New Lattice Model for Adsorption of Small Molecules in Zeolite Micropores

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A new adsorption model is developed for small molecules in zeolites whose form is based on features revealed by molecular simulation. Adsorption is assumed to occur onto a 3-D polyhedral lattice, and both the energy and entropy of the lattice sites are accounted for using a statistical mechanics approach. Energetic interactions are described by an Ising model with both 2- and multibody nearest-neighbor interactions. Entropic interactions are included by an adsorption site volume term which accounts for the loss of translational freedom associated with lattice crowding.

The model is applied to a system of small molecules (xenon, methane) adsorbed in idealized zeolite NaA, where adsorption has been shown by computer simulation to occur on finite, cuboctahedral lattices (Van Tassel et al., 1992). The model quantitatively predicts the simulated isotherm over the entire pressure range. Comparison is made with a Langmuir model and a van der Waals gas model which, although valid at low pressures, fail at high pressures due to overestimation of translational entropy and inaccurate portrayal of sorbate-sorbate interaction energy.

Introduction

Adsorption in microporous solids such as zeolites is an important component of many catalytic and separations processes. Since process models must be constructed to quantitatively account for both the extent and heat of adsorption (to satisfy mass and energy balances), it is to the chagrin of design engineers that adsorption in zeolites is poorly modeled by conventional means. Thermodynamic treatments of capillary condensation fail for micropores, while overly simplistic molecular adsorption models fail to account for the dependence of adsorbed-phase thermodynamics on loading and micropore geometry. New theories are clearly needed, yet have been slow to develop due to a poor overall understanding of the physics of adsorption in micropores.

It has long been recognized that a Langmuir model fails to adequately describe microporous adsorption due to the overrestrictive assumption of independent, noninteracting sites. Recognizing this shortcoming, researchers have shied away from theories incorporating adsorption sites in favor of those describing a delocalized adsorbed phase. Lee and Basmadjian (1970) calculate an isotherm which treats the adsorbed phase as a mobile fluid in a pore of uniform potential energy. A mean field attraction between hard-sphere adsorbates is imposed, and a surface energy term accounts for the surface tension between adsorbates at high loadings. A flaw is that the polarization energy, whose form is well known and readily calculable, is left as an adjustable parameter. Ruthven (1971) proposes a statistical mechanical model which treats the adsorbed phase as a van der Waals gas (as hard-sphere molecules with a mean field attraction) in the mean potential field of a micropore. This model is conceptually simple and describes many absorption systems quite well, particularly at low loading. Suwanayuen and Danner (1980) introduce an isotherm equation using the concept of vacancies: they hypothesize a binary solution of adsorbates and vacancies. The complicated sorbate-sorbent interactions are accounted for by activity coefficients which represent the nonideality of the solution. This thermodynamic treatment offers only a slight improvement over the statistical mechanical model of Ruthven. More recently, density functional theory has been applied to molecular adsorption in smooth, geometrically shaped micropores by Evans and Tarazona (1984) and Peterson et al. (1988, 1990). In this approach, a free energy functional is minimized with respect to the adsorbate density distribution. Although an elegant and useful method, its application to more realistic,

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atomically structured microporous adsorbents may be computationally expensive.

In the absence of a universal theory, computer simulation techniques have provided a great deal of insight into microporous adsorption (Soto and Myers, 1981; Kono and Takasaka, 1986; Woods et al., 1988; Woods and Rowlinson, 1989; June et al., 1990; Razmus and Hall, 1991; Van Tassel et al., 1991, 1992, 1993a; Snurr et al., 1991; Karavias and Myers, 1992), but at great computational expense and with limited predictive power. It would be beneficial to use the detailed molecular level information provided by simulation to develop tractable, predictive and physically meaningful models of microporous adsorption.

One particular feature evident from simulation, which is in contrast to the assumptions made in the previous models, is that adsorption often occurs onto discrete sites in the micropore. Examples include xenon and methane in zeolites X and Y (Woods et al., 1988; Woods and Rowlinson, 1989) and silicalite (June et al., 1990); and xenon in zeolite NaA (Van Tassel et al., 1992, 1993b), zeolite rho (Vernov et al., 1993), and mordenite (Nivarthi et al., 1993). A lattice model of adsorption would seem appropriate for these systems and perhaps for other systems as well.

The term "lattice model" is used to describe any model in which molecules are assumed to occupy discrete positions in space. In many cases, they are more useful than continuous models because of the availability of closed form solutions. Lattice models have found use in various disciplines ranging from the thermodynamics of the liquid state to the mobility of defects in the solid state (Hill, 1956). Additionally, they have become a valuable tool to chemical engineers in describing molecular adsorption on flat surfaces, that is, in two dimensions (Hill, 1960; McQuarrie, 1976).

To model adsorption in zeolite pores, a similar strategy may be employed using a three-dimensional lattice whose geometry represents the preferred adsorption sites in the pore space. In this article, we develop such a model for small molecules in zeolites. The physics and thermodynamics of the adsorbed phase are regulated by the geometry of the lattice and the nearest neighbor interactions between lattice sites. Hints to the mathematical form of the model have come from considering molecular simulation studies. We apply this new model to xenon and methane adsorbed in zeolite NaA and note excellent agreement over the entire pressure range and a significant improvement over existing adsorption models.

Lattice Model

Zeolites are crystalline aluminosilicates composed of connected, cage-like structures which are large enough to house a small number of guest molecules (generally less than 20). To a first approximation, the adsorbates in a given cage occupy discrete sites and interact only with other adsorbates in the same cage. A lattice of adsorption sites may be constructed by postulating that the sites occur at the minimum energy positions in the zeolite pore. Since these positions tend to be located near ring apertures in the crystal (Figure 1a), the lattice may also be determined from the known van der Waals diameters of the ring oxygen atoms and the adsorbate. It has been pointed out that these positions coincide with simulated adsorption sites over a wide range of loading, so one can in general postulate the lattice very easily without extensive simulation. For example, Xe has been shown to reside near the four-membered rings in NaA over a range of loading (Van Tassel et al., 1992, 1993b). Since each cage possesses many elements of symmetry, the lattice representing the adsorption sites in a given cage will be both finite and polyhedral (Figure 1b).

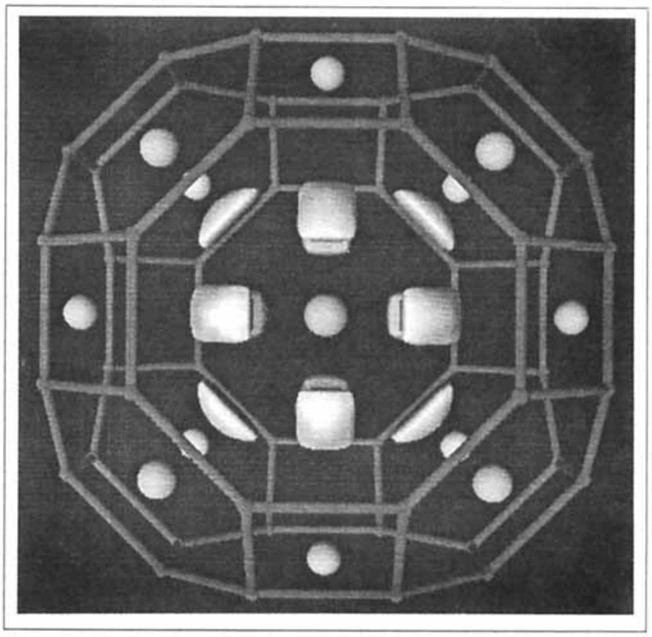

Figure 1a. NaA alpha cage.

Vertices represent silicon or aluminum atoms connected by bridging oxygen atoms (not shown). Sodium ions appear as spheres and are located in the centers of the 6- and 8-membered rings. White clouds represent an isosurface of constant potential energy of −26 kJ/mol. Alpha cages are connected to one another by the 8-membered rings.

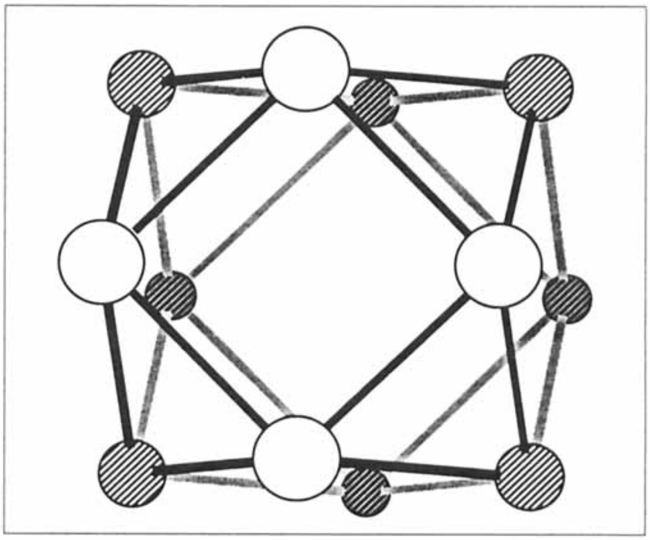

Figure 1b. Cuboctahedral arrangement of adsorption sites in the alpha cage whose positions correspond to potential energy minima.

Nearest neighbor sites are connected by line segments.

The physics of the adsorbed phase is accounted for by the interactions between the adsorbates on the lattice sites. The proposed model includes nearest neighbor energetic and entropic interactions between occupied sites.

Sorbate-sorbate energetic interactions

We start by considering the energetic interactions between adsorbates located on a lattice of sites. The distances between neighboring sites may be slightly larger or smaller than the diameter of the adsorbate. However, we assume that provided the lattice is not too crowded, an adsorbate is free to "relax" to an optimal distance from its neighbors so as to enjoy an attractive interaction. When the lattice becomes crowded, though, some of the adsorbates will not be able to enjoy an optimal separation from its neighbors. For larger adsorbates, the interaction may become repulsive due to crowding. For smaller adsorbates, the interaction may become small since neighboring adsorbates will have "relaxed" to positions closer to other neighbors.

We propose a sorbate-sorbate interaction energy for the *i*th lattice site as:

$$\begin{aligned} E_i &= -n_i\epsilon/2 \qquad n_i<N_{\text{coord}} \\ &= \gamma\epsilon/2 \qquad n_i=N_{\text{coord}} \end{aligned} \tag{1}$$

where n_i is the number of nearest neighbor adsorbates to site i, ϵ is the pairwise energy parameter in the Lennard-Jones potential, N_{coord} is the coordination of the lattice (the maximum number of nearest neighbors), and γ is a parameter accounting for crowding. The interaction is pairwise attractive *if* the number of occupied nearest neighbors is less than the coordination of the lattice. If all nearest neighbor sites are occupied, the interaction is governed by a repulsive parameter, γ, which accounts for a multibody crowding interaction due to the inability of adsorbates on the nearly filled lattice to "relax" to optimal separations (γ is not a function of temperature). γ may be left as an adjustable parameter or it may be set so that E_i is equal to the repulsive energy experienced by the adsorbate when it is forced to be at the separation dictated by the lattice. The factor of 1/2 is to compensate for double counting. The sorbate-sorbate interactions are essentially those of an Ising model for a finite lattice with two- and multibody interactions.

Sorbate-sorbate entropic interactions

We introduce the concept of an adsorption site volume to account for the translational freedom of an adsorbate in a lattice site. While an adsorption site is actually represented by a potential energy minimum in the zeolite, it is useful to approximate this minimum by a cubic well (a square well in three dimensions). The energy inside the site is equal to the average potential energy of an isolated adsorbate and the energy outside of the site is zero. Using this approximation, the volume of an adsorption site at zero coverage (with all neighboring sites unoccupied, so $E_i=0$) is determined by considering the statistical mechanical partition function for a single site:

$$q_{\text{site}}=\frac{1}{\Lambda^3}\int_{\text{site}} e^{-\Phi(\mathbf{r})/kT}d^3r \cong \frac{V^0_{\text{site}}}{\Lambda^3}\, e^{-\langle\Phi\rangle_1/kT} \tag{2}$$

where Λ is the de Broglie wavelength, k is the Boltzmann factor, T is the absolute temperature, V^0_{site} is the volume of the adsorption site at zero loading, $\Phi(r)$ is the potential energy at position r within the site which accounts for the interaction of an adsorbate with all of the zeolite framework atoms (Bezus et al., 1977; Van Tassel et al., 1991), and $\langle\Phi\rangle_1$, is the average potential energy of a single adsorbate. Note that this form of $\Phi(r)$ assumes a spherical adsorbate. Since, in general, the site is not a cubic well, $\langle\Phi\rangle_1$ is evaluated from the potential map in the following way:

$$\langle\Phi\rangle_1=\frac{\displaystyle\int_{\text{site}}\Phi(\mathbf{r})e^{-\Phi(\mathbf{r})/kT}d^3r}{\displaystyle\int_{\text{site}} e^{-\Phi(\mathbf{r})/kT}d^3r} \tag{3}$$

The domain of integration is the region of an adsorption site. Note that $\langle\Phi\rangle_1$ and V^0_{site} depend somewhat on temperature.

As neighboring sites become occupied, the effective volume of a given site is reduced because of crowding; the adsorbates are more restricted translationally than those in a nearly empty cage. The crowding experienced by an adsorbate due to the presence of nearest neighbor adsorbate occurs along a direction connecting the two sites. Therefore, a reasonable way to approximate the decrease in site volume between two adjacent sites is to consider the crowding between one-dimensional, hard-rod adsorbates. The statistical mechanics of hard rods is discussed by Percus (1976) and Vanderlick et al. (1988). The configuration integral of two hard rods (of diameter σ) confined between hard walls separated by a distance L (Figure 2a) is given as:

$$\begin{aligned} Z_2 &= \int_{\sigma/2}^{L-3\sigma/2} dx_1 \int_{x_1+\sigma}^{L-\sigma/2} dx_2 \\ &= \frac{1}{2}\,[L-2\sigma]^2 \end{aligned} \tag{4}$$

We wish to extend this argument to hard rods of length σ whose centers are confined to two consecutive adsorption sites, each with a length of $2r$ and separated by a distance d (Figure 2b). The first adsorbate may traverse the distance $-r$ to r, and the second adsorbate the distance from $d-r$ to $d+r$. Taking into account the nonoverlapping nature of the adsorbates, the configuration integral is:

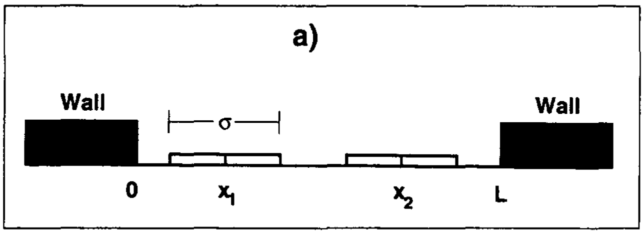

Figure 2a. Two 1-D molecules of length σ confined between walls separated by distance L (Percus, 1976; Vanderlick et al., 1989).

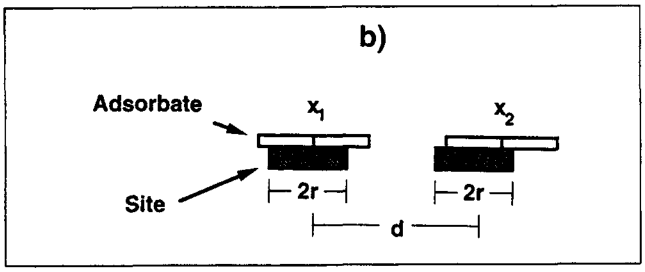

Figure 2b. 1-D adsorbates of length σ whose centers are confined to adsorption sites of length $2r$ and separation d.

$$Z_2=\int_{-r}^{d-\sigma}dx_1\int_{d-r}^{d+r}dx_2+\int_{d-\sigma}^{r}dx_1\int_{x_1+\sigma}^{d+r}dx_2$$

$$=(2r)^2\left[1-0.5\left(\frac{d-\sigma}{2r}-1\right)^2\right]\quad \sigma>d-2r \tag{5}$$

The two-body configuration integral, Z_2, is equal to the square of the 1-D site "volume," $(2r)^2$, times a correction factor which accounts for the steric interaction of an occupied neighbor. In the special case where adsorbates do not crowd into neighboring sites ($\sigma\leq d-2r$), the configuration integral is simplified:

$$Z_2=\int_{-r}^{r}dx_1\int_{d-r}^{d+r}dx_2=(2r)^2\quad \sigma\leq d-2r \tag{6}$$

By analogy, we propose the following expression for the pore adsorption site volume as a function of number of occupied neighbor sites:

$$V_{\mathrm{site}}=V_{\mathrm{site}}^0\left[1-0.5\left(\frac{d-\sigma}{2r}-1\right)^2\right]^{n_i/2}\quad \sigma\geq d-2r$$

$$=V_{\mathrm{site}}^0\qquad \sigma<d-2r \tag{7}$$

where V_{site}^0 is determined from Eq. 2, r is determined by assuming the sites are approximately spherical:

$$r=\left(\frac{3V_{\mathrm{site}}^0}{4\pi}\right)^{1/3} \tag{8}$$

d is the spacing between the sites, σ is the Lennard-Jones size parameter, and n_i is the number of occupied nearest neighbor sites. The exponent in Eq. 7 is $n_i/2$ because the site volume decrease due to more than one occupied nearest neighbor site is multiplacative, for example, if one nearest neighbor causes the site volume to decrease by a factor of 2, two will cause the site volume to decrease by a factor of 4.

Alternatively, more empirical methods may also be used to determine the site volume as a function of loading. Since simulation has shown that the site volume decreases in an approximately sigmoidal fashion with loading (Van Tassel et al., 1993b), one such method is to approximate the site volume as a sigmoidal function antisymmetric about a loading of half-saturation,

$$V_{\mathrm{site}}=V_{\mathrm{site}}^0\{0.5-0.5\tanh[\beta(N-M/2)]\} \tag{9}$$

where M is the total number of sites and β is an adjustable parameter. Again, V_{site}^0 is taken from the definition in Eq. 2. In the next section, we will present isotherms predicted by this new lattice theory using the one-dimensional (Eq. 7) and the empirical (Eq. 9) site volume reduction formulas. The disadvantage of this second approach, of course, is the introduction of the adjustable parameter β which can be predicted only through simulation.

Isotherm calculation

The grand canonical partition function for M sites is:

$$\Xi=\sum_c e^{N(\mathrm{c})\mu/kT}\left(\frac{V_{\mathrm{site}}}{\Lambda^3}\right)^{N(\mathrm{c})}e^{-N(c)\langle\Phi\rangle_1/kT}e^{-\Psi(c)/kT} \tag{10}$$

so the isotherm may be calculated as:

$$\langle N\rangle=\frac{1}{\Xi}\sum_c N(\mathbf{c})e^{N(\mathrm{c})\mu/kT}\left(\frac{V_{\mathrm{site}}}{\Lambda^3}\right)^{N(\mathrm{c})}e^{-N(\mathrm{c})\langle\Phi\rangle_1/kT}e^{-\Psi(\mathrm{c})/kT} \tag{11}$$

where the vector $\boldsymbol{c}$ is the summation index and denotes the configuration of sorbates on the lattice, $N(\boldsymbol{c})$ is the number of adsorbates on the lattice for configuration $\boldsymbol{c}$, μ is the chemical potential, and $\Psi(\boldsymbol{c})$ is the total site-site interaction energy summed over nearest neighbor pairs. It has been suggested to us that this summation may be shortened since many configurations possess the same energy (Schick, 1992).

The summation over $\boldsymbol{c}$ is a sum over all configurations of the system of adsorbates located on the lattice of adsorption sites. For a collection of M sites, there are 2^M distinct configurations, each of which may be characterized by a configuration vector defined as:

$$\boldsymbol{c}=(c_1, c_2, \ldots, c_M)\quad c_i=1 \text{ if } i\text{th site occupied}$$

$$c_i=0 \text{ if } i\text{th site empty} \tag{12}$$

The sum over configurations is handled by summing over scalar values from 0 to 2^M-1, converting the scalar to a base 2 number and assigning each digit to a vector component. For example, on a lattice of 12 sites there are 4,096 configurations, so the summation index i would range from 0 to 4,095. For $i=3{,}000$, i(base 2) = 101, 110, 111, 000, and $c_1=1$, $c_2=0$, $c_3=1, \ldots,$ so sites 1, 3, 4, 5, 7, 8, and 9 would be occupied. This results in a one-to-one correspondence between scalars and configurations, ensuring that all configurations are summed over.

The number of adsorbates in the cage for a given configuration is the sum of the elements of $\boldsymbol{c}$:

$$N(\boldsymbol{c})=\sum_{i=1}^{M}c_i \tag{13}$$

A connectivity matrix for the sites on the cuboctahedral lattice is defined as:

$L=\{L_{ij}\}\quad L_{ij}=1$ if sites i and j are nearest neighbors

$$L_{ij}=0 \text{ otherwise} \tag{14}$$

The number of occupied nearest neighbor sites to site i is then

$$n_i=\sum_{j=1}^{M} L_{ij}c_j \tag{15}$$

The vector describing the number of occupied nearest neighbor sites is:

$$\boldsymbol{n}=\boldsymbol{L}\cdot\boldsymbol{c} \tag{16}$$

A vector describing the energy of each site may be expressed as:

$$\boldsymbol{E}=(E_1, E_2, \ldots, E_M) \tag{17}$$

where the elements are determined from Eq. 1 with n_i obtained from Eq. 15. The total sorbate-sorbate interaction energy for configuration $\boldsymbol{c}$ is then

$$\Psi(\boldsymbol{c})=\boldsymbol{E}\cdot\boldsymbol{c} \tag{18}$$

Previous Adsorption Models

We will compare the results of the new model isotherm with those predicted by other commonly used microporous adsorption models. The Langmuir model of adsorption is based on the postulate of discrete, independent, and noninteracting adsorption sites. For a finite system of M sites, the Langmuir isotherm becomes (McQuarrie, 1976):

$$\langle N\rangle=\frac{\sum_{N=0}^{M} N\frac{M!}{N!(M-N)!}q_{\text{site}}^{N}e^{N\mu/kT}}{\sum_{N=0}^{M}\frac{M!}{N!(M-N)!}q_{\text{site}}^{N}e^{N\mu/kT}} \tag{19}$$

The zeolite adsorption model proposed by Ruthven (1971) treats the adsorbates in a zeolite cavity as a van der Waals gas, that is, as molecules with a hard-core repulsion and a mean field attraction (Hill, 1986; Davis, 1993). Its isotherm for a pore of maximum occupancy of M is:

$$\langle N\rangle=\frac{\sum_{N=0}^{M} NQ_1^N(1-\lambda N)^N e^{N\mu/kT}e^{-\lambda N\epsilon/kT}}{\sum_{N=0}^{M} Q_1^N(1-\lambda N)^N e^{N\mu/kT}e^{-\lambda N\epsilon/kT}} \tag{20}$$

where ϵ is the interaction energy between a pair of adsorbates (the Lennard-Jones energy parameter), λ is a measure of the maximum occupancy of the cage, and Q_1 is the partition function of a single adsorbate in the entire alpha cage:

$$Q_1=\frac{1}{\Lambda^3}\int_{\text{cage}} e^{-\Phi(\mathbf{r})/kT}d^3r=Mq_{\text{site}} \tag{21}$$

where q_{site} is defined in Eq. 2.

Although other models have appeared which are also based on the assumptions of a delocalized adsorbed phase (see Introduction), we will consider only Ruthven's van der Waals (VDW) model from among these since it has the most straightforward partition function and is the most widely cited. These two models represent two extreme views of the adsorbed phase: one as a collection of isolated lattice sites and the other as a pore volume filling fluid.

Results

Zeolite NaA provides an ideal system to which the lattice model may be applied. Its crystal structure is simple [it is composed of alpha cages (Figure 1a) connected together in a cubic arrangement], and there exists an abundance of simulated data to which the model isotherm may be compared (Van Tassel et al., 1992, 1993a-c). The minimum energy positions for small absorbates (xenon and methane) in NaA are near the four-membered rings, so the appropriate lattice is a cuboctahedron (Figure 1b) which contains 12 sites, each with four nearest neighbor sites.

The new lattice model, the VDW model, and the Langmuir model are calculated from the equations above. q_{site} and $\langle\Phi\rangle_1$ (and thus also V_{site}^0) are determined by numerical integration using the potential energy field described previously. ϵ and σ are taken as Lennard-Jones parameters. M is equal to 12, corresponding to the vertices of the cuboctahedron, and λ is set to $1/(M+1)$. Estimates of model parameters could also be obtained from the experimental heat of adsorption and the adsorption capacity. γ and β are left as adjustable parameters. Values of the parameters used are given in Table 1.

Figure 3a-3c show the adsorption isotherm obtained from simulation and ones calculated by the new model and two previous models plotted vs. chemical potential for Xe and methane. We have chosen to compare the model isotherms to simulation rather than to experiment. The point is to compare the new model to existing models on an ideal system (with no framework defects or experimental uncertainties) such as one realized through simulation. Also, the potential function used in the simulation may be used to determine the parameters of the models (q_{site}, V_{site}^0, and so on), so a fair competition among the models may be waged since all have an equal *a priori* chance at success. Furthermore, simulated data are available over a wider loading range and have been shown to match the available experimental data quite well (Van Tassel et al., 1993a). It should also be noted that the highest chemical potentials presented here correspond to extremely high pressures for xenon and methane. We investigate high chemical potentials, not

Table 1. Model Parameters

	Xe (T=300 K)	Xe (T=360 K)	CH_4
q_{site}	2.766×10^8	6.555×10^7	2.165×10^5
$\langle\Phi\rangle_1$	−26.0 kJ/mol	−25.2 kJ/mol	−14.58 kJ/mol
V_{site}^0	5.508 Å^3	7.465 Å^3	9.987 Å^3
d	3.58 Å	3.58 Å	3.79 Å
σ	4.10 Å	4.10 Å	3.82 Å
$\gamma(1-D)$	3.0	3.0	−3.0
γ (emp.)	0.0	0.0	−4.0
β^*	0.35	0.35	0.10
λ^*	1/13	1/13	1/13

*γ and β are adjusted to allow the model to best fit the data.

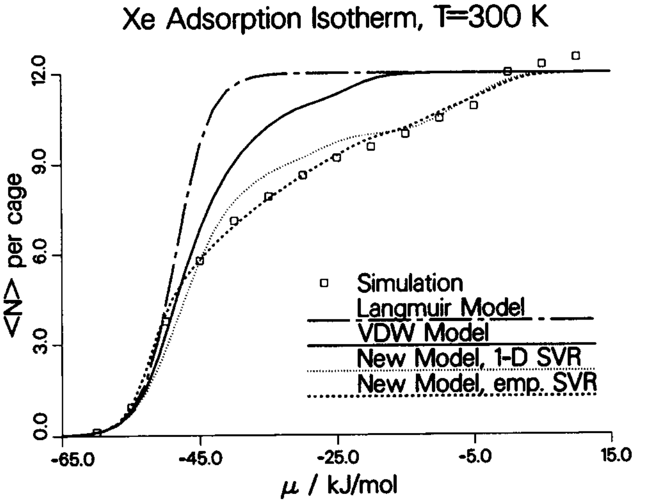

Figure 3a. Xe isotherm at 300 K.

Calculated via simulation (Van Tassel et al., 1993a), Langmuir model, van der Waals model, and new model.

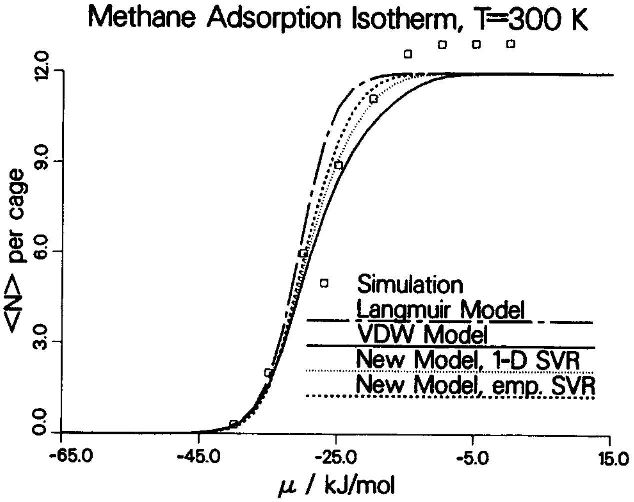

Figure 3c. Methane isotherm at 300 K.

Calculated via simulation (Van Tassel et al., 1993a), Langmuir model, van der Waals model, and new model.

because a high-pressure isotherm model for simple molecules is needed but rather to test whether the model can satisfactorily reproduce the features of the simulated isotherm that are peculiar to a crowded cage. This will also provide insight into the prospects for this model on systems of much more strongly adsorbed species, where liquid-like pore densities may occur at lower pressures.

Each of the models presented here accurately describes adsorption at low loadings, since at low pressure they each reduce to Henry's law. At higher loadings, however, both the Langmuir and VDW models greatly overestimate the amount of adsorbed Xe. The two forms of the new model fit the simulated Xe data accurately over the entire loading regime at both 300 K and 360 K. Furthermore, the new model successfully predicts a plateau at a loading of 10 Xe.

The Langmuir and VDW models describe methane adsorption more accurately than Xe adsorption due to methane's smaller size and lower degree of interaction with neighboring adsorbates. The new model, though, most accurately describes the methane isotherm. Note that the simulation results predict 13 methane to adsorb. The 13th methane resides at the cage center (in the middle of the cuboctahedral lattice of sites) and so is obviously not accounted for by our 12 site model.

Figures 4a-4c show the average energy per adsorbate as a function of loading for each of the three models. The Langmuir model considers the adsorbates to be noninteracting, so the average energy is constant. The assumption in the VDW model is that adsorbates interact via a mean field attraction, resulting in an energy which is slightly lower than in the Langmuir model yet is still independent of loading. The new model accounts for sorbate-sorbate attraction at low to intermediate loadings and repulsion at high loadings in a semiquantitative way. Deviations from the simulated results are due to the neglect of next nearest neighbor interactions.

Figures 5a-5c show the average entropy per adsorbate for

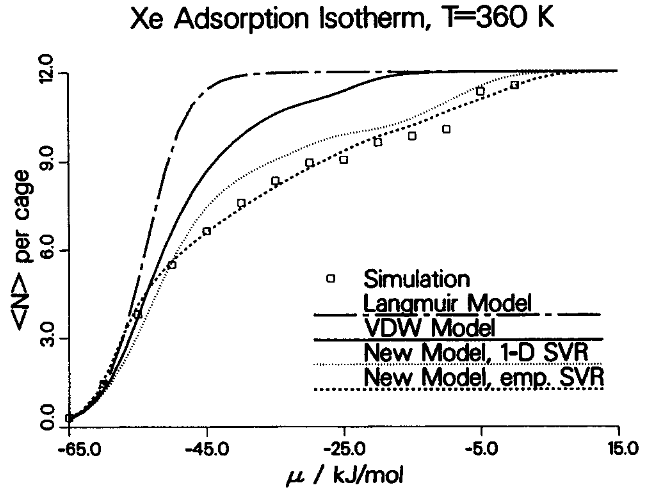

Figure 3b. Xe isotherm at 360 K.

Calculated via simulation (Van Tassel et al., 1993a), Langmuir model, van der Waals model, and new model.

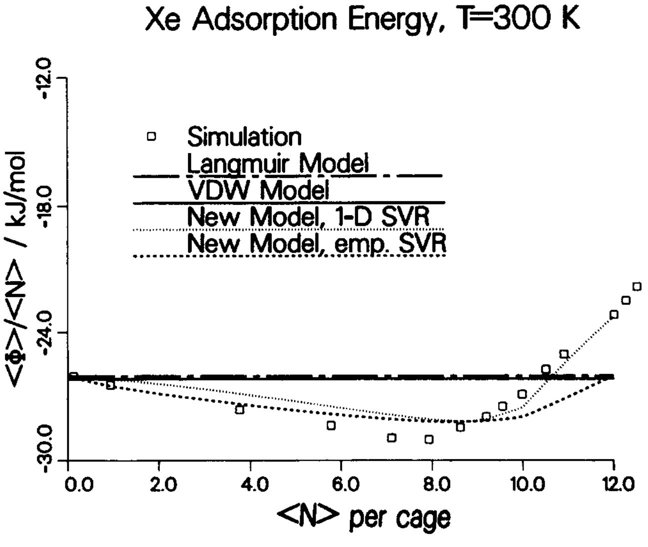

Figure 4a. Xe energy at 300 K.

Calculated via simulation, Langmuir model, van der Waals model, and new model.

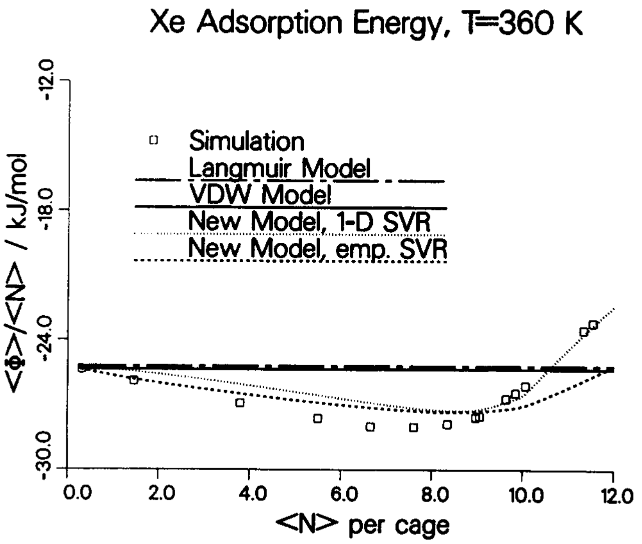

Figure 4b. Xe energy at 360 K.

Calculated via simulation, Langmuir model, van der Waals model, and new model.

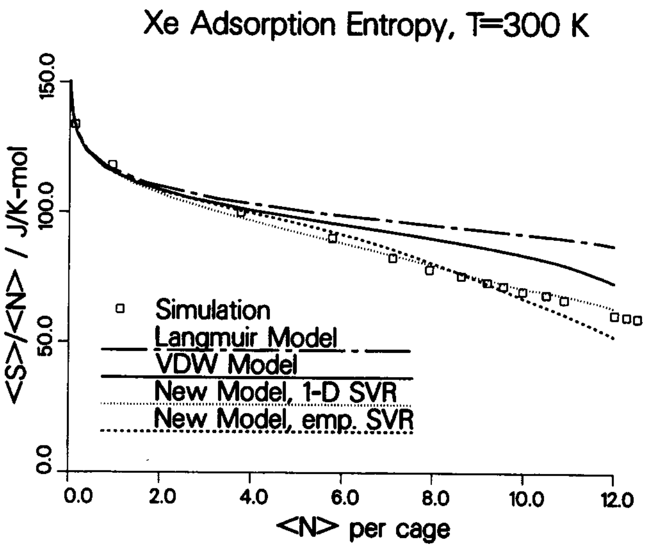

Figure 5a. Xe entropy at 300 K.

Calculated via simulation, Langmuir model, van der Waals model, and new model.

the three models as a function of loading. The Langmuir model overestimates the entropy because it does not account for decreasing site volume, and thus the loss of adsorbate translational freedom, as the sites fill. The van der Waals model accounts for filling of the cage, and so it more accurately predicts the simulated entropy. However, simulations show that not only does the accessible cage volume decrease as the sites fill, but the volume accessible to an adsorbate in a given *site* decreases as well (Van Tassel et al., 1993b). In other words, the adsorption sites become more localized as loading increases. This is taken into account by the new model, which predicts the simulated entropy quite accurately.

To determine the extent to which site volume reduction contributes to the predictive power of the new model isotherm, we have applied our empirical site volume reduction to both the Langmuir and VDW models by multiplying each term of Eqs. 18 and 19 by $V_{\text{site}}/V^0_{\text{site}}$ of Eq. 8. This adjustment improves the predictive capability of these models (Figure 6), but they are still much less accurate than the new model.

Finally, to determine the sensitivity of the new model isotherm to changes in the adjustable parameters, we present isotherms calculated using a range of parameters. Figure 7 shows that the Xe isotherm (using 1-D site volume reduction) changes little for even large changes (~50%) in the single adjustable parameter γ. Essentially, the value of γ affects only the chemical potential at which the transition between isotherm plateaus occurs. It has virtually no effect on the isotherm at low to intermediate loadings. Similarly, Figure 8 shows that the qualitative shape of the empirical form of the new model is accurately predicted for a range of β.

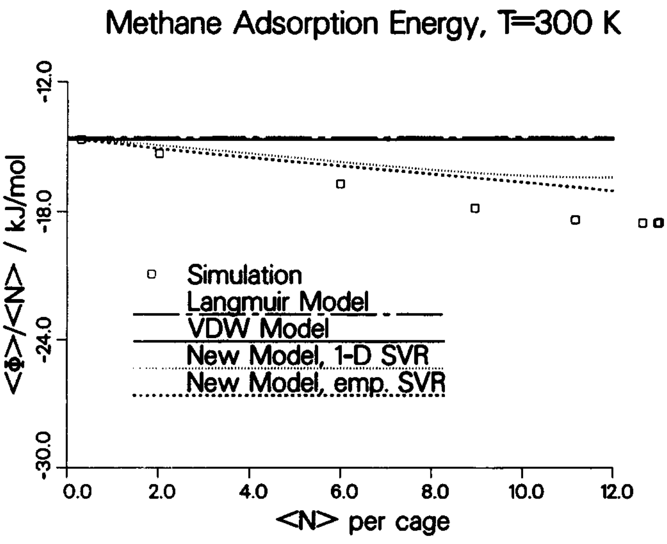

Figure 4c. Methane energy at 300 K.

Calculated via simulation, Langmuir model, van der Waals model, and new model.

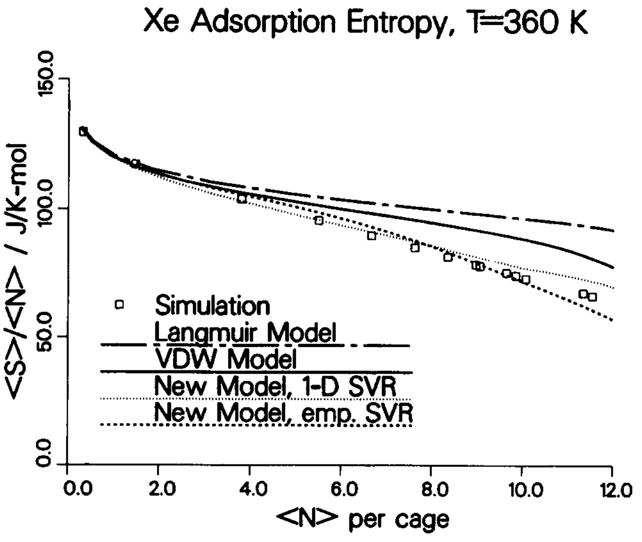

Figure 5b. Xe entropy at 360 K.

Calculated via simulation, Langmuir model, van der Waals model, and new model.

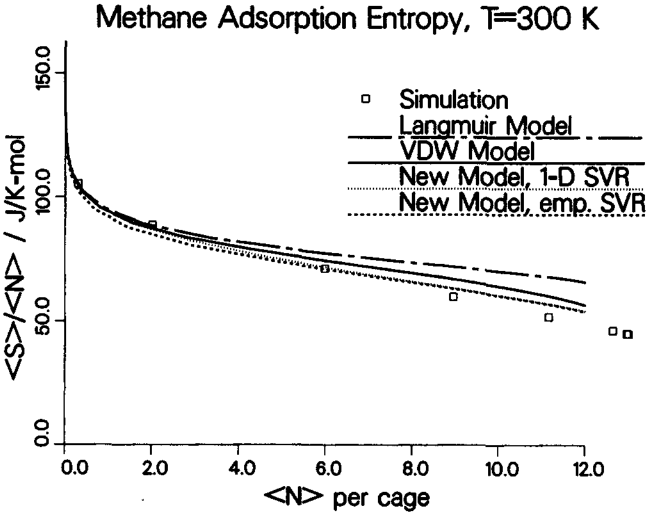

Figure 5c. Methane entropy at 300 K.

Calculated via simulation, Langmuir model, van der Waals model, and new model.

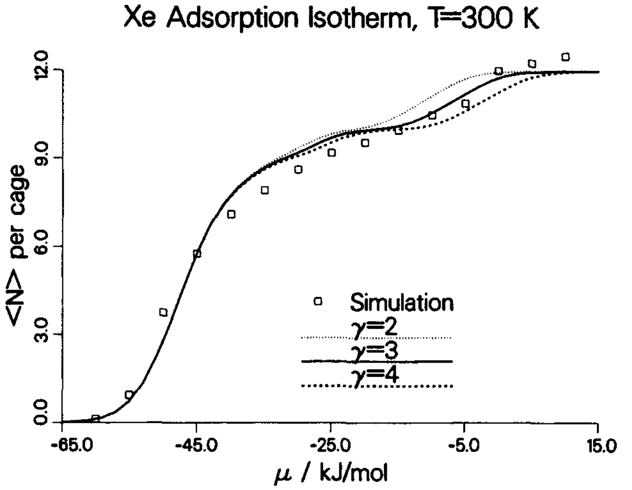

Figure 7. Simulated Xe isotherm and new model isotherm employing 1-D site volume reduction for various values of γ at 300 K.

Discussion

Computer simulation has shown that adsorbates in zeolite pores tend to reside in discrete sites. We suggest modeling zeolitic adsorption using a polyhedral lattice whose neighboring sites interact energetically and entropically. Such an approach accounts for the observed phenomena of sorbate-sorbate attraction, crowding, and translational freedom.

Previously proposed microporous adsorption models do not account for these effects. Thus, they tend to inaccurately predict the isotherm by overestimating the entropy of the adsorbed phase and inadequately portraying the sorbate-sorbate interaction energy. A Langmuir model does not account for sorbate-sorbate interactions or changes in site volume. A VDW model accounts for an overall cage volume change, but considers the adsorbates to be delocalized within the cage. These assumptions result in a) more adsorbate translational freedom than if the adsorbates were confined to sites and b) an inaccurate account of sorbate-sorbate interactions.

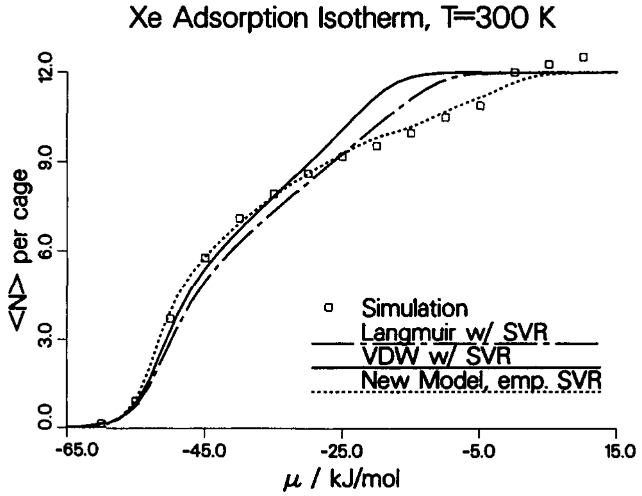

Figure 6. Simulated isotherm(s) calculated via Langmuir model, van der Waals model, and new model (with empirical site volume reduction) at 300 K.

Langmuir and van der Waals models have been modified to include the empirical site volume reduction term.

The new model proposed here has many of the features desired in a tractable model: it reproduces the isotherm over a wide pressure range; it accounts for sorbate-sorbate attraction, repulsion, and site volume reduction; and it has a minimum number of adjustable parameters, one (γ) for the case of 1-D site volume reduction and two (γ and β) for the case of empirical site volume reduction.

The geometry of the lattice is determined by the points of minimum potential energy in the zeolite pore, so a lattice of sites for any zeolite may be determined easily without resorting to simulation. Since these points tend to reside near open ring apertures in the zeolite, their positions may even be estimated using the van der Waals diameters of the ring oxygen atoms and the adsorbate. The lattice is both finite (because the cages which compose the zeolite are small) and polyhedral (because

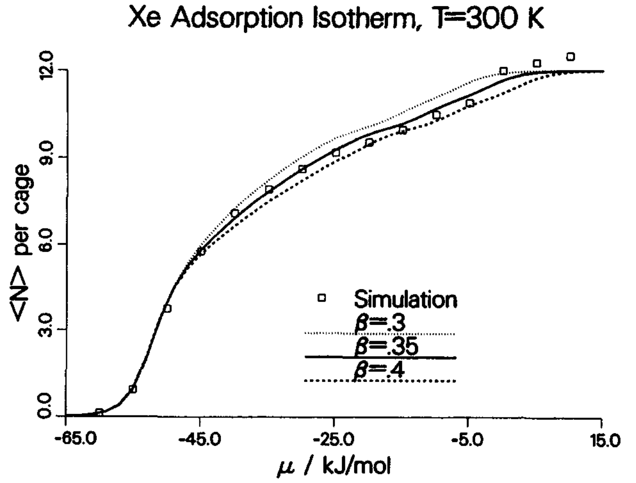

Figure 8. Simulated Xe isotherm and new model isotherm employing empirical site volume reduction for various values of β at 300 K.

the lattice positions are closely related to the symmetry of the zeolite crystal).

A nonmonotonic sorbate-sorbate interaction is proposed here as part of the new model isotherm. Its form implies that for a group of nearest neighbor sites on the lattice, a pairwise attractive interaction will result, provided at least one site is empty. The implication is that even if the adsorbates are somewhat larger than the spacing between sites (the condition of $\sigma \geq d-2r$ of Eq. 7), they may "relax" to positions slightly away from the lattice positions toward the empty site to maximize their pairwise energy. This relaxation may not be possible if all sites are occupied. In this case, the energy of the group of neighbors will depend on the parameter γ and could become repulsive. The adsorption energy predicted by the new model exhibits attractive and repulsive regimes, features consistent with results from simulation and experiment.

The concept of an adsorption site volume reduction is also proposed as part of the new model isotherm in accord with simulation results (Van Tassel et al., 1993b). Physically, this accounts for the loss of the translational freedom of an adsorbate caused by the filling of neighboring sites. The incorporation of a site volume reduction term allows the new model to predict the adsorption entropy more accurately than previously proposed models. This, however, is not the only feature contributing to the new model's predictive capability, since the incorporation of our empirical site volume reduction (Eq. 9) to both the Langmuir and VDW model isotherms only partially improves their accuracy (Figure 6).

Two forms of site volume reduction are presented here: one which is based on 1-D site overlap, the other on an empirical observation of simulation results. Although the empirical form (with an adjustable parameter, β) seems to give a better isotherm fit, the 1-D form (without adjustable parameters) may be of broader use, since it more accurately predicts both the energy and entropy of adsorption. The empirical form of the new model slightly overestimates both the energy and entropy, so its predictive capability is enhanced by a cancelation of errors and thus may be valid over a more limited range of temperatures than the 1-D form. For the temperatures investigated here (300 to 360 K), however, the empirical form of the new model does offer high accuracy.

Methane acts as a nearly "ideal" adsorbate in NaA: it is large enough to be confined to cuboctahedral sites, yet is small enough that the sites may fill without the onset of repulsion. It is thus expected that the Langmuir and VDW model isotherms should adequately describe its adsorption. It is, in fact, a good test of our model that it approaches the simpler model isotherms when the adsorbate becomes more ideal.

Xenon, on the other hand, is nonideal. Repulsion is observed before the sites are filled, leading to an isotherm plateau at a loading of 10 Xe per cage. The new model, because of its two- and multibody sorbate-sorbate energy, predicts this plateau. Isotherm plateaus are often attributed to multilayer adsorption or to the saturation of a class of adsorption sites. Here, the plateau occurs since a loading of 11 Xe is much more crowded than a loading of 10 Xe. Although the jump in the isotherm at a loading of 10 Xe per cage is only approximated by the new model, its mere presence indicates that the essential physics of the sorbate-sorbate interactions are captured in this model.

The new model isotherm depends only weakly on the value chosen for the adjustable parameters. The value of γ essentially affects only the chemical potential at which the transition between isotherm plateaus occurs and has little effect at low to intermediate loadings. We expect that for small adsorbates, γ should approach $-N_{\text{coord}}$ (Eq. 1). For larger adsorbates, γ will be greater. The dependence of the β parameter (in the empirical form of the new model) on the size of the adsorbate is less straightforward. However, although the quantitative fit of the Xe isotherm depends on β, the qualitative shape of the simulated isotherm is accurately predicted for a range of β (Figure 8).

This new model could also be applied to other zeolitic adsorption systems; all that is needed is the adsorption site arrangement. For example, Xe atoms are found to arrange in a cube when adsorbed in zeolite rho (Vernov et al., 1993) and in an octahedron in mordenite (Nivarthi et al., 1993). It will, of course, be very interesting to examine this approach with these and other zeolites—this work is in progress.

Unfortunately, there is a paucity of experimental adsorption measurements compared to simulation results, so almost all of our comparison has been to simulation. Moreover, we have examined only simple adsorbates where we can write reliable, yet tidy, partition functions. These unavoidable limitations, though, do not detract from the conclusions we have drawn. The practice of comparing to simulation allows us to develop a physically insightful, deterministic theory that helps us to understand the complex phenomenon of zeolite adsorption. The chief value of this model is not only that it predicts the adsorption as accurately as simulation, but also that it captures the physics of adsorption and so is predictive in a way that simulation alone cannot be.

Conclusions

A new adsorption isotherm model for small molecules in zeolites is presented which considers adsorbates to reside on discrete lattice sites, a feature consistent with observations from molecular simulation studies. Neighboring sites interact energetically via a nonmonotonic sorbate-sorbate energy function and entropically via a loading-dependent site volume reduction term.

The model is applied to small molecules (xenon, methane) adsorbed in idealized zeolite NaA. Quantitative prediction of the isotherm over the entire loading range is achieved which marks a significant improvement over simple models based on independent sites (Langmuir) and pore-volume filling (van der Waals). These simple models fail to predict the amount adsorbed due to overestimation of translational entropy and neglect of sorbate-sorbate interactions.

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Notation

c = configuration vector
d = distance between nearest neighbor lattice sites
E_i = sorbate-sorbate energy of ith lattice site
k = Boltzmann constant
M = total number of lattice sites
n_i = number of occupied nearest neighbor sites to site i
N = number of occupied sites
N_{coord} = number of nearest neighbor lattice sites
$N(\mathbf{c})$ = number of occupied sites in configuration $\mathbf{c}$
q_{site} = partition function for single adsorption site
r = radius of adsorption site
$\mathbf{r}$ = vector position of adsorbate in zeolite
T = absolute temperature
V_{site} = volume of adsorption site
V^0_{site} = volume of adsorption site at zero loading
Z_2 = configuration integral for two 1-D hard rod adsorbates

Greek letters

β = model site volume parameter
γ = model repulsive parameter
ϵ = Lennard-Jones attractive parameter
Λ = de Broglie wavelength
λ = van der Waals isotherm model crowding parameter
μ = chemical potential
σ = Lennard-Jones size parameter
$\Phi(\mathbf{r})$ = potential energy of interaction between adsorbate and zeolite at position $\mathbf{r}$ in zeolite
$\langle\Phi\rangle_1$ = average potential energy of one adsorbate in zeolite
$\Psi(\mathbf{c})$ = sorbate-sorbate interaction energy of configuration $\mathbf{c}$

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