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Pure Monte Carlo Simulation of Model Heterogeneous Substrates: From Random Surfaces to Many-Site Correlations[†]

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A conceptually simple general method to simulate model heterogeneous surfaces is proposed. It allows one to distribute adsorption energies over a lattice of adsorption sites according to an arbitrary energy distribution which can include spatial site energy correlations. The method provides a powerful tool to simulate either discrete or continuous site energy distributions with any kind of spatial correlations between site energies which makes it useful to test theoretical model of surface processes against MC simulations on the model surface. Effect of correlations on equilibrium and kinetics of gas adsorption, thermal desorption, surface diffusion and reactions can be studied by MC simulation. More sophisticated model heterogeneous surfaces incorporating distributions of saddle point energies (consequently, activation barriers for diffusion) can also be treated. The method is the same as that used for evaluating the equilibrium states of an ensemble of interacting particles through Monte Carlo simulation.

I. Introduction

Adsorption on heterogeneous surfaces has been investigated for many years and is still a very active field of research.^{1,2} Much of the knowledge concerning the adsorption of gases on solid surfaces has come through the study of model systems. Computer simulation has been a particularly useful tool to predict equilibrium as well as dynamical properties of the adsorbate. Many simulation studies of localized adsorption, the kinetics of adsorption, thermal desorption, surface reactions, and the lattice-gas approach to surface diffusion assume that the surface can be represented by a set of adsorption sites arranged in a given geometry.³ A heterogeneous adsorption potential is introduced by assigning an energy to every site of the lattice. This adsorption energy is sampled from preselected energy distribution. However, the surface is

characterized not only by the number distribution of site energies but also by their spatial distribution across the surface. Inasmuch as the average lateral interaction between atoms adsorbed on these sites is quite sensitive to this spatial distribution and, in particular, to the distribution of nearest neighbor pairs of sites, considerable efforts have been made to deal with this part of the problem. This paper is concerned with the computer generation of surface lattices with specified distributions of pairs (or larger clusters) of sites that are consistent with a given number distribution of the site energy. The most widely used spatial descriptions of heterogeneous surfaces have been either the random site⁴ and the large-patch models.⁵ To generate these site distributions is rather trivial. However, it has been argued that real adsorbents are not usually represented by these limiting site topographies but rather exhibit finite-range site–site energy correlations. Moreover, theoretical and simulation results predict that these correlations can strongly affect surface phenomena.^{6–10} Site–site energy correlations characterized by a correlation length were first introduced in the calculation of the virial coefficients for a low-density adsorbed gas through the generalized

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Gaussian model (GGM)⁶ and were later taken into account in high-coverage adsorption studies.^{10,11} In the GGM a multivariate Gaussian density distribution for the site energies is assumed which allows consideration of correlations between multiple-site energies. A very complete study of adsorption of interacting particles on nonuniform no-rearranging surfaces has been carried out by Tovbin *et al.*^{12–15} In their approximation, correlation between multiple adsorption centers can be accounted for in a general fashion for either discrete or continuous distribution of adsorption centers energy. In general terms, they calculate the local density on different adsorption centers taking into account their detailed spatial distribution and interactions between molecules further apart than nearest neighbors. Despite the calculational drawbacks that arise from such a general formulation, this is one of the most exhaustive descriptions of interacting species on heterogeneous substrates. A comprehensive review of many applications to surface phenomena can be found in refs 16–18. A novel description of heterogeneous surfaces incorporating saddle point energies in addition to those of the sites, has been recently formulated through a self-consistent model (dual site-bond description (DD)).^{19,20} The specification of site and saddle point energies determines the barriers to site–site translation. Note that the specification of a saddle point energy requires that the energies of the sites on either side of the barrier (either end of the bond) be lower than the bond energy. This in itself introduces pairwise nearest neighbor correlations of sites with given energies.

Many interesting features arise as a consequence of spatial energy correlation when activated surface diffusion, diffusion-limited aggregation (DLA), and percolation are simulated for these model surfaces.^{20–24} More recently it has been shown that adsorption of large molecules (dimers, trimers, etc.) is very sensitive to short-range site–site energy correlations,^{25,26} and efforts are now being made to obtain information about adsorption site topographies from experimental adsorption isotherms.²

To reproduce a given energy distribution over a set of adsorption sites is by no means easy if spatial correlations are involved. It has already been shown that the usual procedure for assigning adsorption energies to sites through a Markovian sequence can yield altered energy frequencies and spurious site–site correlations compared

to the theoretical input.²⁷ The aim of the present study is to provide a general method for the simulation of model heterogeneous surfaces with arbitrary spatial energy distributions. The basis for the present work can be expressed as: “The whole set of energies distributed over the adsorption sites can be allowed to evolve as an statistical system of objects interacting through their specific correlations.” Accordingly, all adsorption energies will be initially set to appear with the desired frequencies regardless of their spatial correlations. New states for the system which consist in different spatial distributions of the initial set of site energies can be generated by means of transitions conserving the initial frequencies. The transition probability between states must be written to embody the input correlation function for neighboring sites. Successive transitions drive the system from an arbitrary initial spatial distribution toward a stationary sequence of states characterized by the expected energy distribution and spatial correlations. Once equilibrium has been reached, further transitions only switch between configurations having the same statistical features. This method is formally equivalent to that used in MC simulation to reproduce the equilibrium states of interacting particles.

The formulation is given in sections II and III. In section IV an application to the simulation of dual site-bond surfaces (DD) is presented. Discussion and conclusions are drawn in section V.

II. Basic Formulation

The simulation of a model heterogeneous surface as a set of adsorption sites with a given energy distribution requires that the energy frequency density function be known. If no spatial correlations are taken into account, the surface is completely characterized by the single-variable number distribution $f(\epsilon)$, where ϵ is the site energy (as in the random site distribution). Even in the large-patch model, this distribution can be used to specify the size of the patch of a given energy ϵ which is large enough to eliminate any effects of energy differences at the edges of the patches. More generally, let us suppose that the adsorption energies are distributed over a set of M ($M \rightarrow \infty$) sites according to a given bivariate density function $f(\epsilon, \epsilon')$ $d\epsilon d\epsilon'$ which denotes the probability of finding two nearest neighbor (NN) adsorption sites with energies $\epsilon \in (\epsilon, \epsilon + d\epsilon)$ and $\epsilon' \in (\epsilon', \epsilon' + d\epsilon')$, respectively. This is the simplest way of explicitly introducing site–site energy correlations in a model heterogeneous surface. For simplicity, hereafter we will present the ideas in terms of a pair density function $f(\epsilon, \epsilon')$, which is the most appealing manner of taking into account site correlation effects in both theoretical and simulation treatments of surface phenomena. However, as we later present in section III, it can be formally applied to any kind of many-site correlations, be it correlation between pair of sites more distant than NN's or cluster of sites (fragments of the lattice) involving triplets, quarters, or larger sets of sites.

For simplicity, one assumes (this assumption is irrelevant to the final conclusion)

$$f_1(\epsilon) = \int_{\{\epsilon'\}} f(\epsilon, \epsilon') d\epsilon' = \int_{\{\epsilon\}} f(\epsilon, \epsilon') d\epsilon = f_2(\epsilon) \quad (1)$$

for sites 1 and 2.

In general

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$$f(\epsilon, \epsilon') \neq f_1(\epsilon) f_2(\epsilon') \quad (2)$$

In the limiting cases of random and large-patch topography

$$f(\epsilon, \epsilon') = \begin{cases} f_1(\epsilon) f_2(\epsilon') & \text{random topography} \\ f_1(\epsilon) \delta(\epsilon - \epsilon') & \text{large-patch} \end{cases} \quad (3)$$

Provided that eq 1 represents the adsorption energy frequency regardless of the nature of the spatial correlation, an energy value sampled from $f_1(\epsilon)$ can be assigned to every site. This yields what we hereafter call the initial state of the whole set of M sites denoted by \mathbf{x}_0

$$\mathbf{x}_0 = \{\epsilon_1, \epsilon_2, \dots, \epsilon_M\} \quad (4)$$

where ϵ_i is value of the energy of the i th site. Although this initial state will have the desired overall energy frequencies, it is clear that the frequency of energy pairs (ϵ, ϵ') will differ significantly from the desired $f(\epsilon, \epsilon')$. In order to get the appropriate pair distribution, the initial set of energies has to be spatially rearranged on the lattice. Any spatial rearrangement changes the state of the whole set. A sequence $\mathbf{x}_0 \rightarrow \mathbf{x}_1 \rightarrow \dots \rightarrow \mathbf{x}_N$ of different states can be obtained by transitions conserving the initial frequencies (i.e., every state of the chain satisfies eq 1). For any pair of arbitrary states \mathbf{x}, \mathbf{x}' , the transition probability from \mathbf{x} to \mathbf{x}' , $W(\mathbf{x} \rightarrow \mathbf{x}')$ can be written as follows²⁸

$$W(\mathbf{x} \rightarrow \mathbf{x}') = \min \left\{ 1, \frac{P(\mathbf{x}')}{P(\mathbf{x})} \right\} \quad (5)$$

where $P(\mathbf{x})$ is the probability of finding the lattice in a given state \mathbf{x} .

The definition of $W(\mathbf{x}, \mathbf{x}')$ in this way allows the principle of microscopic reversibility (also called detailed balance principle) to be fulfilled³¹

$$P(\mathbf{x}) W(\mathbf{x} \rightarrow \mathbf{x}') = P(\mathbf{x}') W(\mathbf{x}' \rightarrow \mathbf{x}) \quad (6)$$

Consequently, the sequence of states converges to an stationary one with distribution according to $P(\mathbf{x})$. Nevertheless, $P(\mathbf{x})$ has not yet been explicitly specified, and its definition should embody the theoretical input pair density function so that the desired pair distribution will be reached as a state of the stationary sequence.

In order to obtain an expression for $P(\mathbf{x})$, let us consider a lattice with M adsorption sites and connectivity c . It is tacitly assumed that the number M of adsorption sites is large enough to permit a good representation of the continuous function $f(\epsilon, \epsilon')$. An arbitrary adsorption site denoted by i has an energy ϵ_i and c nearest neighbor sites with energies $\{\epsilon_{i1}, \epsilon_{i2}, \dots, \epsilon_{ic}\}$. The probability of finding this particular local configuration of adsorption energies around the site i can be written as

$$P_c(\epsilon_p \{\epsilon_{i1}, \epsilon_{i2}, \dots, \epsilon_{ic}\}) \propto f(\epsilon_p \epsilon_{i1}) f(\epsilon_p \epsilon_{i2}) \dots f(\epsilon_p \epsilon_{ic}) \quad (7)$$

Any particular state of the whole system is completely defined by labeling every adsorption site and specifying

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its adsorption energy. If ϵ_i denotes the energy of the i th site, the probability for the state $\mathbf{x} = \{\epsilon_1, \epsilon_2, \dots, \epsilon_M\}$ is therefore

$$P(\mathbf{x}) \propto \prod_{i=1}^M P_c(\epsilon_i \{\epsilon_{i1}, \epsilon_{i2}, \dots, \epsilon_{ic}\}) = \prod_{i=1}^M \prod_{k=1}^c f(\epsilon_i \epsilon_{ik}) \quad (8)$$

The simplest way to change the spatial distribution of adsorption sites is by switching the values corresponding to any pair of i and j sites picked at random on the lattice. Thus, if the energies of these sites are exchanged, the corresponding initial and final system states are respectively

$$\mathbf{x} = \{\epsilon_1, \dots, \epsilon_p, \dots, \epsilon_j, \dots, \epsilon_M\}$$

$$\epsilon_i \rightarrow \epsilon'_i = \epsilon_j$$

$$\epsilon_j \rightarrow \epsilon'_j = \epsilon_i$$

$$\mathbf{x}' = \{\epsilon_1, \dots, \epsilon'_i, \dots, \epsilon'_j, \dots, \epsilon_M\} = \{\epsilon_1, \dots, \epsilon_j, \dots, \epsilon_p, \dots, \epsilon_M\}$$

Now, by using eq 8, the probability ratio yields

$$\frac{P(\mathbf{x}')}{P(\mathbf{x})} = \prod_{k=1}^c \frac{f(\epsilon'_i, \epsilon_{ik}) f(\epsilon'_j, \epsilon_{jk})}{f(\epsilon_p \epsilon_{ik}) f(\epsilon_j \epsilon_{jk})} = \prod_{k=1}^c \frac{f(\epsilon_j \epsilon_{ik}) f(\epsilon_p \epsilon_{jk})}{f(\epsilon_p \epsilon_{ik}) f(\epsilon_j \epsilon_{jk})} \quad (9)$$

Note that site-site correlation $g(\epsilon_p, \epsilon_{ik})$ can be explicitly introduced by writing

$$f(\epsilon_p \epsilon_{ik}) = f_1(\epsilon_p) f_2(\epsilon_{ik}) g(\epsilon_p \epsilon_{ik}) \quad (10)$$

In this case eq 9 becomes

$$\frac{P(\mathbf{x}')}{P(\mathbf{x})} = \prod_{k=1}^c \frac{g(\epsilon_j \epsilon_{ik}) g(\epsilon_p \epsilon_{jk})}{g(\epsilon_p \epsilon_{ik}) g(\epsilon_j \epsilon_{jk})} \quad (11)$$

The new state \mathbf{x}' is accepted if (see eq 5)

$$\xi < W(\mathbf{x} \rightarrow \mathbf{x}') \quad (12)$$

where ξ is a random number uniformly distributed over the interval (0,1). We should notice that $P(\mathbf{x})$ in eq 8 is unnormalized. Normalization is not necessary provided that $W(\mathbf{x} \rightarrow \mathbf{x}')$ only depends on the ratio of probabilities.

In order to demonstrate that the initial energy pair distribution is the desired one, we can calculate the mean number of (ϵ, ϵ') pairs, $\langle N(\epsilon, \epsilon') \rangle$, in the stationary distribution. At any equilibrium state \mathbf{x} , $N_{\mathbf{x}}(\epsilon, \epsilon') d\epsilon d\epsilon'$ is the number of pairs having energies $\epsilon \in (\epsilon, \epsilon + d\epsilon)$ and $\epsilon' \in (\epsilon', \epsilon' + d\epsilon')$. Thus

$$N_{\mathbf{x}}(\epsilon, \epsilon') d\epsilon d\epsilon' \propto \sum_{i=1}^M \sum_{j=1}^c \delta(\epsilon_i(\mathbf{x}) - \epsilon) \delta(\epsilon_{ij}(\mathbf{x}) - \epsilon') d\epsilon d\epsilon' \quad (13)$$

where $\epsilon_i(\mathbf{x})$ and $\epsilon_{ij}(\mathbf{x})$ denote the energy of the site i and its j -labeled (out of c) NN sites in the state \mathbf{x} .

The mean number $\langle N(\epsilon, \epsilon') \rangle$ is obtained by averaging over all possible states

$$\langle N(\epsilon, \epsilon') \rangle \propto \int_{\{\mathbf{x}\}} N_{\mathbf{x}}(\epsilon, \epsilon') P(\mathbf{x}) d\mathbf{x} \quad (14)$$

$$\langle N(\epsilon, \epsilon') \rangle \propto \int \dots \int_{\{\mathbf{x}\}} \sum_{i=1}^M \sum_{j=1}^c \delta(\epsilon_i - \epsilon) \delta(\epsilon_{ij} - \epsilon') \times \prod_{i=1}^M \prod_{j=1}^c f(\epsilon_i, \epsilon_{ij}) d\epsilon_1 \dots d\epsilon_M \quad (15)$$

where the integration over the set $\{\mathbf{x}\}$ is constrained by the frequency functions being fixed. Since the energy ϵ_{ij} can also be denoted ϵ_k being k ($k \neq i$) the label number of the corresponding NN site of the site i , the integration in eq 15 can be more clearly written as

$$\langle N(\epsilon, \epsilon') \rangle \propto \int \dots \int_{\{\mathbf{x}\}} \sum_{i=1}^M \sum_{k \in \mathbf{K}_i} \delta(\epsilon_i - \epsilon) \delta(\epsilon_k - \epsilon') \times \sum_{i=1}^M \sum_{k \in \mathbf{K}_i} f(\epsilon_i, \epsilon_k) d\epsilon_1 \dots d\epsilon_M \quad (16)$$

where \mathbf{K}_i is a small subset containing the label numbers of the NN sites of site i . After integrating over the pairs (ϵ_i, ϵ_j) , one gets

$$\langle N(\epsilon, \epsilon') \rangle \propto f(\epsilon, \epsilon') \sum_{i=1}^M \sum_{k \in \mathbf{K}_i} \left(\int \dots \int \prod_{\substack{k' \in \mathbf{K}_i \\ k' \neq k}} f(\epsilon, \epsilon_{k'}) \times \sum_{i \neq 1}^M \sum_{j \in \mathbf{K}_i} f(\epsilon_i, \epsilon_j) d\epsilon_1 \dots d\epsilon_{i-1} d\epsilon_{i+1} \dots d\epsilon_{k-1} d\epsilon_{k+1} \dots d\epsilon_M \right) \quad (17)$$

The proportionality comes from the fact that $P(\mathbf{x})$, defined by eq 8, is unnormalized and also that each pair of energies is counted twice in definition 13. From eq 17, it follows that

$$\langle N(\epsilon, \epsilon') \rangle d\epsilon d\epsilon' \propto f(\epsilon, \epsilon') d\epsilon d\epsilon' \quad (18)$$

which means the frequency of any arbitrary energy pair (ϵ, ϵ') on the simulated lattice equals that of the input frequency function. The proportionality constant in eq 18 must equal $Mc/2$ for consistency. (Strictly speaking, boundary conditions have to be assumed in order to have all sites with connectivity c .)

It is worth noting that every trial based upon eq 9 requires only the evaluation of the pair energy distribution function $f(\epsilon, \epsilon')$ (or the site-site correlation function $g(\epsilon, \epsilon')$), which is the function defining the model heterogeneous surface. It should also be pointed out that the alternative procedure to get an energy distribution over adsorption sites consists of the following steps: (a) starting from the empty lattice, an energy ϵ_1 for the first site is specified; (b) the energy values for the c neighboring sites are sampled from the conditional frequency function $f_c(\epsilon_1 | \epsilon_1) = f(\epsilon_1, \epsilon_1) / f_1(\epsilon_1)$, where j denotes one of the c nearest neighbor sites. Step b is then repeated up to lattice completion. However, this requires the inverse functions of the distributions associated with $f_1(\epsilon_1)$ and $f_c(\epsilon_1 | \epsilon_1)$ to be known, which is a hopeless task if many-site correlations are taken into account. Moreover, even in the simplest case of pair correlations only, this procedure yields an incorrect simulated distribution.²⁷ The problem arises with lattices with connectivity great than 2, since then assignment of an energy to a new site often finds that two (or more) of its nearest neighbor sites have assigned energies and, eventually, it becomes very difficult to satisfy the probability distributions for both sites at once. Attempts to remedy this problem lead one to triplet (or higher-order) site energy distributions.

III. The General Case: Many-Site Correlation

In the previous section we have presented the formulation in terms of a joint distribution of pairs of energies corresponding to NN sites. Since in most cases heterogeneous substrates are represented by the simple picture of either a totally random or patchwise distribution local properties of sites,² the consideration of correlations between NN sites is appealing because of the simplicity of the simulation and its relative tractability in theoretical calculations.^{2,18,11}

Site energy correlation can be introduced in a more general way by allowing a site to be statistically correlated to many others. Let us assume the function $f(e_1, e_2, \dots, e_n | \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) d\epsilon_1 d\epsilon_2, \dots, d\epsilon_n$ represents the probability for a cluster of n sites with positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$ with energies e_1, e_2, \dots, e_n within the intervals $(e_1, e_1 + d\epsilon_1), (e_2, e_2 + d\epsilon_2), \dots, (e_n, e_n + d\epsilon_n)$, respectively. If the distribution is statistically homogeneous over the lattice, then f depends only on the relative positions of the sites (we can also assume isotropy so that only the distances between sites counts), say, $|\mathbf{r}_{21}| \equiv |\mathbf{r}_2 - \mathbf{r}_1|, \dots, |\mathbf{r}_{n1}|, |\mathbf{r}_{32}|, \dots, |\mathbf{r}_{n(n-1)}|$.

By simplifying the notation \tilde{f} can be written as $\tilde{f}(\mathbf{e}_n, \mathbf{R}_n)$, where the sets \mathbf{e}_n and \mathbf{R}_n contain the energies and relative positions of the n sites

$$\mathbf{e}_n = \{e_1, \dots, e_n\}$$

$$\mathbf{R}_n = \{|\mathbf{r}_{21}|, \dots, |\mathbf{r}_{n1}|, |\mathbf{r}_{32}|, \dots, |\mathbf{r}_{n2}|, \dots, |\mathbf{r}_{n(n-1)}|\} \quad (19)$$

Analogous to eq 8, the probability for a given state $\mathbf{x} = \{\epsilon_1, \epsilon_2, \dots, \epsilon_m\}$ of the whole lattice to occur can be written in terms of the cluster distribution f (which is assumed to be known)

$$P(\mathbf{x}) \propto \prod_{\{\mathbf{e}_n\}} f(\mathbf{e}_n, \mathbf{R}_n) \quad (20)$$

where the product runs over all possible clusters of n sites sorted from the lattice in the state \mathbf{x} . We define as $\mathbf{A}_{in}(\mathbf{B}_{in})$ the set including all possible sets of energies (relative positions) of n -size clusters having the site i as a member. Accordingly,

$$\mathbf{A}_{in} = \{\mathbf{e}_{in}^1(\mathbf{x}), \dots, \mathbf{e}_{in}^{N_i}(\mathbf{x})\} \quad (21)$$

$$\mathbf{B}_{in} = \{\mathbf{R}_{in}^1(\mathbf{x}), \dots, \mathbf{R}_{in}^{N_i}(\mathbf{x})\} \quad (21)$$

where N_i is the total number of such a clusters and each element $\mathbf{e}_{in}^k(\mathbf{x})$ ($\mathbf{R}_{in}^k(\mathbf{x})$) is a set that includes the energies (relative positions) of the site i and $(n-1)$ remaining sites when the whole lattice is in the state \mathbf{x} .

The probability W for the most elementary transition $\mathbf{x} \rightarrow \mathbf{x}'$, involving the exchange of energies between the sites i and j picked at random, is given by

$$W(\mathbf{x} \rightarrow \mathbf{x}') = \min \left\{ 1, \frac{P(\mathbf{x}')}{P(\mathbf{x})} \right\} = \min \left\{ 1, \prod_{k_1}^{N_i} \frac{f(\mathbf{e}_{in}^{k_1}(\mathbf{x}'), \mathbf{R}_{in}^{k_1}(\mathbf{x}')) f(\mathbf{e}_{jn}^k(\mathbf{x}), \mathbf{R}_{jn}^k(\mathbf{x}'))}{f(\mathbf{e}_{in}^k(\mathbf{x}), \mathbf{R}_{in}^k(\mathbf{x})) f(\mathbf{e}_{jn}^{k_1}(\mathbf{x}), \mathbf{R}_{jn}^{k_1}(\mathbf{x}))} \right\} \quad (22)$$

The transition will be accepted if condition 12 happens to be true.

In practice, if many-site correlation is to be considered, transitions switching the energies on many sites at once could favor the approach to the statistical equilibrium of the spatial distribution of energies.

One example of many-site correlation is given by the multivariate Gaussian distribution³³

$$f(e_1, \dots, e_n | \mathbf{r}_{12}, \dots, \mathbf{r}_{(n-1)n}) = (2\pi)^{-n/2} (\det \mathbf{C})^{-1/2} \times \exp \left[-\frac{1}{2} \sum_{i,j=1}^n (e_i - \bar{e}_i) C_{ij}^{-1} (e_j - \bar{e}_j) \right] \quad (23)$$

where $C_{ij} = \overline{(e_i - \bar{e}_i)(e_j - \bar{e}_j)}$ are the elements of the covariance matrix \mathbf{C} , and C_{ij}^{-1} the elements of the inverse matrix \mathbf{C}^{-1} . The distribution (23) is completely determined by the mean values \bar{e}_i and the covariance matrix \mathbf{C} . This distribution has already been used as a representation of the continuum stochastic adsorption field in the GGM⁶ in the calculation of the equation of state for adsorbed gas on heterogeneous substrate at low coverage.

To give an example of the usefulness of this distribution, suppose one is interested in a model surface on which the correlation between pairs of site energies decays exponentially with the distance between sites. One then should use the distribution of eq 23 with $n = 2$ and

$$C_{12}(|\mathbf{r}_{12}|) = \overline{(e_1(\mathbf{r}) - \bar{e})(e_2(\mathbf{r} + \mathbf{r}_{12}) - \bar{e})} = \sigma^2 G(|\mathbf{r}_{12}|) = \sigma^2 \exp \left(-\frac{|\mathbf{r}_{12}|}{r_0} \right) \quad (24)$$

where $\sigma^2 = C_{12}(0)$ is the variance of the distribution and r_0 the typical correlation length. (For simplicity we assume that all sites on the lattice are equivalent so that $\bar{e}_1 = \bar{e}_2 = \bar{e}$). $G(|\mathbf{r}_{12}|)$ denotes the pair correlation of the energy distribution. Thus, eq 23 becomes

$$f(e_1, e_2 | \mathbf{r}_{12}) = \frac{1}{2\pi\sigma^2 \sqrt{1 - G(|\mathbf{r}_{12}|)}} \times \exp \left[-\frac{1}{2} \frac{(e_1 - \bar{e})^2 + (e_2 - \bar{e})^2 - 2G(|\mathbf{r}_{12}|)(e_1 - \bar{e})(e_2 - \bar{e})}{2\sigma^2(1 - G(|\mathbf{r}_{12}|)^2)} \right] \quad (25)$$

To assign energies to adsorption sites according to (24) and (25), the correct energy frequencies must be produced at the beginning by distributing values at random from the marginal frequency density function

$$\bar{f}(e) = \frac{1}{\sqrt{2\pi}\sigma^2} \exp \left[-\frac{1}{2} \frac{(e - \bar{e})^2}{\sigma^2} \right] \quad (26)$$

Then, realizations of the correct spatial distribution of site energies complying with the correlation function of eq 24 can be accomplished after a number of transitions with probabilities given by using eq 25 in eq 22. The relaxation to statistical equilibrium can be monitored by comparing the theoretical correlation function (eq 24) with that calculated over successive realizations of the lattice.

IV. Application to the Dual Site-Bond Description (DD) of Heterogeneous Surfaces

A common feature of most heterogeneous surface models is that they assume the adsorption sites to be the only elements of the adsorption field. However, in dealing with surface diffusion, a more appropriate description requires that the saddle point energies be introduced also as an important element of the continuum adsorption potential.

The saddle point energy represents the maximum of the particle–substrate interaction along the path connecting two nearest neighbor sites. Once site and saddle point energies have been assigned, the activation barriers for diffusion are therefore specified. An alternative description of heterogeneous surfaces incorporating adsorption sites and saddle point energies (hereafter called bonds) has been proposed in refs 19 and 20. Here we briefly summarize its formulation.

Sites as well as bonds, observed independently in the adsorption field, are statistically characterized by their energy probability density functions $f_s(\epsilon_s)$ and $f_b(\epsilon_b)$, respectively. Here, s and b denote site and bond properties, respectively. We denote the corresponding cumulative distributions as

$$S(\epsilon_s) = \int_0^{\epsilon_s} f_s(\epsilon) d\epsilon \quad (27)$$

and

$$B(\epsilon_b) = \int_0^{\epsilon_b} f_b(\epsilon) d\epsilon \quad (28)$$

The simplest way of introducing the spatial alternation of site and bond energies over the surface is through the joint distribution of nearest neighbor site-bond energies $f(\epsilon_s, \epsilon_b)$. This function can be obtained from $f_s(\epsilon_s)$, $f_b(\epsilon_b)$, and the construction principle (CP) which states: the absolute value of the energy of every adsorption site must be greater than, or at least equal to, the energy of any its neighboring bonds. After some analysis, this finally yields^{19,29,30}

$$f(\epsilon_s, \epsilon_b) = f_s(\epsilon_s) f_b(\epsilon_b) \Phi(\epsilon_s, \epsilon_b) \quad (29)$$

where $\Phi(\epsilon_s, \epsilon_b)$ is a correlation function with the general properties that

$$\Phi(\epsilon_s, \epsilon_b) = \begin{cases} 0 & \forall \epsilon_s < \epsilon_b \\ \frac{1}{[B(\epsilon_b) - S(\epsilon_b)]} \exp \left(-\int_{B(\epsilon_b)}^{\epsilon_s} \frac{dB}{B - S} \right) & \forall \epsilon_s \geq \epsilon_b \end{cases} \quad (30)$$

In general, f_s and f_b are arbitrary functions only constrained to fulfill the following condition

$$B(\epsilon) \geq S(\epsilon) \quad (31)$$

which assures that there are enough bonds with energy ϵ or lower, to link the sites with energy ϵ or lower (otherwise, it would not be possible to combine both distributions in a whole lattice of sites separated by bonds without violating the CP).

If we denote as Ω the overlap area between $f_s(\epsilon)$ and $f_b(\epsilon)$ (the common area of these functions plotted against ϵ), Φ has the following properties: (i) $\Phi_{\Omega \rightarrow 0}(\epsilon_s, \epsilon_b) = 1 \forall \epsilon_s, \epsilon_b$ (sites and bonds are distributed completely at random); (ii) $\Phi_{\Omega \rightarrow 1}(\epsilon_s, \epsilon_b) \propto \delta(\epsilon_s - \epsilon_b) \forall \epsilon_s, \epsilon_b$ (large-patch limit).

It has already been shown that simulation of dual-site bond heterogeneous surfaces becomes a difficult problem if there exists a high overlap between $f_s(\epsilon_s)$ and $f_b(\epsilon_b)$ (strong energy correlation).²⁷ The simulated density functions can be very distorted, and any attempt to correct this distortion may give rise to spurious energy correlations. There is strong evidence that the assignation of energies to sites and bonds through a deterministic sequence of sites over the lattice can produce as a consequence strong anisotropy in the correlation between elements of the lattice.²²

(33) Adler, R. J. *The Geometry of Random Fields*; Wiley: New York, 1981.

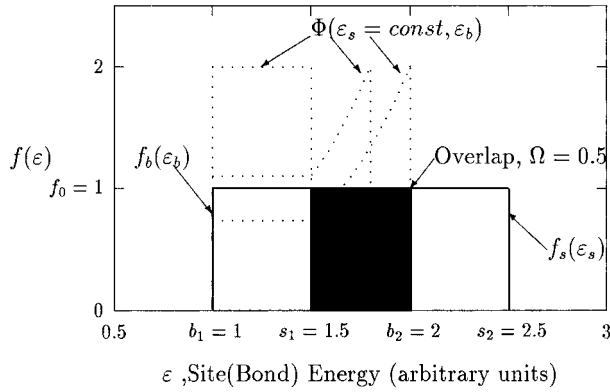


Figure 1. Uniform site and bond energy frequency functions $f_s(\epsilon_s) = f_0 = 1, \forall \epsilon_s \in (1.5, 2.5)$ and $f_b(\epsilon_b) = f_0 = 1, \forall \epsilon_b \in (1, 2)$. This case corresponds to a degree of overlap $\Omega = 0.5$ (blacked area). Also shown are the theoretical correlation functions $\Phi(\epsilon_s, \epsilon_b)$ calculated in refs 19 and 20 for three fixed values of ϵ_s .

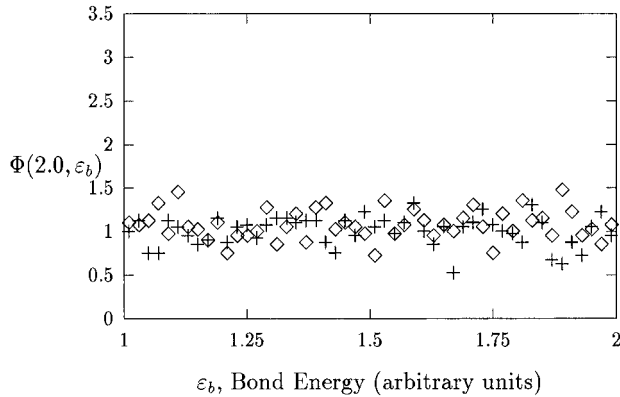


Figure 2. Site-bond energy correlation function $\Phi(\epsilon_s = 2.00, \epsilon_b)$ versus ϵ_b for random configurations of site and bond energies (initial state of the simulation) for two different degrees of overlap: $\diamond, \Omega = 0.5$; $+, \Omega = 0.7$.

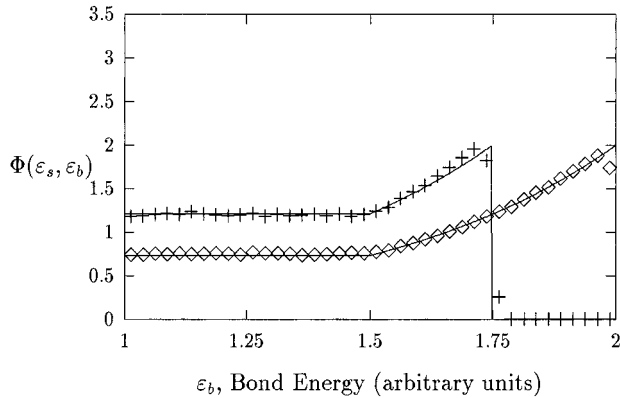


Figure 3. Site-bond energy correlation function $\Phi(\epsilon_s, \epsilon_b)$ for a one-dimensional site-bond heterogeneous chain plotted against ϵ_b for two different values of ϵ_s : $\diamond, \epsilon_s = 2.00$; $+, \epsilon_s = 1.75$. Symbols and lines correspond to simulation and theoretical results, respectively. The overlap between frequency functions $f_s(\epsilon_s)$ and $f_b(\epsilon_b)$ is $\Omega = 0.5$.

We can formally apply the method proposed in section II to simulate a site-bond heterogeneous surface as a lattice of these two elements with an energy distribution according to eq 29. After selection of the desired lattice geometry, site energies from $f_s(\epsilon_s)$ and bond energies from $f_b(\epsilon_b)$ are randomly distributed over the array of sites connected by bonds (evidently, each bond connects two nearest neighbor sites). Then, spatial site and bond rearrangements are carried out with transition probability given by eq 5. For the following formulas, we assume that the j th site and k th bond are labeled by ϵ_{sj} and ϵ_{bk}

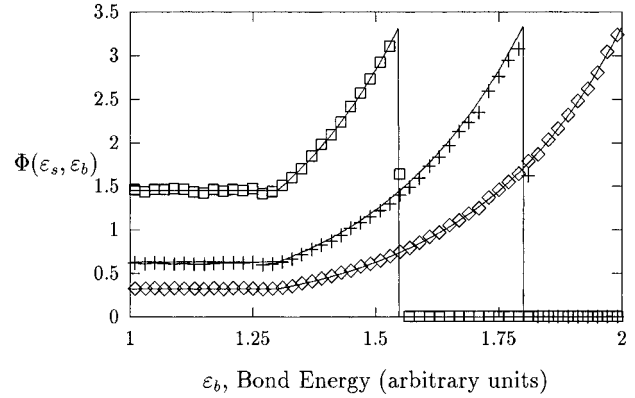


Figure 4. Same as Figure 3 but for $\Omega = 0.7$ (stronger energy correlation): $\diamond, \epsilon_s = 2.05$; $+, \epsilon_s = 1.80$; $\square, \epsilon_s = 1.60$. In all cases the bond energy range was kept unchanged, $(b_1, b_2) = (1, 2)$, and the site energy range (s_1, s_2) was shifted in order to get the correct overlap.

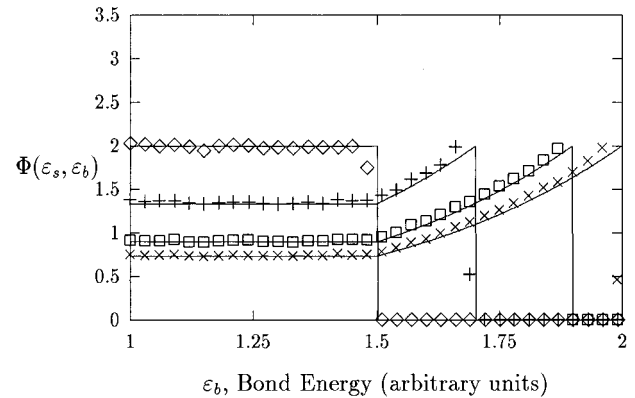


Figure 5. Same as Figure 3 but for a two-dimensional lattice and $\Omega = 0.5$; $\times, \epsilon_s = 2.00$; $\square, \epsilon_s = 1.9$; $+, \epsilon_s = 1.7$; $\diamond, \epsilon_s = 1.5$.

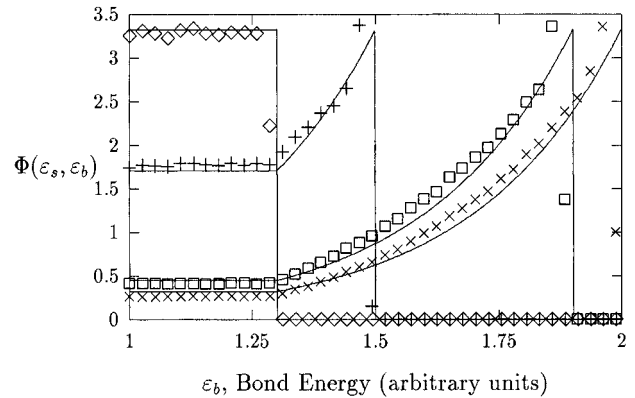


Figure 6. Same as Figure 5 but for $\Omega = 0.7$; $\times, \epsilon_s = 2.00$; $\square, \epsilon_s = 1.9$; $+, \epsilon_s = 1.5$; $\diamond, \epsilon_s = 1.3$.

respectively. Hereafter, we use the notation $\epsilon_{s1}^k, \epsilon_{s2}^k$ in order to distinguish the energy between the two sites linked by the k th bond, and $\epsilon_{b1}^j, \epsilon_{b2}^j, \dots, \epsilon_{bc}^j$ for the c bonds directly connected to the j th site.

If the trial state \mathbf{x}' is reached from the state \mathbf{x} by only interchanging energies of sites i and j , the transition probability will be determined by the ratio (see eq 9)

$$\frac{P(\mathbf{x}')}{P(\mathbf{x})} = \prod_{k=1}^c \frac{\Phi(\epsilon_{sj} \epsilon_{bk}^i) \Phi(\epsilon_{si} \epsilon_{bk}^j)}{\Phi(\epsilon_{si} \epsilon_{bk}^i) \Phi(\epsilon_{sj} \epsilon_{bk}^j)} \quad (32)$$

where the index k runs over the bonds connecting the site i and its nearest neighbors j .

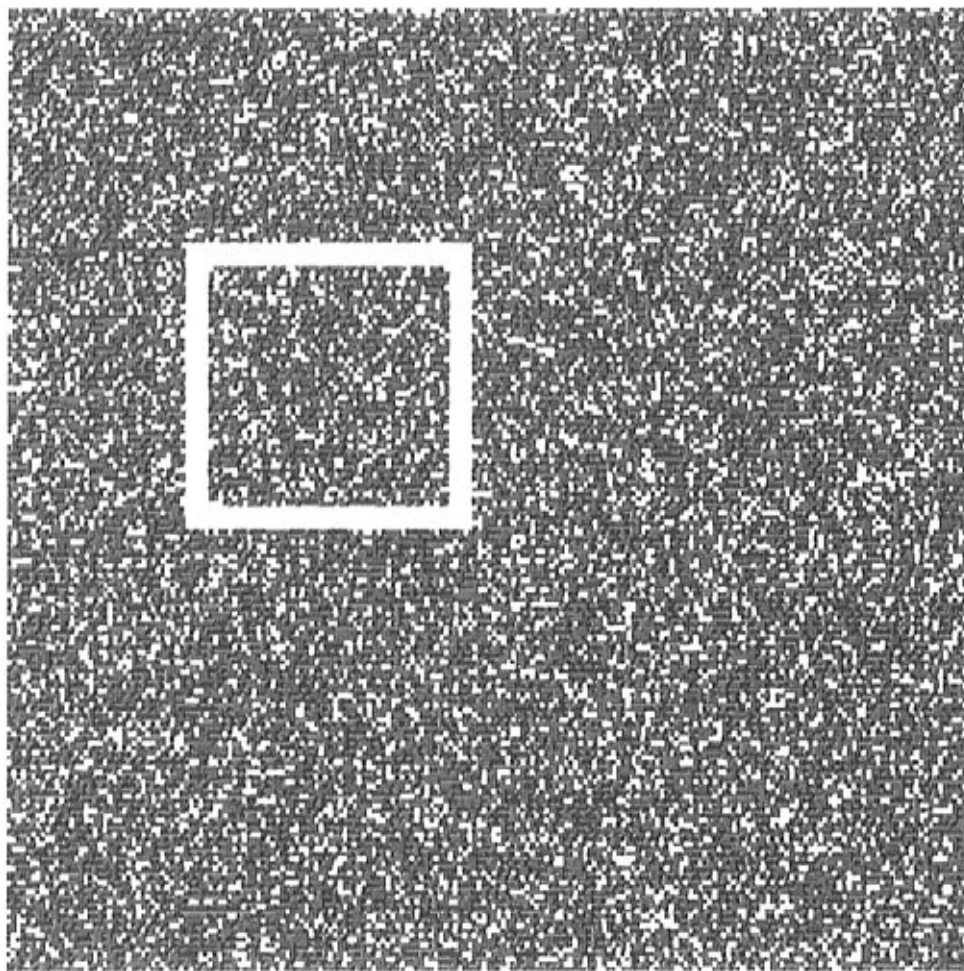


Figure 7. Color representation of a simulated square lattice of sites (square tiles) connected by bonds (not shown) for $\Omega = 0.1$ ($f_s(\epsilon_s) = 1, \forall \epsilon_s \in (1.9, 2.9)$ and $f_b(\epsilon_b) = 1, \forall \epsilon_b \in (1, 2)$). The colors white, green, gray, and red correspond to site energy intervals (1.9, 2.15), (2.15, 2.4), (2.4, 2.65), and (2.65, 2.9), respectively.

Another simple case corresponds to a trial state \mathbf{x}' which is obtained from the state \mathbf{x} by exchanging the energy of the k th and l th bonds. In this case eq 9 gives

$$\frac{P(\mathbf{x}')}{P(\mathbf{x})} = \prod_{i=1}^2 \frac{\Phi(\epsilon_{sb}^k \epsilon_{bl}) \Phi(\epsilon_{sb}^l \epsilon_{bk})}{\Phi(\epsilon_{sb}^k \epsilon_{bk}) \Phi(\epsilon_{sb}^l \epsilon_{bl})} \quad (33)$$

Using the following property of Φ ^{19,29}

$$\Phi(\epsilon_s', \epsilon_b) = \Phi(\epsilon_s, \epsilon_b) \exp\left(-\int_{B(\epsilon_b)}^{B(\epsilon_s')} \frac{dB}{B - S}\right)$$

eqs 32 and 33 finally yield

$$\frac{P(\mathbf{x}')}{P(\mathbf{x})} = \begin{cases} 1 & \text{if construction principle is} \\ & \text{satisfied for the state } \mathbf{x}' \\ 0 & \text{otherwise} \end{cases} \quad (34)$$

This is a remarkable consequence which means that the final spatial distribution of site and bond energies from arbitrary distributions $f_s(\epsilon_s)$ and $f_b(\epsilon_b)$ can be obtained through transitions with only two typical values, namely, 1 (acceptance) for those satisfying CP and 0 (rejection) otherwise. Furthermore, it is no longer necessary to know the explicit form of $\Phi(\epsilon_s, \epsilon_b)$.

We now have prescriptions for generating a heterogeneous surface of sites from either a given site–site correlation or from given site and bond distributions. In the case of the site–site correlation, one generates first

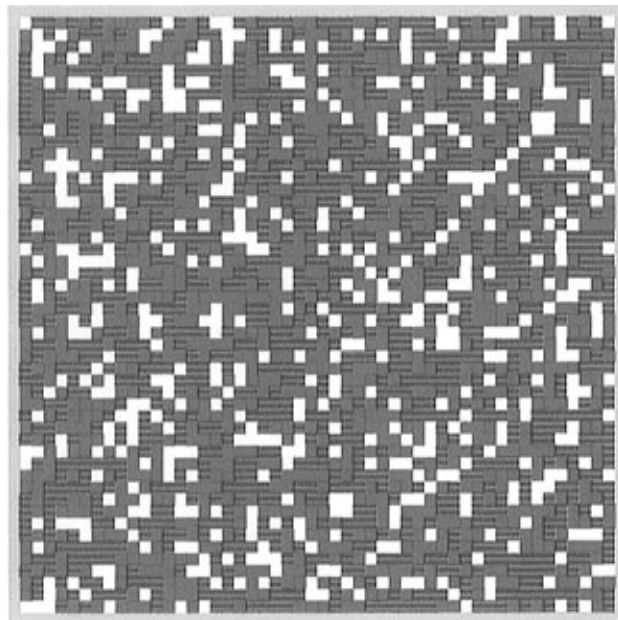


Figure 8. Close up of the yellow-framed area in Figure 7.

a random surface with a number distribution corresponding to the desired $f(\epsilon)$; site energies are then switched pairwise in a Markov chain with acceptance probabilities governed by eqs 5 and 8. Statistical equilibrium is reached when $f(\epsilon, \epsilon')$ or $g(\epsilon, \epsilon')$ for the lattice of sites fluctuates around the initially assumed function. In the case of the site–

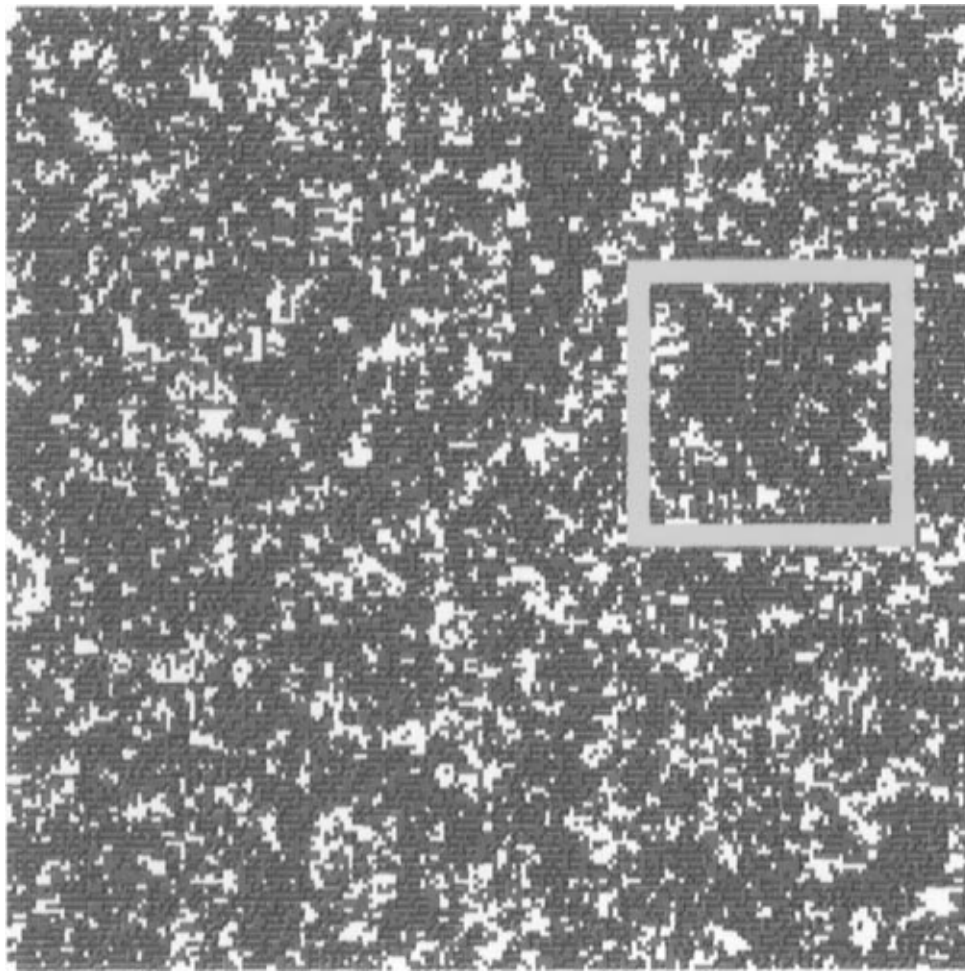


Figure 9. Same as Figure 7 for $\Omega = 0.8$ ($f_s(\epsilon_s) = 1, \forall \epsilon_s \in (1.2, 2.2)$ and $f_b(\epsilon_b) = 1, \forall \epsilon_b \in (1, 2)$). The colors white, green, gray, and red correspond to the site energy subintervals $(1.2, 1.45)$, $(1.45, 1.7)$, $(1.7, 1.95)$, $(1.95, 2.2)$ respectively.

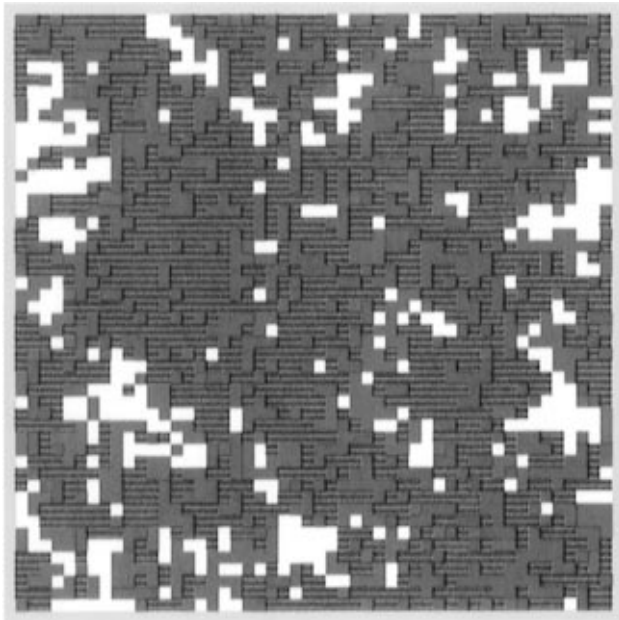


Figure 10. Close up of the yellow-framed area in Figure 9.

bond distribution, one has assumed site and bond number distributions $f_s(\epsilon_s)$ and $f_b(\epsilon_b)$; however, the simulation now consists of switching both site energies (eq 32) and bond energies (eq 33). The correlation function $\Phi(\epsilon_s, \epsilon_b)$ can be calculated from eqs 27, 28, and 30. In the simulation, statistical equilibrium is again reached when $\Phi(\epsilon_s, \epsilon_b)$ for the simulated lattice fluctuates around the assumed

function. At equilibrium, the result in eq 34 means that any change of site and bond energies fulfilling the CP has the same probability of occurring (equal to unity). Accordingly, those trial states violating CP are rejected. The simulation of heterogeneous surfaces (a similar argument holds for the analogous model of porous media) in the framework of this particular model, which appears to be difficult at first glance, turns out to be a simple procedure.

Simulations of a one-dimensional chain (1×10^5 sites, 1×10^5 bonds), and of a two-dimensional square lattice ($L \times L$ sites, $2 \times L \times L$ bonds with $L = 500$) have been performed for different degrees of energy correlation by varying Ω . For simplicity, constant frequency energy distributions were used for ϵ_s and ϵ_b (see Figure 1). Thus, $f_s(\epsilon_s) = f_0 \forall \epsilon_s \in (s_1, s_2)$ and $f_b(\epsilon_b) = f_0 \forall \epsilon_b \in (b_1, b_2)$. The values $f_0 = 1$, $(b_1, b_2) = (1, 2)$ were used throughout the calculations and (s_1, s_2) were shifted in each case to have the desired value of Ω . Accordingly, $s_1 = b_2 - (b_2 - b_1)\Omega$ and $s_2 = s_1 + (b_2 - b_1)$.

The number of transitions needed to reach equilibrium is typically 50 (100) MCS for $\Omega = 0.5$ and 100 (2000) MCS for $\Omega = 0.7$ (1 MCS \equiv one attempted transition per lattice element) in the one (two)-dimensional case. In all cases the initial state was a random distribution of site and bond energies (see Figure 2).

The equilibrium simulated correlation function $\Phi^{\text{sim}}(\epsilon_s, \epsilon_b)$ was compared with the theoretical function $\Phi(\epsilon_s, \epsilon_b)$ calculated elsewhere for these rectangular energy distributions.^{19,20,27} Indeed, given that $\Phi(\epsilon_s, \epsilon_b)$ defines a surface, we have evaluated the dependence of this function upon ϵ_b for several fixed values of ϵ_s . From eq 29

$$\Phi^{\text{sim}}(\epsilon_s, \epsilon_b) = \frac{f^{\text{sim}}(\epsilon_s, \epsilon_b) d\epsilon_s d\epsilon_b}{f_s(\epsilon_s) d\epsilon_s f_b(\epsilon_b) d\epsilon_b} \quad (35)$$

where the superscript *sim* on the right hand means the pair frequency calculated for the simulated lattice. Figure 2 shows the correlation function at the start of the simulation, where the CP is often violated because of the spatially random initial energy assignments. Excellent agreement is found between the final simulated and theoretical correlation functions in both the one- and two-dimensional systems (see Figures 3–6). In the particular case of the DD the only explicit energy correlation taken into account is between pairs of nearest neighbor elements (sites and bonds), as stated above. However, this correlation is effectively propagated to more distant elements in such a way that the site–site (and analogously for site–bond and bond–bond) energy correlation function $C_{ss}(r)$, defined as

$$C_{ss}(r) = \frac{\langle (\epsilon_s(r) - \bar{\epsilon}_s)(\epsilon_s(0) - \bar{\epsilon}_s) \rangle}{\langle (\epsilon_s(r))^2 \rangle} \quad (36)$$

where $\epsilon_s(r)$ and $\epsilon_s(0)$ denote the energies of a pair of sites separated by r lattice units, decays exponentially with r with a typical correlation length r_0 , $C_{ss} = \exp(-r/r_0)$. r_0 depends on the degree of overlap between f_s and f_b so they are empirically related through $r_0 = \Omega/(1 - \Omega)$. This length physically represents the typical size of clusters of sites having very similar energies. Furthermore, the limits $\Omega \rightarrow 0$ ($r_0 \rightarrow 0$) and $\Omega \rightarrow 1$ ($r_0 \rightarrow \infty$) give random and large-patch distribution of site and bond energies, respectively. The larger Ω (or r_0) is, the more patchwise the site and bond topography. These different energy topographies can be appreciated in the pictures shown in Figures 7–10. They represent a square lattice of sites (square tiles) connected by bonds (not shown) obtained by applying the simulation procedure described above. A close up of a smaller area was made in each case (Figures 8 and 10) in order to have a better illustration of the local energy correlations. The site energy interval (s_1, s_2) was divided into four subintervals and a different color was assigned to energies within each subinterval. This gives the following sequence: white, green, gray, and red assigned to sites from the weaker (low ϵ_s) to the stronger (higher ϵ_s) ones (see more details in Figures 7–10). The cases $\Omega = 0.1$ ($r_0 \rightarrow 0$) is displayed in Figures 7 and 8 where different colors appear very scattered. Figures 9 and 10 show the cases $\Omega = 0.8$ ($r_0 \approx 4$ lattice units) where the clustering of similar sites becomes evident.

It should be noted that the pair correlation approximation is only the starting point in a theory in which correlations between triplets, quartets, etc., are taken explicitly into account. As presented in Section III, the methodology is general so that these more complex descriptions can be treated analogously as well. Indeed,

there exist models of heterogeneous surfaces such as the GGM that incorporate multiple site correlations⁶ which could be simulated as described in section 3. However, in practice it is always desirable to reduce multiple correlations by a superposition approximation of pair correlations since the model becomes more tractable analytically and numerically.¹¹

V. Conclusions

A method to simulate the adsorption potential for an adsorbate atom over a heterogeneous surface has been presented. It is particularly useful when spatial energy correlations are present in the model for the surface. Although most of the discussion has been presented here in terms of nearest-neighbor energy correlations only, the formulation is general and heterogeneous surfaces with correlation between pairs of more distant sites or many-site correlations can be simulated as well. In addition, more sophisticated descriptions such as the dual site-bond model, which includes other basic elements of the adsorptive field, can be treated.

Additional applications to the simulation of porous solids are also straightforward. The dual site-bond model was originally formulated to describe random porous networks.³² This problem is formally isomorphous with that of random adsorptive fields. There exist a complete correspondence between pores (throats) and sites (bonds). It has been pointed out that spatial correlation of pore and throat sizes can have a drastic effect on percolation, imbibition, immiscible displacement of fluids, and capillary condensation of gases in the porous space.²⁹ However, it is still very difficult to properly simulate three-dimensional model porous solids in the framework of this description. The pure Monte Carlo method presented here may provide a solution for such a problem. One of its major advantages is that porous networks with correlated pore-neck size distributions (other than uniform) can be simulated. It also encourages the simulation of model porous media with more realistic features as proper pore-neck size distributions and variable connectivity.

It should be noted that we have presented only the general theory. Nothing has been said about the rate of convergence of the pairwise site energy distribution to the equilibrium one. In general, the stronger the energy correlation, the slower the convergence to equilibrium when the starting point is an arbitrary initial state. However, it should be possible to apply the techniques for improving convergence that are available for Monte Carlo simulations in statistical physics.³⁴

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LA9510036

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