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Statistical thermodynamics of lattice models in zeolites: Implications of local versus global mean field interactions

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The statistical thermodynamics of adsorption in caged zeolites is developed by treating the zeolite as an ensemble of M identical cages or subsystems. Within each cage adsorption is assumed to occur onto a lattice of n identical sites. Expressions for the average occupancy per cage are obtained by minimizing the Helmholtz free energy in the canonical ensemble subject to the constraints of constant M and constant number of adsorbates N. Adsorbate–adsorbate interactions in the Brag–Williams or mean field approximation are treated in two ways. The local mean field approximation (LMFA) is based on the local cage occupancy and the global mean field approximation (GMFA) is based on the average coverage of the ensemble. The GMFA is shown to be equivalent in formulation to treating the zeolite as a collection of interacting single site subsystems. In contrast, the treatment in the LMFA retains the description of the zeolite as an ensemble of identical cages, whose thermodynamic properties are conveniently derived in the grand canonical ensemble. For a z coordinated lattice within the zeolite cage, with ϵ_{aa} as the adsorbate–adsorbate interaction parameter, the comparisons for different values of $\epsilon_{aa}^* = \epsilon_{aa}z/2kT$, and number of sites per cage, n, illustrate that for $-1 < \epsilon_{aa}^* < 0$ and $n \geq 10$, the adsorption isotherms and heats of adsorption predicted with the two approaches are similar. In general, the deviation between the LMFA and GMFA is greater for smaller n and less sensitive to n for $\epsilon_{aa}^* > 0$. We compare the isotherms predicted with the LMFA with previous GMFA predictions [K. G. Ayappa, C. R. Kamala, and T. A. Abinandanan, J. Chem. Phys. **110**, 8714 (1999)] (which incorporates both the site volume reduction and a coverage-dependent ϵ_{aa}) for xenon and methane in zeolite NaA. In all cases the predicted isotherms are very similar, with the exception of a small steplike feature present in the LMFA for xenon at higher coverages. © *1999 American Institute of Physics.* [S0021-9606(99)70333-8]

I. INTRODUCTION

Zeolites are microporous crystalline aluminosilicates containing nanometer size pores. The pore structure typically consists of interconnected cavities (channels or cages) that are periodically replicated to form the crystalline zeolite structure. Due to the wide range of pore sizes and compositions, zeolites are used extensively in the industry for gas separations and catalysis. Understanding adsorption, both physical and chemical, of molecules within the zeolite pore is fundamental to zeolite-based processes and technologies.

In the statistical thermodynamic treatment for fluid adsorption in zeolites, the zeolite is modeled as an ensemble of identical non-interacting subsystems, where each subsystem corresponds to a single zeolite cavity. Using this description, the thermodynamics of adsorption has been studied in the grand canonical ensemble where the formulation reduces to studying the adsorption in a single cavity or subsystem.[1,2] When the interactions are described using continuous potentials, the utility of this approach hinges on evaluating configurational integrals within the zeolite cavity.[3]

Lattice models have been recently used to describe adsorption in zeolites.[4–6] Monte Carlo simulations of methane and xenon in zeolite NaA show that adsorption occurs onto a 12-site cuboctahedral lattice. Using this lattice description, the grand partition function is evaluated by computing all possible energetic states for the lattice within a single cage.[4] In an alternate treatment,[5] we have used the Brag–Williams or mean field approximation to treat the adsorbate–adsorbate interactions on the lattice. This results in simplified expressions that can be used to evaluate the adsorption isotherms and other thermodynamic properties of the adsorbed phase. Comparison with grand canonical Monte Carlo simulation data indicate that lattice models, with appropriate description of the site volume reduction and interaction parameters, are able to quantitatively reproduce adsorption isotherms obtained from simulations over a wide pressure range. When applicable lattice models provide an attractive alternate to computation and theory, when compared with continuous potential Monte Carlo simulations, theories based on a virial expansion, or density functional theories. Generally simple molecular statics is sufficient to obtain inputs, such as the adsorbate-adsorbate and adsorbate-lattice interactions for the lattice model.

In our lattice treatment[5] of the adsorption of nonpolar molecules into zeolite NaA, the model is developed by treating the zeolite as a large collection of identical sites. With this approach the notion of the zeolite as a collection of

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identical cages is circumvented. In order to rationalize this description and contrast it with the description involving discrete cages, we present an alternate perspective for developing the statistical thermodynamics for the zeolite. The ensemble consists of a large collection of identical cavities (M), within which adsorption occurs onto a finite number of adsorption (lattice) sites. The derivation consists of minimizing the Helmholtz free energy of the ensemble subject to the constraint of constant number of adsorbates (N) and cages (M).

We treat the mean field approximation for the adsorbate–adsorbate interactions in two ways. The first is at the level of the cage, where the interactions are based on the local occupancy in the cage, and the second is based on the global ensemble-averaged coverage. These will be referred to as the local mean field approximation (LMFA) and global mean field (GMFA) approximation, respectively. The free energy minimization technique, as we will illustrate, facilitates the development of the theory in the presence of adsorbate–adsorbate interactions in the GMFA. Using this approach the theory based on the GMFA reduces to a model consisting of a collection of single-site subsystems interacting via the average coverage of the ensemble, providing a basis for the model used in our earlier work.[5] In contrast, the LMFA retains the zeolite cage as the subsystem and the thermodynamic properties are more conveniently developed in the grand canonical ensemble.

The manuscript is organized as follows. In the theory section, Sec. II, we develop the framework for studying the thermodynamics of adsorption based on minimizing the Helmholtz free energy in the canonical ensemble. We derive expressions for the adsorption isotherm, entropy, and heats of adsorption for non-interacting adsorbates and for interacting adsorbates where the interactions are based on both the LMFA and GMFA. In Sec. III, the adsorption isotherms and heats of adsorption are computed and comparisons made between the LMFA and GMFA. Finally, we contrast the performance of both approaches by studying the adsorption of methane and xenon in zeolite NaA.

II. THEORY

The zeolite is assumed to consist of an ensemble of M identical zeolite cages, where each cage can adsorb up to a maximum of n adsorbates. The treatment here is for a single component and each cage is assumed to consist of n identical adsorption sites, with each site having z nearest neighbors within the cage. Let occupation numbers α_i, $i=0,...,n$, denote the number of cages in the ensemble containing i particles. In the canonical ensemble for a fixed number of adsorbates, N, and fixed M, the constraints on α_i are

$$\sum_i i\alpha_i = N \quad \text{and} \quad \sum_i \alpha_i = M, \tag{1}$$

where the integral values of N can vary from 0 to a maximum of nM when all the sites are occupied. The summation notation in Eq. (1) represents the summation of i from 0 to n.

A. Canonical ensemble

The canonical ensemble partition function for constant N, M, and T is

$$Q(NMT) = \sum_{\{\alpha_i\}} \frac{M!}{\alpha_0!\alpha_1!...\alpha_n!} Q_{c0}^{\alpha_0} Q_{c1}^{\alpha_1} \cdots Q_{cn}^{\alpha_n}. \tag{2}$$

The sum in Eq. (2) represents the summation over all possible sets of occupation numbers $\{\alpha_i\}$, where each set is subject to the constraints in Eq. (1). The combinatorial term is the total number of ways a given set of occupation numbers $\{\alpha_i\}$ can be distributed among M cages. Q_{ci} represents the partition function for a single cage containing i particles. For an n-site lattice within each cage containing i adsorbates,

$$Q_{ci} = \frac{n!}{i!(n-i)!} q_s^i e^{-V_{aa}(i)/kT}, \quad i=0,...,n. \tag{3}$$

If the adsorbate–lattice interaction parameter is ϵ_{al} and v is the volume associated with a lattice site, the expression for the site partition function, q_s, for an adsorbate of mass, m, is

$$q_s = \frac{v}{\Lambda^3} e^{-\epsilon_{al}/kT}, \tag{4}$$

where $\Lambda = h/\sqrt{2\pi mkT}$ is the thermal de Broglie wavelength. $V_{aa}(i)$ in Eq. (3) represents the adsorbate–adsorbate interactions in a cage containing i adsorbates. It will be convenient to define $q_0 = v/\Lambda^3$ for later use.

1. Non-interacting adsorbates

In order to compute the adsorption isotherm, one must develop an expression for the average number of particles in the cage when the ensemble of cages is equilibrated with a bulk fluid with chemical potential μ. We illustrate the procedure for deriving the adsorption isotherm by minimizing the Helmholtz free energy of the ensemble, for non-interacting adsorbates, i.e., $V_{aa}=0$. In the canonical ensemble the expression for the Helmholtz free energy in the system is

$$A = -kT \ln Q(NMT). \tag{5}$$

Since the number of cages M and occupation numbers α_i can be made arbitrarily large in Eq. (2), the maximum term principle can be invoked,[2] thereby reducing the contribution to the free energy from that of a single term in the summation over the sets $\{\alpha_i\}$. We next seek the distribution of occupancy numbers α_i which minimizes the free energy subject to the two constraints in Eq. (1). Using the method of Lagrange multipliers,

$$\mathcal{F}(\alpha_1,...,\alpha_n) = A - \mu \sum_i i\alpha_i - \gamma \sum_i \alpha_i \tag{6}$$

is minimized with respect to α_j. The first Lagrange multiplier μ is simply the chemical potential of the fluid with which the ensemble is equilibrated with. Noting that the grand potential, $\Omega = A - \mu N$, minimizing $\mathcal{F}$ is equivalent to minimizing Ω subject to the constraint of constant M. Substituting the expression for A from Eq. (5) and $Q(NMT)$ from Eq. (2) into Eq. (6) and using Stirling's approximation, Eq. (6) reduces to

$$\mathcal{F}(\alpha_1,\ldots,\alpha_n) = -kT\left[\sum_i \alpha_i \ln \sum_i \alpha_i - \sum_i \alpha_i \ln \alpha_i \right.$$
$$\left. + \sum_i \alpha_i \ln Q_{ci}\right] - \mu \sum_i i\alpha_i - \gamma \sum_i \alpha_i. \tag{7}$$

Minimizing $\mathcal{F}$ with respect to α_j, i.e.,

$$\frac{\partial F}{\partial \alpha_j} = 0, \quad j = 0,\ldots,n, \tag{8}$$

and incorporating the constraints from Eq. (1), the expression for the average number of adsorbates per cage, N/M, is

$$\langle i \rangle_c \equiv \frac{N}{M} = \frac{\sum_i i[n!/i!(n-i)!]q_s^i\lambda^i}{\sum_i [n!/i!(n-i)!]q_s^i\lambda^i}, \tag{9}$$

where $\lambda = e^{\mu/kT}$. Noting that the ensemble-averaged coverage $\theta = \langle i \rangle_c / n$, Eq. (9), based on the occupancy within a single cage, can be used to calculate the adsorption isotherm θ vs μ for a given species. For $n=1$, the expression reduces to the equivalent form of the Langmuir isotherm,

$$\theta = \frac{q_s\lambda}{1+q_s\lambda}. \tag{10}$$

The derivation outlined above is analogous in spirit to obtaining the expression for the most probable distribution of energy levels in the canonical ensemble, except that the energy levels are replaced by the cage occupation numbers.

2. Interacting adsorbates—LMFA

In order to include interactions between adsorbates, we assume that each lattice site within the zeolite cage has z nearest neighbors. In our discussion we will assume that the coordination number of the lattice is similar to the number of nearest neighbors per site. In the LMFA, where the interactions are based on the coverage within the cage, the expression for the adsorbate–adsorbate interactions in the Brag–Williams[2] or mean field approximation for a cage containing i adsorbates is

$$V_{aa}^{\text{LMFA}}(i) = \frac{\epsilon_{aa}i^2z}{2n}, \tag{11}$$

where ϵ_{aa} is the adsorbate–adsorbate interaction parameter. Equation (11) is derived by noting that, in the mean field approximation, the number of nearest neighbors per site, in a lattice of n sites with i adsorbates, is iz/n. The factor of 2 accounts for double counting interactions. Following a procedure similar to that outlined above for non-interacting adsorbates the expression for the ensemble-averaged number of particles per cage $\langle i \rangle_c$, obtained by minimizing the free energy $\mathcal{F}$, is

$$\langle i \rangle_c = \frac{\sum_i i[n!/i!(n-i)!]q_s^i e^{-V_{aa}^{\text{LMFA}}/kT}\lambda^i}{\sum_i [n!/i!(n-i)!]q_s^i e^{-V_{aa}^{\text{LMFA}}/kT}\lambda^i}. \tag{12}$$

At this point, it is worth noting that the equations for $\langle i \rangle_c$, in Eqs. (9) and (12) are easily derived in the grand canonical ensemble, providing a more convenient route to developing the thermodynamics of an ensemble consisting of identical subsystems (see Sec. II B). The Lagrange multiplier method as outlined above facilitates the theory when interactions are treated in the GMFA, illustrated next.

3. Interacting adsorbates—GMFA

In the GMFA, the mean field interactions for an adsorbate at a given site are based on the average coverage θ of the ensemble and not on the local coverage within the cage. With this approach, the expression for the adsorbate–adsorbate interaction potential for a cavity with i adsorbates is

$$V_{aa}^{\text{GMFA}}(i) = \frac{\epsilon_{aa}i\theta z}{2}, \tag{13}$$

where $\theta = N/nM$. Unlike in the case of the LMFA, when the GMFA is used, the cage partition functions are now dependent on the occupation numbers α_i, and must be included during the minimization of the free energy in Eq. (8). The resulting expression for the average cage occupancy, obtained after minimizing $\mathcal{F}$ is

$$\langle i \rangle_c = \frac{\sum_i i[n!/i!(n-i)!]q_s^i e^{-2V_{aa}^{\text{GMFA}}(i,\theta)/kT}\lambda^i}{\sum_i [n!/i!(n-i)!]q_s^i e^{-2V_{aa}^{\text{GMFA}}(i,\theta)/kT}\lambda^i}. \tag{14}$$

Note the factor of 2 that arises in the exponential term. Since V_{aa}^{GMFA} is dependent on θ [Eq. (13)], Eq. (14) is implicit in the coverage θ. However, for $n=1$, which is equivalent to stating that each subsystem in the ensemble is a single site, Eq. (14) reduces to

$$\theta = \frac{q_s\lambda e^{-\epsilon_{aa}\theta z/kT}}{1+q_s\lambda e^{-\epsilon_{aa}\theta z/kT}}, \tag{15}$$

which can be rearranged to yield the adsorption isotherm relationship

$$\mu = kT\ln\left(\frac{\theta}{1-\theta}\right) - kT\ln q_0 + \epsilon_{aa}\theta z + \epsilon_{al}. \tag{16}$$

The GMFA implies that the zeolite is no longer thought of in terms of cages or subsystems, but in terms of single site subsystems that interact via the average coverage of the ensemble. This is equivalent to our earlier adsorption model,[5] where the zeolite is modeled as a large collection of identical sites (M). Using this description,[5] the canonical ensemble partition function for an M site lattice with N adsorbates is

$$Q(NMT) = \frac{M!}{N!(M-N)!}q_s^N e^{-V_{aa}^{\text{GMFA}}/kT}. \tag{17}$$

This is similar in form to the cage partition function given in Eq. (3), except that in Eq. (17) both N and M can be made arbitrarily large, allowing the use of Stirling's approximation. The expression for the adsorption isotherm, Eq. (16), is recovered by taking the derivative of the Helmholtz free energy, Eq. (5), with respect to N at constant T and M.

a. Entropy. Using the expression for $Q(NMT)$ from Eq. (17), the entropy

$$S = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right)_{M,N}$$

$$= k \ln \frac{M!}{N!(M-N)!} + Nk \ln q_s + \frac{3}{2} Nk + \frac{NkT}{v} \frac{dv}{dT}. \quad (18)$$

Assuming a temperature-independent site volume, v, Eq. (18) reduces to

$$\frac{S}{kM} = \frac{3}{2} \theta + \theta \ln q_s + \theta \ln \left(\frac{1-\theta}{\theta} \right) - \ln(1-\theta). \quad (19)$$

b. Isosteric heats of adsorption The isosteric heat of adsorption, $q_{st} = -(\bar{H}_a - \bar{H}_g)$ where $\bar{H}_a$ and $\bar{H}_g$ are the partial molal enthalpies of the adsorbed and gas phase, respectively, is obtained from[3]

$$q_{st} = kT^2 \left(\frac{\partial \ln P}{\partial T} \right)_\theta, \quad (20)$$

where P is the pressure of the bulk fluid which is in equilibrium with the zeolite. Assuming that the bulk gas is ideal, the relationship between the chemical potential μ and the bulk pressure P is

$$\mu = \mu_0 + kT \ln P, \quad (21)$$

where the reference chemical potential $\mu_0 = kT \ln(\Lambda^3/kT)$. Using Eq. (21) to relate the chemical potential to the bulk pressure P, the expression for q_{st} for a temperature-independent site volume reduces to

$$q_{st} = kT - \epsilon_{al} - \theta z \epsilon_{aa}. \quad (22)$$

B. Grand canonical ensemble–LMFA

Although the expression for the ensemble-averaged number of adsorbates [Eq. (12)] and hence the coverage can be derived starting with the free energy for the LMFA, it is more convenient to derive the other thermodynamic properties in the grand canonical ensemble. The grand partition function for the ensemble of M cages

$$\Xi = \sum_{N=0}^{nM} Q(NMT) \lambda^N. \quad (23)$$

Substituting the expressions for the canonical ensemble from Eq. (2), and using the multinomial theorem, Eq. (23) reduces to

$$\Xi = \xi(\lambda, T)^M, \quad (24)$$

where

$$\xi(\lambda, T) = (Q_{c0} + Q_{c1}\lambda + \cdots + Q_{cn}\lambda^n), \quad (25)$$

with the expressions for the cage partition functions Q_{ci} given in Eq. (3).

1. Adsorption isotherm

In the grand canonical ensemble, the expression for the average number of adsorbates per cage [Eq. (12)] is derived using

$$\langle i \rangle_c \equiv N/M = \lambda \left(\frac{\partial \ln \xi}{\partial \lambda} \right)_{M,T}. \quad (26)$$

2. Entropy

The entropy is obtained from,

$$\frac{S}{M} = kT \frac{\partial \ln \xi}{\partial T} + k \ln \xi$$

$$= \left(\frac{3k}{2} + \frac{\epsilon_{al}}{T} - \frac{\mu}{T} \right) \langle i \rangle_c + \frac{\epsilon_{aa} z}{2nT} \langle i^2 \rangle_c + k \ln \xi, \quad (27)$$

where $\langle i^2 \rangle_c$ is the second moment of the cage occupation number i.

3. Isosteric heats of adsorption

To obtain the expression for the heat of adsorption, the starting point is

$$\sum_i (n\theta - i) Q_{ci} \lambda_0^i P^i = 0, \quad (28)$$

which is obtained by rearranging Eq. (12) and using Eq. (21) to substitute λ with $\lambda_0 P$, where $\lambda_0 = e^{\mu_0/kT}$. Differentiating Eq. (28) with respect to T at constant coverage θ and simplifying, the expression for the isosteric heat of adsorption, Eq. (20), reduces to

$$q_{st} = kT - \epsilon_{al} - \frac{\epsilon_{aa} z}{2n} \frac{\sum_i (n\theta - i) i^2 Q_{ci} \lambda^i}{\sum_i (n\theta - i) i Q_{ci} \lambda^i}. \quad (29)$$

An alternate form for q_{st}, obtained by substituting relations for the higher moments $\langle i^2 \rangle_c$ and $\langle i^3 \rangle_c$ [which appear in Eq. (29)] by taking derivatives of Eq. (12), is

$$q_{st} = kT - \epsilon_{al} - \theta z \epsilon_{aa} - \frac{\epsilon_{aa} z kT}{2n} \frac{d^2\theta/d\mu^2}{d\theta/d\mu}. \quad (30)$$

When comparing Eq. (30) with the expression for q_{st} obtained from the GMFA [Eq. (22)] we see an additional term which involves derivatives of the adsorption isotherm. To obtain q_{st} from Eq. (29), the adsorption isotherm μ vs θ relationship must be known.

C. Site volume and coverage-dependent interaction

While using lattice models to study adsorption in zeolites, it has been found that the model must incorporate the decrease in the volume of the adsorption site, v, and, for larger molecules, the adsorbate–adsorbate interaction parameter must reflect the increased repulsive interaction at higher coverages. Within the framework of the GMFA, we have modeled the decrease in the site volume using a hard-rod theory[4] and used a coverage-dependent interaction parameter $\epsilon_{aa}(\theta)$ to predict adsorption isotherms for methane and xe-

non in zeolite NaA.[5] Here we only present the expressions for the site volume reduction and the coverage-dependent interaction parameter ϵ_{aa} that will be used to make comparisons between the LMFA and GMFA for the adsorption of xenon and methane in NaA.

Using a hard-rod theory,[5] the site volume v in the GMFA is

$$v = v_0 \left[\frac{1}{2} \left(\frac{l-\sigma}{2R} + 1 \right)^2 \right]^{pz/2}, \qquad (31)$$

where v_0 is the volume of the adsorption site associated with a single adsorbate in the absence of neighboring adsorbates, $p = \theta$ for the GMFA, and $p = i/n$ when used with the LMFA in the grand partition function. R is the site radius obtained by assuming a cubic site of volume v_0, l is the lattice parameter, and σ is the Lennard-Jones molecular diameter. Using the Lennard-Jones potential, the coverage-dependent interaction[5] for the GMFA is

$$\epsilon_{aa}(\theta) = 4\epsilon \left[\left(\frac{\sigma}{r(\theta)} \right)^{12} - \left(\frac{\sigma}{r(\theta)} \right)^{6} \right], \qquad (32)$$

where

$$r(\theta) = (r_2 - r_1)\theta + r_1. \qquad (33)$$

In this manner, ϵ_{aa} is made to vary from ϵ at $r_1 = 2^{1/6}\sigma$ to a final energy determined by r_2 which is treated as an adjustable parameter. While using Eq. (33) with the LMFA, θ is replaced with i/n in the grand partition function. For the LMFA the expressions for the thermodynamic properties incorporating the site volume reduction and coverage-dependent interaction parameter follow in a similar manner as described above, with the appropriate modification to the site partition function q_s [Eq. (4)] to incorporate Eq. (31) and the inclusion of the coverage-dependent ϵ_{aa} in Eq. (11), in the cage partition function Q_{ci}. The expressions (LMFA) for the adsorption isotherm with Eq. (17) as the starting point are given in the reference by Ayappa et al.[5] and the expression for the heat of adsorption is similar to Eq. (22), with a coverage-dependent ϵ_{aa}.

III. RESULTS AND DISCUSSION

The implications of using the GMFA are the following. The zeolite is no longer thought of in terms of cages (subsystems with n sites), but in terms of single-site subsystems ($n=1$) that interact via the average coverage of the ensemble. The formulation based on the GMFA is equivalent to assuming a lattice of single-site subsystems interacting in the mean field and the thermodynamic properties, which are evaluated in the canonical ensemble, result in simple analytic expressions. On the other hand, the thermodynamic properties for the LMFA are conveniently handled in the grand canonical ensemble where the expressions involve summations at the level of the cage. In order to study the implications between the two representations of the mean field, we compared the adsorption isotherms and heats of adsorption from both formulations. Next, we apply the two formulations
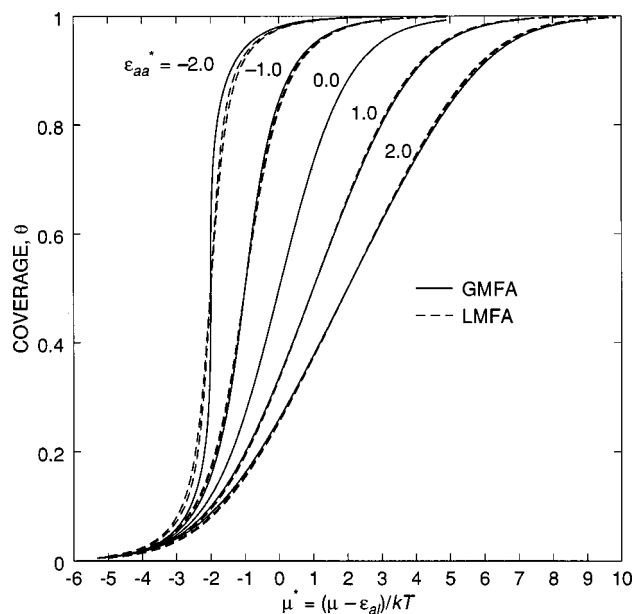

FIG. 1. Adsorption isotherms comparing the predictions between the LMFA [Eq. (12), $n=10$ and 15] and GMFA [Eq. (16)] for different values of $\epsilon^* = \epsilon_{aa}z/2kT$. The deviations from the GMFA are greater for smaller values of n.

to model the adsorption of methane and xenon in zeolite NaA for which simulation data and lattice parameters are available (Table I).[4]

In Fig. 1 we plot the adsorption isotherms evaluated using Eqs. (12) (LMFA) and (16) (GMFA) as θ vs $\mu^* = (\mu - \epsilon_{al})/kT$ for different values of the parameter, $\epsilon_{aa}^* = \epsilon_{aa}z/2kT$, with $q_0 = 1.0$. The dependence on the number of sites, n, in the cage is examined by plotting the isotherms obtained from the LMFA for $n=10$ and 15. For comparison we have also plotted the Langmuir isotherm ($\epsilon_{aa}^* = 0$). For $\epsilon_{aa}^* = -1.0$ the differences between the LMFA and GMFA are small, with the difference decreasing for smaller values of $-\epsilon_{aa}^*$. At a coverage of $\theta = 0.5$, both theories predict the same value of μ^*. The other point to note, fundamental to the different ensembles, is the presence of van der Waal's loops which occurs in the canonical ensemble[2] (GMFA) at lower values of ϵ_{aa}^* (not shown). We also examine the cases of $\epsilon_{aa}^* > 0$, where the agreement between the two theories is seen to be excellent. The shifting of the isotherms to higher μ^* can also occur due to a reduction in the adsorption site volume as we shall see later in the manuscript. In all cases the difference between the two isotherms increases with decreasing n. Increasing n beyond 15 produced a negligible change in the isotherms. The dependence on n reduces with increasing ϵ_{aa}^* and is the least for isotherms with coverages below the Langmuir isotherm.

The isosteric heats of adsorption from Eqs. (22) (GMFA) and (29) (LMFA) are shown in Fig. 2 where $q_{st}^* = (q_{st} + \epsilon_{al})/kT$. The results for the LMFA are shown for $n=10$ and 15. Here again the difference between the two theories increases with decreasing ϵ_{aa}^*, with the LMFA showing both positive and negative deviations from the linear dependence of the GMFA. Equation (30) indicates that the difference between the heats of adsorption from the two theories is
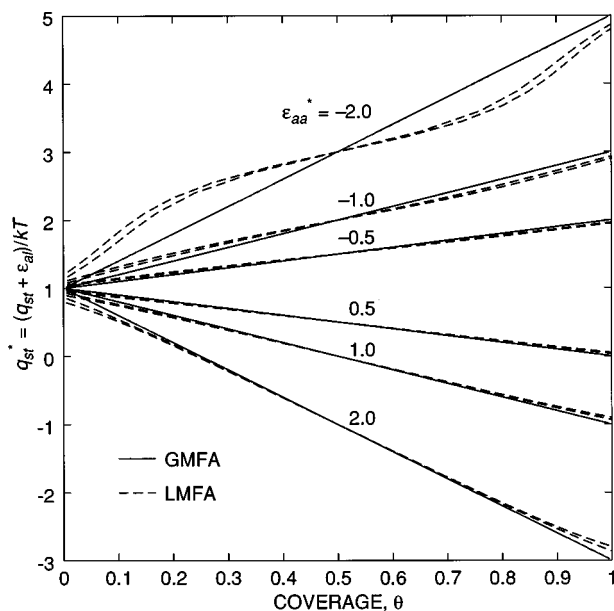
FIG. 2. Reduced isosteric heats of adsorption, q_{st}^* vs θ for the LMFA [Eq. (29)] and GMFA [Eq. (22), $n=10,15$]. The positive and negative deviations from the LMFA about the linear form for the GMFA are larger for $\epsilon_{aa}^*<0$.

FIG. 3. Predicted isotherms for adsorption of xenon in NaA ($n=12$, $T=360$ K) compared with GCMC data (Ref. 4) (●). (a) Mean field with a constant adsorbate–adsorbate interaction parameter, $\epsilon_{aa}=\epsilon$, (b) Langmuir ($\epsilon_{aa}=0$), (c) Mean field with site volume reduction [Eq. (31)], (d) Mean field with site volume reduction and coverage-dependent adsorbate–adsorbate interaction [Eq. (32), $r_2=3.906$ Å]. The differences between the LMFA and GMFA are small. Here $\epsilon_{aa}^*=-1.227$.

due to the last term involving the derivatives of the adsorption isotherm. The identical values for q_{st}^* from both theories at $\theta=0.5$ are due to the vanishing of the second derivative at $\theta=0.5$. For $\epsilon_{aa}^*<0$ the positive deviation in the LMFA at $\theta<0.5$ results from the positive values of $d^2\theta/d\mu^2$ leading to a positive contribution from the last term in Eq. (30) and negative deviation for $\theta<0.5$ results from the negative values of the second derivative. The opposite is true for $\epsilon_{aa}^* >0$. Note that $d\theta/d\mu$ is always positive with a maximum at $\theta=0.5$.

We next computed the adsorption isotherms and heats of adsorption for adsorption for xenon and methane in zeolite NaA. Using MC simulations the adsorption of xenon and methane in NaA has been shown to occur onto a $n=12$ site cuboctahedral lattice.[4] Recently, we have computed the adsorption isotherms for xenon and methane using the GMFA,[5] with the hard-rod site volume reduction [Eq. (31)] and a coverage dependent adsorbate–adsorbate [Eq. (32)] interaction parameter. This approach, with one adjustable parameter (r_2) which controlled the amount of repulsion between adsorbates, was found to yield isotherms in quantitative agreement with the GCMC isotherm data.[5] Here we compute the adsorption isotherms for methane and xenon using the LMFA and compare them with computations using the GMFA.

In all cases $n=12$, and the number of nearest neighbors was $z=4$. Figure 3 illustrates the adsorption isotherms for xenon at 360 K computed from both the GMFA and LMFA as well as with GCMC simulation data.[4] The comparisons are made for the mean field interaction with a constant ϵ_{aa} in the absence of site volume reduction, with the site volume reduction and for a coverage-dependent ϵ_{aa} with the site volume reduction which yields the best agreement with the simulation data. In all cases the predictions from the GMFA
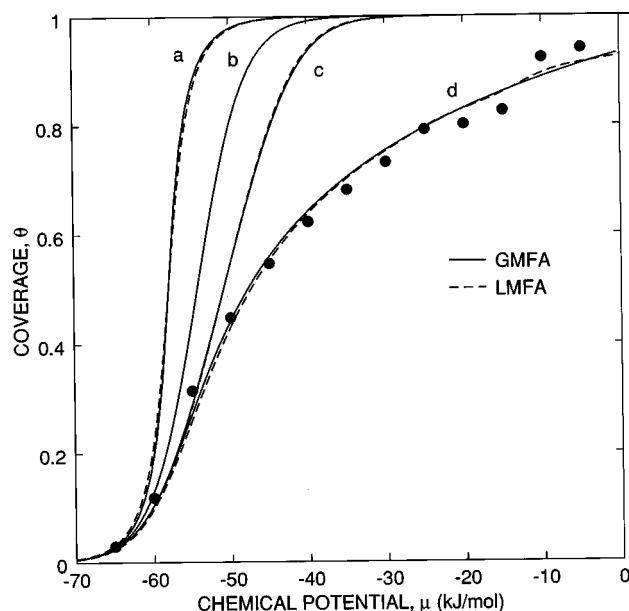
and LMFA are almost identical, with small differences in the LMFA at higher chemical potentials with the coverage-dependent interaction model. The small steplike feature in the LMFA (present also in the simulation data) at higher coverages is absent in the GMFA, indicating the possible loss of such features due to the global averaging of interactions. Based on the value of the Lennard-Jones interaction parameter, $\epsilon_{aa}^*=-1.227$ for xenon. Similar comparisons are
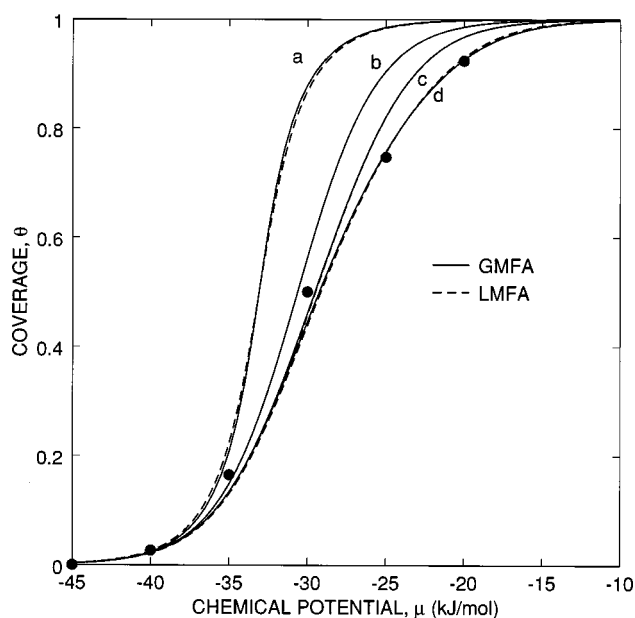

FIG. 4. Predicted isotherms for methane in zeolite NaA ($n=12$, $T=300$ K). (a)–(d) have similar references as that of Fig. 3. Here $r_2=4.0$ Å and $\epsilon_{aa}^*=-0.098$.
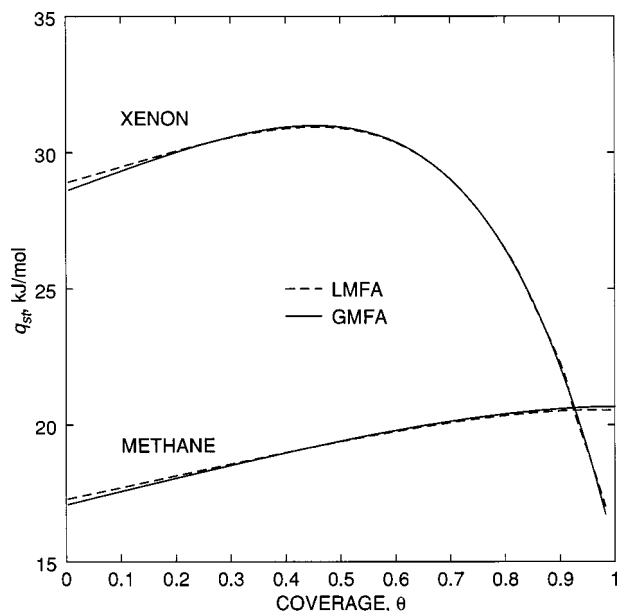
FIG. 5. Isosteric heats of adsorption versus coverage for xenon and methane using the LMFA [Eq. (29)] and GMFA [Eq. (22)]. There is a significant decrease in the heats of adsorption for xenon at higher coverages due to repulsive adsorbate–adsorbate interactions.

TABLE I. Parameters used in lattice model for xenon and methane (data from Ref. 4).

	l (Å)	σ (Å)	ϵ (kJ/mol)	ϵ_{al} (kJ/mol)	v (Å)^3
Xenon	3.58	4.10	1.837	−25.6	7.465
Methane	3.79	3.82	1.230	−14.58	9.987

handled in the grand canonical ensemble, where the model restrains the description of the zeolite as a collection of identical cages and the expressions for the thermodynamic properties involve finite sums within the cage. In addition to the adsorption isotherms we derive expressions for the isosteric heats of adsorption and the entropy in both the LMFA and GMFA.

Comparison of the thermodynamic properties from both formulations based on a parametric study indicates that the adsorption isotherm and heats of adsorption for $\epsilon_{aa}^* > -1.0$ and $n > 10$ predicted from the GMFA are similar to that obtained in the LMFA. For smaller values of n and larger negative ϵ_{aa}^* the deviation from the LMFA is greater. In general, the deviations between the two formulations are smaller when the isotherms lie below (lower coverages) the Langmuir isotherm. The comparisons for the adsorption of methane and xenon in NaA, which incorporates both site volume reduction and a coverage-dependent interaction parameter, indicates that predictions from both models are very similar.

Our analysis shows that the lattice model for zeolites when treated as a collection of single-site subsystems is equivalent to basing the mean field interactions within the cage on a global coverage of the ensemble and provides an analytically tractable description for adsorption of small molecules in zeolites. This approach is expected to work well for systems away from the coexistence region and with positive deviations from the Langmuir isotherm. In these situations it is also expected to provide a favored route to the development of a mixture theory. To conclude, although we have restricted our analysis to zeolite adsorption, the ideas developed here can, in principle, be applied to other adsorption systems which can be modeled as a large collection of identical subsystems, such as adsorption in micellar systems and biological cells.

also shown for methane at 300 K in Fig. 4 where $\epsilon_{aa}^* = -0.098$. Due to the small value of ϵ_{aa}^*, little difference is observed for the isotherms predicted from both theories. The isosteric heats of adsorption for both xenon and methane are plotted in Fig. 5 for both the LMFA and GMFA. Due to the coverage-dependent interaction parameter ϵ_{aa}, the heats of adsorption, although linear at low coverages, show a modest leveling out for methane since the adsorbate–adsorbate interactions are still attractive ($r_2 = 4.0\,\text{Å} > \sigma = 3.82\,\text{Å}$). However, for xenon, where the interactions become repulsive ($r_2 = 3.906\,\text{Å} < \sigma = 4.1\,\text{Å}$), the heats of adsorption shows a significant decrease below a coverage of 0.5. This decrease in the heats of adsorption, attributed to increased repulsive interactions, has also been observed in previous GCMC simulations of small molecules in cagelike cavities[3,7]

IV. CONCLUSIONS

The adsorption and thermodynamics in a zeolite are developed by treating the zeolite as an ensemble of identical cages or subsystems. Using the Helmholtz free energy as the starting point we derive the expressions for the average coverage per cage, for both noninteracting and interacting adsorbates where the adsorbate–adsorbate interactions are treated in the mean field. In the LMFA the mean field approximation is based on the local occupancy within the cage and in the GMFA it is based on the average coverage of the ensemble. We show that the GMFA is equivalent to treating the zeolite as a collection of single-site subsystems interacting via the average coverage, and the thermodynamic properties can be derived in the canonical ensemble. The thermodynamic properties for the LMFA, on the other hand, are conveniently

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