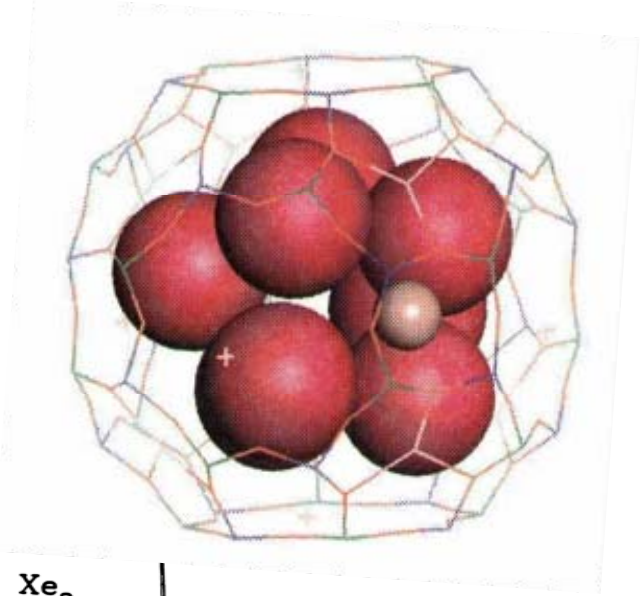
Adsorption and diffusion at the molecular level



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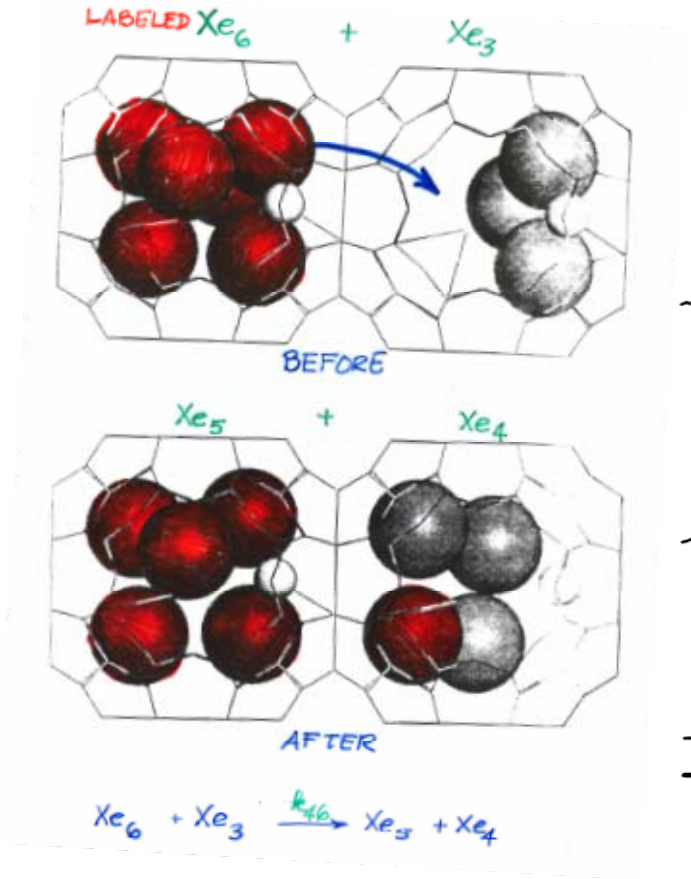
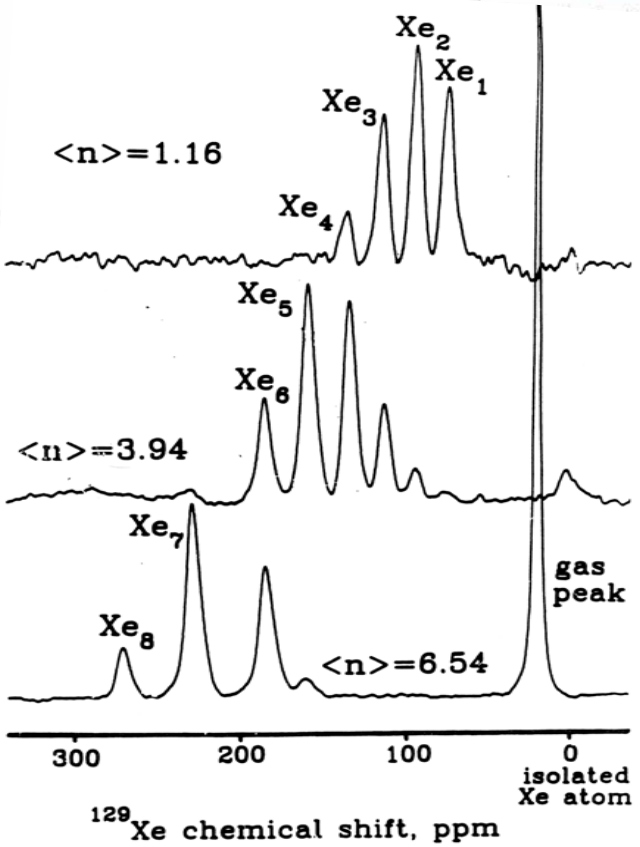




Adsorption and Diffusion

- **The processes of adsorption and diffusion are fundamental to many technological applications of zeolites and other porous solids.**
- **Toward a FUNDAMENTAL UNDERSTANDING of sorption in "micropores" (actually the pores are nanoscale), DETAILED INFORMATION on adsorbate distribution, site occupancy within a cage, rates of site-to-site exchange, cage-to-cage transfer, translation and reorientation dynamics, are extremely important.**
- **Our studies combine NMR spectroscopy and computer simulations to provide a molecular level understanding of the fundamental processes of adsorption and diffusion.**

We use Xe NMR to obtain detailed information about adsorption and diffusion processes

Adsorption (Xe in Na*A*, Xe and other gas in Na*A*)

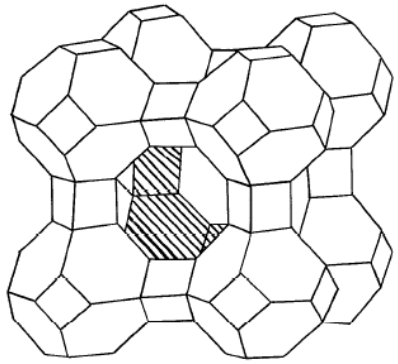
- Partitioning between inside and outside
- Distribution among the cavities
- Distribution within a cavity

Diffusion

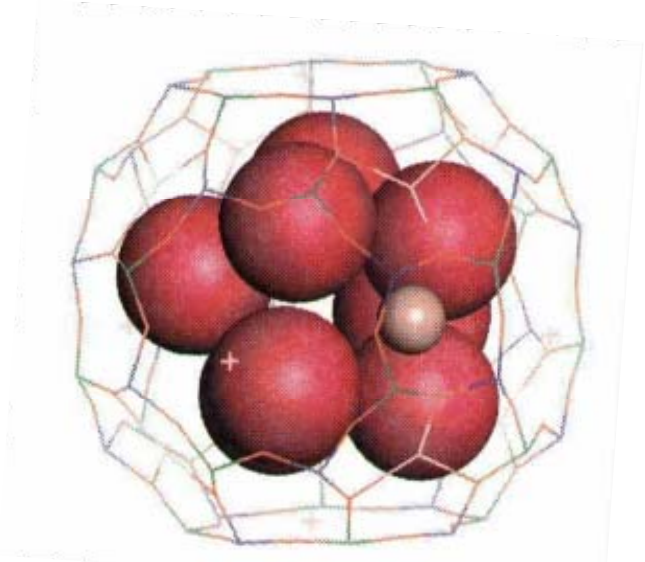
- Intra-crystalline diffusion (Xe in Na*A*)
- Exchange inside $\leftrightarrow$ outside (Xe in silicalite)

Adsorption of one component in a porous solid

Model system: Xe in Na*A*



zeolite Na*A*



7 Xe atoms in a cage of NaA

What information can NMR experiments provide in the model systems Xe in zeolite NaA?

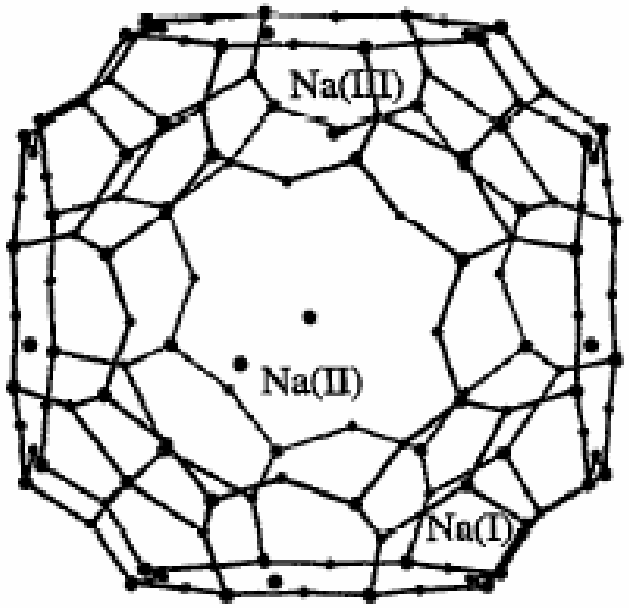
We can answer the following questions:

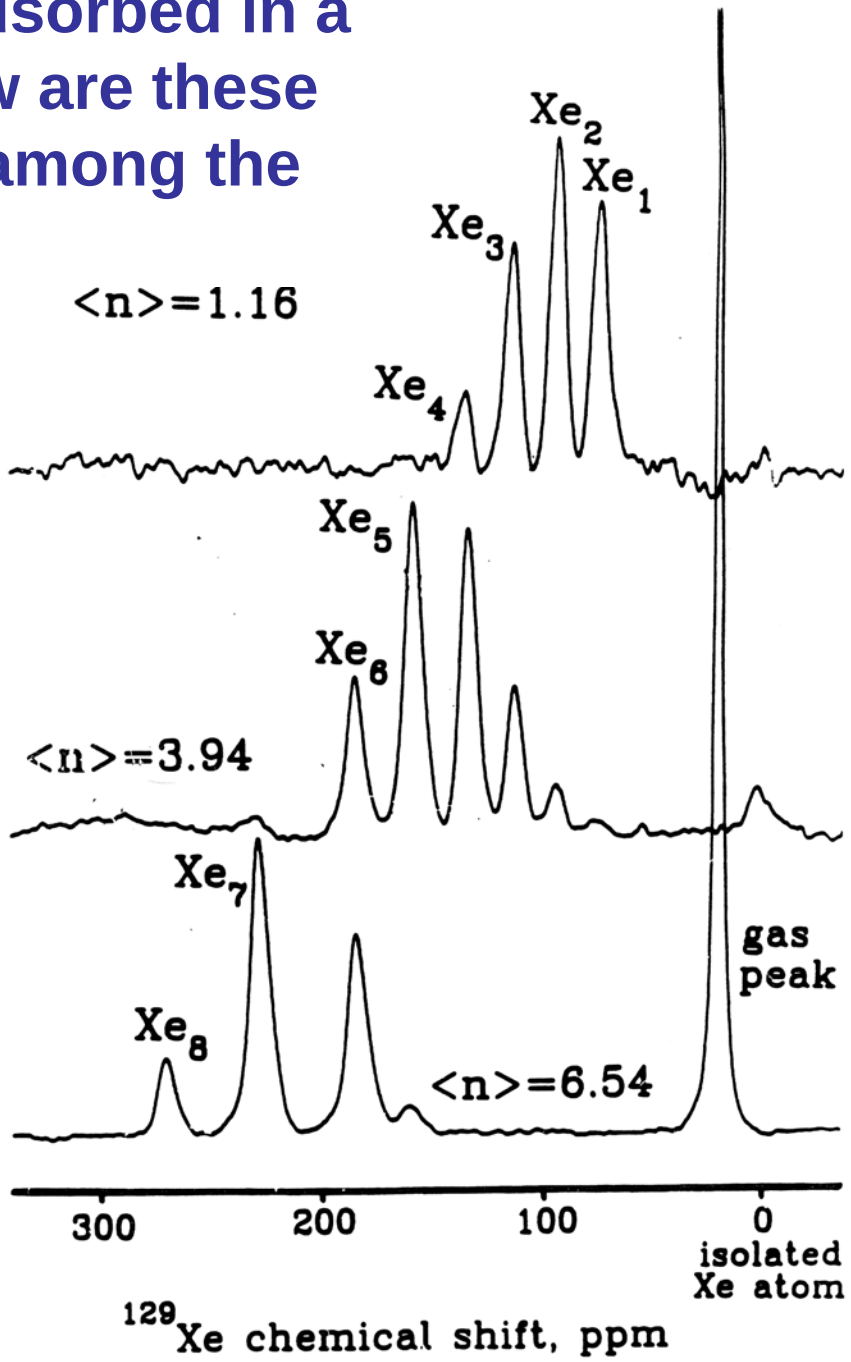
- When molecules are adsorbed in a microporous solid at a given loading, what is the distribution of these molecules among the cavities?
- When the average loading is 0.5 molecules per cavity, can we establish that there are any cavities with more than one molecule?
- Within a cavity, where do the molecules spend most of their time: like a snowball in the middle of the cavity? or like a thin film along the inside walls?

What can we find out about adsorption in zeolites?

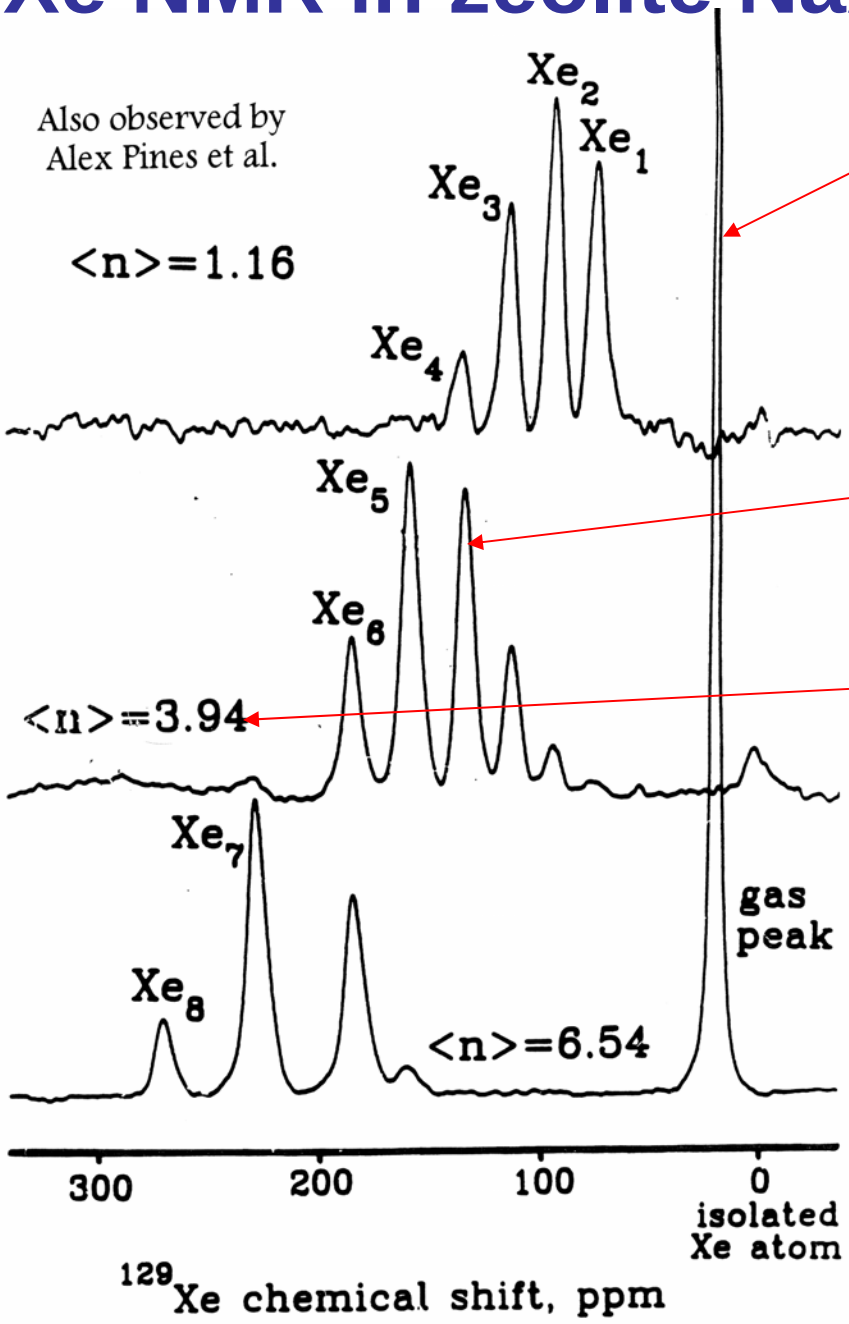
- the density of overhead gas
- fraction of cages which have exactly *n* Xe atoms, P_n
- amount adsorbed, i.e., average occupancy $\langle n \rangle_{Xe}$
- the probability distribution of one Xe atom within the cage
- the distribution of Xe-Xe distances
- the changes of all of the above with temperature and overhead gas pressure

When molecules are adsorbed in a microporous solid, how are these molecules distributed among the cavities?





Xe NMR in zeolite NaA



Xe chemical shift of gas peak provides ρ_{Xe} Xe density in the overhead bulk gas

Relative areas under the peaks provides the fraction of cages containing a number n of Xe atoms and also the average ⟨n⟩. Adsorption isotherm by NMR!

Chemical shift of an individual peak can verify the GCMC *distribution of n Xe atoms within the cavity*.

Grand Canonical Monte Carlo simulations provide atomistic detail with NMR observations

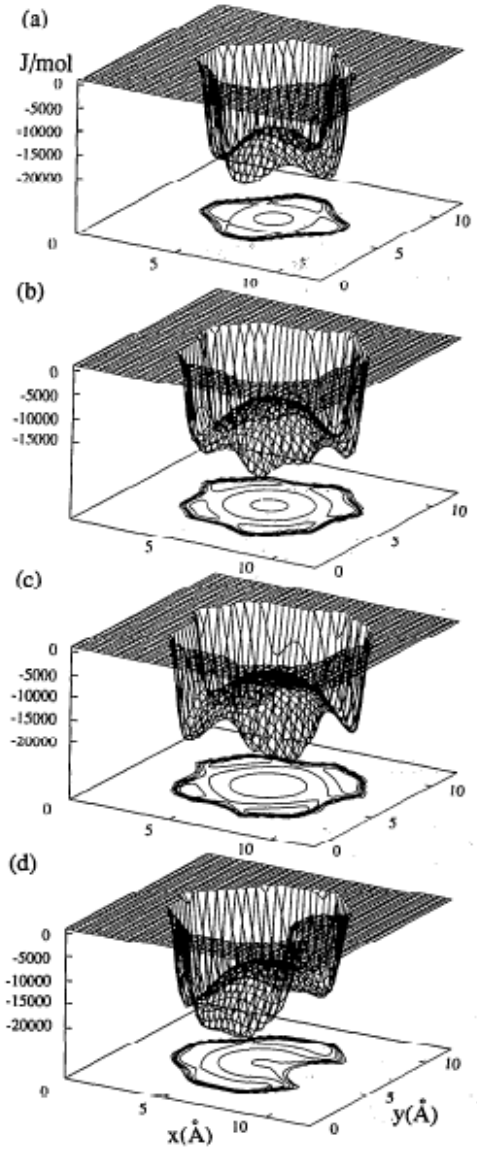
- Individual Xe chemical shifts that are observed correspond to averages over many configurations of Xe inside the zeolite
- Combination of classical probabilities of particular configurations and quantum mechanical Xe nuclear shielding functions lead to predictions of observed distributions of Xe and also the observed Xe chemical shifts.
- Comparison with many detailed experimental observations validate the GCMC results
- Additional details provided by simulations can then be accepted as descriptive of actual systems.

the shielding surface

- **The nuclear magnetic shielding as a function of nuclear coordinates of a molecule.**
- **What is observed experimentally is a dynamic average over this surface. The average arises from the shielding value at each point on the shielding surface being weighted according to the probability of finding the molecular system at that nuclear configuration.**
- **The INTERmolecular chemical shift of ^{129}Xe is the difference between the shielding of ^{129}Xe in an isolated Xe atom and the average shielding of a Xe atom in a supermolecule averaged over all the various configurations.**

What fraction of the time a particular Xe-neighbor configuration is found

- Probability of finding Xe at a particular location depends on the intermolecular potential functions between Xe and the neighbor atoms.



Potential energy surface $U(r^N)$ for one Xe at various planes through the zeolite cage.

in ZEOLITE: Metropolis Monte Carlo

$$\sigma(\mu, T, V) = (1/M)\sum_{i=1}^{M} \sigma_i(\mathbf{r}^N)$$

$$\sigma_i(r^N) = \sigma(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \ldots \text{in zeolite})$$

The configurations i = 1 to M are generated from a probability distribution.

In GCMC the distribution is proportional to

$$\exp\{-[U(\mathbf{r}^N) - N\mu]/kT - ln\ N! - 3N ln(h^2/2\pi mkT)^{1/2} + N ln\ V\}$$

Need 2 functions:

$*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \ldots \text{in zeolite})$ & $U(\mathbf{r}^N)$

GRAND CANONICAL MONTE CARLO

Constant μ, V, T

Norman-Filinov method

equal probability for 3 moves:

2[create/annihilate] + displace; accept or not?

$P_{acc} = \begin{cases} \text{min. } [1, \exp(-\Delta E/k_B T)] & \leq 180 \\ 0 & > 180 \end{cases}$

create $\quad \Delta \mathbf{E} = \Delta \mathbf{U}_{ji}(\mathbf{r}^N) + k_B T \, ln\left(\frac{N}{V\rho^0}\right) - \mu$

or

annihilate $\quad \Delta \mathbf{E} = \Delta \mathbf{U}_{ji}(\mathbf{r}^N) - k_B T \, ln\left(\frac{N+1}{V\rho^0}\right) + \mu$

displace $\quad \Delta \mathbf{E} = \Delta \mathbf{U}_{ji}(\mathbf{r}^N)$

configuration energy

$\Delta \mathbf{U}_{ji}(\mathbf{r}^N) = \mathbf{U}_j(\mathbf{r}^N) - \mathbf{U}_i(\mathbf{r}^N)$

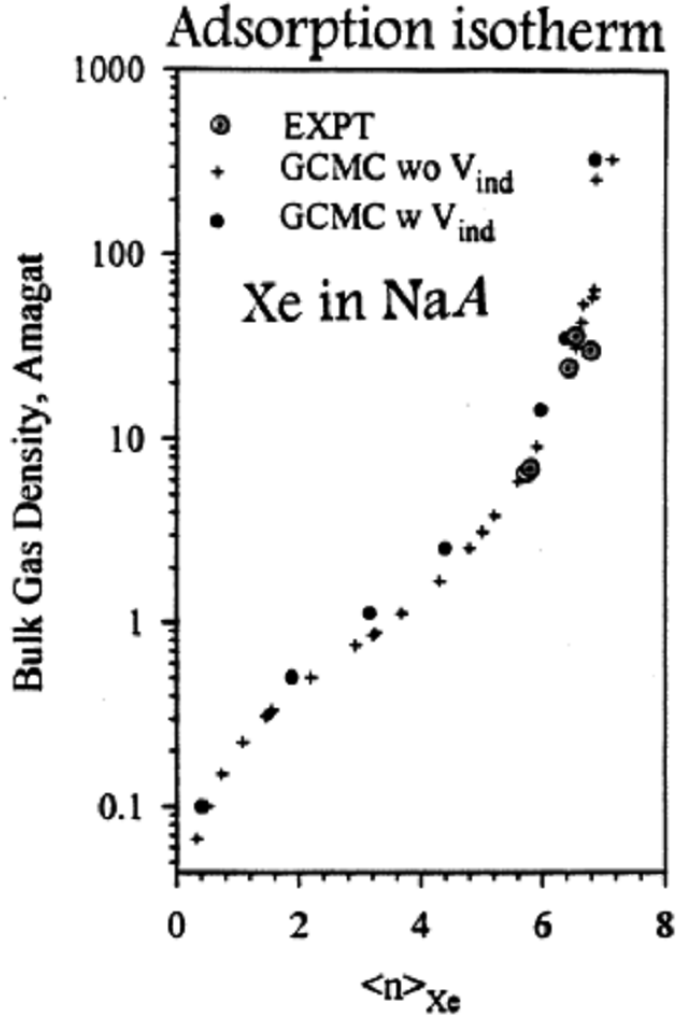
NEW OLD

ASSUME PAIRWISE ADDITIVE!

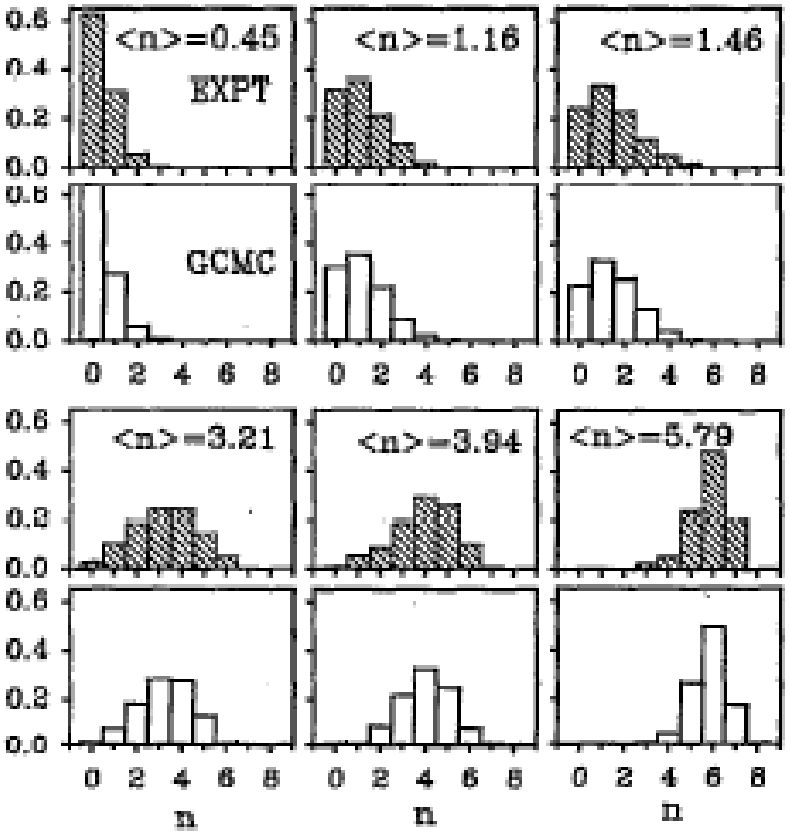
$\langle \mu \rangle_{GCMC} = \mu_{bulk\ gas}$

$\mu_{bulk\ gas} = RT \ln(\rho/\rho_0) + RT(Z-1) + \int_0^{\rho} d\rho \frac{P - RT\rho}{\rho^2}$

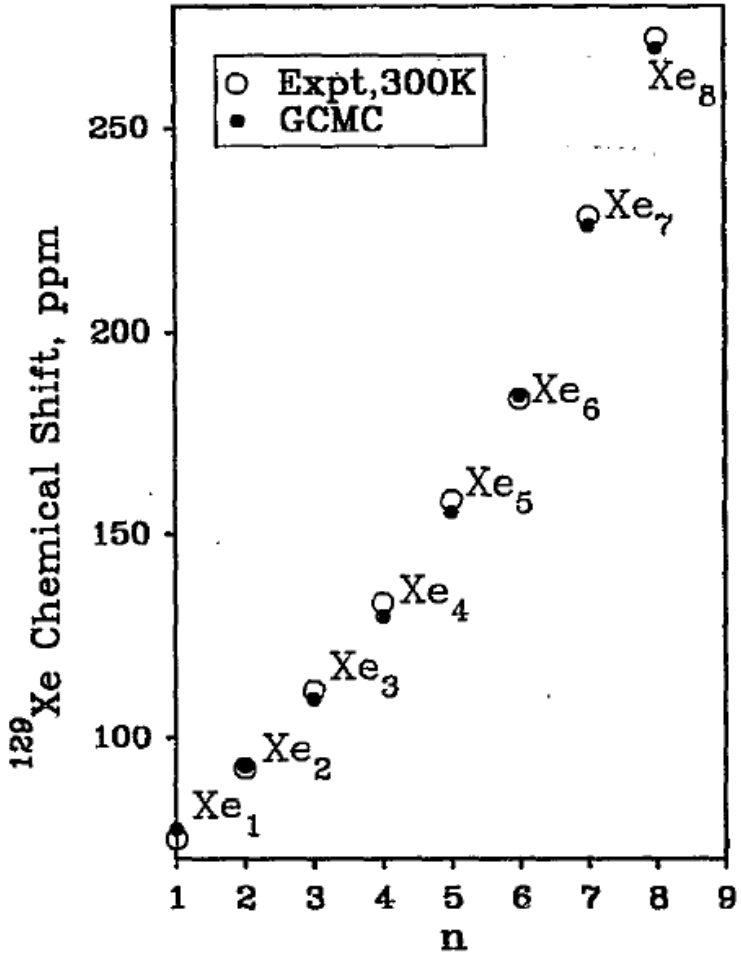
GCMC simulations reproduce the partitioning between Xe in overhead gas and Xe in adsorbed phase



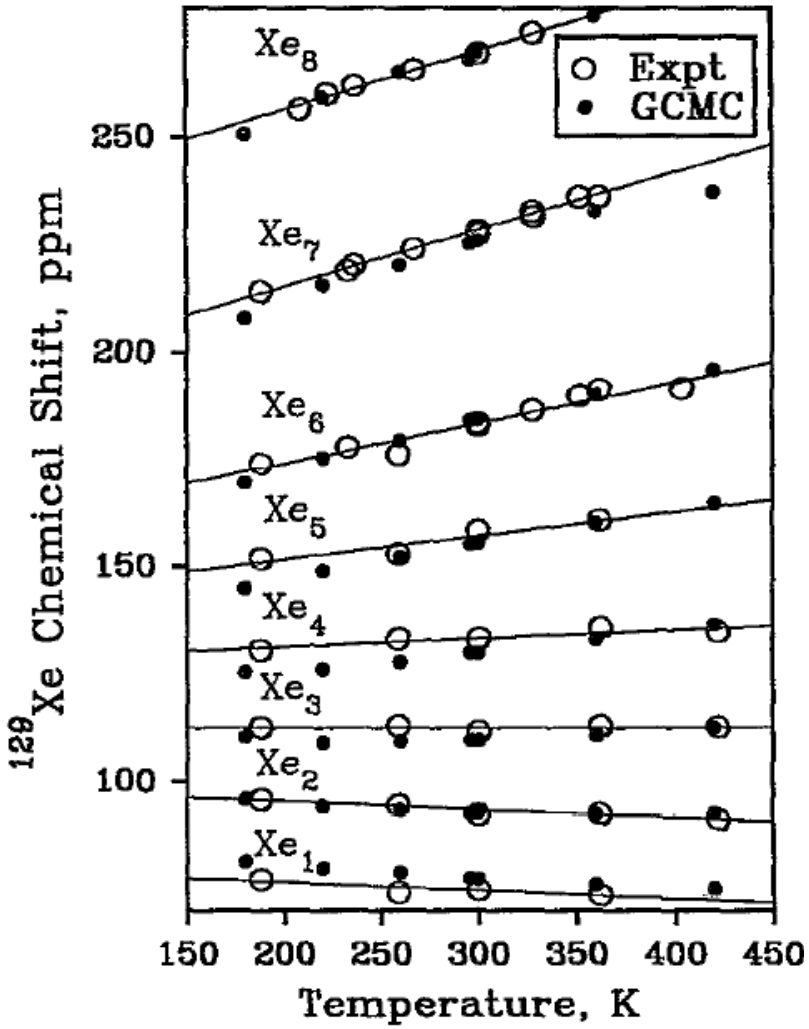
GCMC simulations reproduce the distribution of Xe among the cages



We reproduce the observed individual chemical shifts



and also the temperature dependence of each



These validate (a)the probability distribution of one Xe atom within the cage and (b) the distribution of Xe-Xe distances

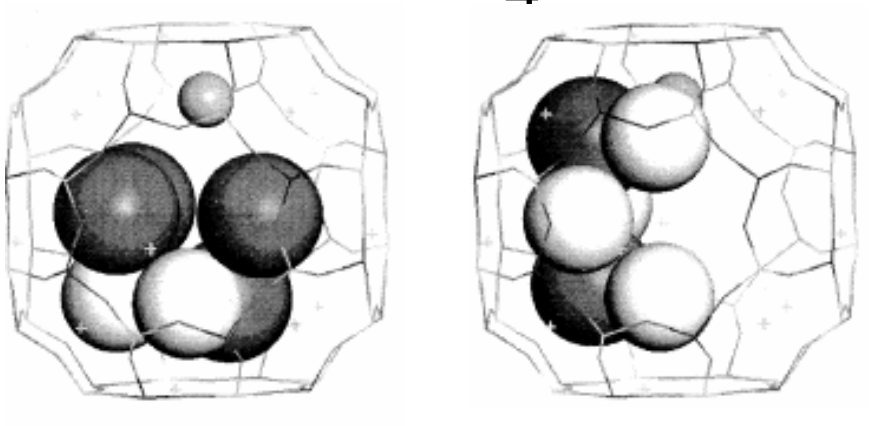
Adsorption of two components in a porous solid

Model systems:

Xe and Ar in Na*A*

Xe and Kr in Na*A*

Xe and CH_4 in Na*A*



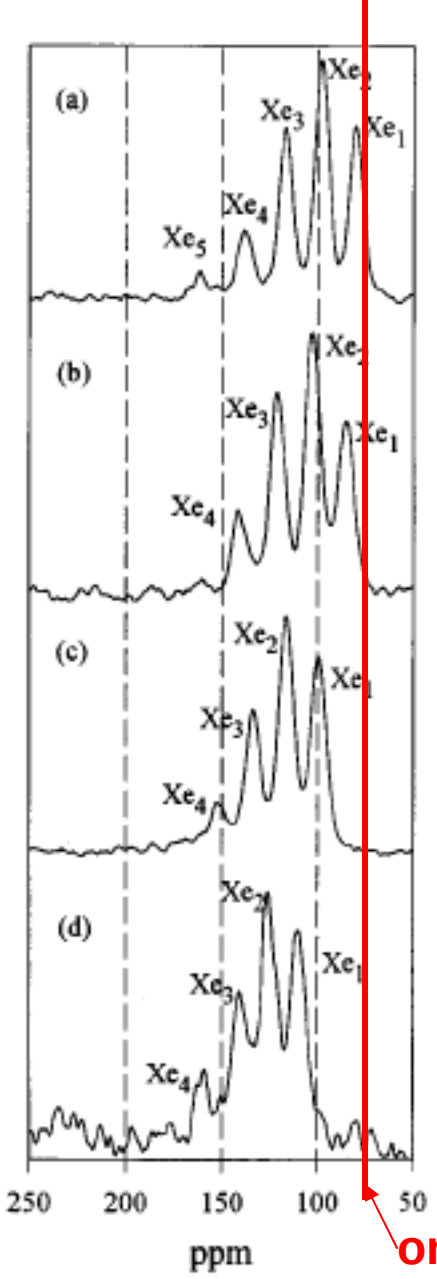
On competitive adsorption of two components, we find the answers to:

- When two types of molecules are adsorbed in a microporous solid, how are these two types of molecules distributed among the cavities?
- How many molecules of type 2 can be found in those cavities that have exactly *n* molecules of type 1?
- Does the distribution of one type of molecule affect the distribution of another?
- For a given composition in the overhead gas, what is the composition in the adsorbed phase?
- Can we predict the adsorption from a mixture of gases from the individual adsorption isotherms?

What can we find out about competitive adsorption in zeolites?

for any chosen sample at (P_{total} , y_{CH4}) in the bulk

- fraction of cages which have exactly n Xe atoms
- average number of CH_4 in same cavity as *n* Xe atoms for any chosen sample (various bulk gas compositions)
- the total amount of gas adsorbed
- the composition inside ($\langle n \rangle_{Xe}$, $\langle m \rangle_{CH4}$)
- the average number of CH_4 found in the same cage as n_{Xe}, while CH_4 are in fast exchange within a single cage
- separation factor = $(x_{Xe}/x_{CH4})/(y_{Xe}/y_{CH4})$



The Xe chemical shift for a specific number of Xe

- is different from that when the overhead gas is pure Xe, and
- depends on the average number of Ar in the same cage as the Xe.

	$\langle n \rangle_{Xe}$	$\langle m \rangle_{Ar}$
(a)	1.54	0.86
(b)	1.36	1.65
(c)	1.22	3.60
(d)	1.23	4.79

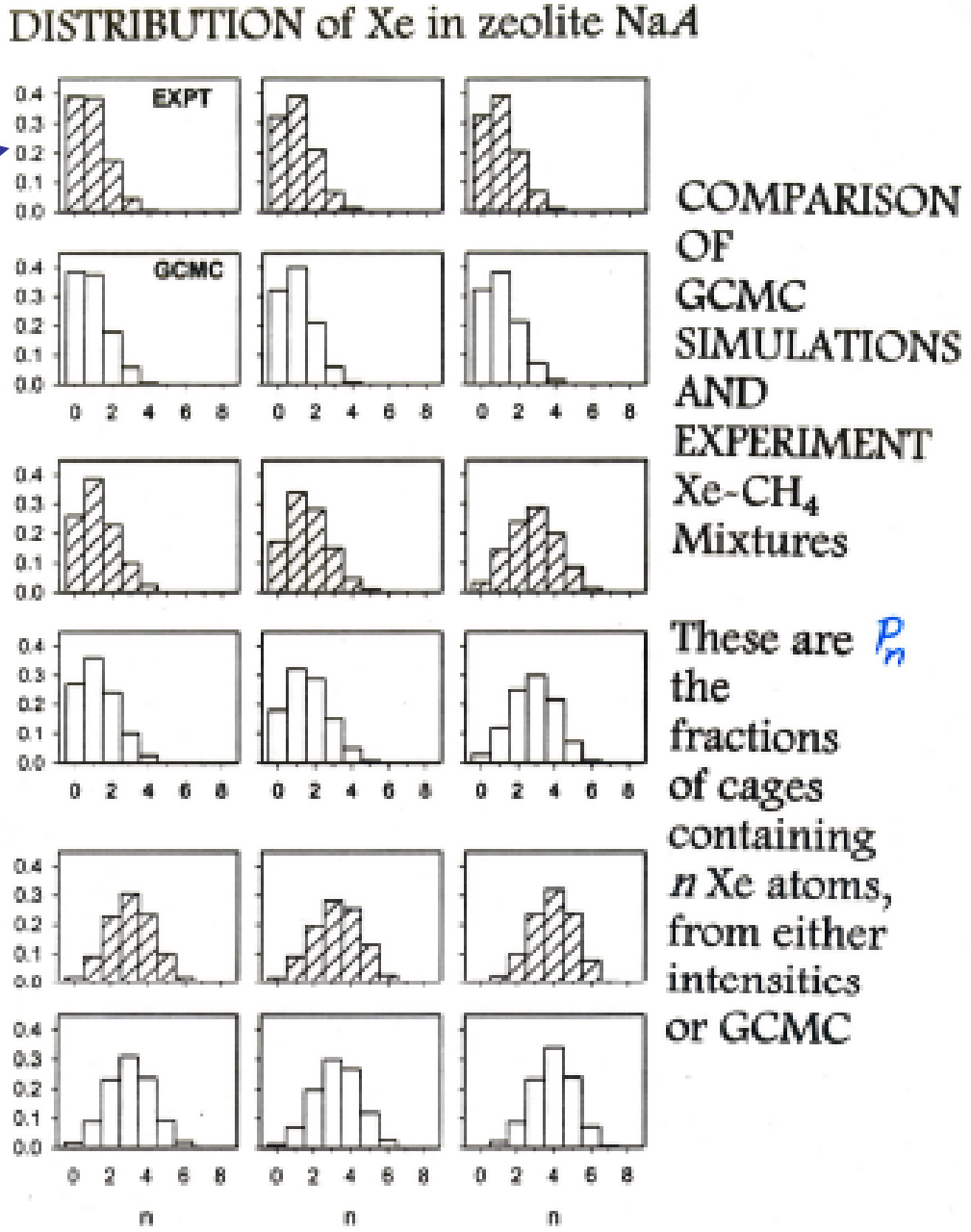
The INTENSITY of the Xe_n peak is a direct measure of the fraction of cages that have exactly *n* Xe atoms

one Xe in a cavity in pure Xe samples

Xe NMR spectra of adsorbed Xe-Ar mixtures in zeolite NaA

DISTRIBUTION of Xe:

from the NMR spectrum we still obtain the distribution of Xe among the cavities from the relative intensities



Distribution of two components inside and outside

from the Monte Carlo simulations

at a given (P_{total} , y_{CH4}) in the bulk, we obtain

- the total amount of gas adsorbed
- the composition inside: $\langle n \rangle_{Xe}$, $\langle m \rangle_{CH4}$

Separation factor

the ratio of mole fractions in the adsorbed phase (***x***) and the bulk gas phase (***y***):

$$S_{Xe,Ar} = \frac{x_{Xe}/x_{Ar}}{y_{Xe}/y_{Ar}}$$

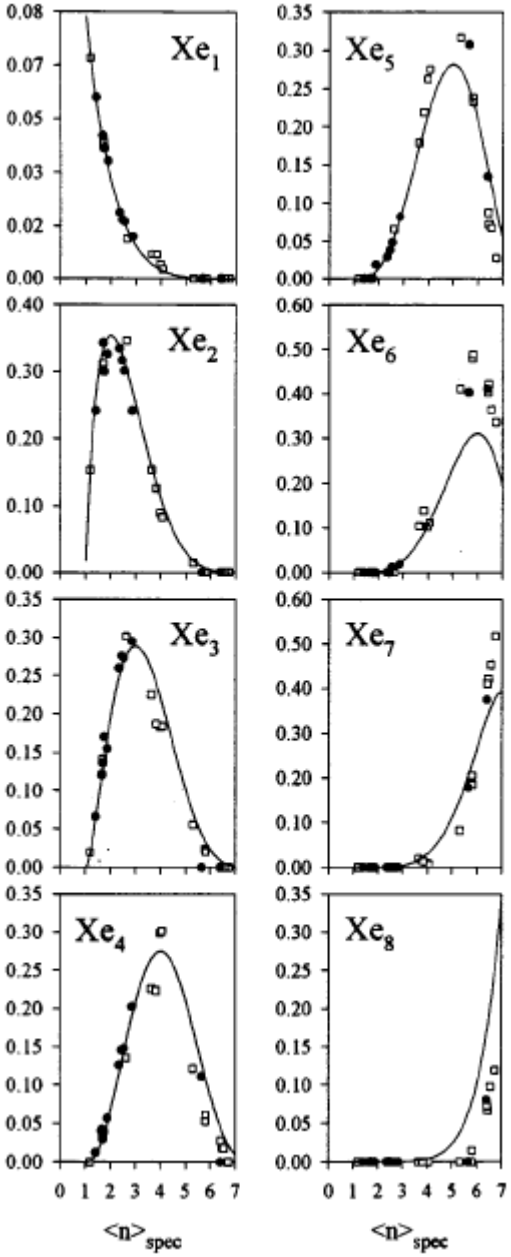
Is the distribution of Xe inside vs. outside affected by the second gas?

Both molecules adsorb, but have different pure adsorption isotherms because of different potential energies of interaction with the atoms of the cavity.

QUESTION:

Is the adsorption isotherm for a mixture the same as that predicted from the individual pure adsorption isotherms?

Ideal Adsorbed Solution theory (IAS) is analogous to Raoult's law for ideal solutions.



! ! Fraction of cages containing a specific number of Xe atoms in zeolite NaA is found to be **independent of whether pure Xe** (□) **or any mixture** (●) of Xe and Ar are overhead

pure Xe (□)
mixture (●) of Xe and Ar
are overhead

Experimental distribution of Xe among cages occupied by Xe atoms

In other words,

the Xe distributes itself among the cages just as it would if the other type of molecule were absent.

Caveat: we can not say the same for the other molecule.

QUESTION:

Does the Xe distribution <u>within the cage</u> change when other molecules are in the cage with it?

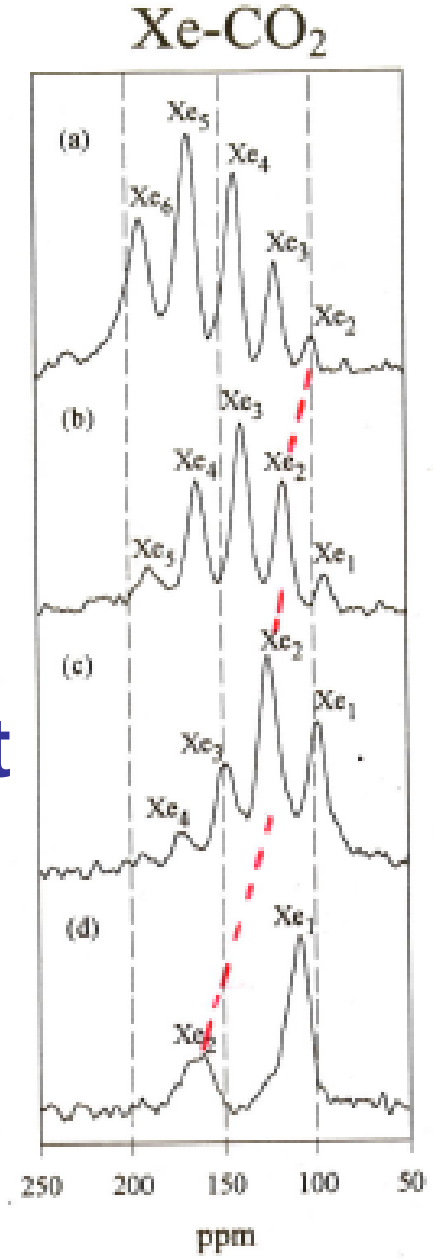
YES, for any Xe_n the available volume within the cage depends on the number of Ar (or other) with it.

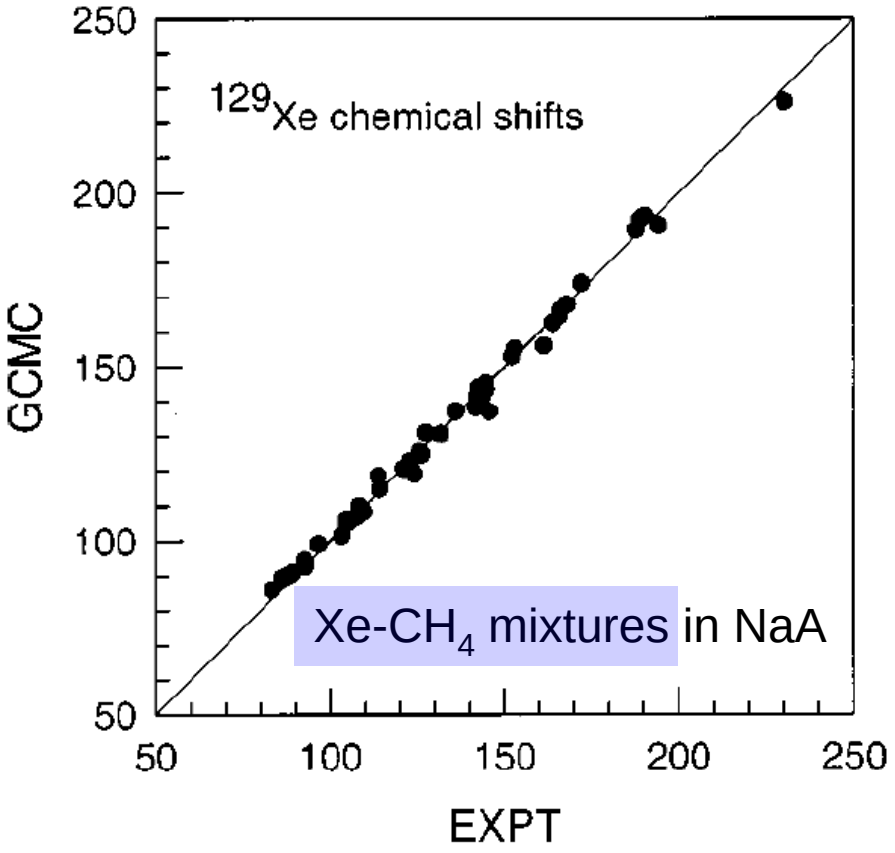
QUESTION:

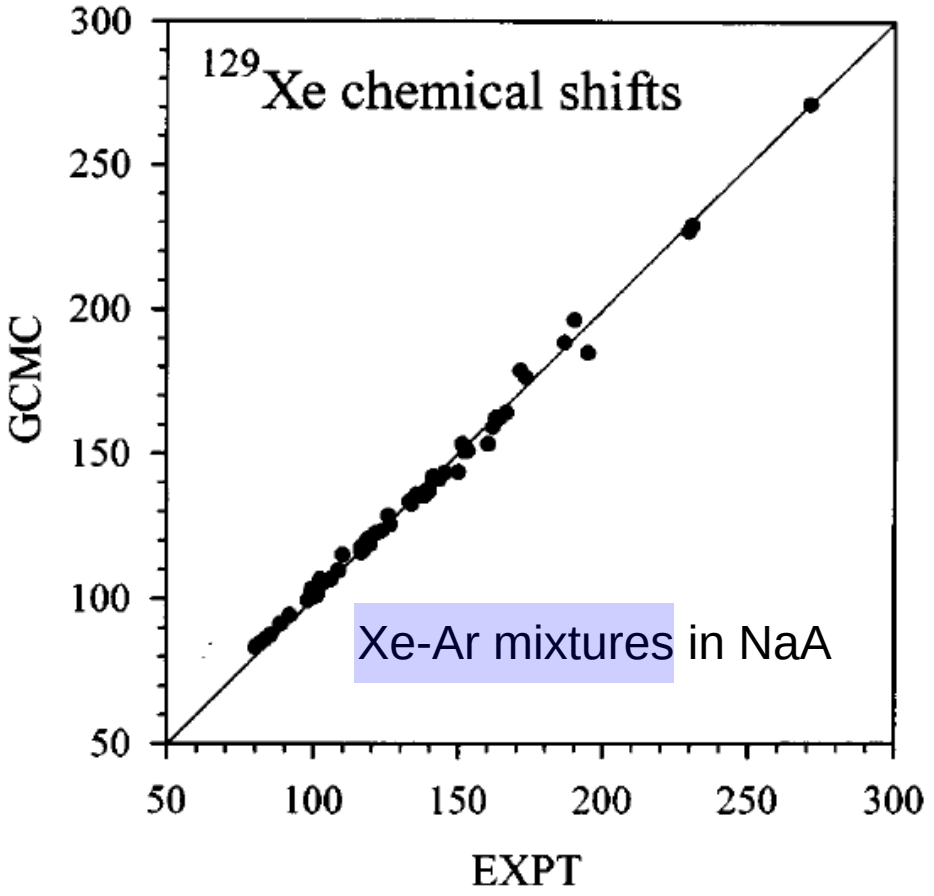
Is the Xe chemical shift affected by the presence of the other gas?

- **Yes, found experimentally, and also by simulations [because the Xe interacts with additional molecules inside the confined space].**

This means that the observed shift in Xe_n peak position in the mixture compared to Xe_n peak in pure Xe can be used to deduce the average number of the other molecules inside the cage with it.







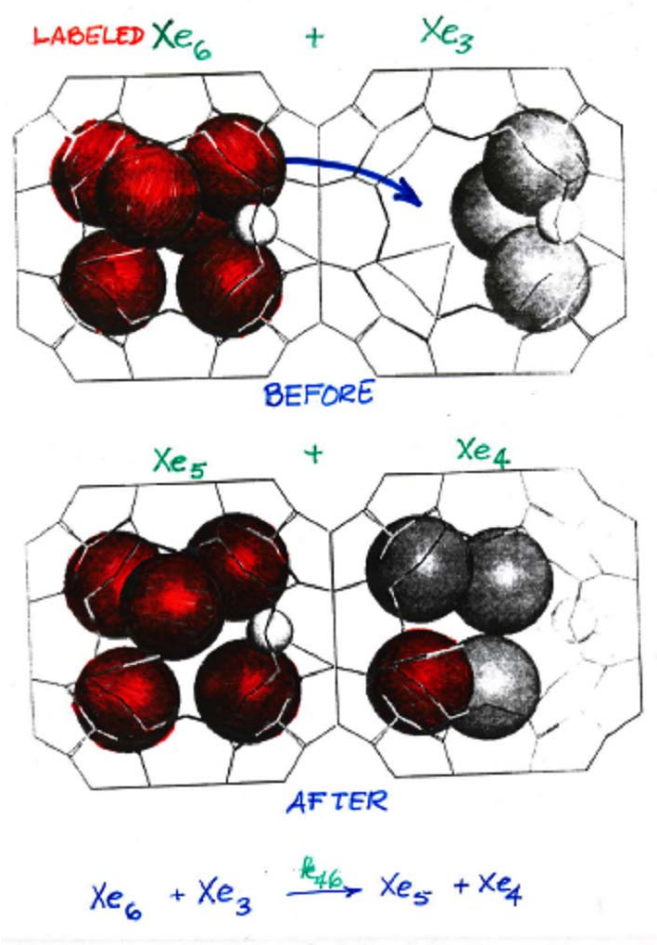
Since we can reproduce the Xe chemical shifts in all the samples of varying Xe-other composition, then the average number of other in the same cage as n Xe atoms is probably well represented by the GCMC results.

We obtain very detailed information about adsorption.

- fraction of cages which have exactly n Xe atoms
- average number of CH_4 in same cavity as *n* Xe atoms for any chosen sample (various bulk gas compositions)
- the total amount of gas adsorbed
- the composition inside ($\langle n \rangle_{Xe}$, $\langle m \rangle_{CH4}$)
- the average number of CH_4 found in the same cage as n_{Xe}, while CH_4 are in fast exchange within a single cage
- separation factor = $(x_{Xe}/x_{CH4})/(y_{Xe}/y_{CH4})$

DIFFUSION

- Intra-crystalline diffusion (Xe in Na*A*)



Intracrystalline diffusion

How fast is the diffusion of Xe atoms within a crystallite?

$$Xe_n + Xe_{m-1} \xrightarrow{k_{mn}} Xe_{n-1} + Xe_m$$

k_{mn} are rate constants for individual jump events

Average rate constant for any given $\langle n \rangle$:

$$\langle k \rangle = \sum_{n=1,8} \sum_{m=1,8} P(m-1) \cdot k_{mn} \cdot P(n)$$

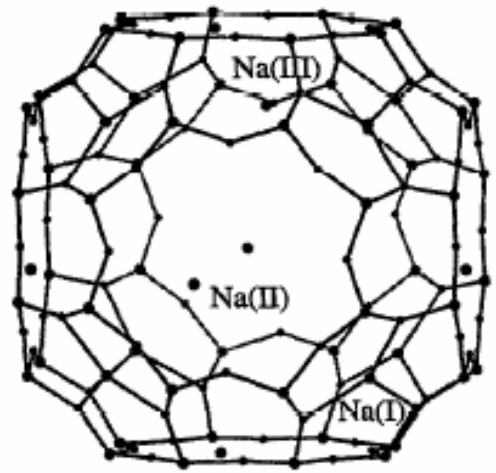
Diffusion coefficient

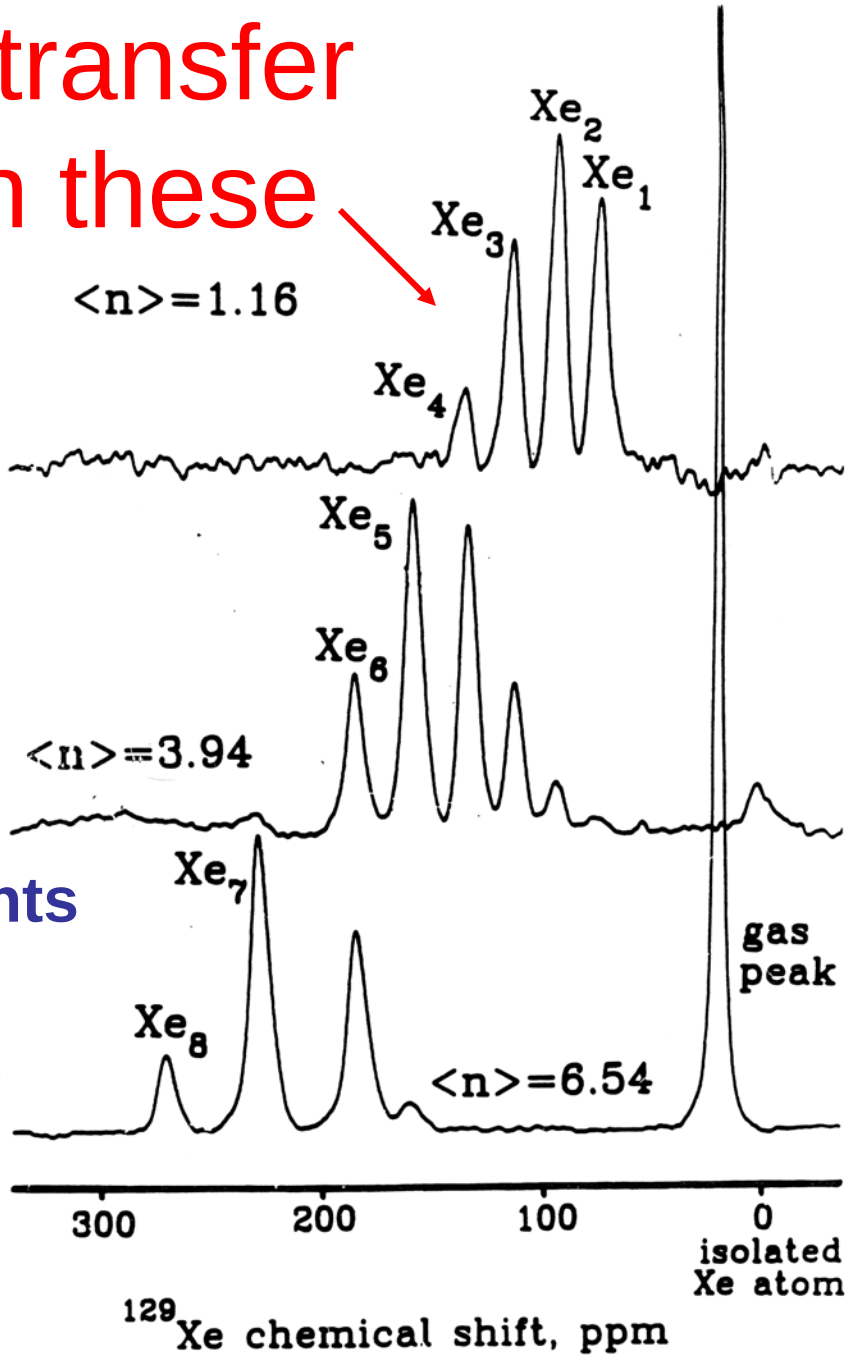
$$D_s = \langle k \rangle / 6$$

Some questions we would like answers to:

- **How often does a molecule migrate from one cavity to another? Can we follow this migration as a function of time?**
- **Does the rate of migration depend on how many other molecules are in the same cavity where it is leaving from? on how many molecules are in the destination cavity ?**

Magnetization transfer experiments on these



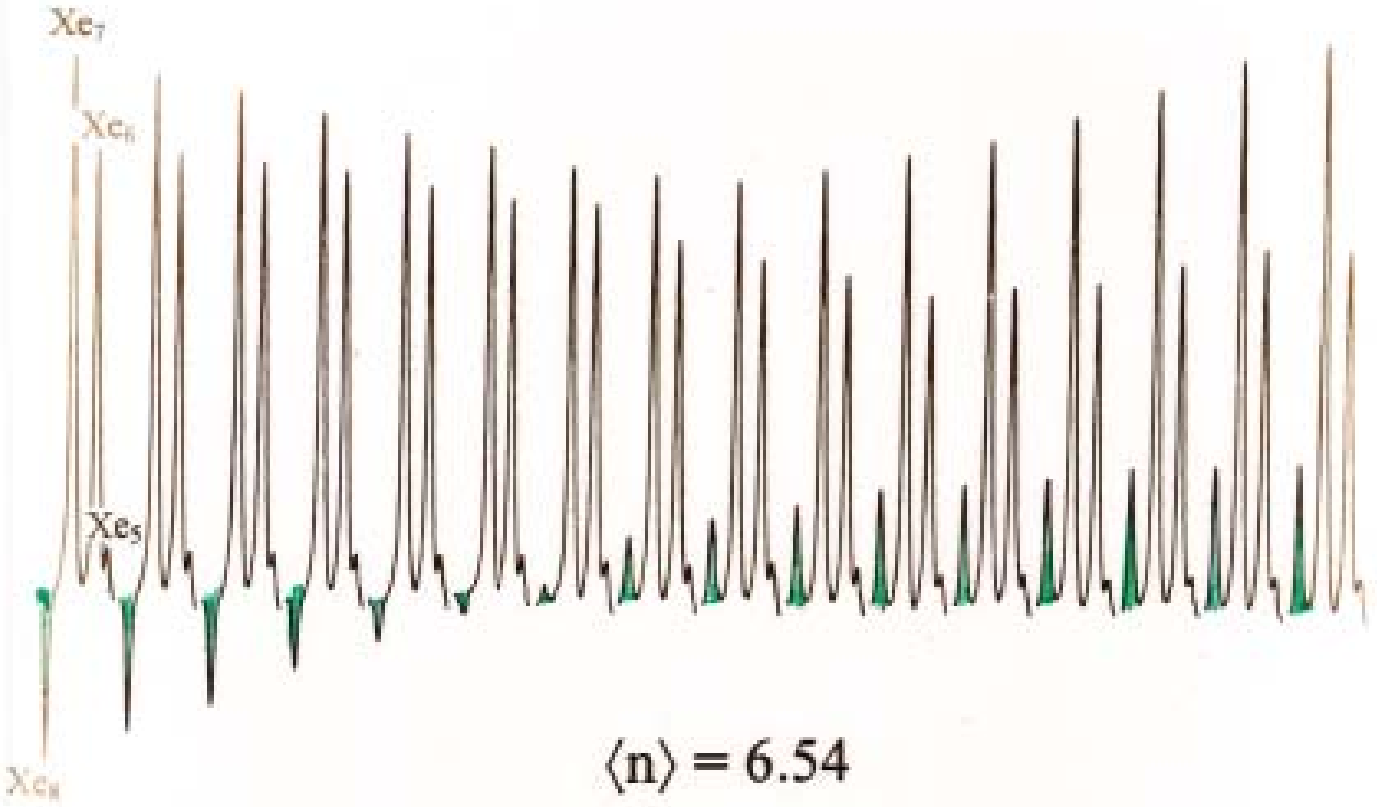


provides these rate constants

$$Xe_n + Xe_{m-1} \xrightarrow{k_{mn}} Xe_{n-1} + Xe_m$$

the 1D-EXSY experiment

Labeling the Xe allows us to observe dynamics and measure rates in a system which is at equilibrium.



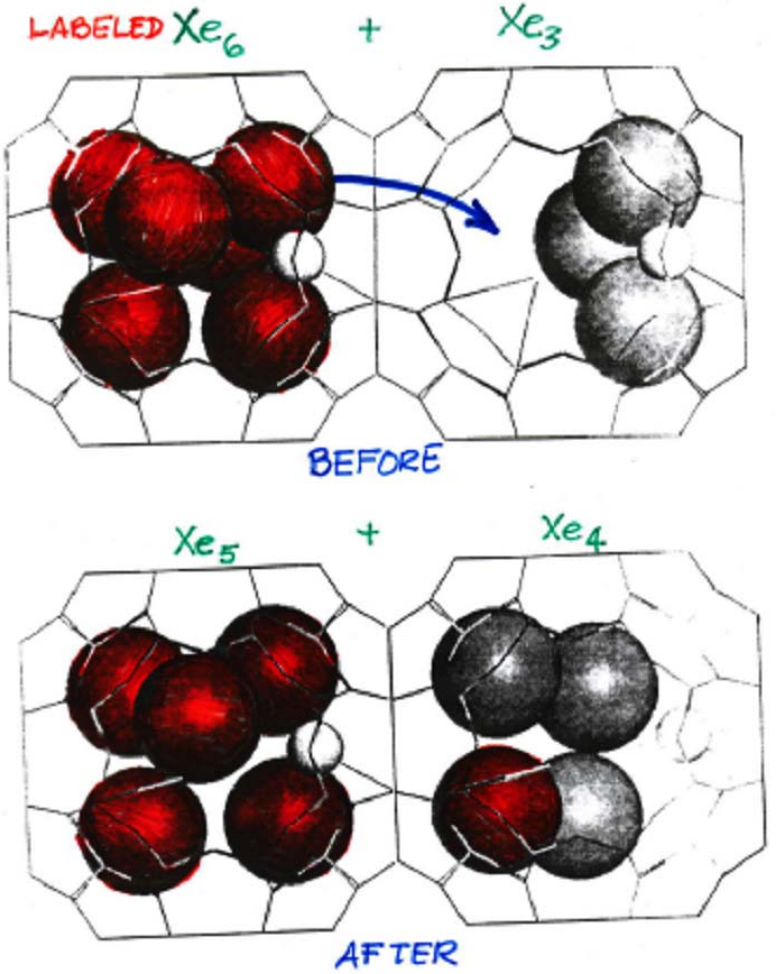
A typical magnetization experiment. This is a Dante experiment on Xe_n in a sample with ⟨n⟩ = 6.54 Xe atoms per alpha cage of zeolite NaA at 300 K. The delay times are (from left to right): 0, 2, 5, 10, 15, 20, 30, 60, 90, 130, 250, 400, 800, 1500, 2500, 3000 ms.

This single jump event affects the intensities of four peaks: Xe_6, Xe_3, Xe_5, and Xe_4.

BEFORE

$$Xe_6 + Xe_3 \xrightarrow{k_{46}} Xe_5 + Xe_4$$

AFTER



phenomenological rate constants K

$$d\mathbf{M}/dt = \mathbf{KM} + \mathbf{M}^{eq}$$

$$K_{ii} = -1/T_{1i} - \Sigma_{i \neq j} K_{ji}.$$

The phenomenological rate constant K_{ji} describes the pseudo-first-order exchange rate from site i to site j.

$$K_{mn} = k_{mn} f(m-1) \quad \text{provided} \quad |n-m| > 1,$$

$$K_{m,m+1} = k_{m,m+1} f(m-1) + m \Sigma_i^8 k_{i,m+1} f(i-1),$$

$$K_{m,m-1} = k_{m,m-1} f(m-1) + \Sigma_i^8 i k_{mi} f(i).$$

Monte Carlo simulations

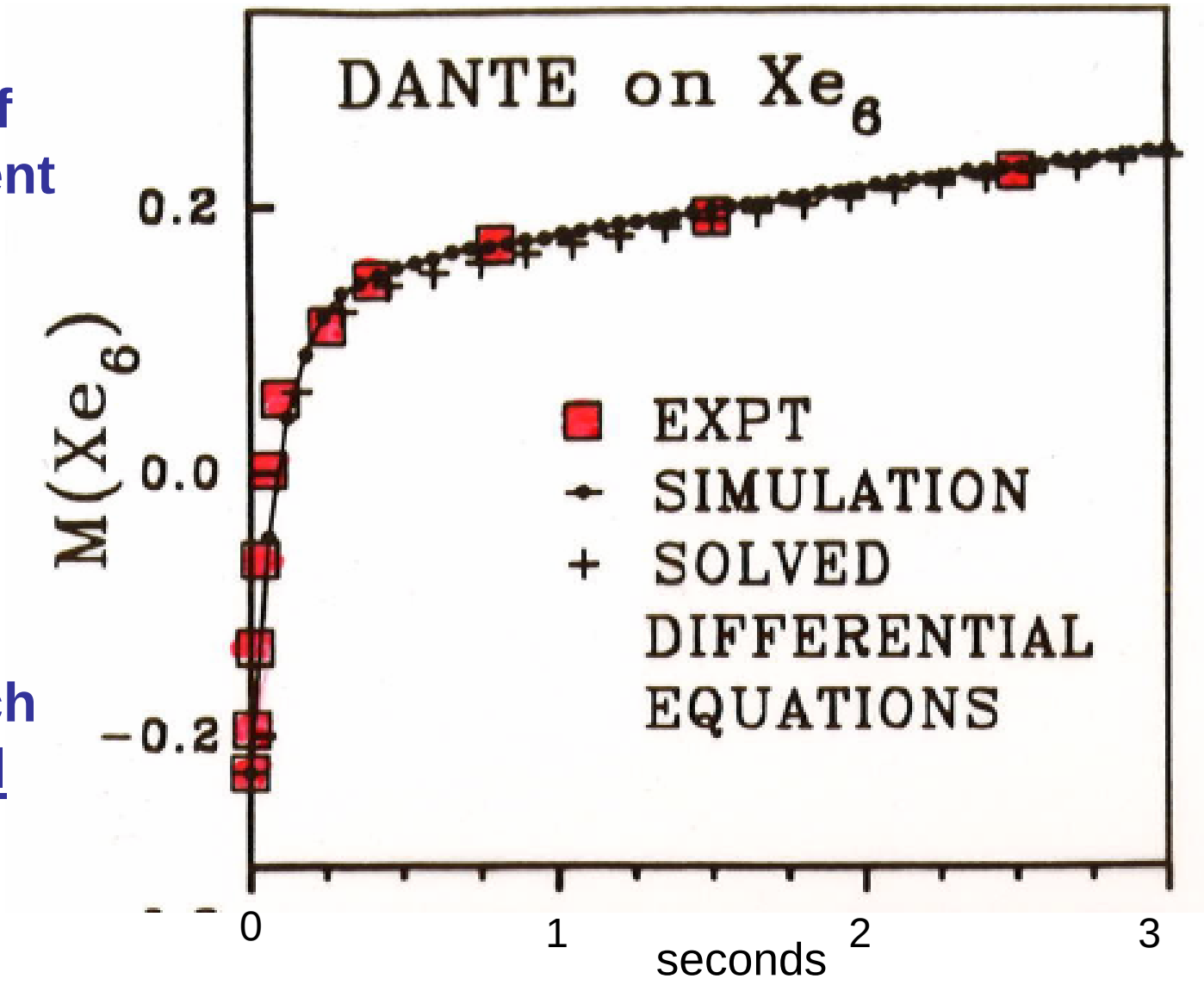
- provide a means of understanding the magnetization transfer experiments
- verify derived relationships between the elementary rate constants k_{mn} (a single atom hopping from a cage to another cage) and the phenomenological rate constants $\boldsymbol{K}$ associated with the magnetization transfer experiment.

Simulations use k_{mn} to define the intrinsic probability of making a jump.

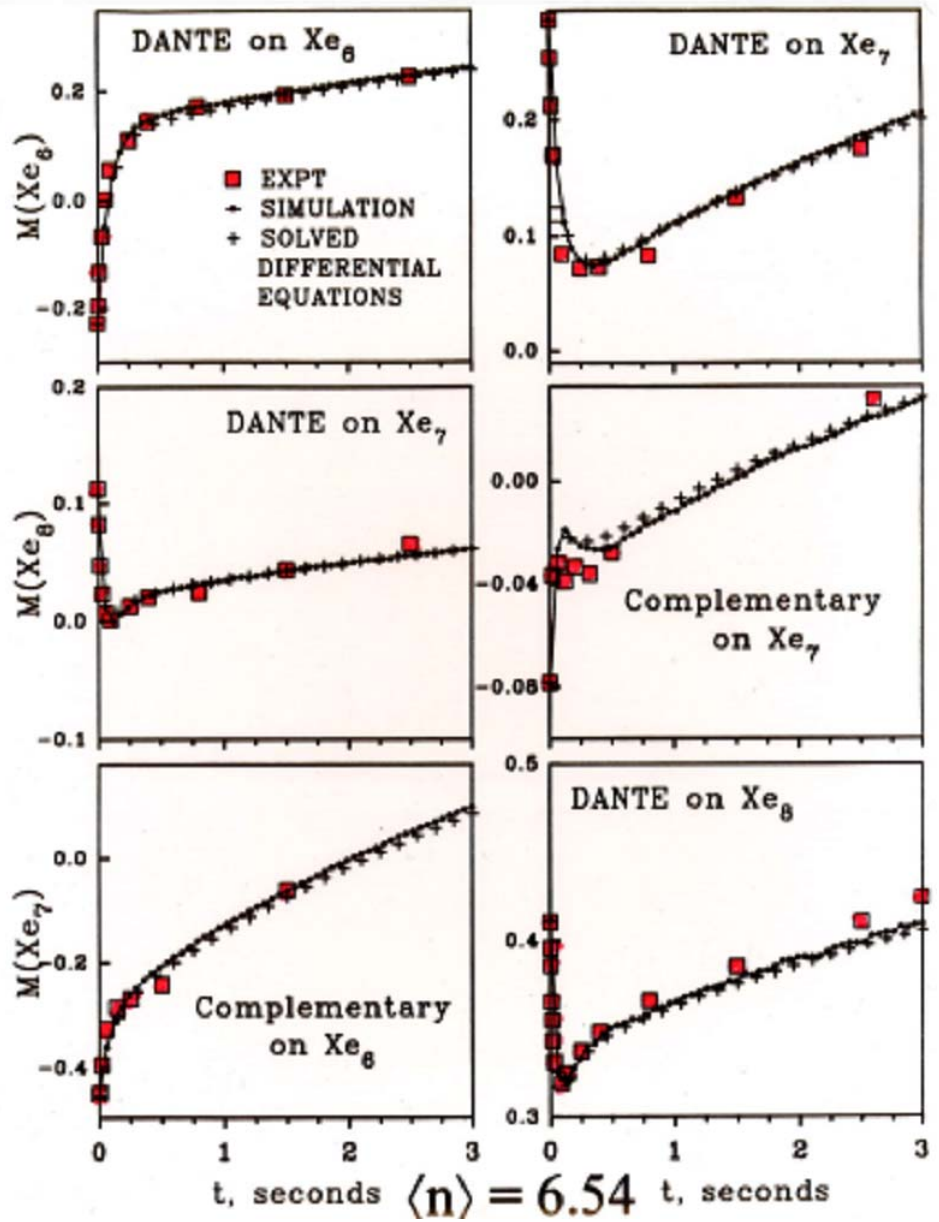
- 5000 cages—as many Xe atoms as needed for ⟨n⟩
- Start with uniform distribution
- 2000 equilibration steps
- Prepare initial labels (alpha and beta spins)
- Random hops as in equilibration but keep track of labels, 100 time steps
- Signal average over 25 "scans"

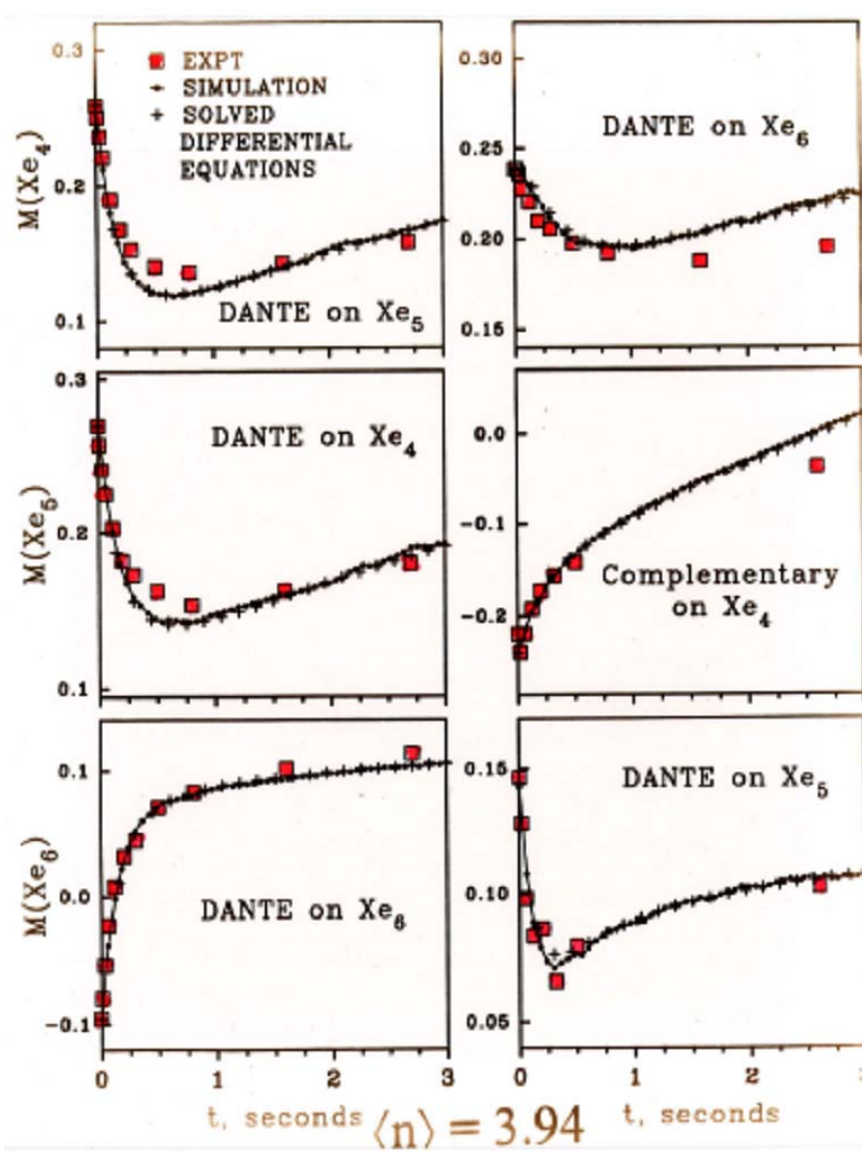
recovery curve after inversion for Magnetization of Xe_6

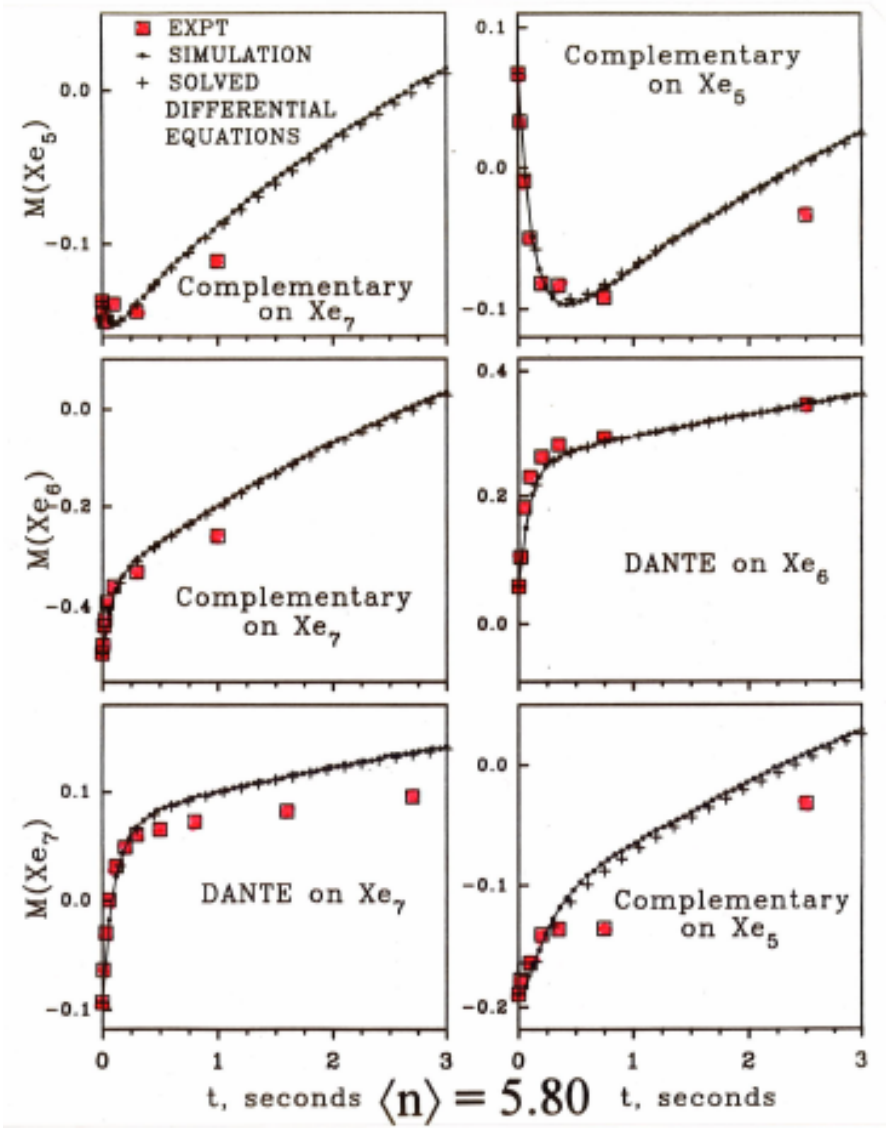
Simulation of the experiment using guessed k_{mn} to define intrinsic probability of making a jump provides such curves <u>for all Xe_n at once</u>.



some decay/recovery curves for one sample







We have 138 such detailed unique curves to provide the rate constants

Does the rate of migration of a Xe depend on how many other Xe are in the same cavity from which it is leaving?

The microscopic rate constants used in the simulations. The notation used is that k_{mn} is for the event in which a single Xe atom leaves the cage containing the cluster Xe_n jumping into the neighboring cage to form cluster Xe_m.

$$Xe_n + Xe_{m-1} \xrightarrow{k_{mn}} Xe_{n-1} + Xe_m$$

Forming \ Leaving	1	2	3	4	5	6	7	8
1	.300	.320	.325	.322	.477	.892	1.20	2.50
2	.351	.320	.325	.322	.477	.892	1.20	2.50
3	.355	.360	.325	.322	.477	.892	1.20	2.50
4.	.289	.364	.319	.322	.477	.892	1.20	2.50
5	(.286)	.381	.334	.322	.477	.892	1.20	2.50
6	(.268)	.357	.341	.322	.477	.892	1.20	2.50
7	(.108)	(.120)	.118	.144	.147	.277	1.20	2.50
8	(.100)	(.115)	(.115)	(.115)	.191	.095	0.456	2.50

The measured individual cage-to-cage migration rate constants k_{mn}

- depend largely on the occupancy of the cage from which the Xe is leaving,
- except that rate constants are significantly smaller when the Xe is going into a cage with high occupancy.

If the resulting equilibrium distribution is hypergeometric, what does this imply about the relative rates of the forward versus reverse process?

STRICTLY STATISTICAL?

Distribution of particles into *N* boxes each having 8 sites (hypergeometric distribution) gives ratios of rate constants, $k_{row,col} / k_{col,row}$:

	1	2	3	4	5	6	7
2	7/8						
3	6/8	6/7					
4	5/8	5/7	5/6				
5	4/8	4/7	4/6	4/5			
6	3/8	3/7	3/6	3/5	3/4		
7	2/8	2/7	2/6	2/5	2/4	2/3	
8	1/8	1/7	1/6	1/5	1/4	1/3	1/2

If the resulting equilibrium distribution is hypergeometric, what does this imply about the relative rates of the forward versus reverse process?

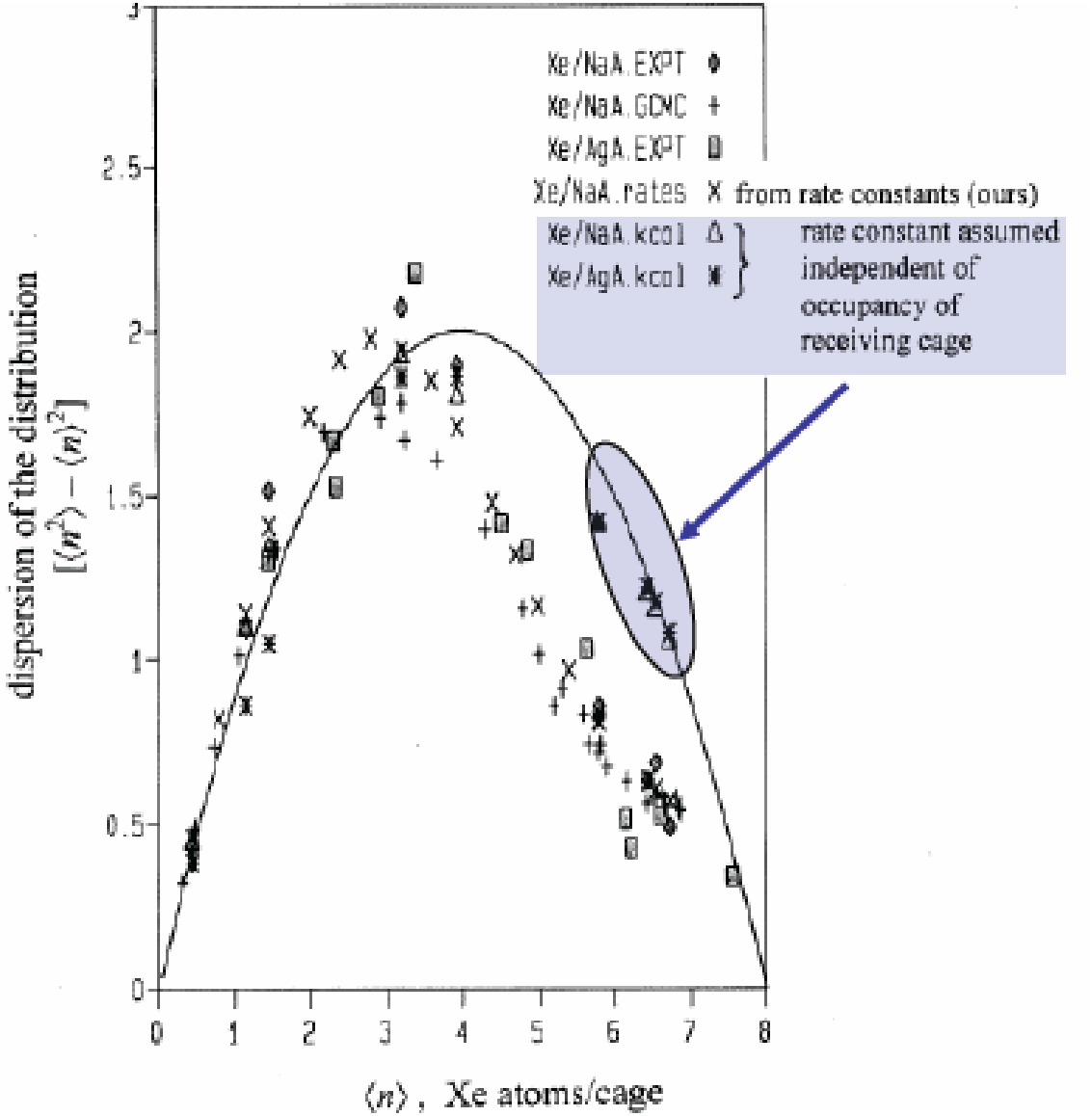
If strictly statistical, the rate constants are in the ratio

	forward/backward =	
$Xe_3 + Xe = Xe_2 + Xe_2$	7/6	***0.90***
$Xe_7 + Xe_3 = Xe_6 + Xe_4$	5/2	***8.3***
$Xe_8 + Xe = Xe_7 + Xe_2$	7/1	***21.7***

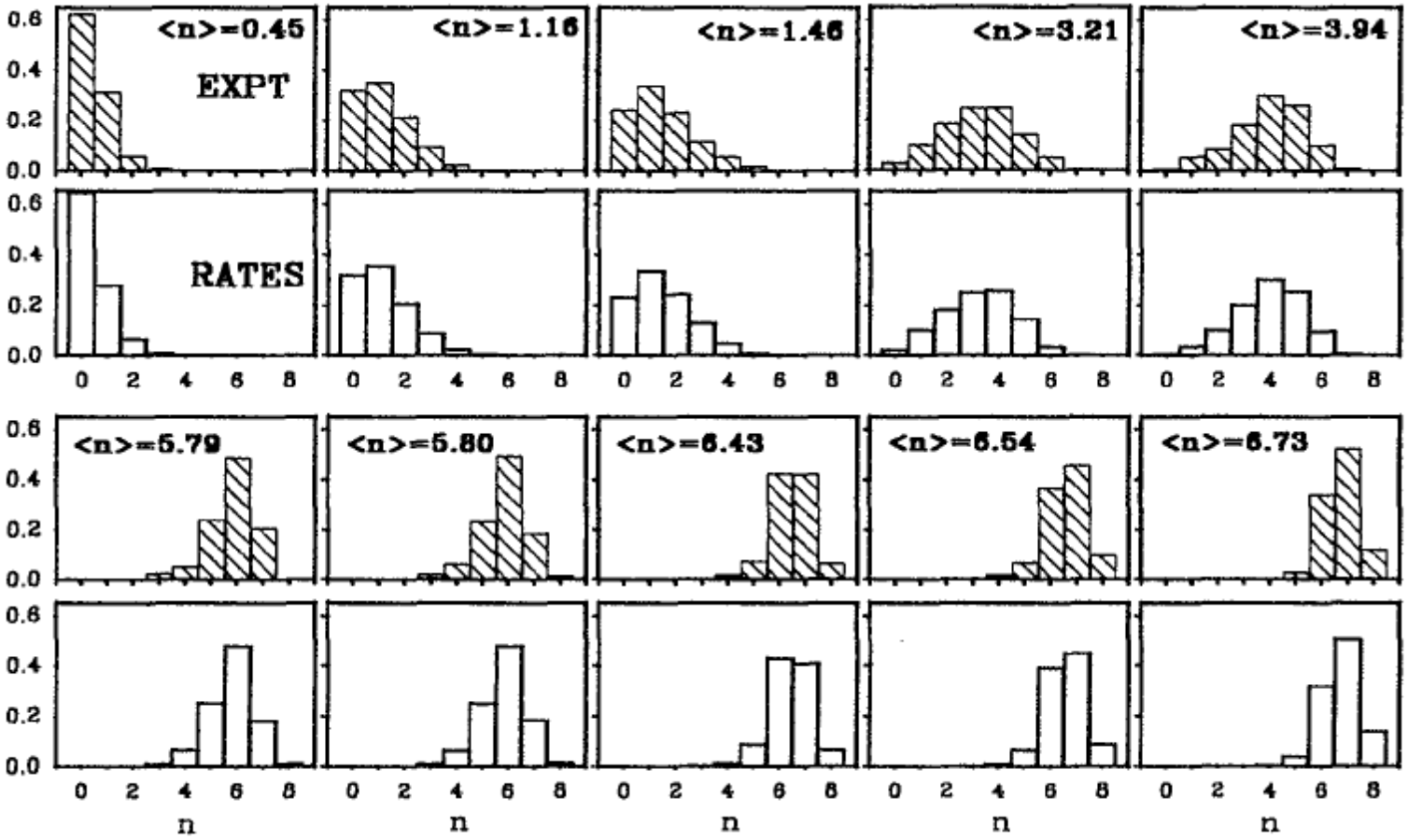
experimental ratios are different

Does the rate constant depend on the occupancy of the receiving cage?

The observed dispersions of the distribution of Xe among the cages reveal that it does.



When the obtained rate constants are used in a Monte Carlo simulation of the cage-to-cage jumps until equilibrium is reached, they reproduce the observed distributions



Two Monte Carlo simulation approaches to the equilibrium distribution of Xe atoms among the cavities of zeolite Na*A* **lead to the same results**, which **agree with experiment**.

RATES

k_{mn} $\rightarrow$ equilibrium P(n)

GCMC

PES $\rightarrow$ equilibrium P(n)

Intra-crystalline diffusion

How fast is the diffusion of Xe atoms within a crystallite?

We measured each one of these rate constants

$$Xe_n + Xe_{m-1} \xrightarrow{k_{mn}} Xe_{n-1} + Xe_m$$

Average rate constant for any given $\langle n \rangle$:

$$\langle k \rangle = \sum_{n=1,8} \sum_{m=1,8} P(m-1) \cdot k_{mn} \cdot P(n)$$

Fraction of cages having n Xe atoms

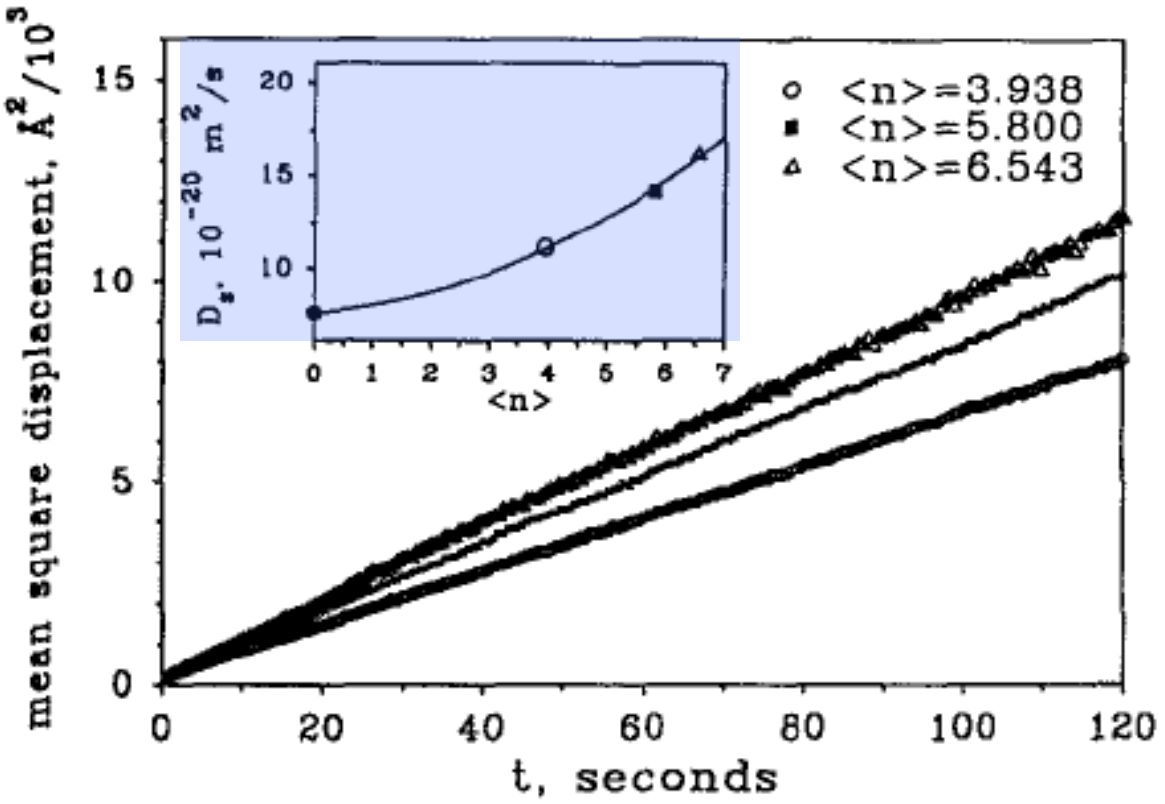
We can get diffusion coefficient

$D_s = \langle k \rangle \, l/6$

but we have more detail than just a diffusion coefficient.

Intra-crystalline diffusion

How fast is the diffusion of Xe atoms within a crystallite?

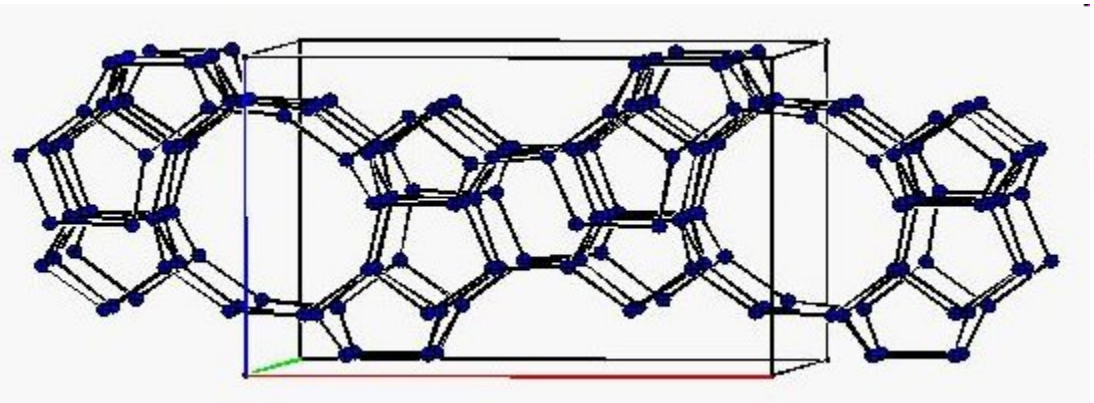


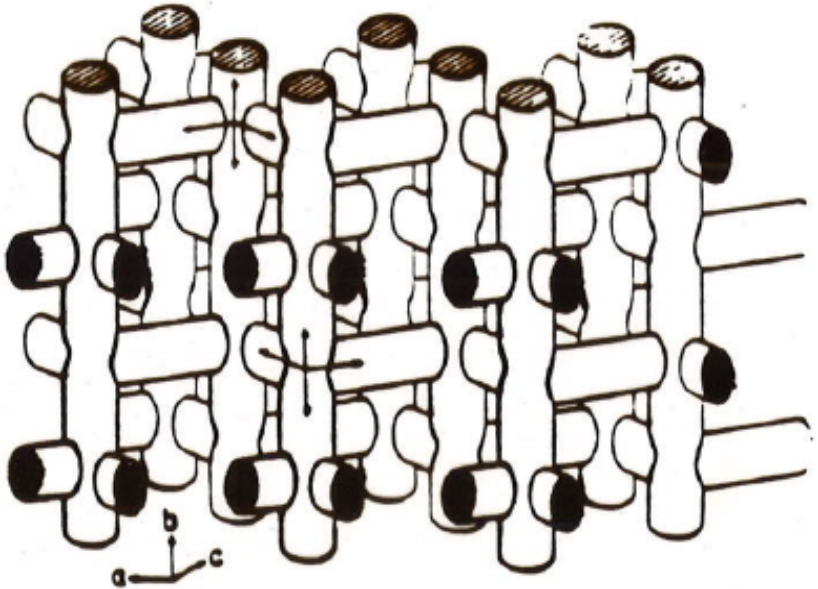
diffusion coefficient of Xe increases with increasing loading of the zeolite

DIFFUSION

- Exchange inside ↔ outside

(Xe in silicalite)





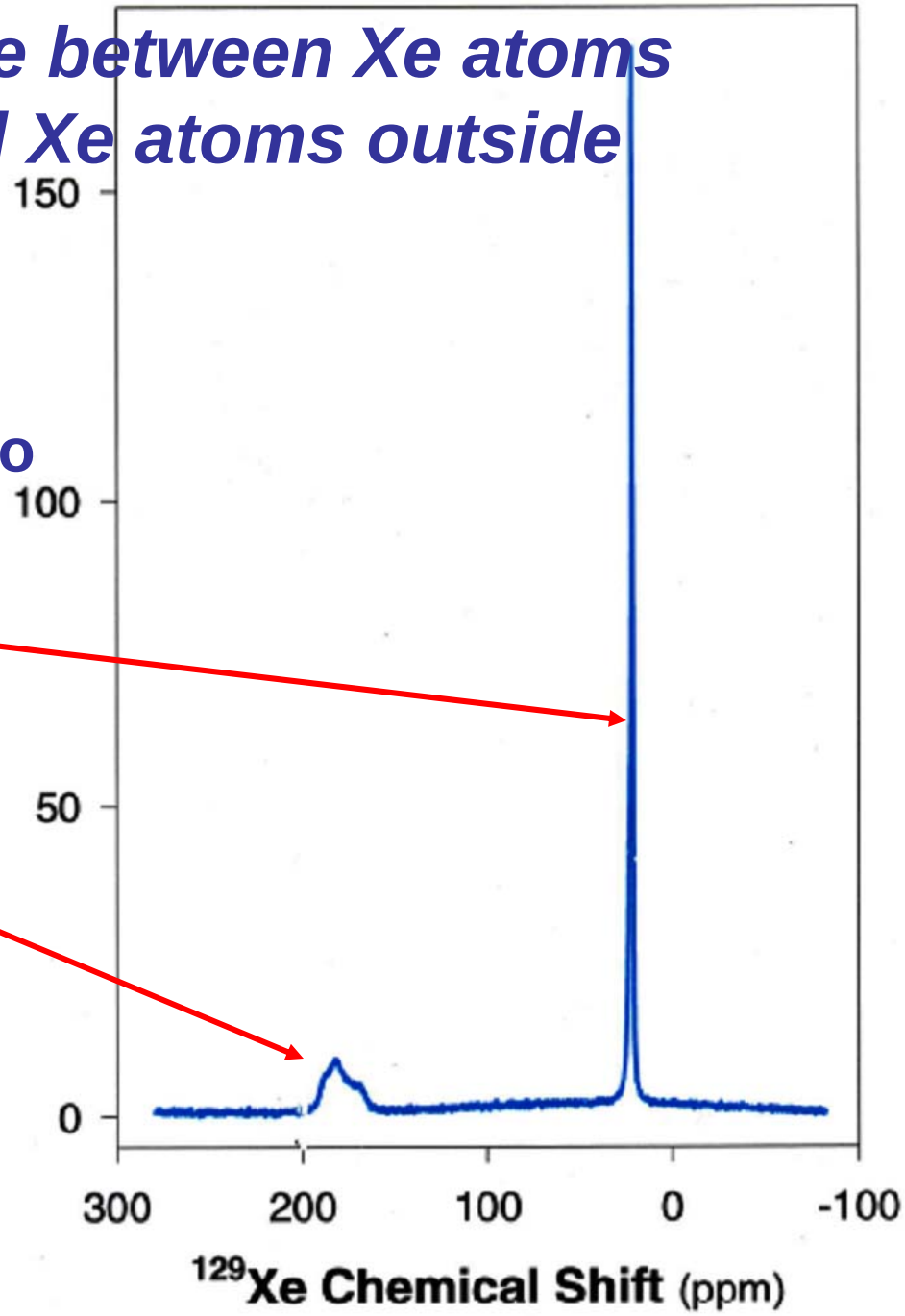
How fast is the exchange between Xe atoms inside the crystallite and Xe atoms outside the crystallite?

It depends on

- **size of crystallites**
- **crystallite packing**
- **overhead Xe pressure**
- **temperature**

How fast is the exchange between Xe atoms inside the crystallite and Xe atoms outside the crystallite?

By using larger crystals we effectively have only two Xe reservoirs:
outside **the crystallite and** ***inside*** **the crystallite.**



How fast is the exchange between Xe atoms inside the crystallite and Xe atoms outside the crystallite?

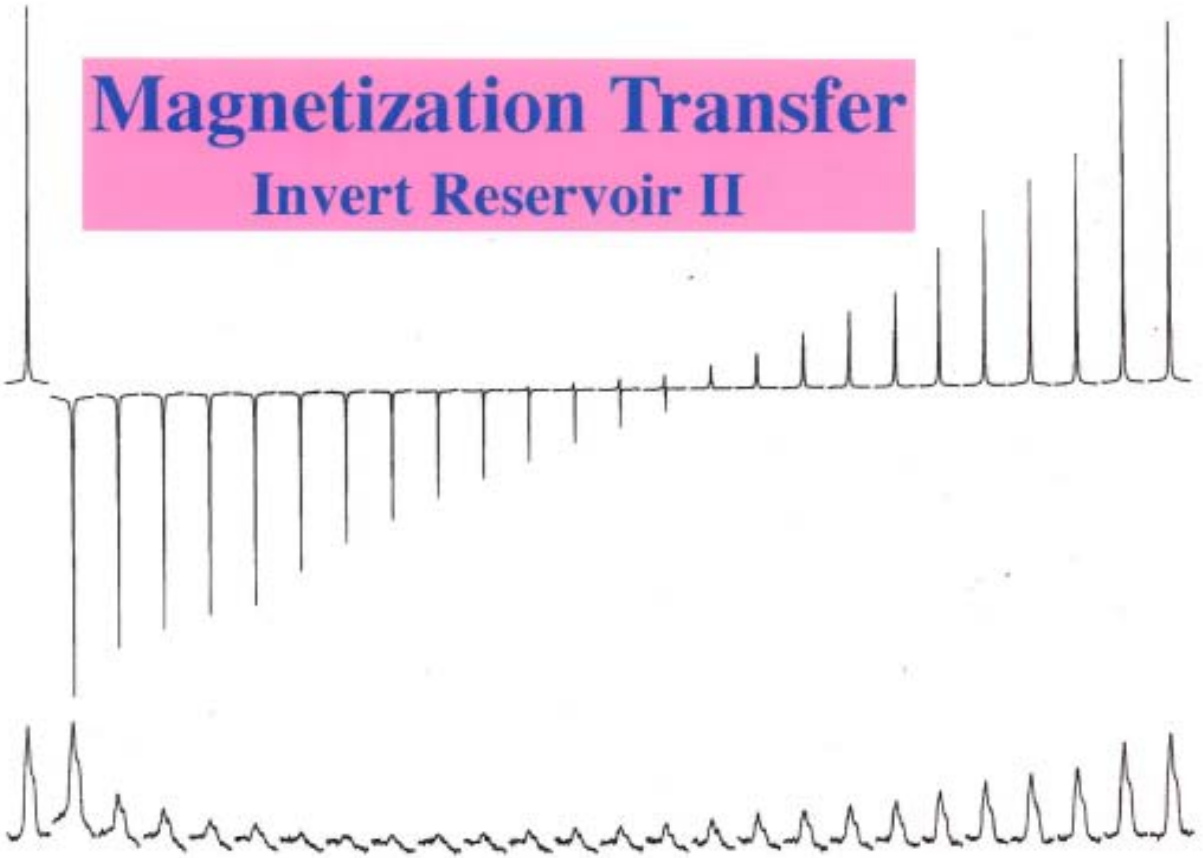
By using larger crystals we effectively have only two Xe reservoirs: *inside* the crystallite and *outside* the crystallite. We have eliminated the dependence on the size of crystallites and the crystallite packing.

Now measure the rate constants for the processes:

$$\text{Xe(adsorbed)} \rightarrow \text{Xe(bulk)}$$
$$\text{Xe(adsorbed)} \leftarrow \text{Xe(bulk)}$$

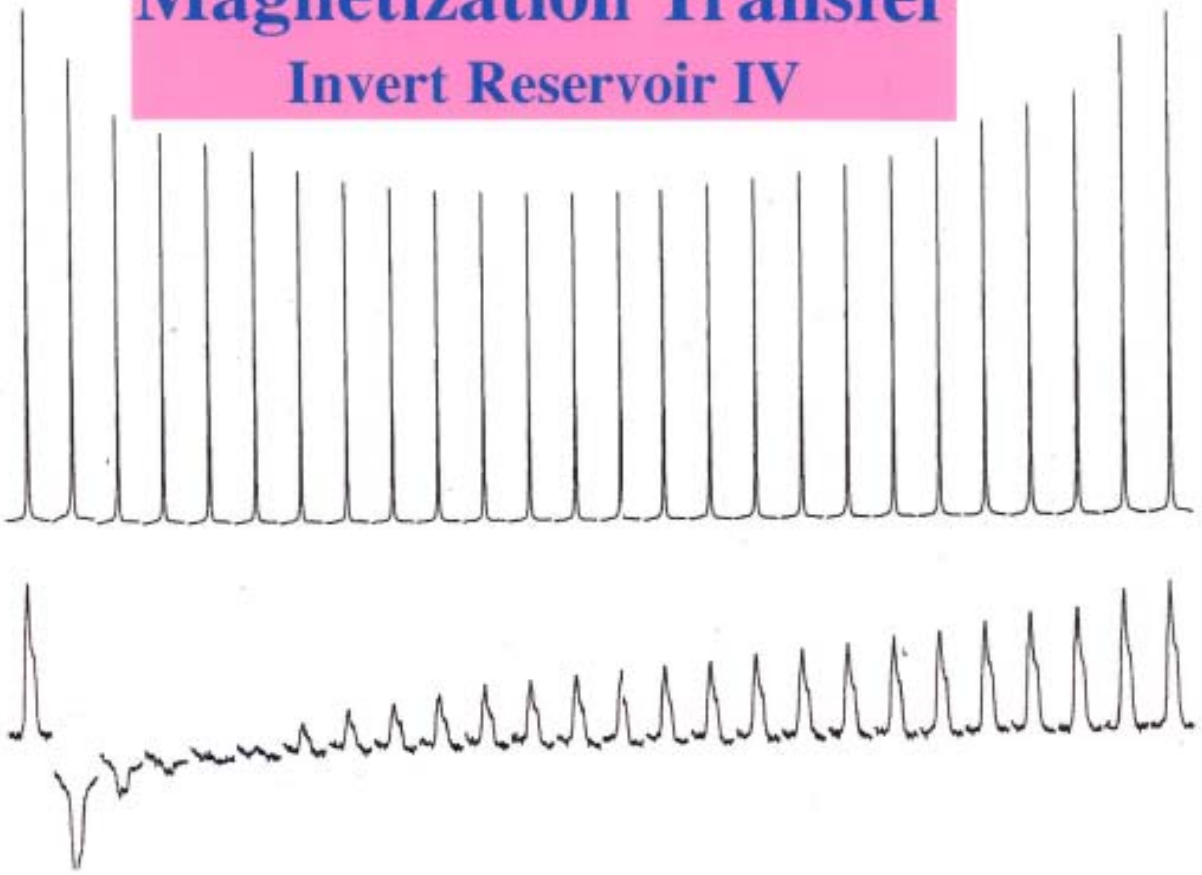
Magnetization Transfer

Invert Reservoir II



Magnetization Transfer

Invert Reservoir IV



How fast is the exchange between Xe atoms inside the crystallite and Xe atoms outside the crystallite?

Analysis of these magnetization transfer curves gives the rate constants for the exchange processes at 300 K in large crystals of silicalite at full loading of Xe:

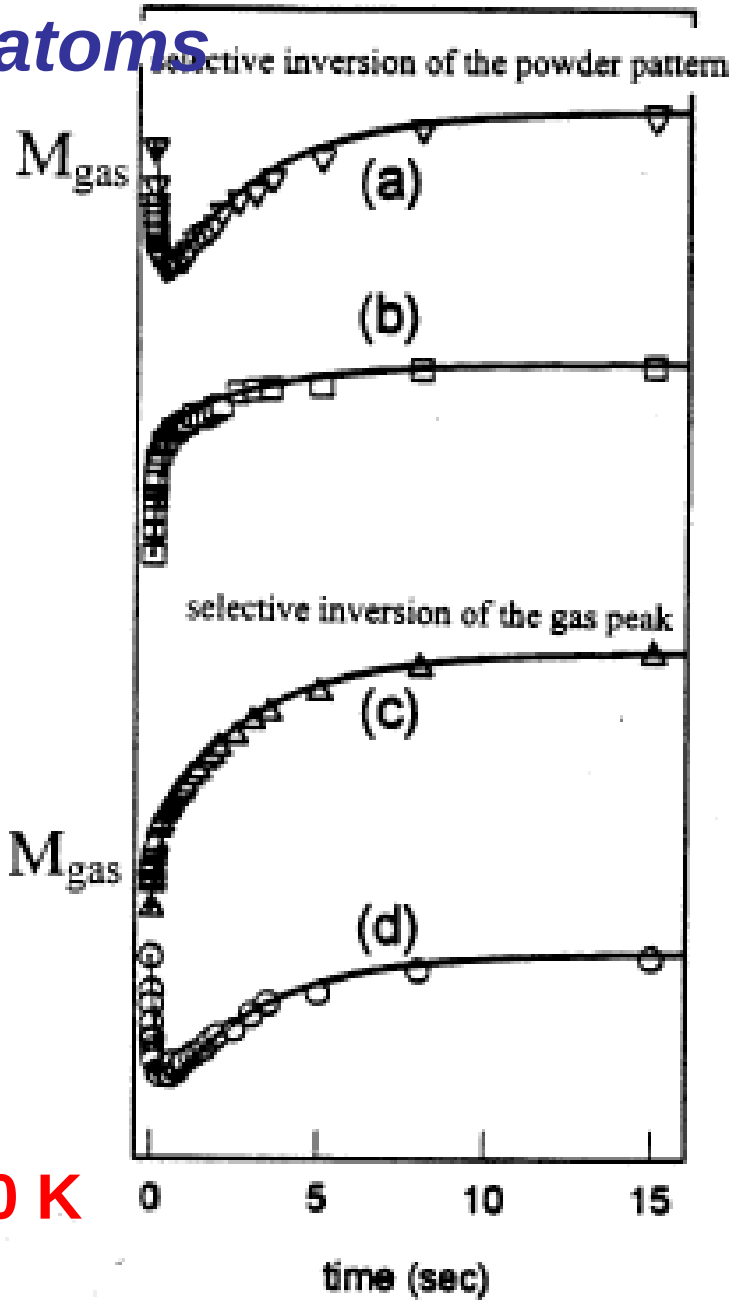
$k = 3.0\ s^{-1}$

Xe(adsorbed) → Xe(bulk)

Xe(adsorbed) ← Xe(bulk)

$k = 1.39\ s^{-1}$

The ratio of the rate constants gives the quilibrium constant, i.e., the adsorption isotherm at 300 K



CONCLUSIONS

We obtain detailed distributions

- **We obtain from intensities directly the distribution of Xe atoms among the cages.**

- **The Xe_n chemical shift in a mixture of Xe and Ar (or CH_4) provides a direct measure of the average number of Ar atoms (or CH_4 molecules) in the same cage as *n* Xe atoms, for a given loading or composition.**

- **The magnitude and the temperature dependence of the chemical shift of Xe_1 contains information about the one-body distribution function of a single Xe atom in the cage. The magnitude and the temperature dependence of the chemical shift difference between Xe_n and Xe_1 contains information about the pair distribution function of an Xe_n cluster.**

CONCLUSIONS

We have detailed information about slow diffusion

- **We can follow the diffusion of Xe atoms from inside the zeolite crystallite to outside the zeolite and obtain the average rate constants for the two processes, Xe(adsorbed) $\leftrightarrow$ Xe(bulk gas). The ratio of these rate constants is related to the adsorption isotherm.**

- **We can follow the cage-to-cage migration of Xe atoms within a crystallite, and obtain the individual rate constants. These provide a truly molecular level picture of the intracrystalline diffusion process. These rate constants reproduce the observed equilibrium distributions.**

CONCLUSIONS…

- **The INTERMOLECULAR CHEMICAL SHIFT makes the above experiments possible, including the experimental determination of the rate constants for cage-to-cage migration of Xe in NaA. Furthermore, the magnitudes of the chemical shifts provide detailed tests of any computer simulation.**

- **Two Monte Carlo simulation approaches to the equilibrium distribution of Xe atoms among the cavities of zeolite Na*A* (GCMC of adsorption and simulations using rate constants) lead to the same results, which agree with experiment.**

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Adsorption

A. Keith Jameson
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Diffusion

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