Adsorption 5, 81–89 (1999)

# A New Approach to the Theory for Adsorption Isotherms on Heterogeneous Surfaces

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**Abstract.** Simulations of the adsorption of nitrogen on several model heterogeneous surfaces (Cascarini de Torre and Bottani, 1997) are analyzed using an alternative description in which the surface is treated as a collection of supersites, each of which can hold 5–6 molecules in the complete monolayer. The local isotherm that is used to describe the sub-monolayer adsorption on a supersite is here taken to be the truncated virial isotherm. This theory fits well to the simulated data. The advantages and disadvantages of this approach are discussed and it is concluded that the supersite concept is a promising approach to the description of adsorption on realistic models of heterogeneous surfaces.

**Keywords:** N2, virial, supersite, local isotherm

## 1. Introduction

Theoretical descriptions of adsorption on heterogeneous surfaces are often based on the idea that the surface can be represented by a lattice of sites with varying adsorption energies (Rudzinski and Everett, 1992; Jaroniec and Madey, 1988). These sites are taken to be independent of each other except possibly for mean field interaction energies with neighboring adsorbed atoms. It is generally assumed that each site is capable of holding only one adsorbed molecule in the monolayer. The adsorptive properties of such a surface are then characterized by the distribution of these sites over their adsorption energies, i.e., by the numbers of sites with given adsorption energies. As is now well-known, this model suffers from a number of defects: it does not readily lend itself to treatments of the adsorption of mixtures of molecules with differing areas, since a site area chosen to accommodate one size molecule will not give a good fit to other size molecules. Indeed, it appears that the final monolayer capacities for different physically adsorbed molecules often do not correspond to adsorption on a fixed number of sites but rather to nearly close-packed arrays of adsorbate molecules. Furthermore, models of the surface of amorphous materials yield complex adsorption energy surfaces (minimum energy as a function of $X$, $Y$, the position over the surface) for which the concept of adsorption sites as a regular array of points is found to be a gross over-simplification (Bakaev and Steele, 1992; Bakaev and Voit, 1990). The actual energy surfaces show extended regions of strong adsorption corresponding to nano-valleys; they also exhibit partial sites, where shallow minima occur in an otherwise rapid monotonic variation of energy with $X$, $Y$; and finally, there are regions of relatively small minimum energy that take up significant fractions of the total area of the surface and thus are hard to account for in the usual site-wise models.

Thus, it would seem useful to develop a model for adsorption on such surfaces that is flexible enough to allow one to avoid some of the deficiencies in the standard model while still retaining the description of heterogeneity in a physically transparent fashion. To this end, it is suggested in this paper that one replace the idea of adsorption site with what we will call "supersites". These supersites are obtained by dividing the surface into a regular lattice of elements that are sufficiently large to hold several adsorbed molecules (on the order of 4–6). Within each supersite, the energy will vary from point to point so that surface heterogeneity is maintained. The "local isotherm" concept is retained, but in a form which allows more than one molecule per site. It can be noted here that patch-wise adsorption can be considered as an example of the supersite model. The patch-wise or homotattic model treats the surface as a collection of patches within which the adsorption energy is constant (Ross and Olivier, 1964). The patches are assumed to be large enough so that edge effects are negligible so that one can represent the adsorption on each patch by the isotherm for an infinite uniform surface. Heterogeneity is included by assuming that different patches can have different adsorption energies. However, collections of very large uniform patches do not appear to represent real surfaces and there has been little work on the determination of the effect of edge effects upon the thermodynamic properties of films on surfaces made up of finite-sized patches.

After presenting the theoretical basis for the supersite approach, computer simulations of nitrogen on an amorphous solid that is modeled as a "Bernal" surface are used to test some of the equations that describe this concept. Advantages and disadvantages of the approach are then discussed.

## 2. Theory

To recapitulate a well-known statistical thermodynamic derivation (Hill, 1960a), the grand partition function (GPF) $\Xi$ for a submonolayer film adsorbed on independent sites can be written as the product of $\xi_i$, the grand partition function for adsorption on a site with energy $\epsilon_i$. The crucial assumption here is that the statistics for adsorption on each site is independent of the status of all other sites. For such a collection of independent subsystems, the GPF becomes:

$$\Xi = \prod_i \xi_i \tag{1}$$

$$= \prod_i [1 + q_i \lambda] \tag{2}$$

where $\lambda$ is the activity $\exp(-\mu/kT)$ and $q_i$ is the canonical partition function for a single molecule adsorbed on the $i$th site. This quantity is often written as $a$ $\exp(-\epsilon_i/kT)$ in the absence of mean field interaction. Here, the constant $a$ is a factor arising from the integrations over the more-or-less quadratic variations in the gas-solid interaction near its minimum. For molecules lacking lateral interactions with molecules on near-by sites, this model gives the local Langmuir equation. An improved theory includes the lateral interactions in a mean field approximation to give a local isotherm that is described as the Bragg-Williams or the Fowler equation, to name only a couple of the titles given to this description (Hill, 1960b). The GPF for the single independent subsystem which is site $i$ is given by $\xi_i$ and Eq. (2) indicates that this site can be in one of two states: empty or occupied by a single adsorbed molecule.

Let us now consider how this argument must be changed to allow for a surface that can hold more than one molecule per supersite. If we continue to assume that the properties of the adsorbed molecules on a supersite are independent of those on neighboring supersites, we have

$$\Xi = \prod_I \xi_I \tag{3}$$

where $\xi_I$ denotes the local GPF for the molecules on the $I$th supersite and which, for monolayer adsorption, is given by:

$$\xi_I = \sum_i \sum_n q_I(n) \lambda^n \tag{4}$$

where now $q_I(n)$ is the canonical partition function for $n$ molecules on the $I$th supersite. If one subdivides that surface into an array of supersites that can hold several molecules in the monolayer, the subsystem GPF will be a sum of several terms for occupancies extending up to $n_I^*$. We then must attempt to derive an accurate local isotherm for the atoms adsorbed on such a supersite and to include interactions with the atoms on neighboring supersites at a mean-field level. The fact that this supersite is actually quite small should help in deriving the isotherm, and actually, the so-called quasi-chemical isotherm for monolayer adsorption has been shown to correspond to adsorption on a surface made up of independent supersites each of which can hold a maximum of two atoms (Steele, 1974; Domb, 1960).

Although the sum over $n$ extends to $n = \infty$ in principle, in practice one can truncate it at the point where the site is fully occupied; i.e., where the total area occupied by $n^*$ atoms adsorbed on the site is equal to the supersite area $\sigma_i$. Thus, $n^* \times a_m$ is essentially equal to the supersite area, if $a_m$ is the area per adsorbed atom. At $n = n^*$, addition of another atom to the limited supersite area will give rise to strongly repulsive interactions between the atoms adsorbed on the supersite and thus, to a vanishingly small $q_I(n)$ for $n > n^*$.

In the presence of lateral interactions arising from atoms adsorbed on nearby supersites, the mean field approximation means that $q_I(n)$ will be multiplied by $\exp(-w/kT)$, where $w$ is the mean energy of interaction of the adsorbed atoms with those on neighboring supersites. The adsorption isotherm can be expressed as $\overline{N}$, the average number of molecules adsorbed, as a function of $\lambda$ and is obtained in the usual way from

$$\overline{N} = \lambda \sum_I \frac{\partial \ln \xi_I}{\partial \lambda} \tag{5}$$

If the configurations of the molecules on the surface are not changed when the lateral interaction energy between the atoms on a given supersite and those on neighboring supersites is included, one will obtain the mean field approximation for this model.

We now see that the supersite concept requires that one estimate the $q_I(n)$ for $n$ equal to a small number. However, this complication is counterbalanced by the advantage that the area per supersite is no longer defined by the requirement that there be a maximum of one molecule per supersite. In this way, occupancy by molecules of differing areas can be handled in a straightforward fashion. Also, the irregular nature of amorphous surfaces is easily taken into account in this picture since much of this irregularity is dealt with by integration over the (small) area of the supersite. Specifically, consider $q_I(1)$, the partition function for a single atom on supersite $I$, which is now

$$q_I(1) = \int_{\mathcal{A}_\mathcal{I}} \exp(-[\epsilon_I(\boldsymbol{\tau}, Z)/kT]\, d\boldsymbol{\tau}\, dZ \tag{6}$$

where $\mathcal{A}_\mathcal{I}$ is the area of the $I$th supersite, $Z$ is the distance perpendicular to the surface, and $\epsilon_I(\boldsymbol{\tau}, Z)$ is the adsorption energy at point $\boldsymbol{\tau}$ ($=X, Y$) and $Z$ in this supersite. Note that an integration over molecular orientation is also required if the molecule is non-spherical with an angle-dependent gas-solid interaction energy.

A direct evaluation of some of the terms involving larger values of $n$ leads to the supersite version of the expansion in powers of $n$ that is essentially the virial adsorption isotherm. Of course, if the supersite is taken to be very large, many terms in the expansion must be included. The point of taking a relatively small supersite is that it allows one to truncate the expansion after a few terms. Here, we concentrate on the evaluation of the first two contributions to the local GPF. A general expression for the canonical partition function of two particles $\alpha$ and $\beta$ on supersite $I$ is:

$$\begin{aligned} q_I(2) = \frac{1}{2} \int_{\mathcal{A}_\mathcal{I}} \int_{\mathcal{A}_\mathcal{I}} & \exp(-[\epsilon_I(\boldsymbol{\tau}_\alpha, Z_\alpha) \\ & + \epsilon_I(\boldsymbol{\tau}_\beta, Z_\beta)]/kT) \\ & \times f(\boldsymbol{\tau}_{\alpha\beta}, Z_{\alpha\beta})\, d\boldsymbol{\tau}_\alpha\, d\boldsymbol{\tau}_\beta\, dZ_\alpha\, dZ_\beta \end{aligned} \tag{7}$$

where $Z_{\alpha\beta}$ is $Z_\alpha - Z_\beta$ and $f(\boldsymbol{\tau}_{\alpha\beta}, Z_{\alpha\beta})$ is a function that is zero when the distance between atoms $\alpha$ and $\beta$ is smaller than their collision diameter $\sigma_{\alpha\beta}$ and is $\exp[-u(\boldsymbol{\tau}_{\alpha\beta}, Z_{\alpha\beta})/kT] - 1$ otherwise.

We can now derive a local isotherm for supersite $I$ from Eqs. (3) and (4). One has

$$\overline{N} = \sum_I N_I \tag{8}$$

with

$$N_I = \frac{\sum_n n q_I \lambda^n}{\sum_n q_I \lambda^n} \tag{9}$$

Keeping only the first two terms in these sums for the moment, we find

$$N_I = \lambda q_I(1) \left[ 1 + \frac{2q_I(2) - q_I^2(1)}{q_I(1)} \lambda + \cdots \right] \tag{10}$$

or, rearranging to a more familiar form,

$$\ln N_I = \ln[\lambda q_I(1)] + \frac{2q_I(2) - q_I^2(1)}{q_I^2(1)} N_I + \cdots \tag{11}$$

In this form, the Henry's Law constant $K_{HI}$ for low coverage adsorption on supersite $I$ is

$$K_{HI} = \frac{1}{kT} \int_V \{\exp(-[\epsilon_I(\boldsymbol{\tau}, Z)/kT] - 1\}\, d\boldsymbol{\tau}\, dZ \tag{12}$$

The second virial coefficient $B_I$ is given by:

$$B_I = -\frac{2q_I(2) - q_I^2(1)}{2q_I^2(1)} \tag{13}$$

and the truncated virial adsorption isotherm is

$$\ln(N_I^*/p) = \ln(K_{HI}) - 2B_I N_I^* + \cdots \tag{14}$$

where $p$ is the pressure of the ideal gas in equilibrium with the adsorbed layer ($K_{HI}$ has units of

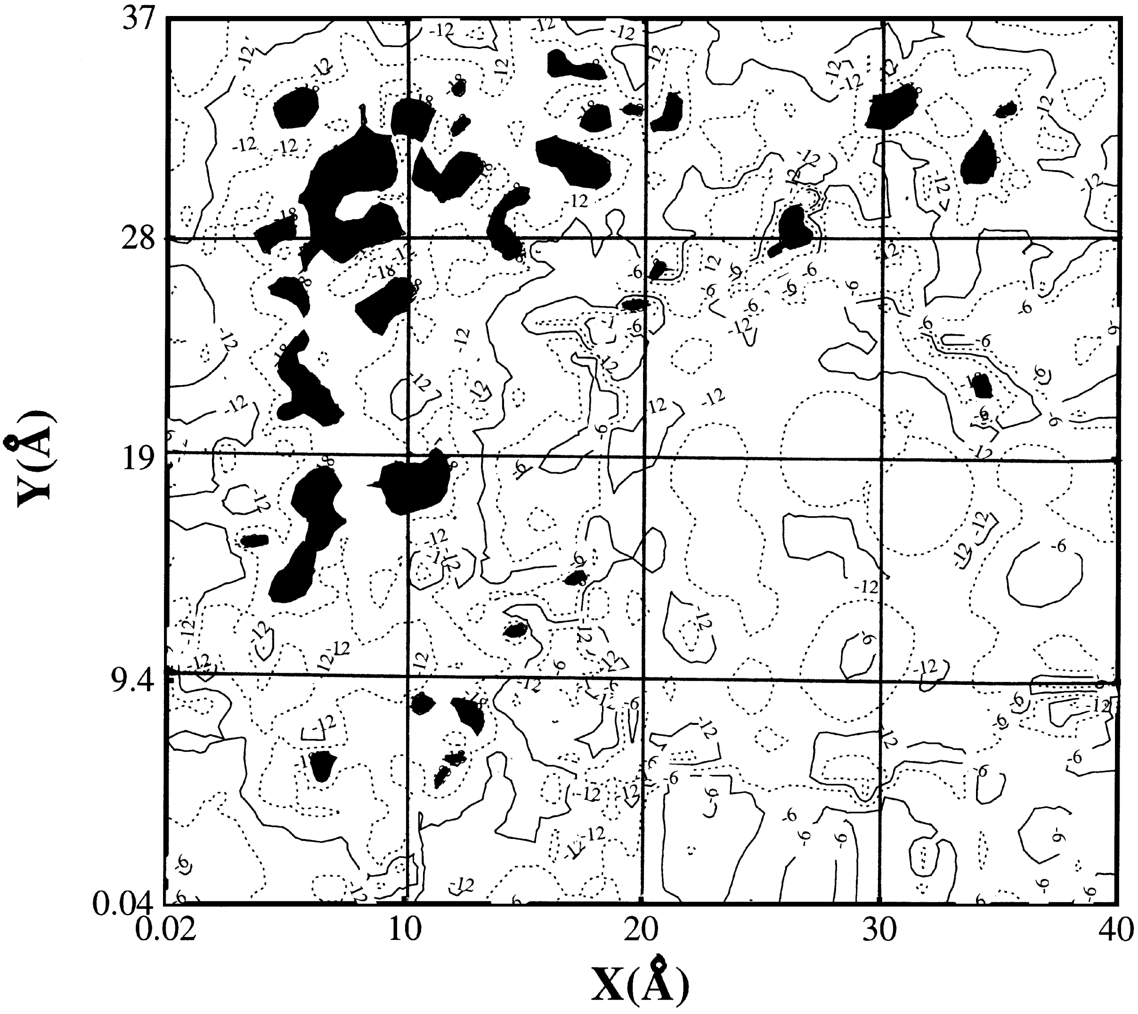

*Figure 1.* Contour lines of constant nitrogen-surface interaction energy for the solid amor1 are shown here. The lines are spaced by 3 kJ/mol and the areas where the energy is less than −18 kJ/mol are colored in black as a guide to the eye. The boundaries of the supersites are shown by straight lines that divide the surface into 16 units.

inverse pressure) and $N_I^*$ is the excess amount adsorbed $= N_I - N_{\text{gas}}$. It should be possible to derive local isotherms that are specifically adapted to deal accurately with adsorption on a very small heterogeneous patch (supersite), but in this paper, we will use only the truncated virial isotherm to compare with simulation results for monolayer adsorption on the arbitrarily chosen set of supersites shown in Figs. 1 and 2.

## 3. Simulations of Local Supersite Isotherms

The initial test of the ideas advanced in the previous section is based on a set of simulations of nitrogen on various amorphous solid surfaces (Cascarini de Torre and Bottani, 1995; Cascarini de Torre et al., 1995). In (Cascarini de Torre and Bottani, 1995), adsorption isotherms of nitrogen at 78 K were simulated using the Grand Canonical Monte Carlo algorithm. Of the various model adsorbent solids used in this work, we have chosen two for further analysis here. These are denoted str5, an unmodified Bernal surface, and amor1, a modified form of str5 obtained by deleting some of the surface atoms in str5. Here, a Bernal solid denotes an adsorbent modeled by constructing a randomly close-packed array of spheres and then assuming that the gas-solid interaction is given by a sum of site-site energies over the atoms in the solid and over the two sites in each nitrogen molecule. The parameters of the

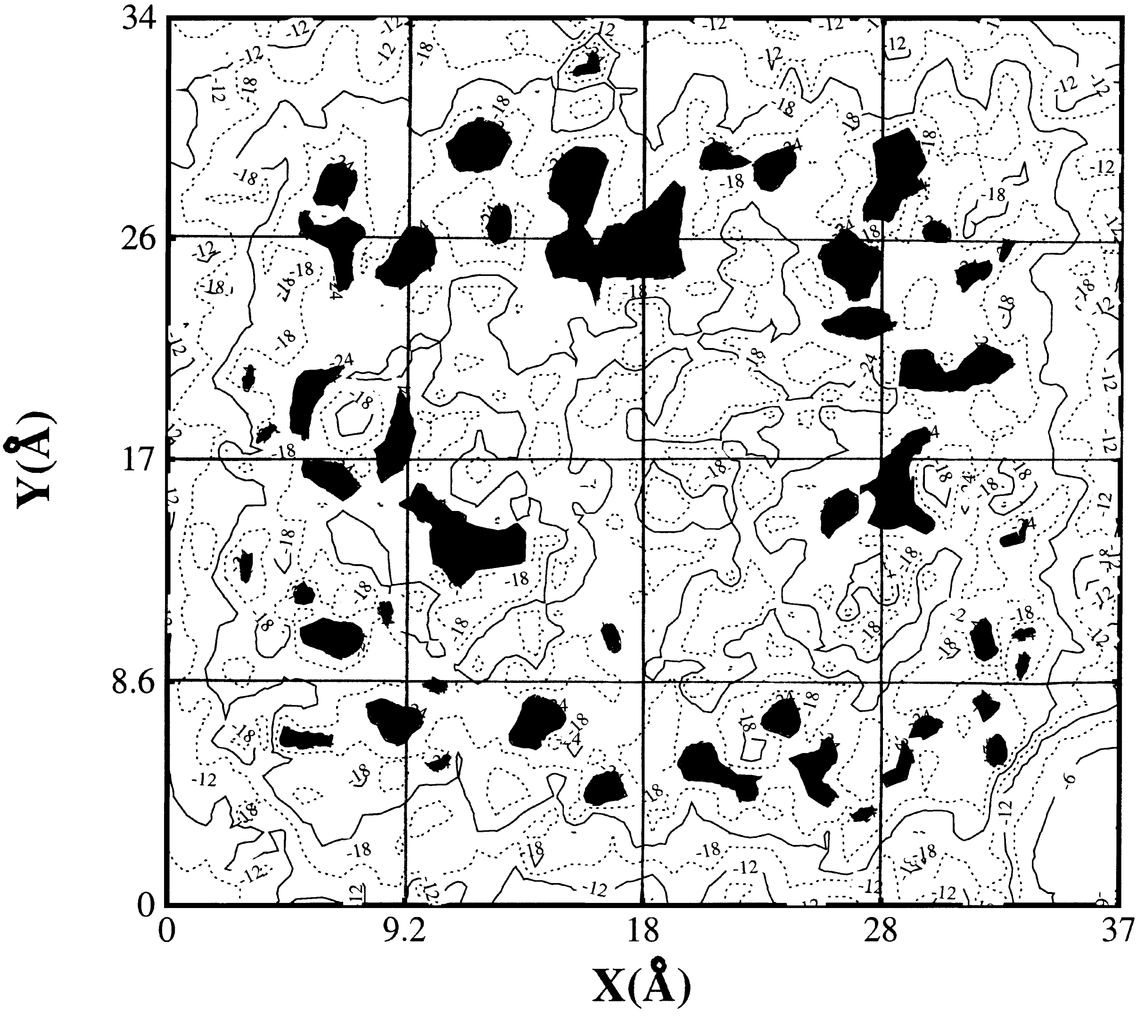

*Figure 2.* Same as Fig. 1, but for the str5 solid. Here, the blackened areas indicate regions where the interaction is less than −24 kJ/mol.

Lennard-Jones 12-6 pair-wise energy functions used in the calculation of the gas-solid energy have been given previously (Cascarini de Torre and Bottani, 1995) and need not be repeated here. The consequence of such a model is a heterogeneous surface with a complex gas-solid energy surface which appears to be well-suited for analysis using the supersite concept.

The solids generated by the Bernal algorithm (Bakaev and Steele, 1992; Bakaev and Voit, 1990) are periodic in the two directions parallel to the surface. In the particular case of str5 and amorl, the dimensions of the solid are 36.8 × 34.4 Å and 40.0 × 37.3 Å, respectively, in the $X$ and $Y$ directions. The potential energies that result from the summations over sites are first minimized with respection to $Z$, the distance perpendicular to the surface, and the orientation of the nitrogen molecule, to obtain the (minimum) adsorption energy as a function of $X$ and $Y$. This process was carried out for a 50 × 50 array of equally spaced points in $X$ and $Y$ to give the adsorption energy surfaces which are shown by the contour plots of Figs. 1 and 2. Here, lines of constant energy (in units of kJ/mol) show how the most negative energy varies across the surface. As an aid to the eye, the favorable adsorption regions are blacked-in. It is evident that the representation of the adsorptive properties of these heterogeneous surfaces by regular lattices of points that are adsorption sites would be a rather poor basis for further analysis.

Thus, the surfaces were divided into supersites for testing purposes. Of course, various levels of division

*Table 1.* Supersite results for amor1.

| Supersite | $\bar{\epsilon}_{\text{ads}}$ (kJ/mol) | $K_{HI}$(calc) (torr$^{-1}$) | $K_{HI}$(sim) (torr$^{-1}$) | $2B_I$ (sim) |
|---|---|---|---|---|
| (1, 1) | −5.92 | 4.32 | 4.45 | 1.60 |
| (1, 2) | −7.13 | 4.71 | 4.53 | 1.55 |
| (1, 3) | −7.27 | 5.44 | 4.61 | 1.57 |
| (1, 4) | −7.18 | 5.57 | 4.57 | 1.50 |
| (2, 1) | −6.08 | 4.87 | 4.30 | 1.15 |
| (2, 2) | −6.37 | 4.92 | 5.23 | 1.03 |
| (2, 3) | −6.12 | 5.34 | 4.84 | 0.90 |
| (2, 4) | −7.74 | 4.62 | 4.56 | 1.55 |
| (3, 1) | −4.00 | 4.30 | 3.92 | 0.86 |
| (3, 2) | −4.99 | 4.19 | 4.42 | 1.16 |
| (3, 3) | −5.04 | 4.44 | 4.14 | 0.90 |
| (3, 4) | −6.37 | 4.80 | 5.38 | 1.00 |
| (4, 1) | −3.87 | 4.76 | 4.18 | 1.05 |
| (4, 2) | −4.23 | 4.48 | 5.00 | 1.35 |
| (4, 3) | −4.92 | 5.59 | 5.22 | 1.00 |
| (4, 4) | −6.44 | 5.98 | 5.40 | 1.52 |

can be made, and, after some preliminary analysis, it was decided to divide the surfaces into the 4 × 4 arrays of supersites that are indicated by the lines overlaying the energy contour diagrams. Clearly, these supersites are large enough to exhibit significant variations in adsorption energy over their surfaces. The sites have geometric areas of about 93 Å$^2$ (amor1) and 79 Å$^2$ (str5), and thus could hold 5–6 nitrogen molecules in the monolayer, based on an area of 16 Å$^2$ per molecule. As a first step, we have averaged the adsorption energies over each supersite for each surface. These are shown in Table 1—the site positions are indicated by $[a, b]$, where the indices $a, b$ run from one to four for increasing $[X, Y]$ coordinates of the supersites. Note that there is a rough correlation between the values of $\bar{\epsilon}_{\text{ads}}$ and the darkened areas of the contour plots: the larger the darkened area in a supersite, the more negative is the average energy for that supersite.

Another way of characterizing the adsorption energies on these surfaces is to construct the histograms that give the frequency of occurrence of an adsorption energy in a given range of energy. For this purpose, we use the 2500 minimum energies evaluated on a uniform 50 × 50 net and assign the energies to intervals of 1 kJ/mol. The results of this calculation are shown in Fig. 3, where it can be seen that the adsorption energies for the two surfaces extend over wide ranges, with the number of strong sites being large for str5 than for amor1. (This is a reversal of the usual result which is that the effect of roughening by deletion is to produce strong adsorption sites. In the present case, the deletion has produced a nano-valley in the center of amor1 which has moderately smooth valley floor and plateau surface.)

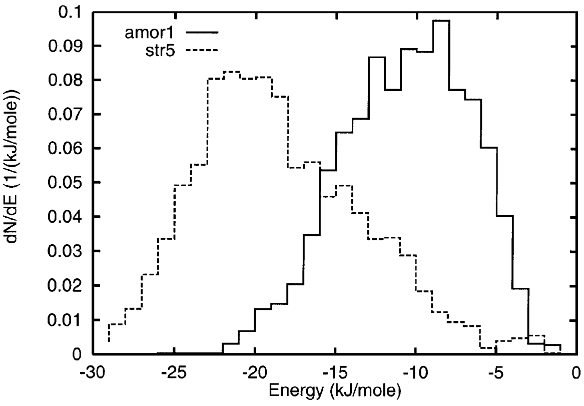

*Figure 3.* Histograms for the adsorption energies of the two solids studied in this paper. Plotted is the fraction of the energies obtained on a net of 2500 equally spaced points over the surfaces of each solid. The interval (bin-width) for these energies was taken to be 1 kJ/mol so that the area under each curve, which is the sum of the heights times the bin-width, is equal to unity.

Although isotherms for these systems are readily simulated well into the multilayer regime, for the present we will limit the analysis to sub-monolayer coverages. Thus, the simulations were modified to give the local isotherm for each supersite by evaluating the average number of atoms over the 16 supersites during the course of a Grand Canonical evaluation of the total number of atoms on the surface at a given pressure (and temperature). Sub-monolayer local isotherms are shown in Figs. 4–7. They are of course not identical, and one might begin by evaluating the Henry's Law constant for each supersite from Eqs. (6) and (11) and comparing the values obtained by fitting the simulated isotherms to Eq. (13). The results are shown in Tables 1 and 2, and indicate moderate agreement, as expected.

At this stage, we take the truncated virial isotherm of Eq. (13) as a first approximation to the submonolayer part of the supersite local isotherm. Rather than attempting the lengthy calculations of the second surface virial coefficients that is indicated in Eq. (7), these coefficients are obtained by fitting the supersite isotherms to Eq. (13). Their values are listed in Tables 1 and 2. Note that the quality of the fit of Eq. (13) to the limited simulation data for local isotherms now available

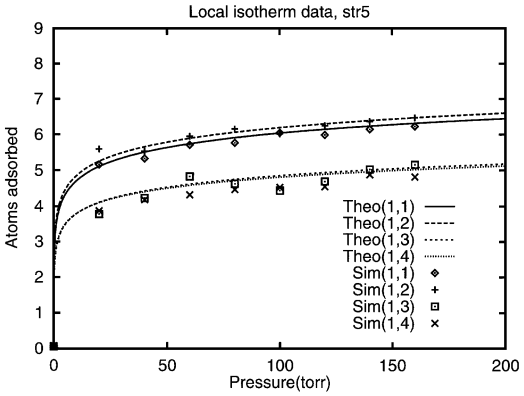

*Figure 4.* Simulated sub-monolayer isotherms for four of the supersites on the amor1 solid are shown here. The number of atoms adsorbed is plotted versus $p$, and the simulated local isotherms are compared with those fitted to the simulations using Eq. (13) and the constants list in Table 1. Values of the fitting parameters are listed in Table 1.

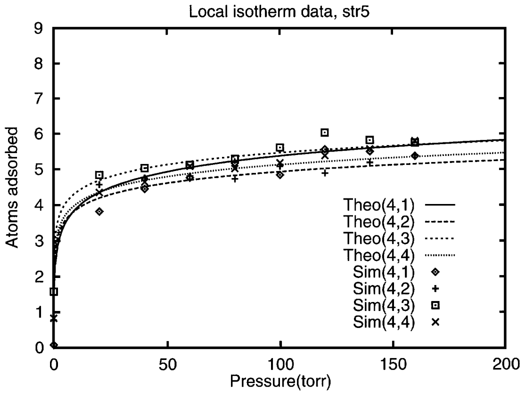

*Figure 5.* Same as Fig. 4 but for four other supersites on the amor1 surface.

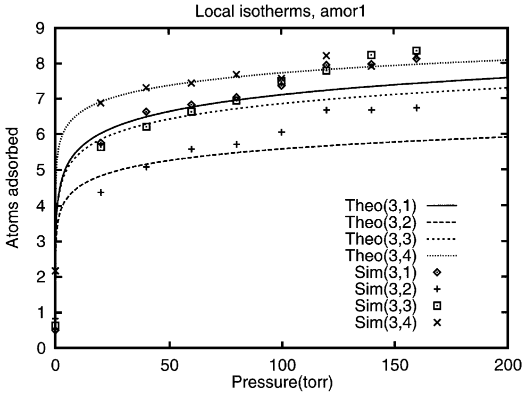

*Figure 6.* Same as Fig. 4 but for the str5 adsorbent, with fitting parameters given in Table 2.

*Table 2.* Supersite results for str5.

| Supersite | $\bar{\epsilon}_{\text{ads}}$ (kJ/mol) | $K_{HI}$(calc) (torr$^{-1}$) | $K_{HI}$(sim) (torr$^{-1}$) | $2B_I$ (sim) |
|---|---|---|---|---|
| (1, 1) | −7.68 | 6.35 | 6.50 | 1.54 |
| (1, 2) | −9.74 | 6.85 | 6.70 | 1.53 |
| (1, 3) | −9.64 | 6.49 | 6.35 | 1.93 |
| (1, 4) | −8.17 | 6.81 | 6.74 | 2.03 |
| (2, 1) | −9.14 | 6.64 | 6.64 | 1.93 |
| (2, 2) | −11.79 | 7.88 | 7.52 | 1.81 |
| (2, 3) | −11.99 | 7.64 | 7.05 | 2.01 |
| (2, 4) | −9.95 | 6.40 | 6.37 | 1.62 |
| (3, 1) | −9.53 | 6.95 | 6.82 | 1.74 |
| (3, 2) | −12.02 | 6.61 | 6.57 | 1.90 |
| (3, 3) | −12.20 | 7.39 | 7.42 | 1.95 |
| (3, 4) | −9.91 | 6.55 | 6.46 | 1.72 |
| (4, 1) | −7.15 | 4.40 | 4.39 | 1.36 |
| (4, 2) | −10.16 | 6.57 | 6.66 | 1.96 |
| (4, 3) | −9.95 | 7.30 | 7.37 | 1.88 |
| (4, 4) | −8.89 | 6.74 | 6.72 | 1.89 |

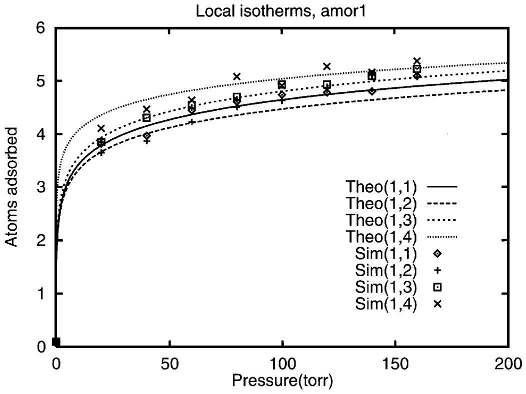

*Figure 7.* Same as Fig. 4 but for four other supersites on the str5 adsorbent. Curves are plotted using fitting parameters given in Table 2.

indicates that the use of this equation might be a reasonable way to proceed.

## 4. Discussion

The comparison presented here between the supersite approach to the description of adsorption on a heterogeneous surface and the standard treatment of adsorption on heterogeneous surfaces reveals several interesting features. In the first place, it should be emphasized that the histograms of adsorption energy given in Fig. 3

differ from the usual number distributions of adsorption site energy in that the histograms include all the minimum energies, not just the lowest energies that one imagines would make up the adsorption sites. Furthermore, these number distributions tell nothing about the spatial distributions of the energy over the surface. In fact, the results of this and other simulations of adsorption on rough surfaces (Bakaev and Steele, 1992; Bakaev and Voit, 1990) indicate that sub-monolayer adsorption proceeds initially as expected: by attachment to the strongest sites (i.e., over the regions of the most negative energy). However, as these areas become covered, additional molecules will be aided by attractive interactions with the previously adsorbed molecules and thus can adsorb on the surface regions of weaker interaction so that the final monolayer coverage is rather close to that for a surface covered with a layer having a liquid-like density regardless of the spatial and number distributions of the gas-solid energies. In addition, previous simulations indicate that the local isotherms are quite sensitive to the spatial distribution of the adsorbing sites (Zgrablich et al., 1996).

The values of *B* that yield the fits of the truncated virial adsorption isotherm to the simulated local isotherms (shown in Figs. 4–7) are all positive, as can be seen in Table 1 and 2. This means that the excluded areas of one $N_2$ by another on the same supersite dominate the virial coefficient calculation at this temperature and for this choice of supersite area.

The simulated multilayer supersite isotherms for these systems have been fitted to the BET theory in the usual way to show that both the total and the individual supersite isotherms yield monolayer capacities that correspond rather well to surfaces covered with a liquid-like layer of nitrogen with the usual area per molecule of 16 $Å^2$. The only exceptions to this finding come from the sites in amor1 that contain the steep walls of the nanovalley created in the modeling process for this solid. These walls cause the BET areas of the these sites to be larger than the geometric area. One consequence is that the total BET area of 1449 $Å^2$ for amor1 is also larger than the geometric area. The dimensions of the str5 sample give the geometric supersite area of 79 $Å^2$. Taking 16.2 $Å^2$ as the area per $N_2$ in the monolayer, these geometric areas lead to the expectation of 4.9 $N_2$ molecules in a complete monolayer on the str5 surface. The analogous numbers for amor1 are slightly different, giving a geometric supersite area of 93 $Å^2$ and an expected monolayer capacity of 5.8 Å. If we compare these expectations with the simulated local isotherms shown in Figs. 4–7, one finds that the knees of these isotherms lead to estimates of the monolayer capacities that appear to be variable and somewhat larger than those obtained from the geometric areas. However, the estimates are generally not too different from those for the geometric areas except for some cases where number of molecules can be 30–50% larger. Although the actual estimates of monolayer capacity are imprecise because these local isotherms have not had the multilayer adsorption subtracted from the totals, the occasional discrepanices observed are most likely due to the presence of the valley walls that can, in effect, give enhanced surface areas for the supersites that contain these walls.

When one compares the range of gas-solid interaction energies that is shown in the histograms with the range of average supersite energies listed in Table 1, it is evident that the supersite approach smooths out many of the details in the interaction energy. Consequently, the average supersite energies listed in Table 1 show a much smaller variation than that shown in the histograms of Fig. 3. Thus any treatment that relies on these averages will necessarily fail to reproduce the actual surface energy distributions. Instead, one will require local supersite isotherms which accurately treat the varying energies within a supersite. Of course, if one were to divide the surface into smaller and smaller supersites, one would approach the limiting capacity of one molecule per "supersite", but these would include very weak sites as noted above and would also give rise to significant problems in accurately dealing with lateral interactions.

A standard calculation in heterogeneous adsorption is to invert experimental adsorption isotherms to extract the site energy number distribution from the data. This remains a formidable problem, especially in view of the need to initially assume both a local isotherm and a spatial site distribution function.

One advantage of the supersite approach is that it allows one to better deal with the effects of lateral interaction. One could conceivably evaluate the mutual interactions between the small numbers of molecules on a supersite to good precision (as in a virial coefficient calculation) and then append a mean field estimate of the interactions between molecules on neighboring supersites. In this way, at least part of this interaction would be accurately calculated and the effects of variations in the spatial distributions of sites over the surface will be minimized. Such studies are reserved for future work.

## Acknowledgments

EJB is a researcher of the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC) and Associate Professor of the Facultad de Ingeniería (Universidad Nacional de La Plata) (UNLP). This research project was partially financed by Consejo Nacional de Investigaciones Científicas y Técnicas, CIC and UNLP. WAS acknowledges financial support by Grant DMR 902 2681 of the Division of Materials Research of the NSF.

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