

The Generalized Gaussian Model for Heterogeneous Surfaces: Achievements and Perspectives

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The statistical description of heterogeneous solid surfaces is reviewed in terms of the Generalized Gaussian Model. Two versions of the model, the continuous and lattice-gas versions, are analyzed. The effects of the adsorptive energy topography on surface processes like adsorption and surface diffusion, as predicted by the model, are thoroughly discussed.

1. INTRODUCTION

The role of the adsorptive surface characteristics in many processes of practical importance is a topic of increasing interest in surface science. Adsorption, surface diffusion and reactions on catalysts are some of the phenomena which are strongly dependent upon surface structure. Most materials have heterogeneous surfaces which, when interacting with gas molecules, present a complex spatial dependence of the adsorptive energy. It is of substantial interest to attempt a complete characterization of such heterogeneity. Through the last 40 years physical adsorption has been used for determining energetic properties of heterogeneous substrates, but this still remains an open problem in many aspects [1-4].

For a very long time in the history of the studies of heterogeneous adsorbents, the adsorptive energy distribution (AED) was considered as the only important characteristic to be known in order to describe the behavior of adsorbed particles, and much effort was dedicated to its determination by inverting the integral equation [5]:

$$\bar{\theta}(T, \mu) = \int \theta(T, \mu, \varepsilon) f(\varepsilon) d\varepsilon \quad (1)$$

where $\bar{\theta}$ is the mean total coverage at temperature T and chemical potential μ , θ is the local coverage (usually called the local isotherm) corresponding to an adsorptive energy ε and $f(\varepsilon)$ is the AED.

It should be noticed that eq. 1 is strictly and generally valid only for non-interacting particles, which is a quite unrealistic case. If adsorbed particles interact with each other, then the local coverage at a point with a given adsorptive energy depends on the local coverage on neighbor points with different adsorptive energies and, in general, eq. 1 should be replaced by a much more complex one, like [6]:

$$\bar{\theta}(T, \mu) = \int \dots \int \theta(T, \mu, \varepsilon_1, \dots, \varepsilon_M) f_M(\varepsilon_1, \dots, \varepsilon_M) d\varepsilon_1 \dots d\varepsilon_M \quad (2)$$

where now θ not only depends on the adsorptive energy at a single point on the surface but also on the adsorptive energy at (in general) M neighbor points, and $f_M(\varepsilon_1, \dots, \varepsilon_M)$ is a multivariate probability distribution which specifies how adsorptive energies are spatially distributed, or in other words, the *energetic topography* of the surface.

We remark that, even for interacting particles, eq. 2 reduces to eq. 1 for two extreme topographies: a) *random sites topography* (RST), where adsorptive energies are distributed totally at random among adsorbing sites, and b) *large patches topography* (LPT), where the surface is assumed to be a collection of homogeneous patches large enough to neglect border effects between neighbor patches with different adsorption energies. Of course, the local adsorption isotherm will be different for these two extreme topographies.

It is by now clear that RST and LPT are particular limiting cases (occurring only rarely in real systems) of heterogeneous surfaces with more general topographies, and that the topography affects strongly many molecular processes occurring on such surfaces, like adsorption, surface diffusion and reactions [6-10], thus making the simple determination of the AED not enough to characterize the heterogeneity. It is then necessary to obtain the multivariate probability distribution, or at least the AED plus the spatial correlation function.

At this point we can precisely see the difficulties involved in the characterization of a general heterogeneous surface. As it is well known, eq. 1 for the simple cases of the two extreme topographies, is an ill-posed problem for the determination of the AED $f(\varepsilon)$ due to the form of the kernel of the integral equation determined by the local isotherm. The determination of the AED from experimental adsorption isotherms requires elaborated computational methods, which have been developed with much effort in many years [5]. When treating with more general topographies, eq. 2 must be used, where the local isotherm is a much more complex equation (if available at all) and we must deal with a multiple integral on the energy and the unknown quantity to be calculated is the multivariate adsorptive energy distribution. Even in the simplest case in which

the topography could be described by a two-point correlation function, the problem cannot be solved by inverting the multidimensional integral equation.

It is then of great importance to develop simple models capable of describing the energetic topography on the basis of a few parameters and to study the effects of these parameters on several surface processes, with the hope that, in such a process, methods to obtain the relevant parameters from experimental data will be envisaged. The present work is devoted to review the efforts done in this direction, following the ideas behind the development of the Generalized Gaussian Model, and to point out some new possible routes to follow. In Section 2 the basic concept of the *Adsorptive Energy Surface* is introduced on the basis of a simple example and the characteristics determining the topography are discussed. In Section 3 the Generalized Gaussian Model is reviewed and its predictions for the equation of state of the adsorbate are analyzed. A lattice-gas approximation to this model to obtain mean-field isotherm equations is given in Section 4, along with the calculation of topography effects on an important surface process: surface diffusion. Finally, in Section 5 we give our conclusions and an outlook of possible future developments.

2. THE ADSORPTIVE ENERGY SURFACE (AES)

In order to base our analysis on a well defined simple system, let us consider an heterogeneous solid consisting of a regular crystal of atoms A (for example an hcp crystal) where a small fraction is substituted by impurity atoms B . We move a probe atom P on the (X, Y) surface of the crystal; the probe interacts with atoms A and B with a Lennard-Jones potential:

$$U_{PS}(r) = -4\epsilon_{PS} \left[\left(\frac{\sigma_{PS}}{r} \right)^6 - \left(\frac{\sigma_{PS}}{r} \right)^{12} \right] \quad (3)$$

where S stands for the substrate atom, A or B , and ϵ and σ are the usual energy depth and particle-diameter parameters, respectively. At each point $i=(X, Y)$ the total interaction energy of the probe atom is calculated as a function of Z by summing up all pairwise interactions with the substrate's atoms within a cutoff distance $r_c = 4\sigma_{PS}$:

$$E(X, Y, Z) = \sum_{r_{ij} \leq r_c} U_{PS}(r_{ij}) \quad (4)$$

Then, by finding the minimum in the coordinate Z , we obtain the equilibrium height Z_0 and the adsorptive energy at position (X, Y) on the surface. What we get in this way is the *adsorptive energy surface* (AES) seen by the probe atom, defined as $E(X, Y, Z_0) = \min_Z \{E(X, Y, Z)\}$.

Figure 1 shows this energy surface for a crystal with 20% of impurity atoms with $\varepsilon_{PA}/k_B = 160$ K, $\varepsilon_{PB}/k_B = 480$ K and $\sigma_{PS} = 0.35$ nm; darker regions represent stronger adsorptive energy, while brighter ones correspond to weaker adsorptive energy. In part (a) we see a general view where significant correlation is seen to be present, in the sense that strong adsorptive regions appear to be quite larger than one lattice size in spite of the low density of impurity atoms, reflecting the fact that the probe atom interacts with many atoms of the substrate at once. As a first rough approximation the energy surface could be considered as a collection of irregular patches of different strengths. However the energetic topography shows a quite greater complexity and such a picture could lead to an oversimplified model not reflecting important behaviors in molecular processes occurring on the surface. The cuts on the borders of the sample give the adsorptive energy profiles along X and Y directions, reinforcing the idea of a high complexity. The problem is: how to model in a simple, and still realistic way, such a complex behavior? In other words, which are the characteristic (and relevant) quantities necessary to construct simple models capable of reproducing in a statistical sense the main topographic features?

In a very general way, we can say that the AES is mathematically described by a *stochastic process* [11,12], i.e. a random function depending on some parameter. In our case, the adsorptive energy is a random function of the position on the surface, $\hat{E}(\vec{R})$, where the symbol (^) indicates a random quantity and \vec{R} is the position vector on the surface whose components are (X, Y) . A particular realization of the stochastic process $\hat{E}(\vec{R})$ is the function $E(X, Y)$ represented in Figure 1 (we can drop the dependence with Z_0). The statistical description of such a stochastic process could be very complex. However, some simplifying assumptions, based on physical grounds, may reduce greatly this complexity. In fact, it is reasonable to assume that the surface is statistically homogeneous, i.e. any macroscopic portion of the surface has all the meaningful information, and that the adsorptive energy distribution can be approximately described by a multivariate gaussian distribution depending on the distance between pairs of points on the surface. This approach leads to the *Generalized Gaussian Model* (GGM) [13,14], which is capable of describing the energetic topography on the basis of the mean and the dispersion of the adsorptive energy, and a correlation function depending on the distance on the surface.

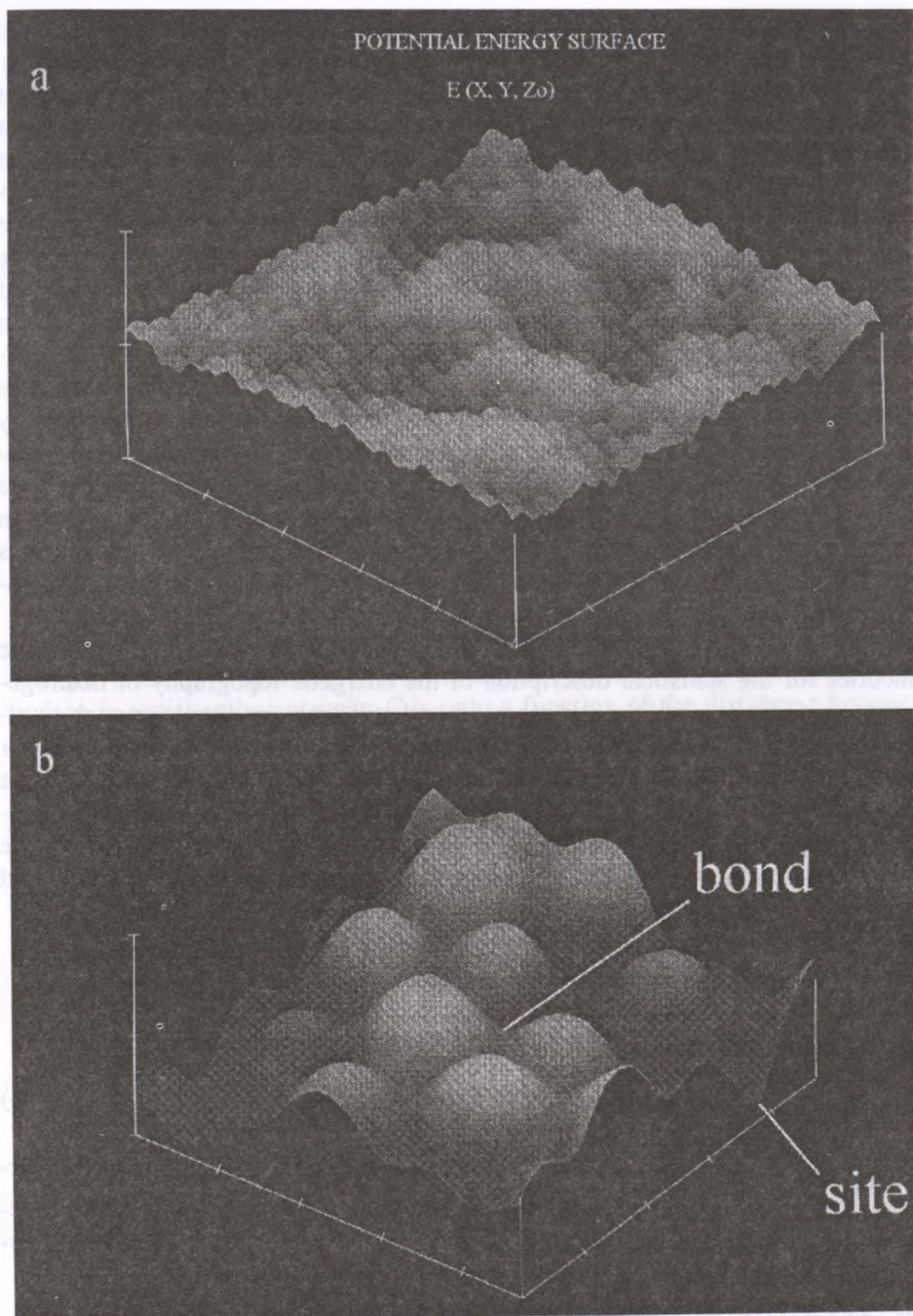


Figure 1. Adsorption Energy Surface (AES) for a crystal of atoms A with 20% impurity of atoms B. (a) general view, (b) enlargement of a small area

In part (b) of Figure 1 we can see an enlarged picture of a small region of the adsorptive energy surface. There we can distinguish two fundamental elements: *sites*, or energy wells where an adsorbed molecule will spend a much greater time, and *bonds*, or energy saddle points through which a molecule will most probably jump to migrate from one site to another. A site may be connected to several bonds, and in general we may have a variable connectivity on the surface, while a bond is always connected to two sites. A quite realistic assumption is that we do not lose relevant information by disregarding the behavior of the energy at all other (X, Y) positions. In fact, sites are the places where adsorbed particles will spend most of the time and their energy play a fundamental role in the adsorption-desorption equilibrium, while bonds (this widely accepted terminology comes from percolation theory) act as connecting channels between sites and their energy, together with those of sites, determine the jumping probability for particle diffusion assumed as an activated process. Along this line of reasoning, a minimum realistic statistical description of the topography will require three functions: the site and bond energy distributions and the spatial correlation function for these elements. Different forms of the site and bond distributions and different correlation's functions are able to generate a variety of topographies. This approach leads to the *Dual Site-Bond Model* (DSBM) [15,16].

The two above mentioned models, GGM and DSBM, are the most complete theories for the statistical description of the energetic topography of heterogeneous surfaces available at the moment, and still they are simple enough to allow the theoretical prediction of molecular processes on these surfaces, like for example adsorption, surface diffusion and others. The two models are in some sense complementary to each other: the GGM is in its most general form a continuous model, while the DSBM is a lattice model. In the present review we focus our attention on the first of these models, in particular the formulation and predictions of the GGM model, and discuss new possible developments.

3. GENERALIZED GAUSSIAN MODEL (GGM)

We start by assuming the validity of the *statistical homogeneity hypothesis*:

$$\langle \hat{E}(\vec{R}_1 + \vec{a}, \dots, \vec{R}_n + \vec{a}) \rangle = \langle \hat{E}(\vec{R}_1, \dots, \vec{R}_n) \rangle \quad (5)$$

where $\langle \dots \rangle$ denotes average over an ensemble of many realizations of the surface. The most general statistical information for a continuous stochastic process is given by its generating functional. If we assume that the AES is a *gaussian stochastic process*, then its generating functional is given by [12,13]:

$$F(\alpha) \equiv \left\langle \exp \left\{ \int d^2 \vec{R} \alpha(\vec{R}) [\hat{E}(\vec{R}) - \bar{E}] \right\} \right\rangle = \exp \left[\frac{1}{2} \iint d^2 \vec{R} d^2 \vec{R}' \alpha(\vec{R}) H(\vec{R}, \vec{R}') \alpha(\vec{R}') \right] \tag{6}$$

where $H(\vec{R}, \vec{R}') = \langle [\hat{E}(\vec{R}) - \bar{E}] [\hat{E}(\vec{R}') - \bar{E}] \rangle$ is the covariance function and $\bar{E} = \langle \hat{E}(\vec{R}) \rangle$. From the generating functional, the multivariate probability density distribution for the adsorptive energies at n points on the surface is obtained as:

$$\begin{aligned} \Phi_n(E_1, \dots, E_n) &\equiv \left\langle \prod_{i=1}^n \delta[\hat{E}(\vec{R}_i) - E_i] \right\rangle \\ &= [(2\pi)^n \det H]^{-1} \exp \left[-\frac{1}{2} \sum_{i,j=1}^n (E_i - \bar{E})(H^{-1})_{i,j} (E_j - \bar{E}) \right] \end{aligned} \tag{7}$$

where, by virtue of the condition (5), the covariance matrix

$$H_{i,j} = \langle (E_i - \bar{E})(E_j - \bar{E}) \rangle = \sigma^2 C(\vec{R}_i - \vec{R}_j) \tag{8}$$

is a function of the relative position vector between two points. Here σ is the adsorptive energy dispersion and C the correlation function. If furthermore the surface is statistically isotropic, C is only a function of the distance r between two points.

In this model the mean value of any macroscopic quantity of interest depending on the AES could then be evaluated by knowing \bar{E} , σ and $C(r)$. The correlation function $C(r)$ carries all the useful information about the energetic topography and should, in principle, be determined from the geometric and chemical structure of the adsorbent (even though the methodology to achieve this has not been developed so far). However, we could simplify the model even more by proposing for $C(r)$ a simple gaussian decay like:

$$C(r) = \exp \left[-\frac{1}{2} \left(\frac{r}{r_0} \right)^2 \right] \tag{9}$$

where r_0 is a *correlation length*. This expression, which we do not intend to take as a realistic correlation function valid for any surface, simply tells us that the spatial correlation between adsorptive energies at points separated by a distance $r < r_0$ is very high (close to 1) while for $r > r_0$ is very low (close to 0). Thus the present model becomes very attractive in the sense that the energetic topography is characterized by a single parameter, the correlation length, and this opens the possibility for the determination of the three simple parameters of the model (\bar{E} , σ and r_0) by, for example, fitting experimental adsorption iso-

therms. It is worth to remark that the present model is a continuous one and not a lattice model of adsorption sites. This is an appealing feature, since, as we can see from Figure 1, adsorption sites hardly form a regular lattice and furthermore many of them are so shallow that an adsorbed particle will most probably be quite mobile on appreciably large regions.

To obtain an evaluable equation for the adsorption isotherm in this model, without loosing the generality of a continuous model (in the next Section we develop a lattice formulation of the GGM), we make use of a virial expansion for the two-dimensional spreading pressure ϕ of the adsorbed phase [17]:

$$\phi = k_B T \rho \left[1 + \sum_{n \geq 2} B_n(T) \rho^{n-1} \right] \quad (10)$$

where ρ is the adsorbate surface density and $B_n(T)$ is the n th two-dimensional virial coefficient. If the adsorbed phase is in equilibrium with an ideal gas phase whose density is ρ_0 and whose pressure is p , then making use of Gibbs equation $\rho_0 d\phi = \rho dp$, the adsorption isotherm equation is given by:

$$p = K(T) \rho \exp \left[\sum_{n \geq 2} \frac{n}{n-1} B_n(T) \rho^{n-1} \right] \quad (11)$$

where $K(T)$ is an integration constant. By assuming that the potential energy of the system of adsorbed particles is the sum of the interparticle potential $U_{ss}(|\vec{R}_i - \vec{R}_j|)$, and the gas-solid potential [18]

$$U_{gs}(\vec{R}, Z) = \frac{1}{2} k_z (Z - Z_0)^2 + \hat{E}(\vec{R}), \quad (12)$$

and that the stochastic process $\hat{E}(\vec{R})$ has the distribution given by eq. (7), then the coefficients in eq. (11) are obtained as [13]:

$$K(T) = (k_B T k_z / 2\pi)^{1/2} \exp \left[\frac{\bar{E}}{k_B T} - \frac{1}{2} \left(\frac{\sigma}{k_B T} \right)^2 \right] \quad (13)$$

$$B_n(T) = -\frac{1}{n(n-2)!}$$

$$\int \dots \int d\vec{R}_1 \dots d\vec{R}_n \delta(\vec{R}_1 + \dots + \vec{R}_n) S'_{1, \dots, n} \prod_{i>j=1}^n \exp \left[\left(\frac{\sigma}{k_B T} \right)^2 C(\vec{R}_i - \vec{R}_j) \right] \quad (14)$$

where

$$S'_{1,2} = f_{1,2} = \exp\left[-U_{ss}(\bar{R}_i - \bar{R}_j)/k_B T\right] - 1$$

$$S'_{1,2,3} = f_{1,2}f_{1,3}f_{2,3}$$

$$S'_{1,2,3,4} = f_{1,2}f_{1,3}f_{1,4}f_{2,3}f_{2,4}f_{3,4} + 6f_{1,2}f_{1,3}f_{1,4}f_{2,3}f_{3,4} + 3f_{1,2}f_{2,3}f_{3,4}f_{1,4}$$

and so on. Eq. 14 can be diagrammatically represented as in Figure 2.

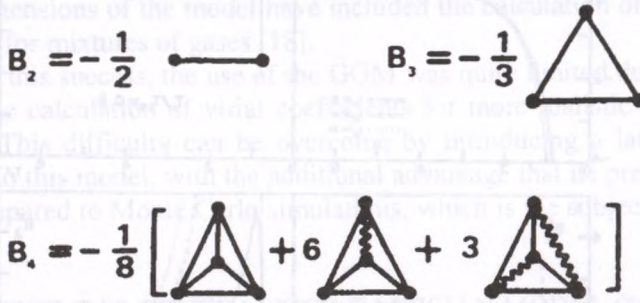


Figure 2. Schematic representation of virial coefficients B_n , eq. 14. A solid line represents a factor $f_{i,j} \exp[H_{ij}/(k_B T)^2]$ and a wiggly line a factor $\exp[H_{ij}/(k_B T)^2]$

In order to study how the virial coefficients depend on the energetic topography, they were calculated for an interparticle interaction given by a square-well potential:

$$U_{ss}(r) = \begin{cases} \infty & \text{for } r < a \\ -k_B T_{ss} & \text{for } a < r < b \\ 0 & \text{for } r > b \end{cases} \quad (15)$$

In this case, and with the change of notation $\bar{E} = -k_B T_a$, $\sigma = k_B T_s$ and $B_n^* = B_n / (\pi a^2 / 2)^n$, the first few coefficients can be evaluated in terms of the relevant parameters [13], and the results are shown in Figure 3.

A deeper discussion of the behavior of B_n^* is given in ref. [13], here we only want to remark that they, and therefore the adsorption isotherm, are appreciably affected by the adsorptive energy topography, described here by the correlation length r_0 , and this effect seems to be stronger when the adsorptive energy dispersion is comparable or greater than the interparticle interaction strength ($T_s \geq T_{ss}$). We also want to stress that here the energetic topography is simply represented by the correlation length r_0 , and that the classical RST and LPT models are now the extreme particular cases corresponding to $r_0 \rightarrow 0$ and $r_0 \rightarrow \infty$, respectively.

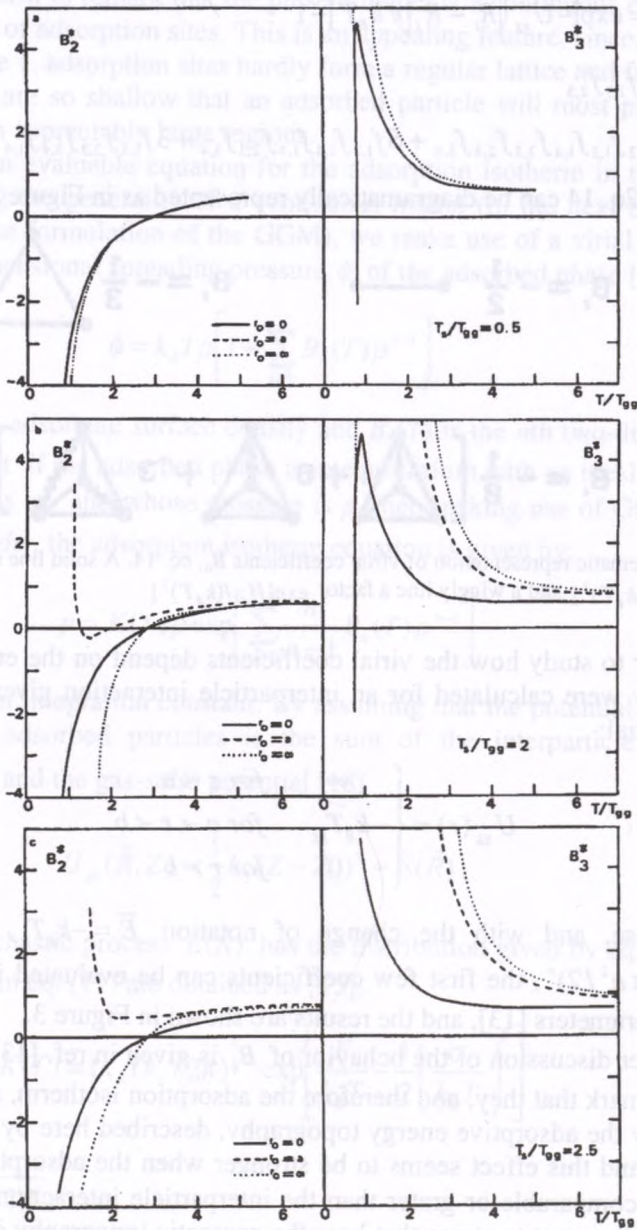


Figure 3. Normalized virial coefficients for a square-well potential, as a function of the reduced temperature T/T_{gg} , for different values of the correlation length r_0 and standard deviation of the adsorptive potential $k_B T_s$.

Applications of the GGM to the analysis of adsorption isotherms of several gases on carbon blacks graphitized at different temperatures (producing different heterogeneity degrees) were performed in Ref. [14]. The model gave good fits of the adsorption isotherms with values of the energetic topography parameters in reasonable agreement with the physical process: T_s decreased and r_0 increased with increasing graphitization temperature (meaning a more extended graphite structure).

Further extensions of the model have included the calculation of the adsorption isotherm for mixtures of gases [18].

In spite of this success, the use of the GGM was quite limited due to the difficulties in the calculation of virial coefficients for more realistic interparticle interactions. This difficulty can be overcome by introducing a lattice-gas approximation to this model, with the additional advantage that its predictions can be easily compared to Monte Carlo simulations, which is the subject of the next section.

4. LATTICE-GAS GENERALIZED GAUSSIAN MODEL (LGGM)

To obtain the lattice-gas version of the GGM [6,19], we drop the AES picture as a whole, and consider that only adsorption sites are important and that these sites form a regular lattice. Of course, the adsorptive energy at these sites will be statistically described by the multivariate distribution, eq. 7, thus keeping the essential feature of spatial energy correlations.

We assume that the surface, which is represented by a lattice of M ($M \rightarrow \infty$) sites with adsorptive energies ε_i , $i=1, \dots, M$, is exposed to an ideal gas phase and the system reaches equilibrium at chemical potential μ and temperature T . We further assume that single occupancy of adsorption sites can occur. The hamiltonian of the adsorbed phase can then be written as:

$$h = \sum_{i=1}^M \varepsilon_i n_i + \sum_{i \neq j} U_{ij} n_i n_j = \sum_{i=1}^M n_i \left[\varepsilon_i + \sum_{j \neq i} U_{i,j} n_j \right] \quad (16)$$

where n_i is the occupation number of site i and U_{ij} is the interaction energy between molecules adsorbed at sites i and j . The expression in brackets is the energy field "seen" by a particle located at site i , and we approximate it by the mean field energy:

$$W_i = \varepsilon_i + \sum_{j \neq i} U_{ij} \theta_j \quad (17)$$

where $\theta_j = \langle n_j \rangle$ is the mean occupation number (or local coverage) at site j .

Then, with the mean field hamiltonian

$$h' = \sum_{i=1}^M n_i W_i \tag{18}$$

the grand partition function for the system is given by:

$$\Theta = \sum_{states} e^{-(h'-N\mu)/k_B T} = \sum_{n_1, n_2, \dots} e^{-[n_1(W_1-\mu)+n_2(W_2-\mu)+\dots]/k_B T} \tag{19}$$

This, as well known, leads to the Fermi-Dirac statistics for the mean occupation number of a single particle state i :

$$\theta_i = \frac{\exp[-(W_i - \mu)/k_B T]}{1 + \exp[-(W_i - \mu)/k_B T]} \quad ; \quad i = 1, \dots, M \tag{20}$$

We recall that, as W_i is a function of all θ_j (for $j \neq i$), eq. 20 actually represents a system of M coupled transcendental equations.

Now, if our heterogeneous surface is characterized by the multivariate distribution, $\Phi_M(\varepsilon_1, \dots, \varepsilon_M)$, which describes the statistical ensemble of surfaces, then for a given member of such an ensemble, i.e. for a given realization of $\varepsilon_1, \dots, \varepsilon_M$, we can define a local coverage

$$\theta = \frac{1}{M} \sum_{i=1}^M \theta_i \tag{21}$$

and consequently obtain the mean surface coverage $\bar{\theta}$ as the mean over the total ensemble:

$$\bar{\theta}(T, \mu) = \int \dots \int \Phi_M(\varepsilon_1, \dots, \varepsilon_M) \theta(T, \mu, \varepsilon_1, \dots, \varepsilon_M) d\varepsilon_1 \dots d\varepsilon_M \tag{22}$$

Equations 20 to 22 constitute the formal mean field solution of the LGGM. In this way the adsorption isotherm could in principle be numerically calculated. However this is not practical, since M is a much too big number. However, we can take further advantage of the fact that usually intermolecular interactions are short ranged, and that the energetic topography is characterized by a correlation length r_0 (measured in units of the lattice spacing a), in such a way that we could expect that within a distance r_0 the adsorptive energy has a small probability of changing appreciably. With this in mind, we consider three regions around a given site i , as illustrated in Figure 4: a nearest-neighbor region A_N (containing N sites) where detailed interactions will be considered, the region of sites j not belonging to A_N but included in the circle of radius r_0 and the region outside this circle. The effective mean field seen by a molecule adsorbed on site i can therefore be written as

$$W_i = \varepsilon_i + \sum_{j \neq i, \in A_N} U_{ij} \theta_j + \lambda_0 \theta + \lambda \bar{\theta} \tag{23}$$

where

$$\theta = \frac{1}{N} \sum_{i=1}^N \theta_i ; \quad \lambda_0 = \sum_{j \in A_N: r_{ij} \leq r_0} U_{ij} ; \quad \lambda = \sum_{j \in A_N: r_{ij} > r_0} U_{ij}$$

This means that the interaction between a molecule adsorbed at site i and the remaining adsorbate has been split in three terms: a detailed interaction with $N-1$ closest sites belonging to A_N , a mean field interaction $\lambda_0\theta$ within the region represented by the shadowed area in Figure 4 and another mean field interaction $\lambda\bar{\theta}$ with the rest outside r_0 . Note that the mean coverage on the shadowed area cannot considerably differ from that on A_N (due to strong correlation within r_0), while outside r_0 sites can have, in average, all possible energies so that the coverage there is represented by the mean coverage on the whole surface.

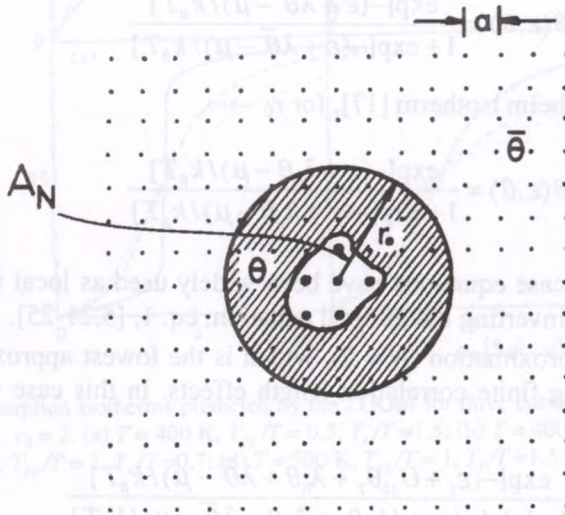


Figure 4. A square lattice of adsorption sites showing zones of different mean field approximations

The isotherm equation is now determined by the more manageable set of equations:

$$\bar{\theta}(T, \mu) = \int \dots \int \Phi_N(\epsilon_1, \dots, \epsilon_N) \theta(T, \mu, \epsilon_1, \dots, \epsilon_N) d\epsilon_1 \dots d\epsilon_N \quad (24)$$

$$\theta = \frac{1}{N} \sum_{i=1}^N \theta_i \quad (25)$$

$$\theta_i = \frac{\exp\left[-\left(\varepsilon_i + \sum_{j \neq i, \in A_N} U_{ij}\theta_j + \lambda_0\theta + \lambda\bar{\theta} - \mu\right)/k_B T\right]}{1 + \exp\left[-\left(\varepsilon_i + \sum_{j \neq i, \in A_N} U_{ij}\theta_j + \lambda_0\theta + \lambda\bar{\theta} - \mu\right)/k_B T\right]} \quad (26)$$

$i = 1, \dots, N$

Several approximation degrees can be now investigated, by giving N different values:

a) First order approximation ($N = 1$), where no detailed interactions are involved, leads to two well-known local adsorption isotherms depending on the limiting value of r_0 considered: Hill isotherm [20], for $r_0 = 0$,

$$\theta(\varepsilon, \theta) = \frac{\exp[-(\varepsilon + \lambda\bar{\theta} - \mu)/k_B T]}{1 + \exp[-(\varepsilon + \lambda\bar{\theta} - \mu)/k_B T]} \quad (27)$$

and Fowler-Guggenheim isotherm [17], for $r_0 \rightarrow \infty$,

$$\theta(\varepsilon, \theta) = \frac{\exp[-(\varepsilon + \lambda_0\theta - \mu)/k_B T]}{1 + \exp[-(\varepsilon + \lambda_0\theta - \mu)/k_B T]} \quad (28)$$

These two limiting case equations have been widely used as local isotherms to determine $f(\varepsilon)$ by inverting the integral equation, eq. 1, [5,21-25].

b) Second order approximation ($N = 2$), which is the lowest approximation capable of determining finite correlation length effects. In this case we have for the local isotherm:

$$\theta_1 = \frac{\exp[-(\varepsilon_1 + U_{12}\theta_2 + \lambda_0\theta + \lambda\bar{\theta} - \mu)/k_B T]}{1 + \exp[-(\varepsilon_1 + U_{12}\theta_2 + \lambda_0\theta + \lambda\bar{\theta} - \mu)/k_B T]} \quad (29)$$

$$\theta_2 = \frac{\exp[-(\varepsilon_2 + U_{12}\theta_1 + \lambda_0\theta + \lambda\bar{\theta} - \mu)/k_B T]}{1 + \exp[-(\varepsilon_2 + U_{12}\theta_1 + \lambda_0\theta + \lambda\bar{\theta} - \mu)/k_B T]} \quad (30)$$

$$\theta(T, \mu, \varepsilon_1, \varepsilon_2) = (\theta_1 + \theta_2)/2 \quad (31)$$

Adsorption isotherms for the second order approximation LGGM were calculated by replacing eqs. 30 and 31 in eq. 24 with $N = 2$ [6]. Results, given in Figure 5, show the effects of the correlation length on adsorption for different values of interparticle interactions and adsorptive energy dispersion. In general we see that for a surface with a higher correlation length, adsorption is stronger at low coverage and weaker at high coverage. This topography effect is highly coupled to interparticle interactions; in fact it is null for non-interacting adsorbates (not shown), very weak for $T_{gg}/T = 0.5$ (Figure 5a) and much stronger for

$T_{gg}/T = 1$ (Figure 5b), while the other parameters are the same. On the other hand, a higher adsorptive energy dispersion (higher heterogeneity) smoothes out the correlation length effect, as it can be seen by comparing Figure 5c, for a small dispersion $T_s/T = 0.7$, to Figure 5d, for $T_s/T = 1.5$, with the same values for the remaining parameters.

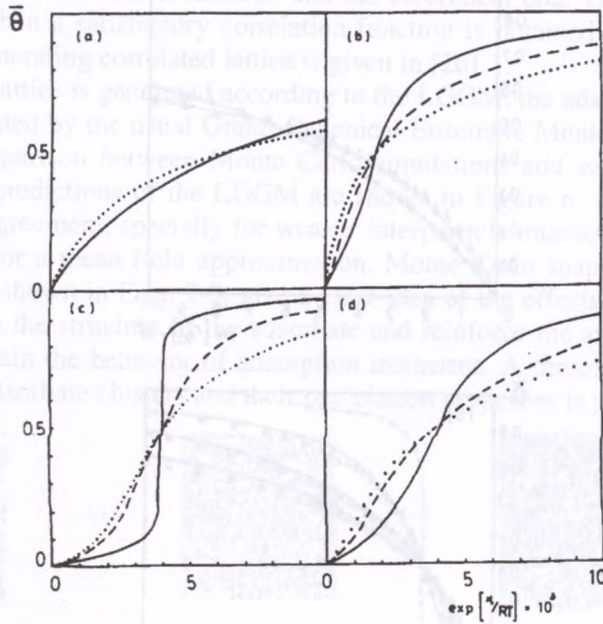


Figure 5. Adsorption isotherms predicted by the LGGM for three correlation lengths: — $r_0 = 0$; - - - $r_0 = 1$; $r_0 = 2$. (a) $T = 400$ K, $T_{gg}/T = 0.5$, $T_s/T = 1.5$; (b) $T = 400$ K, $T_{gg}/T = 1$, $T_s/T = 1.5$; (c) $T = 500$ K, $T_{gg}/T = 1$, $T_s/T = 0.7$; (d) $T = 500$ K, $T_{gg}/T = 1$, $T_s/T = 1.5$

The coupling between interparticle interactions and the energetic topography can be used to explain the main feature of these adsorption isotherms. For a correlated surface, $r_0 > 0$, a strong adsorptive site is likely to be surrounded by similar sites and this, combined with attractive lateral interactions, enhances adsorption at low coverage in comparison to an uncorrelated surface. On the contrary, at high coverage only weak adsorptive sites remain uncovered, which for a correlated surface are likely to be surrounded by other weak sites, resulting in a smaller adsorption than in the case of uncorrelated surfaces.

A much richer picture of the effects of the topography on the adsorbed phase can be obtained by performing Monte Carlo simulations on surfaces characterized by the LGGM. In order to generate a surface with a given r_0 [6], circles of radius r_0 centered on randomly chosen sites are considered and the energies for the sites belonging to each circle were sampled from the conditional probability distribution to find a site with energy $\leq \epsilon'$, given a central site with energy ϵ :

$$F_\varepsilon(\varepsilon', r) = \frac{\int_0^{\varepsilon'} \Phi_2(\varepsilon_1, \varepsilon) d\varepsilon_1}{\int_0^\infty \Phi_2(\varepsilon_1, \varepsilon) d\varepsilon_1} \quad (32)$$

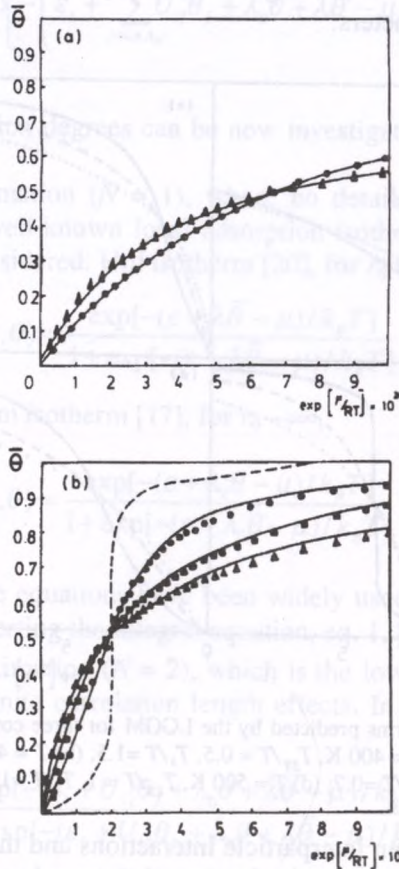


Figure 6. Comparison between Monte Carlo simulated isotherms (symbols) and LGGM predictions with $N = 2$ (solid lines): \bullet $r_0 = 0$, \blacksquare $r_0 = 1$, \blacktriangle $r_0 = 2$. (a) $T_{gg}/T = 0.5$, (b) $T_{gg}/T = 1$. The broken line represents the homogeneous case with $\bar{\varepsilon} = -3$ Kcal/mol

Values of ε for the central sites are sampled from a gaussian distribution, provided that the centers of the circles are separated at least a distance $2r_0$. Any site which has already been assigned an energy value is "marked". When no more marked circles of radius r_0 can be found (at this point the surface has been covered up in a coarse-grained sense and only smaller regions or interstitial sites between circles are still unmarked) the procedure is started again with a smaller radius and this goes on until all sites have been marked. At this stage the generated lattice shows a correct correlation between the energies of sites belonging

to the same circle but the overall correlation function is far from the desired theoretical one (eq. 9) due to border effects between circles. A relaxation method is then started, where pairs of sites are randomly selected and an energy replacement for one of them is attempted by sampling a new value from eq. 32. The change is made if it goes in the direction of minimizing the difference between the actual correlation function and the theoretical one. The procedure is terminated when a satisfactory correlation function is obtained. An alternative method of generating correlated lattice is given in [26].

Once the lattice is generated according to the LGGM, the adsorption process can be simulated by the usual Grand Canonical Ensemble Monte Carlo method [27,28]. Comparison between Monte Carlo simulations and second order approximation predictions of the LGGM are shown in Figure 6, where we see a satisfactory agreement, specially for weaker interparticle interactions, as was to be expected for a mean field approximation. Monte Carlo snapshots of adsorbate clusters, shown in Figs. 7-9, give a clear idea of the effects of the correlation length on the structure of the adsorbate and reinforce the arguments given above to explain the behavior of adsorption isotherms. A through study of the behavior of adsorbate clusters and their percolation properties is given in [6].

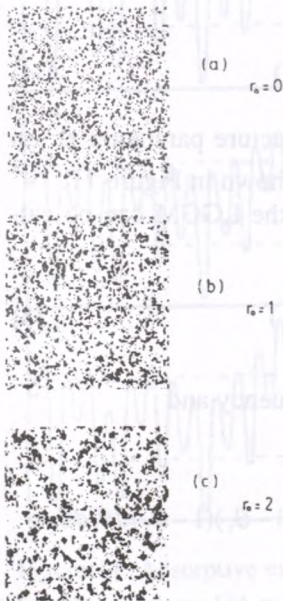


Figure 7. Snapshots of non-interacting adsorbate at $T = 100$ K and $\bar{\theta} = 0.3$

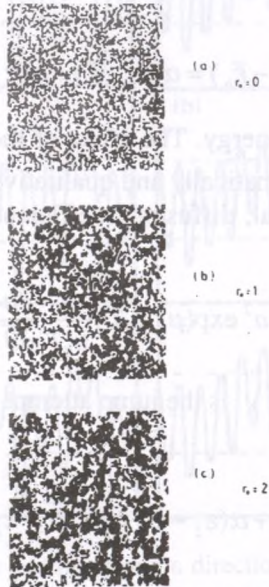


Figure 8. Snapshots of non-interacting adsorbate at $T = 100$ K and $\bar{\theta} = 0.56$

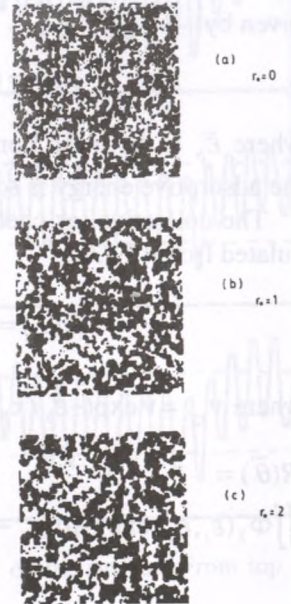


Figure 9. Snapshots of an adsorbate with attractive nearest-neighbor interactions of -0.5 Kcal/mol at $T = 100$ K and $\bar{\theta} = 0.56$

Another molecular process which is expected to be strongly influenced by the energetic topography is surface diffusion. A general account of surface diffusion of adsorbates on heterogeneous surfaces is given in [29]. Here we focus on the description of such a process from the point of view of the LGGM. Since in this model the statistical information concerns only adsorption sites, to treat surface diffusion we need to somehow relate the energy of the barriers connecting pairs of sites to the energies of the sites. A reasonable assumption could be that the correlation function for site energies should be similar to that for any other points of the AES, and in particular for energy barriers between sites. With this in mind, it was proposed [30] that the variation in activation energy for a jump from a site i to a nearest-neighbor site j , due to heterogeneity, could be expressed as a weighted average of the adsorptive energies of those sites (see Figure 10), in the form:

$$\Delta E_{i \rightarrow j}^a = (\alpha - 1)(\varepsilon_i - \bar{\varepsilon}) + \alpha(\varepsilon_j - \bar{\varepsilon}) \quad (33)$$

where $\bar{\varepsilon}$ is the mean site energy and $0 \leq \alpha \leq 1/2$ is a structure parameter taking into account the influence of the destination site on the jump. In terms of the saddle point energy (bond energy) between sites i and j , ε_b^{ij} , its variation is given by:

$$\Delta \varepsilon_b^{ij} = (\varepsilon_b^{ij} - \bar{\varepsilon}_b) = \alpha(\varepsilon_i - \bar{\varepsilon}) + \alpha(\varepsilon_j - \bar{\varepsilon}) \quad (34)$$

where $\bar{\varepsilon}_b$ is the mean bond energy. The effect of the structure parameter α on the adsorptive energy is schematically and qualitatively shown in Figure 11.

The collective, or chemical, diffusion coefficient in the LGGM can be calculated from [29,30]:

$$D(\bar{\theta}) = v_{eff} a^2 \exp(\mu/k_B T) \frac{1}{k_B T} \frac{\partial \mu}{\partial \bar{\theta}} R(\bar{\theta}) \quad (35)$$

where $v_{eff} = v \exp(-\bar{\varepsilon}_b/k_B T)$, v is the jump attempt frequency and

$$R(\bar{\theta}) =$$

$$\iint \Phi_2(\varepsilon_1, \varepsilon_2) \exp\{-[\alpha(\varepsilon_1 - \bar{\varepsilon}) + \alpha(\varepsilon_2 - \bar{\varepsilon}) + W * \bar{\theta}]/k_B T\} (1 - \theta_1)(1 - \theta_2) d\theta_1 d\theta_2$$

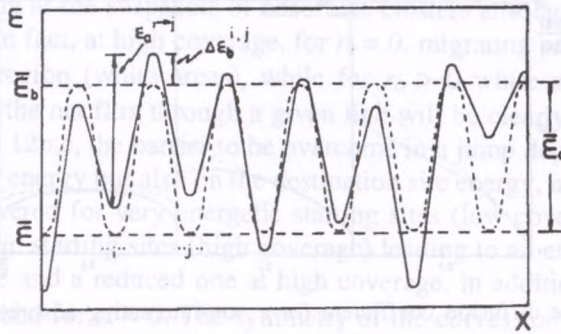


Figure 10. Adsorptive energy variation along a direction X on the surface showing the heterogeneous potential (full line) as a random perturbation of the periodical homogeneous potential (broken line)

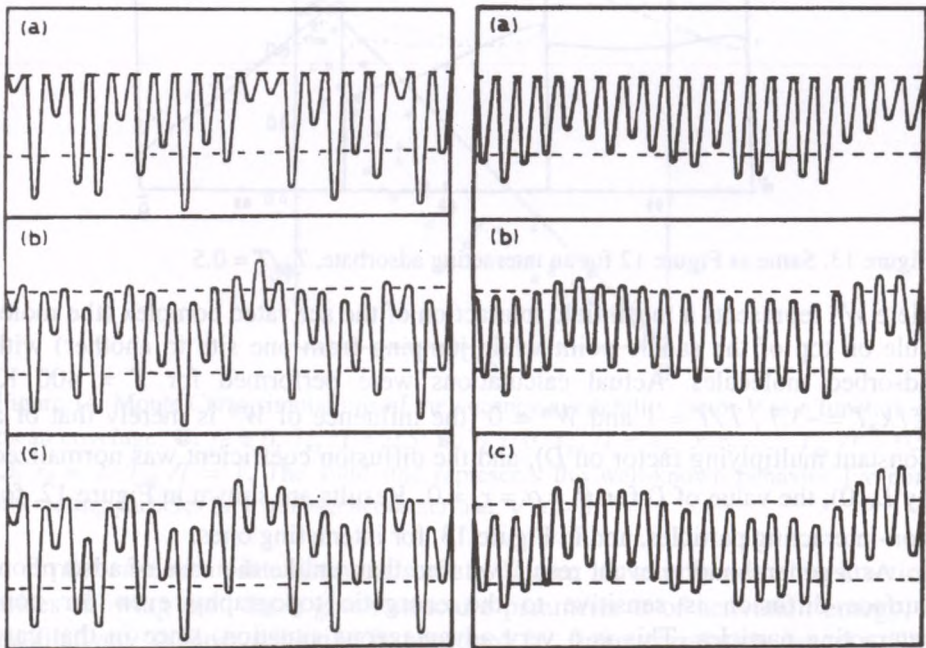


Figure 11. Adsorptive energy profiles along a direction X on the surface. From top to bottom: $\alpha = 0, \alpha = 1/4, \alpha = 1/2$. Left, $r_0 = 0$; right, $r_0 \cong 1$

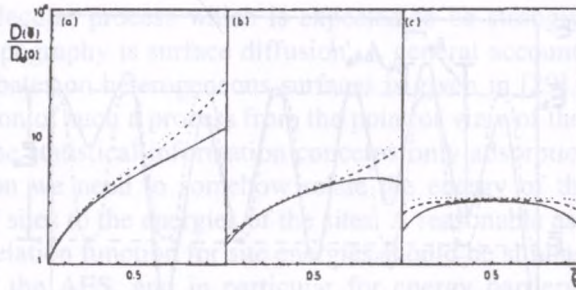


Figure 12. Surface diffusion coefficient for a non-interacting adsorbate, $T_{gg}/T = 0$: — $r_0 = 0$; --- $r_0 = 1$; $r_0 = 2$. (a) $\alpha = 0$, (b) $\alpha = 1/4$, (c) $\alpha = 1/2$

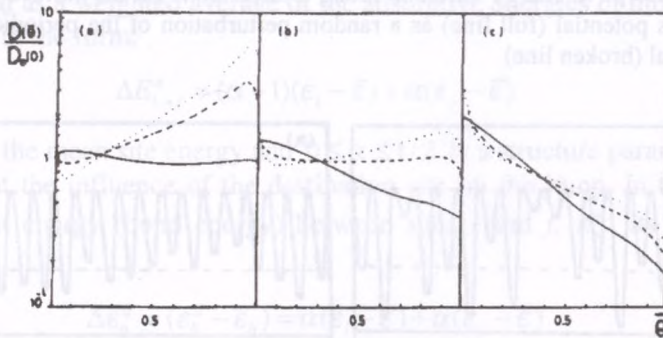


Figure 13. Same as Figure 12 for an interacting adsorbate, $T_{gg}/T = 0.5$

Here W^* represents a mean field interaction of the activated complex (the molecule on top of the saddle point while jumping from one site to another) with adsorbed molecules. Actual calculations were performed for $T = 400$ K, $\bar{E}/k_B T = -3.7$, $T_g/T = 1$ and $W^* = 0$ (the influence of W^* is merely that of a constant multiplying factor on D), and the diffusion coefficient was normalized by $D_0(0)$, the value of D for $\bar{\theta} = \alpha = r_0 = 0$. Results are shown in Figure 12, for non-interacting particles, and in Figure 13, for interacting ones.

As a general and relevant result, we find that, unlike the case of adsorption, surface diffusion is sensitive to the energetic topography even for non-interacting particles. This is a very advantageous situation, since in that case topography effects can be studied without the interference of competing lateral interactions. In Figure 12a ($\alpha = 0$) we have the case of a trap surface (see also Figure 10a), a surface which has received much theoretical attention for random topography [31-33]. We see that the diffusion coefficient steadily increases with coverage for all values of r_0 , due to the fact that the activation energy decreases as particles are forced to adsorb on less energetic sites (less deep traps) as coverage increases. However, curves for $r_0 = 1, 2$ show a much faster increment for $\bar{\theta} > 0.2$ and reach much higher values for $\bar{\theta} \approx 1$. This behavior can be under-

stood by looking at the snapshots of adsorbate clusters at relatively high coverage, Figure 8. In fact, at high coverage, for $r_0 = 0$, migrating particles move in a very intricate region (white areas), while for $r_0 > 0$ white areas form larger patches so that the net flux through a given line will be clearly enhanced. As α increases, Figs. 12b,c, the barrier to be overcome in a jump depends not only on the starting site energy but also on the destination site energy, in such a way that barriers are lowered for very energetic starting sites (low coverage) and raised for less energetic starting sites (high coverage) leading to an enhanced mobility at low coverage and a reduced one at high coverage, in addition to the general behavior described for $\alpha = 0$. The symmetry of the curves for the limiting case $\alpha = 0.5$, showing a maximum at $\bar{\theta} = 0.5$, is a consequence of the symmetrical role played by the initial and final sites of a jump in determining the activation energy and the assumed symmetry of the site energy distribution.

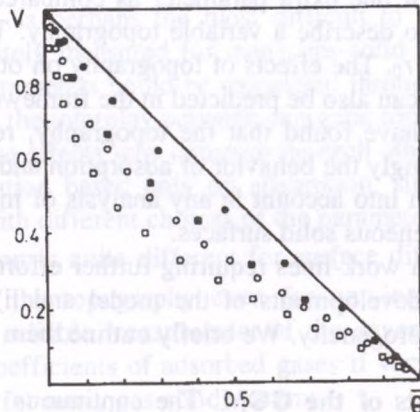


Figure 14. Monte Carlo simulations of the vacancy availability factor V as a function of mean coverage. ●: $r_0 = 0$, $T_{gg}/T = 0.5$; ■: $r_0 = 0$, $T_{gg}/T = 1$; ○: $r_0 = 2$, $T_{gg}/T = 0.5$; □: $r_0 = 2$, $T_{gg}/T = 1$. The solid line represents the well-known behavior for non-interacting particles on a homogeneous surface, $V = 1 - \bar{\theta}$

In the case of an interacting adsorbate, Figure 13, a more complex situation arises showing that, for a given structure parameter α of activation energy, a qualitatively distinct behavior is produced by finite correlation lengths. The minimum and maximum displayed in Figs. 13a,b, for $r_0 = 1, 2$, in contrast to the case $r_0 = 0$, is a manifestation of the vacancy factor, whose effects become more important when lateral interactions are present, as can be seen from Figure 14. The competing effects of decreasing activation barriers as $\bar{\theta}$ increases and the strong decrease in the vacancy factor as r_0 increases, yield the minimum at low coverage for $\alpha = 0$ and $r_0 = 1, 2$. The maximum at high coverage can be understood by considering the mobility of vacancies instead of particles. For $\alpha = 0.5$, Figure 13c, the effect of decreasing activation barriers as coverage

increases is not sufficiently strong and the minimum and maximum disappear. In addition, as compared to the non-interacting case, there is an overall decreasing factor due to the effect of attractive lateral interactions.

Monte Carlo simulations on surface diffusion for the LGGM, which have not been reported to the date, could be helpful to check and extend the above results.

5. CONCLUSIONS AND PERSPECTIVES

We have seen that the GGM is a general enough model as to be able to take into account the spatial distribution of adsorptive energy, i.e., the energetic topography, of a heterogeneous surface. At the same time, the model is simple enough to allow the calculation of adsorption isotherms, on the basis of few parameters, indeed just one extra parameter as compared to classical models, which were not able to describe a variable topography. This new parameter is the correlation length, r_0 . The effects of topography on other surface processes, like surface diffusion, can also be predicted in the framework of the GGM. As a main conclusion, we have found that the topography, represented by the parameter r_0 , affects strongly the behavior of adsorption and surface diffusion and then it should be taken into account in any analysis of molecular processes interacting with heterogeneous solid surfaces.

There are two main work-lines requiring further efforts to answer still open problems: i), further developments of the model and ii), the problem of the characterization of heterogeneity. We briefly outline them below.

Further Developments of the GGM. The continuous version of the GGM, described in Section 3, is a very appealing one to describe the physical adsorption of gases on heterogeneous surfaces. This is so because, on one hand, the whole adsorptive energy surface is taken into account instead of just the adsorptive sites (whose role is under revision at least for physical adsorption [34]), providing a more realistic picture when the adsorbate is mobile. On the other hand, the continuous version provides a direct derivation of an isotherm equation, the virial isotherm, which, like the case of real gases in three dimensions, should be a very reliable equation of state when the adsorbed phase is not near a phase transition. However, due to the greater facility to perform computer simulations, the LGGM has received more attention in the past.

It is then worth to develop some improvements to make the GGM more realistic. The computing power available on desktop to many researchers nowadays, makes it possible to consider more realistic adsorbate-adsorbate interaction potentials, like the Lennard-Jones potential, instead of the square-well potential used in eq. 15. Good multidimensional integration subroutines can be used to calculate now in reasonable computing times up to the third virial coefficient. This greater disposability of computer power makes it also possible to

check or improve the assumptions of a multivariate gaussian distribution, eq. 7, and the gaussian decay of the correlation function, eq. 9. In fact, model heterogeneous surfaces can be generated by computers, like in Section 2, and the multivariate energy distribution and the correlation function can be numerically measured and compared to those assumed in the GGM. Furthermore, adsorption of a gas on such an heterogeneous surface can be simulated by a Grand Canonical Monte Carlo method in the continuum and the results compared to the predictions of the GGM in which the actual (numerically measured) correlation function is used. This would provide a strong test for the reliability of the GGM and the virial adsorption isotherm and new insight for further developments.

The Problem of the Characterization of Heterogeneity. The problem of obtaining information on the energetic topography of an heterogeneous surface from the measurement of quantities involved in gas-solid processes, the *characterization problem*, is perhaps the most difficult to solve. Adsorption isotherms can be accurately measured for many gas-solid systems and isotherms depending on few parameters could be calculated through the GGM and fitted to the data. However, the interplay between energetic topography and interparticle interactions, whose effects may compensate each other [8], makes it impossible the characterization based only on adsorption, since the same isotherm could be generated with different choices of the parameters. As we have seen in Section 4, the situation is quite different for surface diffusion, since $D(\bar{\theta})$ is strongly affected by the topography even for non-interacting particles. The problem here is that reliable measurement of the coverage dependence of the chemical diffusion coefficients of adsorbed gases is very difficult and data are practically inexistent for many gas-solid systems.

According to our results, the simultaneous analysis of adsorption and surface diffusion data obtained for the same gas-solid system could give positive results, however these data are not available at present and their obtention is strongly encouraged. In the mean time some advancement in this field could be given by working on computer generated ideal systems.

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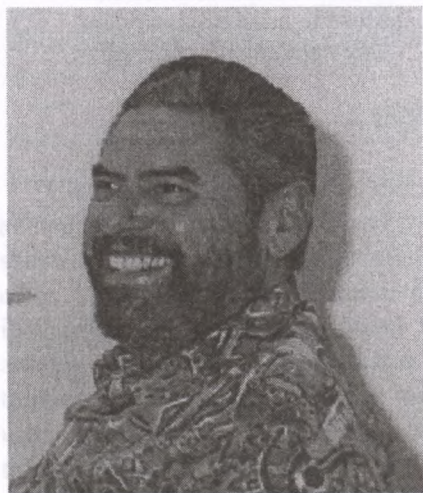
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CURRICULUM VITAE



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Since the beginnings of the 90's he has been in close contact with the Lublin Group led by Professor W. Rudzinski, who have strongly influenced his work.

