

A Simulated Annealing Method for Determining Atomic Distributions from NMR Data: Silicon and Aluminum in Faujasite

Brian K. Peterson[†]

Air Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, Pennsylvania 18195-1501

Received: November 23, 1998; In Final Form: March 3, 1999

Simulated annealing is applied to the determination of distributions of silicon and aluminum atoms on the faujasite lattice from ^{29}Si NMR data. The method is described and compared to others. The local silicon environments, $\text{Si}(n\text{Al})$, $n = 0-4$, are reproduced to high accuracy by the technique. More detailed features of local structure are then available, such as numbers of Al on different ring systems in the zeolite. Dempsey's rule is found to be strictly followed in the four rings of the zeolite X sample studied, while this is not the case for zeolite Y—in agreement with previous work. The results are consistent with a possible small violation of Lowenstein's rule in the zeolite X sample.

Introduction: Silicon and Aluminum Distributions in Faujasite

X-ray diffraction of single crystals or powders provides structural data for many materials including zeolites. Atomic identities, fractional occupancies, and average positions are often found with great precision. Because of the similar scattering factors for silicon and aluminum atoms, however, it is usually impossible to distinguish between them on the basis of XRD analysis alone. The topology and dimensions of a zeolite framework might then be known, but the ordering (or disorder) of the Si and Al among the tetrahedral sites of the framework is not determined.

Complementary short-range information can be obtained from nuclear magnetic resonance experiments, particularly ^{29}Si NMR.¹ A high-symmetry zeolite with only one crystallographically unique tetrahedral site, (Tsite) will, in general, exhibit ^{29}Si NMR spectra with up to five lines; one for each possible number of aluminum neighbors for a given silicon atom, $n = 0-4$. Zeolites X and Y, which have the FAU framework topology, are such zeolites, and many studies have derived some information on the silicon/aluminum distributions in these materials by combining the local environment information from NMR, the framework topology from crystallography, other chemical information, and modeling. Various attempts have used the analysis of models of ordered subunits of the framework,²⁻⁴ subunits plus symmetry constraints,⁵ random distributions,^{6,7} Monte Carlo annealing studies with either simplified or realistic energetics,⁸⁻¹¹ order plus disorder models,¹² and combinations of methods including molecular dynamics.¹³ Recently, an approach using simulated annealing has been tried on other Si/Al framework materials.¹⁴ In all cases, the results of the modeling have been compared to the known ^{29}Si NMR spectra or to the integrated intensities that give the relative populations of $\text{Si}(n\text{Al})$ environments. Lowenstein's rule¹⁵ (Al on adjacent Tsites not allowed) is usually enforced. The results from many of these studies have fit the available experimental information quite well and have provided useful information, but they are sometimes contradictory and there is room for a more complete and accurate picture.

We have applied simulated annealing^{16,17} to this problem. We are able to include the long-range topology and order of the framework, can enforce Lowenstein's rule if desired, and fit the available NMR data to high precision using few extraneous assumptions. The resulting distributions of silicon and aluminum should prove useful in better understanding the structure and performance as catalysts and adsorbents of these industrially important zeolites.

Method

Simulated Annealing. The method of simulated annealing (SA) was developed by Kirkpatrick et al.¹⁶ as an optimization method for combinatorially large problems. A description of the general method and its application to the traveling salesman problem can be found in the Numerical Recipes book.¹⁷ Annealing is the process of using slow cooling from an initial high temperature to remove high-energy structures and defects, e.g., applied to liquid freezing. The slow cooling allows time for thermal motions in the system to overcome local potential energy barriers. If the cooling is slow enough, a state very near the global minimum energy condition (a defect-free crystal) should be reached. The opposite, rapid quenching, tends to freeze-in high-energy defects.

Consider a Monte Carlo simulation of a simple liquid such as one consisting of atoms interacting with the Lennard-Jones intermolecular potential. To an initial configuration of the molecules is applied some trial change of the system. This is probably just a slight displacement of one of the atoms. If the energy of the system is decreased by the trial move, the move is accepted, the new configuration becomes the configuration of the system, and the next trial move is attempted. If the energy of the system is increased by the move, the Metropolis¹⁸ criterion is used to determine if the move is accepted or rejected, in which case the old configuration of the system is retained. The Metropolis criterion uses a random number, r , between 0 and 1 such that if $e^{-\delta E/KT} < r$, the move is accepted, and otherwise, it is rejected. This process is repeated many times and after a sufficient number of steps, the system should take up an equilibrium (Boltzmann) distribution of states. If, after a certain number of steps, the temperature of the simulation is decreased, the system will fall into the equilibrium state at the new

[†] Phone: 610-481-3850. E-mail: petersbk@apci.com.

temperature. If the temperature is slowly decreased to some very low value, the state of the system should be that which minimizes the energy of the system, in the case of the Lennard-Jones fluid, a defect-free crystal.

Simulated annealing borrows this process to minimize functions other than the energy of a physical system. Consider an objective function that we will still call E (but which may have any units or no units at all) and a fictitious temperature T (with the same units; we absorb Boltzmann's constant into the temperature). Some initial state is again perturbed by trial moves, the trials are accepted or rejected, and the fictitious temperature is decreased by some amount after each set of a certain number of moves. The process continues until T is some predetermined small value. You need to define four things to make this work: a starting configuration, a set of trial moves with sufficient power to enable all relevant states to be generated, an energy (objective) function, and a schedule for decreasing the temperature.

Application to Silicon and Aluminum Distributions. For the problem of interest here, the starting configuration is a lattice of Tsites in the FAU topology. Some of these sites are populated by silicon and some by aluminum atoms. Often a randomly populated system was chosen, or pure Si, or a system with Si/Al = 1 and Si and Al in alternating positions throughout the lattice. Lowenstein's rule was enforced (unless explicitly mentioned otherwise) and periodic boundary conditions (PBC) were used. These PBC ensure that the small crystals used in the simulations (1–125 unit cells) behave as if the entire system was in the bulk.

The objective function that was used most often was a sum-of-squares of differences in the relative numbers of Si atoms with n Al neighbors:

$$E = \sum_{n=0,4} \left(\frac{\text{ASi}(n\text{Al})_{\text{experiment}}}{A_{\text{total}}} - \frac{\text{Si}(n\text{Al})_{\text{simulation}}}{n\text{Si}} \right)^2 + \alpha \left[\left(\frac{n\text{Si}}{n\text{Al}} - R \right) / R \right]^2 \quad (1)$$

where $\text{ASi}(n\text{Al})_{\text{experiment}}$ is the peak area for the $\text{Si}(n\text{Al})$ environment from a ^{29}Si NMR experiment, A_{total} is the total area attributed to tetrahedral Si environments, $\text{Si}(n\text{Al})_{\text{simulation}}$ is the number of T-sites occupied by Si that have n Al nearest neighbors, and $n\text{Si}$ is the total number of silicon sites in the simulated lattice. The second term, with weight α , was sometimes added to force the Si/Al ratio of the simulated lattice to match a desired ratio, R .

The trial moves consist of three types:

1. swapping the positions of a randomly chosen Al with that of a randomly chosen Si
2. converting an existing Si to an Al
3. converting an existing Al to an Si

It is easy to see that any possible configuration is reachable from any starting configuration since you can simply convert all of the Al to Si and then convert selected ones back. The first move, a swap, is added for efficiency and to allow runs at fixed Si/Al. The relative ratios of these types of moves are user-selectable, but we usually chose 80% of the moves as type 1 and 10% for each of types 2 and 3.

For the annealing schedule, we used the usual one, $T_i = f T_{i-1}$, where T_i is the i th temperature used (for some subset of the total number of Monte Carlo steps) and the scaling factor f is in the range $0.8 < f < 1.0$, and usually $f > 0.95$ for slow cooling. The annealing was continued until the objective function or the

temperature reached a predetermined value or did not change for all of the moves over several temperatures. We usually found better results or faster convergence if at each new temperature, or after several tens of temperatures had been run, the best previous result was re-instated as the current configuration. This somewhat defeats the purpose of simulated annealing to allow the system to find and surmount local energy barriers, but it also prevents the system from wandering away from a promising low-energy region.

Programming Details. Several arrays were used in a FORTRAN implementation of the algorithm. One binary array of length N holds the identity of a given Tsite,

tsite(i) = 0; site i occupied by Si

1; site i occupied by Al

Another array holds the adjacency information, $\text{enviro}(i,j) = k$; $i = 1 - N$, $j = 1 - 4$ if site k is the j th tetrahedral neighbor of site i . Certain auxiliary arrays were also found useful; one to hold a list of all of the sites currently occupied by Si and a similar array for Al. These were used when randomly choosing, for example, a silicon to be replaced in a trial move of type 2. These arrays are all loaded at the start of the program after choosing a starting configuration. Each time a trial move is accepted, the arrays dependent on the Si and Al populations are updated.

The value of the objective function, E , can be calculated by considering each Si site in the current configuration and determining with the *enviro* and *tsite* arrays the number of its nearest neighbors that are occupied by Al. We sometimes added the second term in eq 1 to force the system to match the experimentally determined (either from chemical analysis or from the NMR peaks¹) Si/Al ratio, though this is not necessary unless Lowenstein's rule is not being enforced by the program.

Our code can perform other analyses and can be restarted for convenience and to recover from software or hardware problems.

Testing. Initial testing of the program proceeded by using several starting configurations and objective functions corresponding to easily recognized cases; $\text{ASi}(n\text{Al})/A_{\text{tot}} = (1,0,0,0,0)$ ($n = 0-4$) for a pure Si system (every Tsite is Si and is surrounded by four Si) and $\text{ASi}(n\text{Al})/A_{\text{tot}} = (0,0,0,0,1)$ for Si/Al = 1.0. If Lowenstein's rule is enforced, the final configuration for this latter system consists of alternating $-\text{Si}-\text{Al}-\text{Si}-\text{Al}-$ etc. throughout the crystal; every Si is surrounded by four Al and every Al is surrounded by four Si. All such tests were satisfied perfectly; we could start from pure Si or from a random Si/Al system and produce the alternating structure if $\text{ASi}(n\text{Al})/A_{\text{tot}} = (0,0,0,0,1)$ and we could start from the alternating structure or a random distribution and produce a pure Si system if $\text{ASi}(n\text{Al})/A_{\text{tot}} = (1,0,0,0,0)$. The objective function could be driven to $E = 0$, and the results were insensitive to starting structure as long as a sufficiently slow annealing schedule was used.

For testing the program against experimental data, we used the results of Melchior, Vaughan, and Pictroski,¹⁹ as these consist of carefully controlled NMR experiments and an interesting analysis producing a detailed picture of short- and intermediate-range order. Their Table 5 contains the integrated peak areas (expressed as the average number of Si per sodalite unit) for 14 samples with $1.26 \leq \text{Si/Al} \leq 4.60$ covering zeolites X ($1.0 \leq \text{Si/Al} \leq 1.5$) and Y ($\text{Si/Al} > 1.5$).²⁰ These counts of $\text{Si}(n\text{Al})$ are very slightly dependent upon their analysis and so, therefore, will be our results. We here present results for two

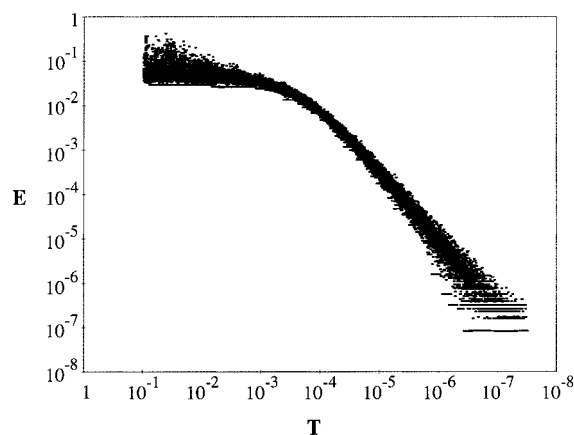


Figure 1. Improvement in fit to ^{29}Si NMR as annealing temperature decreases for a $3 \times 3 \times 3$ supercell of zeolite Y. The objective function, E , is defined in eq 1, and the annealing schedule is defined in Table 1.

TABLE 1: System and Annealing Parameters

supercell size	$3 \times 3 \times 3$ or $5 \times 5 \times 5$
tetrahedral sites	5184 or 24 000
starting configuration	Si/Al = 1.0 & insert random Si to yield experimental Si/Al
initial temp	0.1
final temp	10^{-8}
early termination criteria	$E < 10^{-10}$ or constant for 200 T
moves per temp	100 000
attenuation factor, f	0.999
no. of replicates	6
reset to lowest E every 50 T ?	yes

typical members of this set, the zeolite X with Si/Al = 1.26 and the zeolite Y with Si/Al = 2.60. Our results will be presented in terms of the integrated areas or counts of local Si environments rather than trying to reproduce any detailed peak shapes.

There are several possible ways of using the simulated annealing procedure to determine Si and Al distributions which yield the experimental local environments. A single run of the program will produce one such distribution if the procedure is terminated at very low temperature. We have usually chosen to run several replicates with different starting configurations (different random number seeds) and to average these data in order to improve the statistics and to probe the uniqueness of the results. An alternative approach¹⁴ is to produce a long run, terminating at higher temperatures and to average the results over the course of the simulation. The amount of possible nonuniqueness varies in a nonmonotonic way with the Si/Al ratio; there are large numbers of different structures that could reproduce a given spectra at some intermediate Si/Al and only one possible structure at Si/Al = 0 or Si/Al = 1.0 (if Lowenstein's rule holds).

Results and Discussion

Zeolite Y. For the Y zeolite we set up the objective function as in eq 1 with the Si(n Al) counts from Melchior et al.,¹⁹ ASi-(n Al) = (1.76, 6.40, 7.37, 1.70, 0.10) for $n = 0-4$ with a total of 17.34 Si per 24 Tsites (Si/Al = 2.60). The starting configuration was the Si/Al = 1.0 alternating structure with additional Si randomly replacing Al until the nominal Si/Al from the experimental spectra was reached. We show in Figure 1 the value of E at the end of every set of 100 000 attempted moves for one run on a $3 \times 3 \times 3$ supercell with the annealing parameters defined in Table 1. Note the spread in E at any given range of T , an effect that is necessary for overcoming local

TABLE 2: Zeolite Y

	experiment	$3 \times 3 \times 3$	$5 \times 5 \times 5$
E		8.24×10^{-8}	2.59×10^{-8}
Si/Al	2.60	2.6025	2.6020
Peak Areas			
0	0.1015	0.1017 (0)	0.1015 (0)
1	0.3691	0.3693 (0)	0.3693 (2)
2	0.4250	0.4251 (2)	0.4253 (0)
3	0.0979	0.0980 (1)	0.0981 (1)
4	0.0058	0.0059 (0)	0.0058 (0)

energy barriers. Also noticeable, as apparent horizontal lines forming a lower envelope in some ranges of T , are the effects of resetting to the best fit configuration after every 50 temperatures. E can obviously be driven to very low values by the procedure.

For data analysis, we averaged the results of six runs and show in Table 2 the final objective function value, Si/Al, and the fractional peak areas. For each run, the procedure terminated when the objective function value did not change for 200 consecutive temperatures at a T slightly above the specified final T ($T \sim 3 \times 10^{-8}$ for the $3 \times 3 \times 3$ cases). The fractional Si-(n Al) populations were extremely close to the "desired" ones from the experiments. In Table 2, the numbers in parentheses are two standard deviations for the last digit; these were calculated from the six replicates. The replicates gave almost identical results for the relative environment counts. This should not be construed to mean that the detailed Si and Al distributions were the same and there were small differences in other statistics, such as the probability distributions for numbers of aluminum atoms in various substructures such as double-six-rings or β cages.

The correspondence with experiment is closer than is warranted by the accuracy of the experimental data, which is $\sim 1\%$. The important point is that the procedure can produce a configuration of Si and Al that very closely matches any Si-(n Al) ratios consistent with the assumptions used.

The number of attempted steps can be very large if the program proceeds to the lowest temperature and these runs took about 5 h on a fast workstation. The number of temperatures is $n_T = \log(T_f/T_i)/\log(f) \sim 16\,000$, or $n_{\text{steps}} = \sim 1.6 \times 10^9$. Reasonable results could be obtained on a single unit-cell system in a few seconds or with fewer steps per temperature and/or temperatures for the larger systems. In these runs the objective function reached $\sim 2 \times 10^{-4}$ when $T \sim 1 \times 10^{-5}$ and the results would be within the experimental error after $< 1/2$ of the time actually used. Runs with larger numbers of Tsites can more closely reproduce any particular input peak area since the smallest increment in fractional peak area available is 1 Tsite or about $1/N_{\text{Si}} = 0.0002$ in the $3 \times 3 \times 3$ system and only 0.005 for a $1 \times 1 \times 1$ unit-cell system with 192 Tsites. The close correspondence between the $3 \times 3 \times 3$ and the $5 \times 5 \times 5$ results indicates that size dependent effects are not important at or above 27 unit cells for this zeolite Y. We did find some evidence of size dependence for smaller systems.

A brief look at some features of the resulting structures may be useful. Let us define a cluster (as in percolation theory²¹) of silicon as a portion of the lattice, every Tsite of which contains a Si and every Tsite of which is a nearest neighbor (on the tetrahedral lattice, we are ignoring the oxygen bridges altogether) to at least one other silicon. A cluster is bounded by only Al atoms. That is, a cluster is a piece of the crystal that consists of Si "bonded" to only Si and "bonded" means residing within one nearest-neighbor distance. Inspection of a cluster size distribution for the simulated Y system shows that it consists

TABLE 3: Zeolite X

experiment		$3 \times 3 \times 3$	$5 \times 5 \times 5$	$3 \times 3 \times 3$ (all Si start)
<i>E</i>		$4.6(3.4) \times 10^{-4}$	$3.7(0.2) \times 10^{-4}$	$1.7(1.0) \times 10^{-4}$
Si/Al	1.255	1.266	1.275	1.2705
Peak Areas				
0	0.0307	0.0416 (40)	0.0448 (13)	0.0401 (22)
1	0.0411	0.0438 (38)	0.0452 (09)	0.0446 (22)
2	0.1369	0.1233 (66)	0.1263 (07)	0.1303 (23)
3	0.3022	0.2966 (20)	0.2959 (05)	0.2970 (17)
4	0.4899	0.4947 (26)	0.4879 (05)	0.4880 (12)

of a continuous phase of Si and a very small number of other small clusters containing four to nine Si atoms. The Al atoms are distributed within the almost continuous sea of Si.

The Al are evenly, but not randomly, distributed. In an Si/Al = 1.0 system with the alternating structure, one can identify a sublattice on which all of the Al atoms lie. The opposite sublattice is occupied by Si, and the ratio of Al on one sublattice to the other would be 0. In this higher Si/Al zeolite Y, the results show that on average the ratio of Al on one sublattice to the other is 0.96; very near 1.0. The Al are evenly distributed in this sense; there is no apparent influence of long-range ordering of aluminum.

The system is, however, not completely random in the way that aluminum exists. If you consider the four-ring (4R) substructures in the FAU lattice (square rings of four Tsites), there are three possibilities consistent with Lowenstein's rule: zero, one, or two Al atoms and in the latter case the Al atoms are next nearest neighbors; they sit diagonally across the 4R. A tendency known as Dempsey's rule²² states that next-nearest-neighbor Al's are to be avoided and the number of 2-Al 4R will be minimized to some extent. For this zeolite Y we found that the probability of such 4R was 0.21, while the minimum such probability consistent with the Si/Al ratio is $(3 - R)/(1 + R) = 0.11$ and the maximum is $2/(R + 1) = 0.56$. In 4R, Dempsey's rule is partially, but not completely, followed in this case. This was also found by Melchior et al.¹⁹ and other workers for zeolite Y (see below for the situation in X).

We will present further discussion of detailed local structures and Si/Al distributions in a future publication.

Zeolite X. Application of the algorithm to the zeolite X sample was done with the same parameters as for zeolite Y. The objective function had the relative peak areas from Melchior et al.,¹⁹ $ASi(nAl) = (0.41, 0.55, 1.83, 4.04, 6.55)$ with $A_{tot} = 13.37$. The results, shown in Table 3, required approximately the same CPU time as in the previous case.

The fit is not as close as for zeolite Y, but the results are within the experimental uncertainties. The poorer fit is somewhat unique to this sample, as other X's at different Si/Al are fit to the same low objective function value as the zeolite Y shown above. We do not know the cause of the discrepancy, but it could be due to experimental error (most of the contribution to *E* is from the smallest peak), to compositional heterogeneity on length scales larger than the size of the systems studied here, or to an incorrect assumption used in the modeling (see below). The numbers in parentheses are again 2 times the standard deviations estimated from the six replicates, this time reported to two digits. The standard deviations are also larger than in the Y case; the different replicates were not so uniform. To test for dependence on starting conditions more drastically different than different random number seeds, we performed six more runs, which started from $3 \times 3 \times 3$ systems with all sites filled by Si. These results are given in the last column of Table 3. The results are somewhat better, on average, than the other 3

TABLE 4: Relaxing Lowenstein's Rule for Zeolite X

experiment		$3 \times 3 \times 3$
<i>E</i>		3.3×10^{-6}
Si/Al	1.255	1.255
Peak Areas		
0	0.0307	0.0319
1	0.0411	0.0416
2	0.1369	0.1366
3	0.3022	0.3016
4	0.4899	0.4884

$\times 3 \times 3$ systems, but all peaks but one are within the estimated two standard deviations of each other. The different starting conditions yield very similar results.

As expected, the structure is very different from the zeolite Y and it exhibits long-range order. The ratio of Al on the two sublattices now averages 0.08; the system is more like the alternating (Si/Al = 1.0) structure interrupted by small antidomains of Al (surrounded by Si) on the opposite sublattice. The silicon clusters are also different, as is expected for this system with many fewer silicon atoms in the same volume. There are clusters of size 1–25 and we no longer have the continuous Si phase as in the zeolite Y. The basic picture is now one of the alternating structure plus defects rich in silicon. These defects within themselves may contain Al on the sublattice opposite to the main one. For Y, the picture was one of a continuous silicon phase containing small defects rich in aluminum. This picture is consistent with the different space groups usually used in refinements of zeolites X (Fd-3) and Y(Fd-3m).

The 4R distributions for zeolite X are interesting. The fraction of 4R with 2Al was found (in the $3 \times 3 \times 3$ cases) to be absolutely at the minimum. The fraction was 0.765 to be compared with $(3 - R)/(1 + R) = 0.765$ for the theoretical minimum. For Si/Al < 3, the minimum occurs when the number of 0-Al 4R is also minimized at 0. There were no 0-Al 4R found in any of the final configurations. This implies that Dempsey's rule is strictly obeyed for 4R (not necessarily for 6R) in zeolite X.¹⁹

Relaxing Lowenstein's Rule. In principle, it should not be necessary to enforce Lowenstein's rule in order to generate structures that match the ²⁹Si NMR. If Lowenstein's rule holds, the results should be consistent with it. However, without some constraint on the overall Si/Al ratio, the program would generate fragments of FAU that did produce the desired relative NMR peak counts, surrounded by regions with only Al on the Tsites. These pure-Al regions would have no direct effect on the local environment ratios and so could grow or shrink to allow the Si-containing regions to have the best possible match with the experiment. To generate a structure that had no such Al impurities, the weighting factor, α , was set to nonzero and a desired Si/Al ratio was input to the program. One could also constrain Si/Al by setting $\alpha = 0$ and eliminating moves other than swaps, but we thought a weak constraint is better since the actual Si/Al ratio will be different than that calculated from the experimental peaks due to the usual calculation's dependence on Lowenstein's rule.

When the final structure from one of the $3 \times 3 \times 3$ zeolite X simulations discussed above was used as a starting point for an annealing run with $T_i = 0.5 \times 10^{-5}$, $\alpha = 0.1$, $R = 1.255$, and all other parameters unchanged, better correspondence between the experimental and simulated Si environments was obtained, as shown in Table 4.

The resulting structure contained 21 pairs of Al–Al neighbors; $42/2299 = 1.8\%$ of the Al did not obey Lowenstein's rule. These Al–Al pairs were evenly distributed throughout the

structure. If the Si/Al ratio was constrained to be less than the Si/Al ratio derived from the ^{29}Si NMR, a good fit to the peaks was obtained, but unrealistic numbers of non-Lowensteinian Al were created.

As a check, we also did not enforce Lowenstein's rule in a run starting from the final structure of one of the zeolite Y cases and using $R = 2.60$ and $\alpha = 0.1$. The resulting fit of the NMR peaks was slightly poorer and the objective function value increased to $E = 7 \times 10^{-7}$ with Si/Al = 2.595 and about half of the final E coming from the new constraint and half from the lack of fit of the experimental peaks. Several (11) non-Lowenstein Al/Al pairs (1.5% of Al) were created. In this case, disobeying Lowenstein led to a slightly poorer fit.

In summary, we were able to improve the fit to the environment counts in zeolite X by relaxing Lowenstein's rule. To do this we also had to place a constraint on the Si/Al ratio to prevent the system from producing large regions of pure AlO_2 . So constrained, small amounts of non-Lowensteinian Al were created. It is not clear if this result reflects physical reality (it would be difficult to determine experimentally if there were only $\sim 1\%$ non-Lowensteinian Al in a zeolite sample) or if it just represents an increased flexibility in the system to fit the noise in the data.

Comparison to Other Methods. Melchior, Vaughn, and Pictroski,¹⁹ whose experimental data we used, fit the entire line shapes to a distribution of local environments. They then use these more detailed environment counts along with equation-based constraints derived from the FAU topology to derive a picture of the Si and Al distributions on the lattice. While a comparison with their results will be forthcoming in a future publication, we can say that our results are qualitatively consistent with theirs, as far as the local environment populations are concerned.

Our results should, in general, be preferable to theirs because *all* of the constraints due to the FAU topology are automatically included in our analysis. We do not have to make any approximations as they did to make the analysis tractable. In general, one can expect the SA algorithm to produce structures that are consistent with the data and with all the constraints imposed by the lattice, but which are otherwise random. This is valuable when looking for hints of mechanistic information in the structures, since no patterns will emerge that are not required by the NMR and the topology. We do very slightly *overconstrain* our system with the periodic boundary conditions, but this is unlikely to lead to error with system sizes such as those employed here.

Since Melchior et al.¹⁹ found that overlap among the Si(n Al) peaks was rather small, the simulated annealing on a lattice can get reasonable results fitting only to the five Si(n Al) peaks and not explicitly using the detailed local environments provided by their analysis. We could, however, take advantage of the increased resolution by fitting to these local environments which are easily counted on our lattice. Including this information, if accurate, would determine our solutions almost completely uniquely and this might be tried in the future.

Our simulated annealing procedure is most like Dove and Heine's,¹⁴ of which we were unaware until this work was nearly completed. There are differences in the use of the simulated annealing and in our codes. Dove and Heine's code is very general, allowing for any crystal structure, including other topologies with more than one crystallographically distinct Tsite. We concentrated on FAU, with a single kind of Tsite, and our code can perform detailed counts of different kinds of β cages,

double six-rings, etc. in FAU and can perform percolation calculations and other analyses.

We also used the codes differently. We have driven the objective function to as near zero as possible with very slow annealing to low temperatures and we then usually average the results of several replicates of this procedure. Dove and Heine's code can also be used to lower the temperature, but they used fewer temperatures and attempted moves and found significant effects of starting condition when studying ordered structures.²³ They usually used a single run at some temperature, which is equivalent to about 10^{-5} , as we have defined it, and then inspected the final configuration. The same annealing procedure could be performed with either code, at least with only slight modifications, and the results would likely be equivalent. We did, as they suggested was possible, make our code more efficient by calculating the objective function via updates instead of looping through all of the Si and counting neighbors at each step. This is important when working with large unit cells and supercells in zeolites as we did. Dove and Heine chose to allow violations of Lowenstein's rule and fixed the Si/Al ratio by using the experimental value from chemical analysis and allowed only Si/Al swaps. Our code allows the user to select whether Lowenstein's rule is to be strictly enforced.

The fundamental data structure for this algorithm is a binary string; the tsite array containing the identities, 0 or 1, of the Tsite atoms. The procedure consists of making modifications to this string and sifting out the good ones through the annealing process. These similarities to a Genetic Algorithm indicate that GAs or more general forms of evolutionary algorithms²⁴ might be good alternative methods. However, some of the power of a standard GA would be lost on this problem for the following reasons. Lowenstein's rule (whether strictly or more weakly adhered to) incorporates correlations between Tsites that are far from each other on the tsite array but that are near in 3D physical space or 2D topological space. Any attempt at crossover would improve the objective function with very low probability since this is equivalent to attempting to cut out large portions of a crystal and then put them back together in different ways—many Al/Al pairs would likely be created. Either very substantial bookkeeping would have to be incorporated, or the set of allowed transformations would have to be limited to simple bit-flipping mutations or other local modifications. The simulated annealing procedure uses similar moves, but concentrates on one structure instead of a population. It would be interesting to try a GA-like approach on a population of tsite vectors.

A different approach to determining Si/Al distributions in zeolites has been used by several workers.^{8–11} They used simulations on lattices with interaction energies defined either between nearest and next-nearest neighbors or more realistically between Si/Al/O and extraframework cations. These are more standard energetic Monte Carlo calculations. In some cases the authors avoided local minima by annealing the systems by dropping the temperature from initially high values. (We would prefer not to call this procedure *simulated annealing*, however, since that term is usually reserved for procedures where the "energy" does not correspond to something with units of energy, and the temperature is a purely fictitious scaling variable. In their method the energy and temperature correspond to real energies and temperatures for their model. They are annealing a simulated system but not doing simulated annealing.) In this lattice MC method, the thermodynamically stable states at a given temperature can be found for a system with their model Hamiltonian. It has not, however, been established that the distributions of Si and Al in zeolites are determined solely by

the thermodynamics of the zeolite lattice; kinetics could play a role. Methods that directly use the NMR information with no approximate Hamiltonians involved (for which some fitting of parameters is necessary) will give less biased results. It might be interesting to compare the present simulated annealing results with those of energetic MC calculations to determine if the Si/Al distributions are consistent with the Hamiltonian models and thermodynamic control.

Conclusions

The simulated annealing method was able to generate Si and Al distributions that closely match the experimental Si(*n*Al) counts from ^{29}Si NMR experiments for zeolites X and Y. For $3 \times 3 \times 3$ supercells, size dependent effects are minimal and different starting conditions yield very similar final structures; the resulting configurations should be very representative of the best possible fits to the experiments. The configurations are then available to investigate more detailed structural features exemplified here by the ratios of aluminum atoms on two different sublattices and the probabilities of 4-rings containing certain numbers of Al. Zeolite X is closely related to the low-silica (Si/Al = 1.0) FAU end-member with an ordered arrangement of Si and Al and all the Al on one sublattice. Small clusters of Si are inserted on this lattice and these clusters can in turn contain Al atoms on the minority sublattice. For zeolite Y, the picture is the expected one where Al atoms are evenly distributed in a continuum of Si.

A benefit of the method is the choice of whether to enforce Lowenstein's rule. The fit for zeolite X was somewhat improved by relaxing Lowenstein's rule and approximately 2% of the Al were then found adjacent to other Al. It is not clear if this is a physical effect or an artifact of the increased flexibility in fitting. The fit for Y was not improved by relaxing Lowenstein's rule.

Future work will deal with a broader range of Si/Al ratios and a more detailed look at intermediate and long-range ordering of Si and Al on the Faujasite lattice. There is no theoretical obstacle to applying this method to other NMR nuclei or, as shown by Dove and Heine,¹⁴ to other framework materials.

Acknowledgment. Thanks to Air Products and Chemicals, Inc. for permission to publish this work. Discussions or correspondence with T. R. Gaffney, J. B. Higgins, J. E. MacDougall, P. L. McDaniel, and M. T. Dove were helpful.

References and Notes

- (1) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Zeolites and Related Systems*; John Wiley and Sons: London, 1987.
- (2) Engelhardt, G.; Lippmaa, E.; Magi, M. *J. Chem. Soc., Chem. Commun.* **1981**, 712.
- (3) Engelhardt, G.; Lohse, U.; Patzelova, V.; Magi, M.; Lippmaa, E. *Zeolites* **1983**, 3, 239.
- (4) Melchior, M. T.; Vaughan, D. E. W.; Jacobson, A. J. *J. Am. Chem. Soc.* **1982**, 104, 4859.
- (5) Ramdas, S.; Thomas, J. M.; Klinowski, J.; Fyfe, C. A.; Hartman, J. S. *Nature* **1981**, 292, 228. Klinowski, J.; Ramdas, S.; Thomas, J. M.; Fyfe, C. A.; Hartman, J. S. *J. Chem. Soc., Faraday Trans. 2* **1982**, 78, 1025.
- (6) Peters, A. W. *J. Phys. Chem.* **1982**, 86, 3489.
- (7) Vega, A. J. *J. Phys. Chem.* **1996**, 100, 833.
- (8) Herrero, C. P. *J. Phys. Chem.* **1991**, 95, 3282.
- (9) Herrero, C. P.; Ramirez, R. *J. Phys. Chem.* **1992**, 96, 2246.
- (10) Soukoulis, C. M. *J. Phys. Chem.* **1984**, 88, 4898.
- (11) Ding, D.; Li, B.; Sun, P.; Jin, Q.; Wang, J. *Zeolites* **1995**, 15, 569.
- (12) Takaishi, T. *J. Phys. Chem.* **1995**, 99, 10982. Takaishi, T. *Zeolites* **1996**, 17, 389.
- (13) Himei, H.; Yamadaya, Y.; Oumi, Y.; Kubo, M.; Stirling, A.; Vetrivel, R.; Broclawik, E.; Miyamoto, A. *Microporous Mater.* **1996**, 7, 235.
- (14) Dove, M. T.; Heine, V. *Am. Mineral.* **1996**, 81, 39.
- (15) Lowenstein, W. *Am. Mineral.* **1954**, 39, 92.
- (16) Kirkpatrick, S.; Gelatt, C. D.; Vecchi, M. P. *Science* **1983**, 220, 671. Kirkpatrick, S. *J. Stat. Phys.* **1984**, 34, 975.
- (17) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in FORTRAN: The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1992.
- (18) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, 21, 1087.
- (19) Melchior, M. T.; Vaughan, D. E. W.; Pictroski, C. F. *J. Phys. Chem.* **1995**, 99, 6128.
- (20) Breck, D. W. *Zeolite Molecular Sieves*; R. E. Krieger Publishing: Malabar, FL, 1984.
- (21) Stauffer, D.; Aharony, A. *Introduction to Percolation Theory*, 2nd ed.; Taylor and Francis: London, 1992.
- (22) Dempsey, E. *J. Phys. Chem.* **1969**, 73, 3660.
- (23) Dove, M. T. Personal communication.
- (24) Fogel, D. B. *Evolutionary Computation*; IEEE Press: New York, 1995.