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# Is there a spatial correlation in the distribution of adsorbed atoms in the cages of a zeolite?

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Monte Carlo simulations of the cage-to-cage jumps of Xe atoms in a crystalline zeolite using the experimentally observed molecular rate constants for cage-to-cage jumps were carried out to determine if there is a systematic spatial correlation of the distributions of Xe atoms among the cages at equilibrium. The neighbours of cages having an Xe occupancy that is *less* than the average occupancy are found to have distributions that are skewed toward *higher* occupancy compared with the overall distribution. On the other hand, the neighbours of cages having an Xe occupancy that is *greater* than the average occupancy are found to have distributions that are skewed toward *lower* occupancy than the overall distribution.

## 1. Introduction

Zeolite Na*A* has a well-known structure of cages of uniform size and shape, called alpha cages, in which xenon atoms (or other atoms and molecules) may be adsorbed and trapped. Each alpha cage is joined to each of six other alpha cages via a shared eight-oxygen-ring $(Al–O–Si–O)_4$ window in which an $Na^+$ ion sits off-centre, coordinated to three of the oxygen atoms. In Xe NMR, the residence time of the Xe atoms in each cage is sufficiently long that the NMR spectrum of the Xe adsorbed in an Na*A* sample at equilibrium with the bulk Xe gas shows individual distinct peaks corresponding to the Xe chemical shifts of $Xe, Xe_2, Xe_3, \ldots, Xe_8$ [1, 2]. The relative intensities of these peaks provide the fraction of cages containing $1, 2, 3, \ldots, 8$ Xe atoms. The distribution of Xe in the cages of zeolite Na*A* can be completely characterized in terms of the distribution of Xe between the bulk phase and the adsorbed phase, the distribution of Xe atoms among the cages, and the one- and two-body distribution functions of Xe within a cage. (a) We have measured the partitioning of Xe atoms between the adsorbed phase and the bulk phase; for a given temperature and bulk gas density, we have determined the average occupancy $\langle n \rangle$ Xe atoms per cage [1]. (b) From the relative intensities of the individual peaks we have directly observed the equilibrium distribution of Xe atoms among the cages [1]. Namely, we found $P(n)$, the fraction of cages in the zeolite that are occupied by exactly $n$ Xe atoms, the normalized probability of finding a cage occupation number equal to $n$. The peak corresponding to those Xe atoms that are in the cages occupied by exactly $n$ Xe atoms has a signature chemical shift at a given temperature and this shift systematically changes with increasing $n$ [1]. (c) The temperature dependence of the magnitude of the chemical shift relative to the free Xe atom is determined by the distribution of the Xe atoms within the internal volume of the cage [3, 4]. The quantitative characterization of distributions as described in (a)–(c) has been established for Xe in zeolites Na*A* [1], K*A* [5] and Ag*A* [6], and grand canonical Monte Carlo simulations have interpreted the Xe distributions and the Xe chemical shifts successfully in Na*A*, K*A* and Ag*A* [3–5, 7].

Given that we have the observed equilibrium distribution of Xe atoms among the cages of Na*A*, a point of curiosity is the uniformity of the distribution. Is there a spatial correlation of Xe distributions in cages of Na*A*? An explicit statement of this question is as follows: given an average occupancy $\langle n \rangle$, if we examine only those cages that have $n$ Xe atoms, do we find their neighbours to have a distribution that is different from the overall average distribution $P(n)$? Let $Q^n(m)$ be the distribution of Xe atoms in the cages that are adjoining to a cage containing $n$ Xe atoms. Do we find $Q^n(m) = P(m)$? If not, is there a systematic correlation of the distributions? That is, for which $n$ and $m$ are we more likely to find the distribution in the adjacent cages to be systematically greater than the average distribution, and for which $n$ and $m$ are we more likely to find the distribution in the adjacent cages to be systematically less? Explicitly, in a sample of a given $\langle n \rangle$, for which $n$ and $m$ is $Q^n(m) > P(m)$, and for which $n$ and $m$ is $Q^n(m) < P(m)$?

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## 2. Method

From magnetization transfer experiments, otherwise known as 1D-EXSY experiments, we have determined the molecular rate constants for the specific jumps, for example the rate constant, per Xe per second, for the single Xe jump from a cage containing $n$ Xe atoms to the adjacent cage containing $(m-1)$ Xe atoms, resulting in the first cage being left with $(n-1)$ Xe atoms and the destination cage with $m$ Xe atoms [8]. This set of 64 rate constants (only $n = 1$ to 8, $m = 1$ to 8, since an occupancy number greater than eight has never been observed) has been obtained by us at 300 K using a 1D-EXSY method [8]. In a separate 2D-EXSY study conducted at the same time by the Pines group, the rate constants were found by using the assumption that all rate constants corresponding to the same $n$ are equal [9]. Our own studies show that this assumption is incorrect; the rate constants have to depend on the occupancy of the destination cage, otherwise the set of rate constants would be inconsistent with the measured equilibrium distribution of Xe atoms among the cages. Our set of rate constants is consistent with the equilibrium $P(n)$ for each one of 12 samples covering the entire range of values of average occupancy $\langle n\rangle = 0.1 - 6.75$ Xe atoms per cage [8]. For the Xe in Ag$A$ zeolite (which has the same framework as Na$A$ but with a different counterion), an analysis of the 2D-EXSY experiments without using the assumption that all rate constants corresponding to the same $n$ are equal also leads to a set of rate constants that does change with the occupancy of the destination cage, rate constants being much smaller when the destination cage has an occupancy of six or greater [6].

We use our experimentally determined rate constants which have been found to reproduce the experimental equilibrium distributions for a wide range of adsorbed concentrations of Xe in Na$A$ [8]. We carry out simulations of Xe in 8000 alpha cages, in a simulation box of $20 \times 20 \times 20$ cages, using periodic boundary conditions. For a sample with an adsorbed Xe concentration equal to $\langle n\rangle$, the simulation box is initialized with exactly $n$ Xe atoms in each cage. The rate constants provide the probabilities for Xe jumps from one cage to an adjacent cage through the shared window in a Monte Carlo procedure. After a large number of cage-to-cage jumps have achieved an equilibrium distribution in the 8000 cages, data acquisition is carried out. The occupancies of all the cages are interrogated to find the overall probability of finding a cage with $m$ Xe atoms in the crystal. These are the values $P(m)$. At the same time, the occupancies of the six cages that share a window with a cage containing $n$ Xe atoms are interrogated to collect the information necessary to determine whether the probability of finding $m$ Xe atoms, $Q^n(m)$, is greater or less than the overall probability of finding $m$ Xe atoms in the crystal, $P(m)$. A total of 2.5 to 30 million jump attempts constitutes the data-gathering phase of the simulation.

To readily observe deviations from uncorrelated distributions, we plot difference bar graphs of $Q^n(m) - P(m)$ for $m = 0$ to 8 for a given $\langle n\rangle$. If uncorrelated, we expect to find no trends outside of statistical noise, randomly $+/-$ in the difference bar graphs. On the other hand, if there is correlation in the distributions, we expect to see systematic changes.

## 3. Results

Examples of the equilibrium distributions obtained by a Monte Carlo simulation of jumps from cage to cage using the set of experimental rate constants we reported in [8] in a simulation box of $20 \times 20 \times 20$ cages are shown in figure 1 for $\langle n\rangle = 4.000$. The results for 30 million jump attempts are displayed in terms of the deviations from a spatially uniform distribution, $Q^n(m) - P(m)$, for $n = 0$ to $n = 8$. It is clear that there are systematic deviations from a spatially uniform distribution. The values are shown in table 1 for this simulation.

Given that the overall average occupancy is $\langle n\rangle$ Xe atoms per cage, the overall probability of finding a cage with $m$ Xe atoms is $P(m)$, and the probability of finding a cage with $m$ Xe atoms among the six neighbours of those cages containing $n$ Xe atoms is $Q^n(m)$, the results can be summarized as follows.

(1) The neighbours of cages having $n < \langle n\rangle$ are found to have distributions which are skewed toward higher occupancy compared with the overall distribution. That is, for $n < \langle n\rangle$, it is found that

$$Q^n(m) > P(m) \quad \text{for } m > \langle n\rangle$$

and

$$Q^n(m) < P(m) \quad \text{for } m < \langle n\rangle.$$

(2) On the other hand, the neighbours of cages having $n > \langle n\rangle$ are found to have distributions which are skewed toward lower occupancy compared with the overall distribution. That is, for $n > \langle n\rangle$, it is found that

$$Q^n(m) > P(m) \quad \text{for } m < \langle n\rangle$$

and

$$Q^n(m) < P(m) \quad \text{for } m > \langle n\rangle.$$

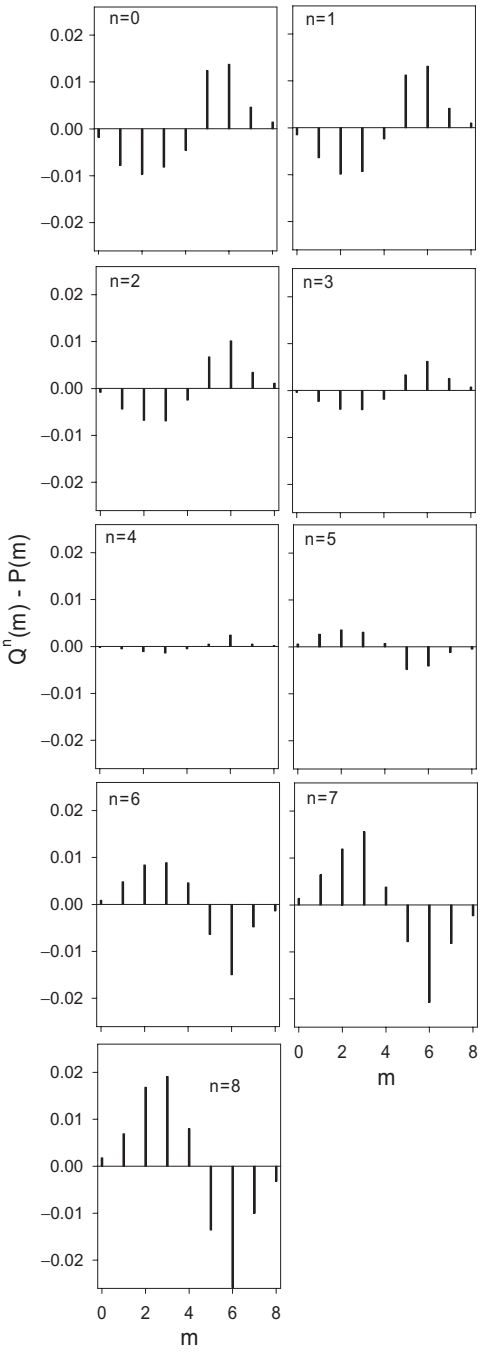


Figure 1. Equilibrium distributions obtained by a Monte Carlo simulation of jumps from cage to cage using the set of rate constants reported in [8] in a simulation box of $20 \times 20 \times 20$ cages. Data were acquired in 30 million jump attempts for $\langle n \rangle = 4.000$. The bar graphs correspond to the deviations from a spatially uniform distribution, $Q^n(m) - P(m)$, for $n = 0$ to $n = 8$.

The results make physical sense. A cage achieves an occupation number smaller than the average $\langle n \rangle$ by having donated one or more Xe atoms to its neighbours. Thus, its neighbours will tend to have distributions skewed toward higher occupancy compared with the overall distribution. On the other hand, a cage achieves an occupation number greater than the average $\langle n \rangle$ by having accepted one or more Xe atoms from its neighbours. Thus, its neighbours will tend to have distributions skewed toward lower occupancies compared with the overall distribution, even in the limit of an infinitely long simulation. In other words, there is something of a trace of the past events in the *local* distributions, analogous to persistence of velocity despite randomizing collisions in the gas phase.

Finally, we comment on the consistency between the experimental rate constants from [8] that we used in this work and the equilibrium distributions of atoms among the cages. In figure 2 we use the dispersion of the distribution, $\langle n^2 \rangle - \langle n \rangle^2$, as a means of inspecting various distributions for a wide range of average occupancies $\langle n \rangle$ in a single plot. A strictly statistical distribution of atoms among the cages is obtained if one assumes that there is a fixed number of sites within a cage which can be occupied by Xe atoms under mutual exclusion (that is, a site can be occupied by only one Xe). Such a distribution, the hypergeometric distribution, is easily calculated in terms of only $\langle n \rangle$ and the number of sites within a cage. For eight sites within a cage, the distribution is shown in figure 2 as a smooth curve. Also shown are the experimental distributions obtained for Xe in Na*A* [1], the experimental distributions obtained in a zeolite that has the same framework, Ag*A* [6], the distributions calculated (this work) from the set of rate constants under the assumption that the rate constants are independent of the occupancy of the destination cage, and the distributions obtained from grand canonical Monte Carlo simulations with assumed potential functions [3, 7]. We see from figure 2 that (a) the grand canonical Monte Carlo simulations provide distributions that are consistent with the experimental distributions, (b) the experimental Xe distributions in Na*A* and in Ag*A* both systematically deviate from the hypergeometric distribution in a manner that is predicted by the grand canonical Monte Carlo simulations, and (c) the set of experimental rate constants we reported in [8] for cage-to-cage migration of Xe atoms in zeolite Na*A* leads to distributions that are consistent with the experimentally observed distributions. Finally, we also show in figure 2 the distributions that would result if we use the assumption that rate constants are independent of the occupation number of the destination cage. To mimic this assumption, the set of experimental rate constants were converted to identical values for the same column. This assumption, used in [9] but not in [8] or [6], leads to distributions at the higher occupancies ($\langle n \rangle > 5$) that are similar to those obtained from the hypergeometric distribution, inconsistent with

Table 1. The overall distribution $P(n)$ (probability of finding a cage with $n$ Xe atoms) compared with the neighbour distributions $Q^n(m)$ for the case where $\langle n \rangle = 4.000$. If the distribution had been spatially uncorrelated, one should find all $Q^n(m)$ to be equal to $P(m)$.

| $n$ | $P(n)$ | $Q^n(0)$ | $Q^n(1)$ | $Q^n(2)$ | $Q^n(3)$ | $Q^n(4)$ | $Q^n(5)$ | $Q^n(6)$ | $Q^n(7)$ | $Q^n(8)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.0093 | 0.0074 | 0.0410 | 0.1010 | 0.1849 | 0.2543 | 0.2191 | 0.1476 | 0.0359 | 0.0087 |
| 1 | 0.0488 | 0.0078 | 0.0424 | 0.1007 | 0.1839 | 0.2565 | 0.2179 | 0.1471 | 0.0354 | 0.0084 |
| 2 | 0.1106 | 0.0084 | 0.0444 | 0.1038 | 0.1862 | 0.2565 | 0.2134 | 0.1441 | 0.0347 | 0.0084 |
| 3 | 0.1932 | 0.0089 | 0.0465 | 0.1067 | 0.1890 | 0.2570 | 0.2100 | 0.1402 | 0.0338 | 0.0080 |
| 4 | 0.2589 | 0.0091 | 0.0483 | 0.1096 | 0.1917 | 0.2584 | 0.2072 | 0.1364 | 0.0318 | 0.0075 |
| 5 | 0.2067 | 0.0098 | 0.0514 | 0.1142 | 0.1963 | 0.2596 | 0.2018 | 0.1298 | 0.0301 | 0.0068 |
| 6 | 0.1340 | 0.0102 | 0.0536 | 0.1190 | 0.2021 | 0.2635 | 0.2003 | 0.1190 | 0.0265 | 0.0059 |
| 7 | 0.0313 | 0.0106 | 0.0552 | 0.1225 | 0.2087 | 0.2627 | 0.1988 | 0.1133 | 0.0231 | 0.0050 |
| 8 | 0.0073 | 0.0110 | 0.0557 | 0.1275 | 0.2123 | 0.2669 | 0.1930 | 0.1082 | 0.0213 | 0.0041 |

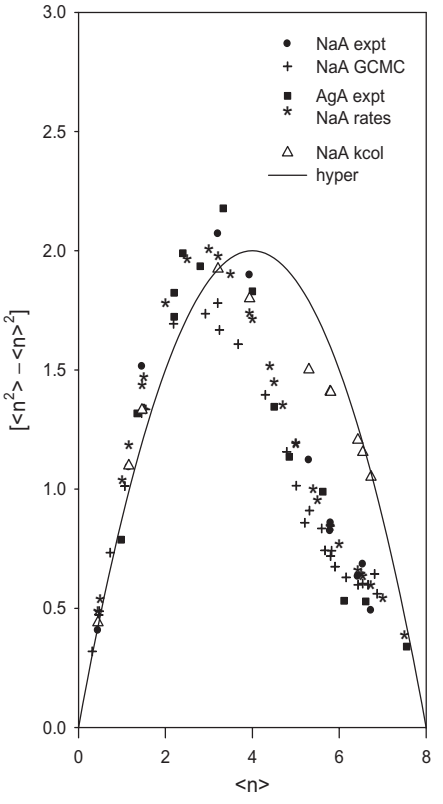


Figure 2. The dispersion of the distribution, $\langle n^2 \rangle - \langle n \rangle^2$, provides a means of comparing distributions for a range of values of average occupancy $\langle n \rangle$. Shown are the distributions obtained experimentally for Xe in Na$A$ (•), the distributions calculated from our set of rate constants [8] (∗), the distributions obtained under the assumption [9] that rate constants are independent of the occupancy of the destination cage in Na$A$ (△), and the distributions obtained from grand canonical Monte Carlo simulations with assumed potential functions [3] (+). The smooth curve is the dispersion of the distribution for the strictly statistical hypergeometric distribution which corresponds to eight adsorption sites for Xe atoms in the cage occupied under the rule of mutual exclusion. Also shown for Xe in Ag$A$ [6] are the distributions obtained experimentally (■).

the experimental distributions in both Na$A$ and Ag$A$, and inconsistent with the grand canonical simulations.

## 4. Conclusions

A systematic spatial correlation of the distributions of Xe atoms among the cages of zeolite Na$A$ at equilibrium is consistent with the set of rate constants that had been derived from magnetization decay/recovery curves in a large number of 1D-EXSY experiments in many samples of various $\langle n \rangle$. The neighbours of cages having an Xe occupancy that is *less* than the average occupancy are found to have distributions that are skewed toward *higher* occupancy compared with the overall distribution. A cage which has less than the average occupancy achieved that lower than average occupancy number by means of a jump that leaves the cage depleted and in the same event increases the occupancy number of an adjacent cage. On the other hand, the neighbours of cages having an Xe occupancy which is *greater* than the average occupancy are found to have distributions that are skewed toward *lower* occupancy than the overall distribution. A cage with greater than the average occupancy had achieved the increased occupancy number by one Xe jumping in from an adjacent cage which itself is left depleted. The overall distributions are the equilibrium distributions; nevertheless, systematic differences are found in the local distributions. How large the deviations are from a completely random spatial distribution is determined by the set of rate constants that give rise to the equilibrium overall distribution.

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