the general features of the majority of adsorption systems in the region of submonolayer coverage, the above three empirical isotherms were good enough.

This observation led Cerofolini⁹ and then Rudzinski and Everett⁶ to postulating the existence of some universal function which could quantify the adsorption energy distribution that describes the energetic surface heterogeneity of all solid surfaces. Unique features of a given solid surface should be accounted for by the values of a few parameters in that function, but the analytical form should be the same for all systems.

Cerofolini, Rudzinski, and Everett developed such an analytical form and used the condensation approximation to develop the corresponding universal equation that describes adsorption on all real heterogeneous solid surfaces. They have shown⁶ that this universal adsorption isotherm reduces to Freundlich's equation at low pressures, and becomes the Langmuir–Freundlich equation at higher submonolayer coverages. That same universal isotherm also predicted the existence of the Dubinin–Radushkevich empirical isotherm.

The theoretical development of that generalized adsorption energy distribution was based on the assumption of a geometrically distorted solid surface and on simple thermodynamic arguments. However, no general relationships were known at that time which would create links between the general features of the adsorption energy distribution, and features of the surface geometric heterogeneity, usually characterized by the pore size distribution function. As a result, when considering energetic heterogeneity, the effects of geometric heterogeneity were ignored as a rule.

Since the 1940s, dozens of papers had been devoted to the theoretical description of adsorption on energetically heterogeneous solid surfaces. It would exceed the scope of this publication to list even the most fundamental of them. Instead, we refer the reader to five monographs devoted to this problem.^{6,8–13} We will call this approach to adsorption science the “energetic approach”.

One can also identify another, distinctly different approach in adsorption research, we call it the “geometric approach”.¹⁴ Here geometric surface heterogeneities are the focus of interest, and the accompanying energetic heterogeneity is ignored as a rule.

For decades, theoretical studies of adsorption on heterogeneous solid surfaces followed either the “energetic” or the “geometric” approach. However, a feeling has grown that there must exist some fundamental relationship between the adsorption energy distribution and the pore size distribution function. In the case of adsorption in mesopores, where capillary condensation takes place, the Kelvin equation is known to relate the pore size distribution to the distribution of the free energies of adsorption. In 1976, Everett and Powl¹⁵ made the first attempt to look for that kind of relationship in the case of adsorption in micropores. Substantial progress was made at the beginning of the 1980s when Horvath and Kawazoe,¹⁶ Gregg and Sing,¹⁴ and other authors^{17–20} developed relationships between pore dimensions and the free energy of adsorption for pores of various geometries. Using such correlations, one may now calculate the adsorption energy distribution from an experimental adsorption isotherm.^{21–24}

However, despite the large variety of pore distributions which one may have to deal with, for all adsorption systems there exists a universal function describing the adsorption energy distribution, as was shown by Cerofolini and by Rudzinski and Everett. This would suggest that there should also exist some universal

function describing the geometric surface heterogeneity of the many adsorption systems.

The break-through came in 1983 with the application of fractal geometry concepts by Avnir and Pfeifer^{25,26} to describe the general features of surface geometric heterogeneity in adsorption systems showing a small degree of surface organization.

The amazing thing about this fractal approach was that it offered a simple universal function to describe the pore size distribution. Only one parameter is required—the “fractal dimension” D —varying between 2 for flat, and 3 for “fuzzy”, irregular surfaces. Numerous adsorption experiments provided convincing proof for the applicability of the simple expressions offered by the fractal approach.^{27–29}

The fractal approach is applicable even in the case of almost ideally flat surfaces, like graphitized carbons, yielding the correct value $D \approx 2$. That means that even in the case of surfaces which are believed to be flat and homogeneous, a certain degree of surface irregularity exists. This has been confirmed by surface images obtained using STM and AFM microscopes. Generally speaking, at a molecular scale, real solid surfaces are less well organized than was previously supposed.

The simplicity and the general applicability of the fractal approach attracted much interest among surface scientists at the end of the 1980s. A rapid decline of interest in this approach followed at the beginning of the 1990s. There are a number of reasons for that. In the end, that approach to surface heterogeneity resulted in a relatively small number of papers offering equations for adsorption isotherms.^{30–52} The situation was reviewed recently by C.-K. Lee, and S.-L. Lee.⁵³ More recently, interesting results have been published by Terzyk et al.^{54–58} One reason for this decline might be the growing number of the papers reporting deviations from the assumed fractal behavior, or showing a limited range for its applicability, though in fact Avnir and Pfeifer themselves have always emphasized that fractal behavior will be observed only in a certain range of pore radii.⁵⁹

Another reason is more fundamental. Adsorption experiments interpreted in this way provide only a single number—the fractal dimension D —characterizing the degree of surface geometric irregularity. No fundamental paper has been published so far that would offer a simple and general way of relating the methods of statistical thermodynamics to that fractal dimension. The paper by Cole et al.³¹ is an example showing how difficult it is to do this even in the relatively simple case of evaluating Henry's constant. The one example of a successful application of the fractal concept, leading to simple results, are the papers on multilayer adsorption on fractal surfaces (the “fractal” FHH isotherm).^{38,39,40,44}

The wide applicability of the fractal approach to adsorption systems and at the same time its limited utility in almost every case, brings one to the following conclusion: solid surfaces are never perfectly regular and never totally irregular (fractal). Real solid surfaces represent an intermediate case. We will call them “partially correlated”.

In this paper we develop a simple generalized approach to such partially correlated surfaces. This approach reduces to the classical fractal approach in the limit of small pore radii, or when $D = 3$. Next, it is shown that there exists a functional relationship between geometric and energetic surface heterogeneities. By applying that relationship it is shown that the generalized pore size distribution developed here from the modified fractal approach becomes the generalized adsorption energy distribution, developed earlier by Cerofolini, Rudzinski,

and Everett using the “energetic” approach. In that way a bridge is built between the “energetic”, and the “geometric” approaches to adsorption on the heterogeneous surfaces of real solids.

Theory

1. Empirical Isotherm Equations and the Integral Equation Approach. 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 approach, the observed adsorption isotherm θ_i is formulated as the following average:

$$\theta_i(p, T) = \int_0^\infty \theta(\epsilon, p, T) \chi(\epsilon) d\epsilon \quad (1)$$

where p is the equilibrium bulk pressure, T is the absolute temperature, and ϵ is the local adsorption energy on a certain part of the solid surface. $\theta(\epsilon, p, T)$ is one of the classical adsorption isotherms, developed for an energetically homogeneous surface, and $\chi(\epsilon)$ is a normalized differential energy distribution function which describes the distribution of surface areas among the corresponding values of adsorption energies.

It is generally believed that the dispersion of the adsorption energy, $\chi(\epsilon)$, is due to a geometric disorder existing on the solid surfaces. As that disorder might be due to various factors, such as the chemical composition of the adsorbent, its preparation, etc., it was surprising to find that the adsorption isotherms $\theta_i(p, T)$ measured in a variety of the adsorption systems could be described by a few empirical equations.

One such isotherm was the empirical Freundlich equation (F) launched in 1909, and its generalized form, the Langmuir–Freundlich equation (LF),

$$\theta_i(p, T) = \frac{K_L p^{\alpha k T}}{1 + K_L p^{\alpha k T}}, \quad 0 < \alpha k T < 1 \quad (2)$$

launched first by Bradley⁶ in 1927. The first attempts to rationalize this empirical equation were made in 1948 by Sips⁶ using the integral eq 1. Also a kinetic derivation of that equation was proposed in 1974 by Cricmore and Wojciechowski.⁶⁰

The LF equation was frequently applied to correlate experimental isotherms of adsorption on what were believed to be nonporous solids, although other formulas have also been used for that purpose.^{6,11,13}

In the case of adsorption by porous adsorbents, activated carbons, for instance, the Dubinin–Radushkevich (DR) equation has been used successfully for decades,

$$\theta_i(p, T) = \exp \left\{ - \left(\frac{kT}{E} \right)^2 \left[\ln \frac{p_0}{p} \right]^2 \right\} \quad (3)$$

Here p_0 was commonly taken as the saturated vapor pressure p_s while E is a fitted constant.

It was also noted that the kinetics of adsorption observed in many adsorption systems can be well described by two empirical formulas: the Elovich and power-law equations.⁷ Besides these examples there are many other, less frequently discussed similarities in the behavior of obviously different gas/solid systems. In view of this it is reasonable to suppose that the heterogeneity of various real solid surfaces must have some common features, independent of the crystallography, chemical composition, and in general the “nature” of the adsorbent. Cerofolini⁹ was the first to show that these general features of

adsorption on heterogeneous solid surface can conveniently be analyzed by using the condensation approximation (CA) approach.

The CA method is based on the postulate that in the case of adsorption on energetically heterogeneous solid surfaces, adsorption on various areas of the surface proceeds from high-to-low energy areas with increasing surface pressure (coverage). There exists a sharp “adsorption front” on the adsorption areas characterized by a “critical” adsorption energy ϵ_c , such that all sites with $\epsilon > \epsilon_c$ are covered, whereas the remaining areas with $\epsilon < \epsilon_c$ are empty. That means that the “local” adsorption isotherm, $\theta(\epsilon, p, T)$, can be represented by the following step function, $\theta_c(\epsilon, p, T)$

$$\theta_c(\epsilon, p, T) = \begin{cases} 1 & \text{for } \epsilon \geq \epsilon_c(p, T) \\ 0 & \text{for } \epsilon < \epsilon_c(p, T) \end{cases} \quad (4)$$

where ϵ_c is found from the condition,⁶

$$\left(\frac{\partial^2 \theta}{\partial \epsilon^2} \right)_{\epsilon = \epsilon_c} = 0 \quad (5)$$

As a consequence, the integral eq 1 can be rewritten in the following form,

$$\theta_i(p, T) = \int_{\epsilon_c}^\infty \chi(\epsilon) d\epsilon \quad (6)$$

According to eq 5, for the Langmuir adsorption isotherm $\theta(\epsilon, p, T)$

$$\theta(\epsilon, p, T) = \frac{Kp \exp\left(\frac{\epsilon}{kT}\right)}{1 + Kp \exp\left(\frac{\epsilon}{kT}\right)} \quad (7)$$

the function ϵ_c takes the form,

$$\epsilon_c = -kT \ln Kp \quad (7a)$$

It takes a similar form for other “classical” adsorption isotherms (for example, that of Volmer, etc.), so that the following conclusions are not limited solely to the Langmuir model of adsorption.

2. Attempts to Rationalize the Adsorption Energy Distributions Recovered from the Empirical Adsorption Isotherms. One intriguing discovery was made by Hobson in 1968. Hobson⁶¹ reported that, at very low surface coverages, where the LF empirical isotherm (eq 2) fails, the Dubinin–Radushkevich equation appears to correlate the experimental isotherms of adsorption on nonporous surfaces very well. Soon more such examples were being reported in the literature.⁶ This could be taken to mean, that low coverage adsorption on nonporous surfaces, and adsorption in porous solids must have some fundamental features in common. That idea lead to initial attempts to formulate the general features of energetic surface heterogeneity of solid surfaces.

From the observation that at low surface coverages the applicable isotherm θ_i is the Freundlich isotherm, while at still lower coverages, on the same adsorbent, θ_i commonly starts obeying the Dubinin–Radushkevich isotherm, Cerofolini put forward the suggestion that these two expressions are particular forms of some more general isotherm equation, one governing adsorption on all energetically heterogeneous solid surfaces.⁹

He followed the already accepted viewpoint, documented by fundamental theoretical consideration and computer simulations,

that ideally smooth surfaces can exist only at $T = 0$ K. At finite temperatures, the formation of a rough surface begins by the displacement of surface atoms into higher energy states. Cerofolini assumed, that the lowest energy u_0 corresponds to a fully coordinated site on the crystal face with the densest packing. Atoms on a rough surface have an “excess energy” $u^{(ex)}$, relative to u_0 . Consideration of the relationship between the roughness of a surface and its adsorptive properties led Cerofolini to postulate that the number of N_i atoms with the excess energy $u_{i(ex)}$ is related to the number N_0 of the atoms in the ground level u_0 by the Boltzman distribution,^{6,9}

$$\frac{N_i}{N_0} = \exp\left(-\frac{u_i^{(ex)}}{kT_f}\right) \quad (8)$$

where T_f is a certain characteristic temperature, not far from the melting temperature. Next Cerofolini expressed the relation between $u^{(ex)}$ and ϵ by using its formal Taylor expansion.

$$u^{(ex)} = \alpha'(\epsilon - \epsilon_0) + \beta'(\epsilon - \epsilon_0)^2 + \dots \quad (9)$$

where α' and β' must be positive for physical reasons. Then,

$$\chi(\epsilon) = \frac{\partial(N/N_0)}{\partial u^{(ex)}} \left(\frac{du^{(ex)}}{d\epsilon} \right) \quad (10)$$

After normalizing this function upon $(\epsilon_0, +\infty)$, he obtained the following expression for $\chi(\epsilon)$

$$\chi(\epsilon) = [\alpha + 2\beta(\epsilon - \epsilon_0) + \dots] \exp\{-\alpha(\epsilon - \epsilon_0) - \beta(\epsilon - \epsilon_0)^2 + \dots\} \quad (11)$$

where

$$\alpha = \frac{\alpha'}{kT_f}, \quad \text{and} \quad \beta = \frac{\beta'}{kT_f} \quad (11a)$$

ϵ_0 in the Cerofolini's derivation is the lowest adsorption energy on a given solid surface.

Applying the CA approach, eq 6, one arrives at the following general adsorption isotherm,

$$\theta_i(p, T) = \exp\{-\alpha(\epsilon_c - \epsilon_0) - \beta(\epsilon_c - \epsilon_0)^2 + \dots\} \quad (12)$$

At higher adsorbate pressures, where $\alpha(\epsilon_c - \epsilon_0) \gg \beta(\epsilon_c - \epsilon_0)^2$, eq 12 reduces to the Freundlich isotherm.

$$\theta_i = \exp\{-\alpha(\epsilon_c - \epsilon_0)\} = K_L p^{\alpha kT} \quad (13)$$

where

$$K_L = \left[K \exp\left(\frac{\epsilon_0}{kT}\right) \right]^{\alpha kT} \quad (13a)$$

When $\alpha(\epsilon_c - \epsilon_0) \ll \beta(\epsilon_c - \epsilon_0)^2$, which may happen at very low adsorbate pressures, eq 12 becomes the Dubinin–Radushkevich isotherm,

$$\theta_i = \exp\{-\beta(\epsilon_c - \epsilon_0)^2\} = \exp\left\{-\left(\frac{kT}{E}\right)^2 \left[\ln\left(\frac{p_0}{p}\right)\right]^2\right\} \quad (14)$$

in which

$$\beta = \frac{1}{E^2} \quad \text{and} \quad \ln p_0 = -\ln K - \epsilon_0/kT \quad (14a)$$

Notice that Cerofolini's development does not explain the energetic origin of the Langmuir–Freundlich isotherm (eq 2).

Rudzinski and Everett⁶ have further modified Cerofolini's concept by assuming that surface atoms are in different energy states u_i , but their chemical potential μ is the same throughout the system. The occupancy of the energy states is given by the Fermi–Dirac distribution because surface atoms are localized and distinguishable by their Cartesian coordinates,

$$N_i = \left[1 + \exp\left(\frac{u_i - \mu}{kT_f}\right) \right]^{-1} \quad (15)$$

where T_f is the temperature which could have led to the formation of the actual heterogeneous solid surface. The heterogeneous surfaces are therefore considered to be “frozen in states”, equilibrium structures representing conditions at an imaginary temperature.⁶

The function $(u_i - \mu)/kT_f$ is now written as its Taylor expansion, as in Cerofolini's eq 9. This led Rudzinski and Everett to the following adsorption energy distribution,

$$\chi(\epsilon) = \frac{[\alpha + 2\beta(\epsilon - \epsilon_0) + \dots] \exp\{\alpha(\epsilon - \epsilon_0) + \beta(\epsilon - \epsilon_0)^2 + \dots\}}{[1 + \exp\{\alpha(\epsilon - \epsilon_0) + \beta(\epsilon - \epsilon_0)^2 + \dots\}]^2} \quad (16)$$

normalized to unity upon the $(-\infty, +\infty)$ energy limits. Now, ϵ_0 no longer represents the minimum energy of adsorption found on the surface.

In the region of smaller adsorption energies such that $\alpha \gg 2\beta(\epsilon - \epsilon_0)$, eq 16 becomes the Gaussian-like adsorption energy distribution

$$\chi(\epsilon) = \frac{\alpha \exp\{\alpha(\epsilon - \epsilon_0)\}}{[1 + \exp\{\alpha(\epsilon - \epsilon_0)\}]^2} \quad (17)$$

centered at $\epsilon = \epsilon_0$.

Application of the CA approach (eq 6) yields the Langmuir–Freundlich isotherm,

$$\theta_i = \frac{\exp\{\alpha(\epsilon_0 - \epsilon_c)\}}{1 + \exp\{\alpha(\epsilon_0 - \epsilon_c)\}} = \frac{K_L p^{\alpha kT}}{1 + K_L p^{\alpha kT}} \quad (18)$$

This happens at higher adsorbate pressures such that $\alpha \gg 2\beta(\epsilon_c - \epsilon_0)$. At lower adsorbate pressures, when adsorption is taking place on higher-energy sites, and the exponential term in the denominator is much smaller than unity, adsorption is governed by the $\chi(\epsilon)$ function defined in eq 11. In this way we come to the conclusion that one should observe the following sequence of applicability of the empirical isotherm equations as the adsorbate pressure (surface coverage) decreases.

Langmuir–Freundlich \rightarrow Freundlich \rightarrow

Dubinin–Radushkevich

We see that the “energetic” approach is able to explain the origin of all the empirical equations and the sequence of their applicability from low to higher adsorbate pressures. We will postpone discussion of the adsorption isotherms at still higher adsorbate pressures, where multilayer adsorption and capillary condensation may take place. Limiting discussion to submonolayer adsorption should make it easier to study the relationship between geometric and energetic heterogeneities. These two approaches have developed along two separate paths, with a

slowly growing exchange of ideas. At this point we are still far from understanding the fundamental relationship between energetic and geometric heterogeneities of real solid surfaces but it seems reasonable to assume that a fundamental relationship does exist. Moreover, there are good reasons to presume that the relationship should be simple. Consider the following justification for such a hypothesis.

Considerations of the general features of the energetic heterogeneities were based on simple assumptions and led to simple expressions for the general form of adsorption energy distribution $\chi(\epsilon)$. In the same way, looking at a fractal picture of geometric surface heterogeneities leads to simple expressions for pore size distribution.

It seems therefore reasonable that there should be a simple relationship between the energetic and geometric surface heterogeneities. A kind of mapping of energy heterogeneity onto geometric heterogeneity. Keller,⁴⁸ as well as Giona et al.⁵¹ and Ehrburger–Dolle,⁵² for instance, arrived at the conclusion that it is the fractal nature of a heterogeneous solid surface that may be the source of the Freundlich, and more generally the power-law expressions, which describe the behavior of experimental adsorption isotherms.

3. Functional Relationship between the Geometric and the Energetic Surface Heterogeneities. In considering this issue, we focus our attention on works offering a simple expression for the general form of a pore volume distribution on fractal surfaces. We recall that the basic property of fractal surfaces is that the number of (spherical) molecules n , necessary to cover such surfaces with a monolayer blanket, scales with their radius r , according to

$$n \sim r^{-D} \quad (19)$$

where D is the fractal dimension of the surface accessible for adsorption. The volume of this blanket V therefore scales as

$$V \sim r^3 r^{-D} = r^{3-D} \quad (20)$$

The pore walls create local minima in the gas–solid interaction potential–adsorption sites. Every adsorption site is in turn associated with a certain volume, so that the total volume of the blanket can be divided into subvolumes, each of them associated with one adsorption site. Thus, the total number of adsorption sites N , should be proportional to V .

It is known that gas–solid interactions are related to the curvature of the pore; therefore, we can write,

$$\frac{\partial N}{\partial \epsilon} \sim \left(\frac{\partial V}{\partial r} \right) \frac{dr}{d\epsilon} = C(3-D)r^{2-D} \left(\frac{dr}{d\epsilon} \right) \quad (21)$$

where C is a proportionality constant. Recall that, in the development of the fractal approach to adsorption on solids, it was usually assumed that fractal features are manifested only in the case of pores having radii smaller than $r = r_m$. This implies that the normalized pore size distribution $\rho(r)$ should have the following form:

$$\rho(r) = \frac{3-D}{r_m^{3-D}} r^{2-D} \quad (22)$$

The reported results in the literature considerations suggest that the function $r(\epsilon)$ behaves like an exponentially decreasing function.^{15–20} Therefore, we postulate the following relationship to exist:

$$r = e^{-F(\epsilon)} \quad (23)$$

where $F(\epsilon)$ is a function of ϵ describing the individual features of the adsorption system under consideration. We replace the function $F(\epsilon)$ by its Taylor expansion around $\epsilon = \epsilon_0$,

$$F(\epsilon) = F(\epsilon_0) + \left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \frac{1}{2} \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0)^2 + \dots \quad (24)$$

Thus, $(\partial N / \partial \epsilon)$ now takes the form,

$$-\left(\frac{\partial N}{\partial \epsilon} \right) = C(3-D)r^{3-D} \frac{dF}{d\epsilon} = C \left[\left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} + \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \dots \right] \exp \left\{ -(3-D) \left[F(\epsilon_0) + \left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \frac{1}{2} \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0)^2 + \dots \right] \right\} \quad (25)$$

After normalizing the function $(\partial N / \partial \epsilon)$ between the energy limits $(\epsilon_1, +\infty)$, it becomes the function $\chi(\epsilon)$,

$$\xi \int_0^\infty \left(\frac{\partial N}{\partial \epsilon} \right) d\epsilon = 1 \quad (26)$$

and the normalization factor ξ reads,

$$\xi = [C r_m^{3-D}]^{-1} \quad (27)$$

where $r_m = r(\epsilon = \epsilon_1)$. Finally, the general form of the adsorption energy distribution on fractal surfaces takes the form,

$$\chi(\epsilon) = (3-D) \left(\frac{r_0}{r_m} \right)^{(3-D)} \left[\left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} + \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \dots \right] \exp \left\{ -(3-D) \left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} (\epsilon - \epsilon_0) - \frac{1}{2} (3-D) \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0)^2 + \dots \right\} \quad (28)$$

where $r_0 = r(\epsilon_0)$.

The function $\chi(\epsilon)$ in eq 28 has the same form as that of the Cerofolini's adsorption energy distribution in eq 11, which was developed using “energetic” arguments, though function in eq 28 was developed using “geometric” arguments based on theories of adsorption on fractal surfaces.

Our “geometric” derivation of the energy distribution explains Hobson's surprising observation^{6,61} that the DR equation, which describes adsorption in porous sorbents, also describes adsorption on “flat” surfaces at very low adsorbate pressures (surface coverages). It seems that “flat” solid surfaces, which are believed to be nonporous, are in fact porous on a molecular scale. Therefore, even if D is close to 2, there will exist a distribution of “pore” sizes, and a “micropore” region which will first be covered at the smallest pressures. According to the CA approach, adsorption first starts on these highest energy sites, which according to eq 23 are located in micropores. In that case, $(\partial^2 F / \partial \epsilon^2)_{\epsilon_0} (\epsilon_c - \epsilon_0) \gg (\partial F / \partial \epsilon)_{\epsilon_0}$, and adsorption is described by the DR equation

$$\theta_t(p, T) \approx \left(\frac{r_0}{r_m} \right)^{3-D} \exp \left\{ -\frac{1}{2} (3-D) \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (kT)^2 \left[\ln \frac{p_0}{p} \right]^2 \right\} \quad (29)$$

where p_0 is still defined by eq 14a, and the variance E of the

corresponding $\chi(\epsilon)$ is given by

$$E = \left[\frac{2}{(3-D) \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0}} \right]^{1/2} \quad (29a)$$

Equation 29a correctly predicts what should be expected by considering obvious physical arguments: the more porous the surface (i.e., the larger the fractal dimension D) the more energetically heterogeneous it should be. In eq 29a, if D increases, the variance E of the corresponding function $\chi(\epsilon)$ increases too.

At higher adsorbate pressures, such that $(\partial^2 F / \partial \epsilon^2)_{\epsilon_0}(\epsilon_c - \epsilon_0) \ll (\partial F / \partial \epsilon)_{\epsilon_0}$, adsorption is governed by an exponentially decreasing function $\chi(\epsilon)$, defined in eq 11, which combined with the CA approach (eq 6) yields the Freundlich isotherm,

$$\theta_t(p, T) = \left(\frac{r_0}{r_m} \right)^{3-D} \left(\frac{p}{p_0} \right)^{\alpha kT} \quad (30)$$

where

$$\alpha = \left[(3-D) \left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} \right] \quad (30a)$$

Thus, again we observe behavior that is consistent with the idea that when a surface becomes more porous (i.e., the fractal dimension D grows), it becomes more energetically heterogeneous.

4. Pore Size Distribution of the Actual Heterogeneous Solid Surfaces, and the Related Adsorption Energy Distribution Function. According to the above development, the fractal nature of a real solid surfaces will cause the appearance of pressure (coverage) regimes where the Freundlich or the DR behavior will be observed. However, the fractal pore size distribution in eq 22, combined with the postulated functional relationship in eq 23, does not predict the transition of the Freundlich isotherm into the Langmuir–Freundlich isotherm at higher pressures (surface coverages) when adsorption proceeds in larger and larger pores. This is just another evidence for that the classical fractal pore distribution (eq 22) cannot be applied for pores having pore radii larger than a certain value $r = r_m$.

The problem of the limits (r_1, r_m) of the applicability of the fractal approach received remarkable attention of the scientists applying that approach. Certain theoretical considerations have brought Pfeifer⁶² to the conclusion that $r_m/r_1 > 2^{1/D}$. Recently Terzyk et al.^{54–58} have proposed a method to estimate r_1, r_m as best-fit parameters of their new fractal isotherm, used to fit experimental data.

While accepting the classical fractal pore distribution (eq 22), along with its limited range of applicability (r_1, r_m), one can describe only a part of an experimental adsorption isotherm corresponding to pressures at which pore filling proceeds in pores having dimensions larger than r_1 but smaller than r_m . The important experimental finding discussed below suggests another yet way to overcome the problem of the limited applicability of the classical fractal approach.

We will soon demonstrate that in order to arrive at the Langmuir–Freundlich isotherm, one has to assume that the fractal relationship in eq 20 represents a limit, when pore size goes to zero, of the following more general expression:

$$N = \frac{C r^{3-D}}{1 + r^{3-D}} \quad (31)$$

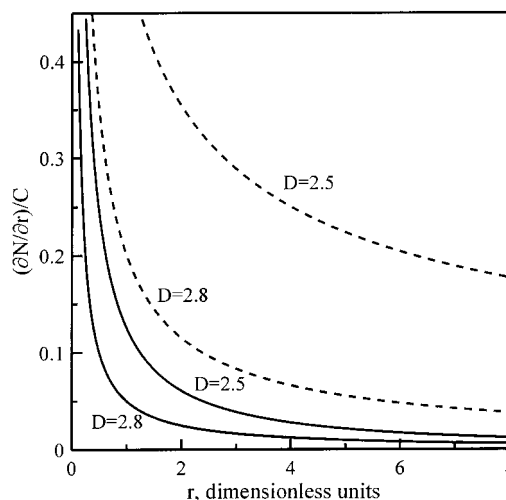


Figure 1. Comparison of our modified fractal pore size distribution $(\partial N / \partial r)$ defined in eq 32 (—), with the “classical” pore distribution $(3-D)r^{2-D}$ (---).

In the limit $r \rightarrow 0$, eq 31 leads to the linear dependence of N on r^{3-D} , and consequently to eq 22. In the other limit, $r \rightarrow \infty$, N becomes equal to C , i.e., the number of adsorption sites on an ideally flat surface ($D = 2$).

However, according to eq 31,

$$\frac{\partial N}{\partial r} = \frac{C(3-D)r^{2-D}}{[1 + r^{3-D}]^2} \quad (32)$$

Because the Langmuir–Freundlich equation applies at all pressures, the modified fractal pore distribution (eq 32) should apply to pores of all dimensions. Thus, considering r_1 or r_m is no longer necessary. In fact, nature does not like discontinuities. Even in the classical fractal pore size distribution (eq 22), r_1 and r_m should not be considered as “sharp” values, but rather as best-fit “transition” values.

Figure 1 shows the features of the modified fractal pore size distribution, defined in eq 32

We can see that for small pores, i.e., in the limit $r \rightarrow 0$

$$\lim_{r \rightarrow 0} \left(\frac{\partial N}{\partial r} \right) = C(3-D)r^{2-D} \quad (32a)$$

and we have arrived at the classical fractal eq 21. On the other hand, in the limit of $r \rightarrow \infty$,

$$\lim_{r \rightarrow \infty} \left(\frac{\partial N}{\partial r} \right) = C(3-D)r^{D-4} \quad (32b)$$

For physical reasons, r cannot be $r = 0$ because of the finite dimensions of adsorbed molecules. However, accepting the lower limit of r at $r_1 = \exp(-F(\epsilon_m))$, where ϵ_m is the maximum adsorption energy, does not change the form of eq 32. The new normalization constant will only change the value of C

$$C \rightarrow \frac{C}{1 + r_1^{3-D}} \quad (33)$$

Thus, the normalized function $(\partial N / \partial r)$ takes the form,

$$\frac{\partial N}{\partial r} = \frac{(1 + r_1^{3-D})(3-D)r^{2-D}}{(1 + r^{3-D})^2} \quad (34)$$

Now consider the adsorption energy distribution related to $(\partial N / \partial r)$ in eq 32:

$$\frac{\partial N}{\partial \epsilon} = \left(\frac{\partial N}{\partial r} \right) \frac{dr}{d\epsilon} = C(3-D)(1+r_1^{3-D}) \left[\left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} + \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \dots \right] \times$$

$$\frac{\exp \left\{ (3-D)F(\epsilon_0) + (3-D) \left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \frac{3-D}{2} \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0)^2 + \dots \right\}}{\left[1 + \exp \left\{ (3-D)F(\epsilon_0) + (3-D) \left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \frac{3-D}{2} \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0)^2 + \dots \right\} \right]^2} \quad (35)$$

This function, upon normalization, will yield the corresponding function $\chi(\epsilon)$.

The limit $(0, +\infty)$, or more generally $(\epsilon_1, +\infty)$, to normalize the function $(\partial N/\partial \epsilon)$ in eq 25 was dictated by the generally expressed view that above a certain maximum radius $r_m = e^{-F(\epsilon_1)}$, the surface no longer behaves as a fractal surface. Now, if we assume that $N(r)$ in eq 31 is valid for all values of r , including $r = \infty$, then according to eqs 23 and 24, we should apply the integration limits $(-\infty, \epsilon_m)$ to normalize the function $(\partial N/\partial \epsilon)$ in eq 35.

$$\chi(\epsilon) = (3-D) \left[\left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} + \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \dots \right] \times$$

$$\left(\frac{1}{r_0} \right)^{3-D} \frac{\exp \left\{ (3-D) \left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \frac{3-D}{2} \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0)^2 + \dots \right\}}{\left[1 + \left(\frac{1}{r_0} \right)^{3-D} \exp \left\{ (3-D) \left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \frac{3-D}{2} \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0)^2 + \dots \right\} \right]^2} \quad (36)$$

At higher surface coverages, adsorption proceeds in larger and larger pores, with smaller and smaller adsorption energies, i.e., ϵ is getting closer and closer to ϵ_0 . Then, the quadratic terms $\sim (\epsilon - \epsilon_0)^2$ terms in eq 36 become small compared to the first-order terms $\sim (\epsilon - \epsilon_0)$, and the energy distribution (eq 36) becomes essentially the Gaussian-like function (eq 17) which corresponds to the Langmuir–Freundlich isotherm. This isotherm is clearly observed at higher surface coverages in the systems with not too strong tendencies to multilayer adsorption “screening” the plateau of the submonolayer adsorption.⁶ Thus, we summarize our consideration as follows:

To arrive at the Langmuir–Freundlich isotherm, so commonly observed in the behavior of real adsorption isotherms, one has to assume that the pore size distribution in real systems is described by the function (eq 32). That function becomes the classical fractal pore size distribution for small pores.

We could also arrive at eqs 35 and 36 by assuming $r_1 \rightarrow 0$. Using this limit will simplify some of our forthcoming considerations, and the results will retain their correct physical meaning when $r_1 > 0$.

Notice that the $(\partial N/\partial r)$ function defined in eq 32, also reduces to the classical fractal function in eq 22 in the limit $D \rightarrow 3$. That means the classical fractal picture of solid surface is valid when $r \rightarrow 0$, or when $D \rightarrow 3$, or in both these cases. This observation will be very important in our discussion aimed at explaining the physical origin of eq 32.

Thus, by assuming that the geometric heterogeneity of solid surfaces is that described by applying the generalized fractal approach (eq 31), we have arrived at the same adsorption energy distribution (eq 16) that was developed earlier by using the “energetic” approach. Because this general form of adsorption energy distribution describes the observed behavior of experimental isotherms at submonolayer coverage, it can be taken to describe the fundamental features of adsorption on real, heterogeneous, solid surfaces.

As for eq 23, the dependence of r on ϵ is simply an empirical postulate, but accepting it leads to the expression for $\chi(\epsilon)$ in eq

36, which then explains, in a consistent way, the general behavior of experimental adsorption isotherms.

In the limit of high adsorption energies (i.e., small pore sizes), when the unity in the denominator of eq 36 can be neglected compared to the exponential term, $\chi(\epsilon)$ takes the following form,

$$\chi(\epsilon) = (3-D)r_0^{3-D} \left[\left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} + \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0) + \dots \right]$$

$$\exp \left\{ -(3-D) \left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} (\epsilon - \epsilon_0) - \frac{3-D}{2} \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} (\epsilon - \epsilon_0)^2 + \dots \right\} \quad (37)$$

which, except for the constant, is identical with eq 28. From now on, we will take eq 37 as the correct form of $\chi(\epsilon)$ for the region of high adsorption energies.

Now, let us consider the adsorption isotherm corresponding to the adsorption energy distribution in eq 36

$$\theta_t = \left[1 + \left(\frac{1}{r_0} \right)^{3-D} \exp \{ \alpha(\epsilon_c - \epsilon_0) + \beta(\epsilon_c - \epsilon_0)^2 + \dots \} \right]^{-1} \quad (38)$$

where

$$\alpha = (3-D)F'_0 \text{ and } \beta = \frac{3-D}{2}F''_0 \quad (38a)$$

and where we used the following shorter notation

$$\left(\frac{\partial F}{\partial \epsilon} \right)_{\epsilon_0} = F'_0 \text{ and } \left(\frac{\partial^2 F}{\partial \epsilon^2} \right)_{\epsilon_0} = F''_0 \quad (38b)$$

5. Real Solid Surfaces Are Partially Correlated. We start with the following fundamental question: What physical factor causes a systematic deviation of $N(D)$ in eq 31 from the ideal fractal behavior with $N = Cr^{3-D}$?

To answer that question, let us invoke a fundamental feature of fractal structures, namely; the same structure is repeated in every scale. Thus, structures which are seen as macroscopically amorphous, i.e., lacking a surface organization, will also be characterized by this lack of organization at the molecular scale. Now, since the fractal picture is believed to be most applicable to highly amorphous structures, ideally fractal behavior can be related to a lack of correlation at the molecular scale.

Let $\bar{\chi}_2(\epsilon_1, \epsilon_2)$ denote the probability of finding two adjacent sites on a heterogeneous surface; one having the adsorption energy ϵ_1 and the other one having the adsorption energy ϵ_2 . For fully amorphous structures, with no correlations at any scale, $\bar{\chi}_2^{(0)}(\epsilon_1, \epsilon_2)$ will simply be the following product:

$$\bar{\chi}_2^{(0)}(\epsilon_1, \epsilon_2) = \chi^{(0)}(\epsilon_1)\chi^{(0)}(\epsilon_2) \quad (39)$$

Let us assume that some correlation exists. Then

$$\bar{\chi}_2(\epsilon_1, \epsilon_2) = \chi^{(0)}(\epsilon_1)\chi^{(0)}(\epsilon_2)\gamma(\epsilon_1, \epsilon_2) \quad (40)$$

Then a universal form of the adsorption energy distribution found for a partially correlated surface $\chi(\epsilon)$, defined in eq 36, will be given by

$$\chi(\epsilon) = \int_0^\infty \chi^{(0)}(\epsilon_1)\chi^{(0)}(\epsilon_2)\gamma(\epsilon_1, \epsilon_2) d\epsilon_2 \quad (41)$$

Our hypothesis therefore states that a systematic deviation from fractal behavior, described in eq 31, and the corresponding

universal form of the adsorption energy distribution given in eq 36, is a result of the fact that solid surfaces are not ideally fractal but have some degree of surface organization. We will call them the “partially correlated”. We first consider this general conclusion in terms of the correlations between adsorption sites located in pores having different radii r .

Begin by considering again the pore size distribution ($\partial N/\partial r$) in eq 32. Let $\rho_1(r)$ denote this function after normalization to unity between the limits $(0, +\infty)$

$$\rho_1(r) = \frac{(3-D)r^{2-D}}{[1+r^{3-D}]^2} \quad (42)$$

In the limit $r \rightarrow 0$, or $D \rightarrow 3$, for fully uncorrelated, amorphous (fractal) surfaces, the function $\rho_1(r)$ tends to behave like the classical fractal pore size distribution

$$\rho_1^{(0)}(r) \sim (3-D)r^{2-D} \quad (43)$$

Let $\rho_2(r_1, r_2)$ denote the probability of finding two pores; one having radius r_1 , and another one having radius r_2 . For fully uncorrelated (ideally fractal) surfaces, $\rho_2(r_1, r_2) = \rho_2^{(0)}(r_1, r_2)$ will be given by

$$\rho_2^{(0)}(r_1, r_2) = \rho_1^{(0)}(r_1)\rho_2^{(0)}(r_2) \quad (44)$$

Also, let $\xi_2(r_1, r_2)$ denote the pore correlation function such that

$$\rho_2(r_1, r_2) = \rho_1^{(0)}(r_1)\rho_2^{(0)}(r_2)\xi_2(r_1, r_2) = B(3-D)^2 r_1^{2-D} r_2^{2-D} \xi_2(r_1, r_2) \quad (45)$$

where B is the normalization constant over the limits $(0, +\infty)$

$$\int_0^\infty B(3-D)^2 r_1^{2-D} r_2^{2-D} \xi_2(r_1, r_2) dr_1 dr_2 = 1 \quad (45a)$$

The function $\xi_2(r_1, r_2)$ must fulfill the two following conditions:

$$\lim_{r_1, r_2 \rightarrow 0} \xi_2(r_1, r_2) = 1 \quad (46)$$

and

$$\int_0^\infty \rho_2(r_1, r_2) dr_2 = \rho_1(r_1) = \frac{(3-D)r_1^{2-D}}{[1+r_1^{3-D}]^2} \quad (47)$$

After replacing $\rho_2(r_1, r_2)$ by expression 45, we have

$$B \int_0^\infty (3-D)^2 r_1^{2-D} r_2^{2-D} \xi_2(r_1, r_2) dr_2 = \frac{(3-D)r_1^{2-D}}{[1+r_1^{3-D}]^2} \quad (48)$$

One can check that the function $\xi_2(r_1, r_2)$ required to solve the above equation while fulfilling condition 46 has the form,

$$\xi_2 = [1 + r_1^{3-D} + r_2^{3-D}]^{-3} \quad (49)$$

when the normalization constant $B = 2$. We conclude that $\xi_2(r_1, r_2)$ is the desired two-pore correlation function for real solid surfaces.

Figure 2 shows the behavior of this correlation function.

Now, consider the site-pair correlation function $\gamma_2(\epsilon_1, \epsilon_2)$ in eq 40. As fractal behavior is observed in the limit $r \rightarrow 0$, i.e., in the limit $\epsilon \rightarrow \infty$, we take the function $\chi(\epsilon)$ in eq 37 to represent $\chi^0(\epsilon)$ after an appropriate constant is introduced. At the same time, we take $\chi(\epsilon)$ in eq 36 to represent $\chi(\epsilon)$ on the left-hand

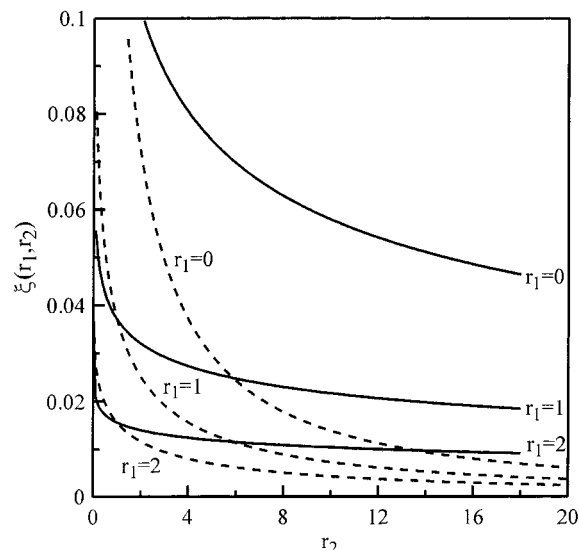


Figure 2. Behavior of the two-pore correlation function defined in eq 49 (---) $D = 2.8$, (—) $D = 2.5$.

side of eq 40. With that it can be shown that the function $\gamma_2(\epsilon_1, \epsilon_2)$ solving eq 41 has the form,

$$\gamma(\epsilon_1, \epsilon_2) = \left[1 + r_0^{3-D} \exp \left\{ - (3-D)F'_0(\epsilon_1 - \epsilon_0) - \frac{3-D}{2} F''_0(\epsilon_1 - \epsilon_0)^2 + \dots \right\} + r_0^{3-D} \exp \left\{ - (3-D)F'_0(\epsilon_2 - \epsilon_0) - \frac{3-D}{2} F''_0(\epsilon_2 - \epsilon_0)^2 + \dots \right\} \right]^{-3} \quad (50)$$

and the integral in eq 41 has to be multiplied by the normalization factor $B = 2$. This function is also obtained from $\xi_2(r_1, r_2)$ in eq 49, by expressing r in terms of ϵ using eqs 23 and 24.

Notice that the correlation function $\gamma_2(\epsilon_1, \epsilon_2)$ is a function of the same parameters ($r_0, \epsilon_0, D, F'_0, F''_0$) that appear in equations for the one-site distribution function $\chi(\epsilon)$. Thus, the surface topography characterized by the two-site correlation function $\gamma_2(\epsilon_1, \epsilon_2)$ is not an independent actor on the scene, as was previously assumed in theories of adsorption on energetically heterogeneous surfaces, but is related to the degree of the dispersion of adsorption energies.

Finally, let us consider the effect of the interactions between the adsorbed molecules. The result of this consideration will provide more proof that eq 31 has its origins in the partial correlations present in surface structure. We use the MFA (mean field approximation) to examine this issue.

In the case of the Langmuir model of adsorption MFA leads to the well-known generalization of the Langmuir equation, called the Bragg–Williams isotherm. Let us take this isotherm to be the local isotherm $\theta(\epsilon, p, T)$ under the integral in eq 1.

$$\theta(\epsilon, p, T) = \frac{Kp \exp\left(\frac{\epsilon}{kT} + \frac{z\omega f}{kT}\right)}{1 + Kp \exp\left(\frac{\epsilon}{kT} + \frac{z\omega f}{kT}\right)} \quad (51)$$

where the form of the function “ f ” depends on the topography of the heterogeneous solid surface.⁶ In the case of a patchwise topography (highly correlated surface structure) $f = \theta(\epsilon, p, T)$, whereas in the case of the fully random (fractal) surfaces $f = \theta(p, T)$. Furthermore, “ z ” is the number of adsorption sites which are nearest neighbors of a selected adsorption site (the coordination number) and “ ω ” is the energy of interaction between two

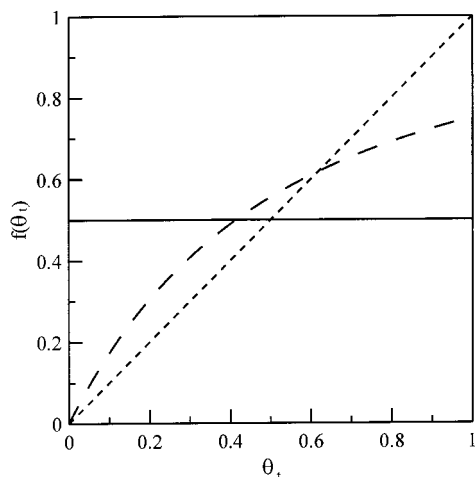


Figure 3. The solid line represents $f = 1/2$ (—) for the highly correlated (patchwise) surface topography, the slightly broken line (—) is the function $f = [1 - 1/(1 + \theta_t)^2]$, and the strongly broken line (- -) is the function $f = \theta_t$ for the fully random (fractal) surface.

molecules adsorbed on neighboring adsorption sites. Now, we apply the CA approach, i.e., eq 6 to evaluate $\theta_t(p, T)$

By applying eq 6 to eq 51 we find two $\epsilon_c(p, T)$ functions. For the patchwise (*highly correlated*) topography $\epsilon_c = \epsilon_c(p)$ takes the following form:⁶

$$\epsilon_c^{(p)} = -kT \ln Kp - z\omega \frac{1}{2} \quad (52)$$

whereas for the random (*weakly correlated*) topography we have⁶

$$\epsilon_c^{(r)} = -kT \ln Kp - z\omega \theta_t \quad (53)$$

We now proceed to calculate the function $\epsilon_c = \epsilon_c^{(c)}$ for the intermediate model of *partially correlated* (c) surfaces. If our hypothesis that eq 31 has its origin in the partial correlations of surface structure is correct, the $z\omega$ in the additional interaction term for these cases should be multiplied by a function lying between $1/2$ and θ_t . This, in fact, appears to be the case. We have shown in the Appendix that

$$\epsilon_c^{(c)} = -kT \ln Kp - \omega z \left[1 - \frac{1}{(1 + \theta_t)^2} \right] \quad (54)$$

Compare the three interaction terms in the ϵ_c functions defined in eqs 52–54. In Figure 3, these three interaction terms are shown as functions of the total surface coverage θ_t .

Looking at Figure 3 we can see that the value of the interaction term in the function $\epsilon_c^{(c)}$ corresponding to our model of a solid surface lies between the two extreme values $1/2$ and θ_t corresponding to highly correlated (patchwise) surface, and the totally uncorrelated (fractal) surface. Our model of the surface is therefore intermediate between those two and agrees with what one would expect from a partially correlated surface.

Of course, spatial (distance) correlations between two pores having certain radii, or between two adsorption sites having certain adsorption energies exist practically at finite distances. That means, that the postulated modified fractal function 31 takes these features into account implicitly.

The generalized isotherm equation taking into account the interaction between the adsorbed molecules is obtained by replacing ϵ_c in eq 38, with the function $\epsilon_c^{(c)}$ defined in eq 73. In

this way, a nonlinear equation for $\theta_t(p, T)$ is obtained. This final form can be easily solved to calculate θ_t as a function of pressure p and temperature T .

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Appendix

We consider the probability of finding, in the vicinity of a fixed adsorption site having energy ϵ_1 , another adsorption site having adsorption energy ϵ_2 . That probability is proportional to $\chi_2(\epsilon_1, \epsilon_2)$. Let us consider this probability in a form normalized to unity with respect to the variable ϵ_2 . That probability, $P(\bar{\epsilon}_1, \epsilon_2)$, now takes the form

$$P(\bar{\epsilon}_1, \epsilon_2) = \frac{\chi^0(\bar{\epsilon}_1) \chi^0(\epsilon_2) \gamma(\bar{\epsilon}_1, \epsilon_2)}{\chi(\bar{\epsilon}_1)} \quad (A.1)$$

where $\chi(\epsilon)$ is given by eq 36, $\chi^0(\epsilon)$ is given in eq 37, and $\gamma(\epsilon_1, \epsilon_2)$ is given in eq 50.

Now, consider the contribution to the total energy of interaction of a molecule adsorbed at a site having adsorption energy $\bar{\epsilon}_1$, due to its interactions with the nearest-neighbor molecules adsorbed on the sites having adsorption energy between ϵ_2 and $(\epsilon_2 + d\epsilon_2)$. This contribution is given by $z\omega \theta(\epsilon_2) P(\bar{\epsilon}_1, \epsilon_2) d\epsilon_2$. Therefore, the total energy of interaction with all the neighboring molecules is given by

$$z\omega \int_{-\infty}^{+\infty} \theta(\epsilon_2) P(\bar{\epsilon}_1, \epsilon_2) d\epsilon_2 = z\omega f(\bar{\epsilon}_1) = \frac{z\omega \chi^0(\bar{\epsilon}_1)}{\chi(\bar{\epsilon}_1)} \int_{-\infty}^{+\infty} \theta(\epsilon_2) \chi^0(\epsilon_2) \gamma(\bar{\epsilon}_1, \epsilon_2) d\epsilon_2 \quad (A.2)$$

Next, we use the CA approach to calculate the integral in eq A.2

$$\int_{-\infty}^{+\infty} \theta(\epsilon_2) \chi^0(\epsilon_2) \gamma(\bar{\epsilon}_1, \epsilon_2) d\epsilon_2 = \int_{\epsilon_c}^{+\infty} \chi^0(\epsilon_2) \gamma(\bar{\epsilon}_1, \epsilon_2) d\epsilon_2 = \left[1 + r_0^{3-D} \exp \left\{ -(3-D) F'_0(\bar{\epsilon}_1 - \epsilon_0) - \frac{3-D}{2} F''_0(\bar{\epsilon}_1 - \epsilon_0)^2 + \dots \right\} + \right]^{-2} \Big|_{\epsilon_c}^{+\infty} + r_0^{3-D} \exp \left\{ -(3-D) F'_0(\epsilon_2 - \epsilon_0) - \frac{3-D}{2} F''_0(\epsilon_2 - \epsilon_0)^2 + \dots \right\} \quad (A.3)$$

Now, by the definition of θ_t in eq 38, we have

$$r_0^{3-D} \exp \left\{ -(3-D) F'_0(\epsilon_c - \epsilon_0) - \frac{3-D}{2} F''_0(\epsilon_c - \epsilon_0)^2 + \dots \right\} = \frac{\theta_t}{1 - \theta_t} \quad (A.4)$$

From eqs A.3 and A.4 we have

$$\int_{\epsilon_c}^{+\infty} \chi^0(\epsilon_2) \gamma'(\bar{\epsilon}_1, \epsilon_2) d\epsilon_2 =$$

$$\left[1 + r_0^{3-D} \exp \left\{ -(3-D) F'_0 (\bar{\epsilon}_1 - \epsilon_0) - \frac{3-D}{2} F''_0 (\bar{\epsilon}_1 - \epsilon_0)^2 + \dots \right\} \right]^{-2} -$$

$$\left[1 + r_0^{3-D} \exp \left\{ -(3-D) F'_0 (\bar{\epsilon}_1 - \epsilon_0) - \frac{3-D}{2} F''_0 (\bar{\epsilon} - \epsilon_0)^2 + \dots \right\} + \frac{\theta_t}{1-\theta_t} \right]^{-2} \quad (\text{A.5})$$

For the model of surface (partially correlated) topography considered here, the related expression for $\epsilon_c = \epsilon_c^{(c)}$, takes the form

$$\epsilon_c^{(c)} = -kT \ln Kp - \omega z f(\epsilon = \epsilon_c) \quad (\text{A.6})$$

where $f(\epsilon_c)$ is obtained by replacing $\bar{\epsilon}_1$ by ϵ_c in eq A.2. Equation A.3 is now inserted into eq A.2, in which

$$\frac{\chi^0(\epsilon_c)}{\chi(\epsilon_c)} = \left[1 + r_0^{3-D} \exp \left\{ -(3-D) F'_0 (\epsilon_c - \epsilon_0) - \frac{3-D}{2} F''_0 (\epsilon_c - \epsilon_0)^2 + \dots \right\} \right]^2 = \left[\frac{1}{1-\theta_t} \right]^2 \quad (\text{A.7})$$

Applying the definition of θ_t in eq A.4 to eqs A.5 and A.6, and inserting the results into eq A.2, we finally arrive at the expression for $\epsilon_c^{(c)}$ in eq 54.

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