Recommended Features of a Good Research Statement

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(a) 5-part layout:
1. *Research theme and motivation* (what is the context of the work? why is it important? what part do I expect to carry out in this grand scheme?)
2. *Previous research accomplishments* (establishes your expertise and background, convinces the reader that you are capable of doing the work that follows, also established methods that you know and can apply)
3. *Future plans* (what will you do as a faculty member, 2-3 defined projects). In each project: why important (motivation for this project)? demonstrate your awareness of other work in the field; what will you do? research methodology you will use; what may be expected; focus on the contribution to scientific understanding; place the work in the big picture; state longer term goals. This should be the longest part of the Research Statement.
4. *Short punch line summary*: say what you propose to determine, how your previous experience equips you uniquely for doing this, what contributions to scientific understanding will result from it.
5. *A few bibliographic references*.

(b) Use of good layout and structure: use bold headings to let the reader catch the topics without reading the whole text

(c) Use of good graphics relieves tedium, spices up the research statement, makes it clearer and easier to understand the proposed work

(d) Use of words and sentence structure that key the reader into what you are leading up to, that is: what you will do? how you will do it? why it is important? what are the contributions to scientific understanding?

(e) The clearly stated research goals, the most compelling motivation, and the general approach you intend to take are in the first ½ page.

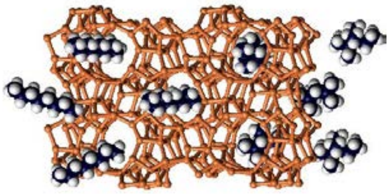
(f) The future plans are built on your prior experience but clearly stated as not direct extensions of previous work.

(g) Research plan is specific, but offers no superfluous details.

Note the recommended features in the following example of a Research Statement.

RESEARCH STATEMENT

THE SIGNIFICANCE AND CONTEXT OF THIS RESEARCH PROGRAM



The molecular level behavior of fluids in porous materials such as zeolites, activated carbons and porous glasses is critical in applications such as heterogeneous catalysis, adsorption separations and oil recovery technology. Perhaps the most fascinating class of heterogeneous catalysts are the zeolites. These materials are all surface, and both the acid sites in their frameworks and the metal ions in the pores are responsible for a huge variety of catalytic processes.

Moreover, the geometries - pore and void dimensions - of the zeolite structures strongly influence the selectivity of the catalysis - that is the ability of the catalytic process to produce a specific product in high yield rather than a range of products. Increasing selectivity as well as better yields at lower temperatures are among the strongest economic pressures in the field of catalysis. Zeolite micropores offer unique reaction fields for catalytic reactions based on narrow pores, a wide variety of channel structure, ion exchangeability and strong solid acid properties. As a negative effect, narrow pore and channels may suppress the diffusivity of reactant molecules and reduce the catalyst effectiveness factor. One example of a key question in an industrial context is, how do the intracrystalline unique reaction fields of zeolite influence HC-SCR, i.e., selective catalytic reduction of NO by hydrocarbons under extreme conditions, i.e. high space-velocity ratio and low content of reactants in exhausts? While the catalytic reaction between active metal atoms and reactants is well-known, the role and importance of the solid support, the zeolite that regulates the traffic of reactant molecules to access these metal atom clusters, and the traffic of product molecules that have to exhaust out is not completely understood. Despite the importance of answers to key questions of this type, the relationship of the structure of the porous material support to the key molecular processes is poorly understood. Zeolite diffusivity in the HC-SCR process is affected by two types of diffusion: *geometry-limited diffusion*, which is determined by the relative size of diffusing molecule and zeolite pore-opening, and *adsorption-controlled diffusion*, which is determined by the strong interaction between diffusing molecule and intracrystalline cation. The key fundamental question here is how the porous material microstructure determines the thermodynamic behavior of confined fluids. What is missing is an approach that can provide molecular level understanding of adsorption, including competitive adsorption, how adsorption isotherms are related to the material microstructure, and understanding of various types of diffusion processes depending on the channel structures and the fluid pressures. In our work we will develop an entirely new experimental-theoretical approach to achieve this fundamental level of understanding.

THE APPROACH

I plan to focus on three important questions about molecules in porous solids:(1) what is the equilibrium distribution of molecules and what factors determine this distribution? (2) what factors determine the diffusion behavior of the molecules that give rise to this equilibrium distribution? (3) how does the presence of another type of molecule affect these two? To illustrate how these questions will be answered in my research, let us consider the many facets included in the first key question. (i) What factors determine how molecules distributed between the bulk phase and the adsorbed phase (adsorption isotherm)? (ii) How are the molecules in the adsorbed phase distributed among the pores of the solid, i.e., for a given overhead pressure of bulk fluid, what fraction of the pores in the solid phase have three adsorbed molecules? (iii) How are the molecules distributed within the pore, i.e., what is the one-body distribution function for a molecule in a pore? What is the pair distribution function, i.e., what is the probability of finding another molecule within a distance of x Angstroms from a molecule? (iv) what is the distribution of the second type of molecule among the pores of the solid containing a first type of molecule, i.e., if a pore contains 3 molecules of the first type, what is the average number of molecules of the second type that are in the same pore, for a given temperature, total pressure, and molar composition of the bulk phase in equilibrium with the adsorbed phase?

The philosophy of my approach is the following: Choose model systems such that rigorous and unique interpretation of the experimental observations can yield results that are sufficiently detailed so that comparisons with first principles calculations and statistical mechanical simulations can yield molecular level understanding. I will explore these questions with three model physical systems of known structure and composition: (system A) Xe and other molecules in a specific crystalline zeolite system where distributions of molecules among the cavities can be directly observed in the spectrum, (system B) Xe and other molecules in specific zeolite systems that have one-dimensional channels, and (system C) Xe and other molecules in open network zeolites. These systems are particularly appropriate because (i) the structures of the porous materials are well-defined by X-ray and neutron diffraction, and (ii) the response of Xe to its electronic environment is particularly large and highly discriminating. I plan to determine the distributions of Xe between pores and bulk gas (adsorption isotherm) and distribution among the cavities in (system A) zeolite NaA, where direct measurement of the distributions is possible, then carry out adsorption and Xe measurements in systems where the latter distributions are not directly measurable for freely diffusing Xe atoms experiencing the entire channel (system B)or open networks (system C), but where the anisotropic environment will provide additional information. The proposed research builds upon my post-doctoral work on Xe NMR spectroscopy, particularly the density and temperature-dependent NMR chemical shifts of Xe in the presence of other simple molecules in gas mixtures. Together with my understanding of the fundamental nature of the NMR chemical shift based on my Ph.D. dissertation, and statistical mechanical averaging by Monte Carlo techniques, the detailed knowledge learned from the studies on systems A and systems B will lead us to understand how to correctly interpret the observations we will make in the more general porous systems of type C. Below I briefly describe my previous work which can provide confidence that I have sufficient expertise in key steps of development of the projects described under future plans, so that they can be carried out successfully by myself as an independent investigator.

RESEARCH ACCOMPLISHMENTS

My research is driven by my attempt to couple experimental measurements on well-characterized model systems with an understanding at the molecular level brought about by computations that include quantum mechanical studies of the electronic aspects of the observable and dynamic averaging of the electronic quantity by statistical mechanical methods such as Monte Carlo or molecular dynamics on an appropriate version of the experimental physical system. Reproducing the experimental results on the chosen model systems provides the molecular level understanding which can illuminate the observations that can be made in future on more complex real systems of practical importance.

High-resolution NMR Experiments:

Gas phase NMR measurements of intermolecular effects on nuclear shielding of Xe in mixtures of Xe with other gases.

In this work, the Xe NMR chemical shifts which arise from intermolecular Xe-Xe interactions and Xe-other interactions were measured as a function of temperature and the densities of Xe and other gas in sealed samples. In pure Xe gas, the intermolecular chemical shift is the average of the Xe-Xe response function (a mathematical function of the Xe-Xe distance) weighted by the probability of finding Xe at these distances, which in turn depends on the intermolecular interaction energy.

Temperature dependence of the ^{19}F NMR chemical shifts in F_2 gas in the zero-pressure limit.

In this work, the temperature dependence of the ^{19}F chemical shift in the gas phase is measured in the limit of zero pressure. The ^{19}F response function (a mathematical function of the F-F distance) is weighted by the probability of finding the molecule with these bond distances, which in turn depend on the anharmonic vibrational wavefunction. Higher vibrational states correspond to longer average bond lengths

Theoretical Computations:

Ab initio calculations of the Xe nuclear shielding in the Xe_2 dimer, Xe_3

In this work, the Xe response function for various configurations of 2 or 3 Xe atoms has been calculated. The magnitude of Xe chemical shifts that are observed in the gas phase and also for Xe in confined spaces arise from the nature of the averaging of these functions under various conditions.

Vibrational averaging of the ^{19}F shielding in HF and F_2 molecule.

In this work, the observed temperature dependence of the ^{19}F NMR chemical shift and the ^{19}F chemical shift arising from D/H substitution are interpreted using the same theoretical framework.

FUTURE PLANS

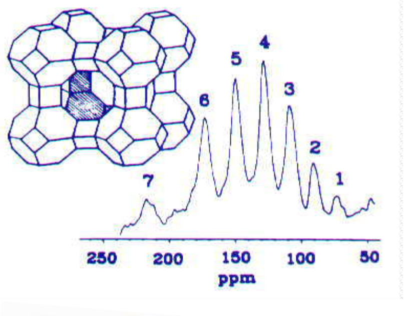
The knowledge gained from the studies on physical model systems chosen here (systems A, B, C), with increasing degree of averaging of NMR response can lead to general understanding in more complex solid nanoporous materials. For system type A (zeolite NaA) we can measure directly the adsorption isotherm, and the fraction of cages containing exactly n Xe atoms, for n = 1, 2, ..., 8. Therefore, for systems of type A only, we can answer questions such as: At a given overhead Xe pressure and temperature, what is the average occupancy of the cavities? For a given occupancy such as $\langle n \rangle = 4.25$, what fraction of cavities have exactly 1 Xe? what fraction have exactly 6 Xe, etc. How are the 6 Xe atoms distributed within the cavity: sticking close to the walls like a film, or in the center like a snowball? Because we can get direct measure of adsorption isotherm and of distributions among cavities from the spectrum, the results of grand canonical statistical averaging simulations can be directly tested against our experiments. When we have agreement with the detailed distributions and the individually observed Xe chemical shifts as a function of pressure and temperature, then the distribution of the 6 Xe atoms within a cavity which is obtained in the same statistical averaging can be believable. In the general case, only an average peak is observed as a function of overhead pressure and temperature, but the underlying distributions that give rise to this peak are those that we have learned from studying systems of type A, therefore we can interpret the experiments with confidence.

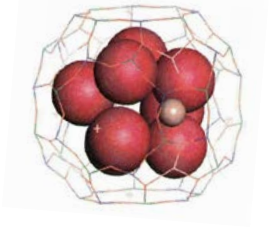
Project 1 Characterization of the distribution of the sorbate species among the pores of the zeolite under various conditions of temperature and pressure

These are the key experiments which will provide the fundamental basis for interpreting the more general case of adsorption and diffusion in porous solids

(a) Study adsorption of Xe in zeolite NaA

M. G. Samant, L. C. deMenorval, R. A. Dalla Betta, and M. Boudart, J. Phys. Chem. 92, 3937 (1988) forced Xe into the cages of zeolite NaA by using high temperature and pressure (40 bar and 525 K and reported 5 peaks in the Xe spectrum. From my previous work on Xe gas density dependence, this indicates that a reasonable explanation for the multiple peaks observed is that Xe atoms in a cavity have chemical shifts which are determined by the number of other Xe atoms in the cavity and that the peaks arise from only those cavities containing n Xe atoms, with n being 1, 2, 3, 4, 5. I propose to prepare Xe in NaA sealed samples in which the moles of Xe and NaA crystals are known.





My preliminary work gives the spectrum shown in the figure. The Xe peak in the overhead gas will report on the Xe density. The fractions of cavities containing n Xe atoms will be measured from the relative areas under each signal. The average number of Xe per cavity will be determined from the assignments of the peaks and the relative peak areas. I plan to carry out temperature dependent studies of these spectra. The distribution of the Xe atoms among the cavities and the average occupancy will change with temperature. Because the peaks are assigned, the temperature dependence of the chemical shift of each Xe_n can be individually determined. This in turn is dependent on the distribution of the n Xe atoms within the cavity.

In parallel, I will use the known x-ray diffraction and neutron diffraction structure of zeolite NaA to model the expected Xe chemical shifts for two Xe atoms in an alpha cage of NaA by using the results of my previous ab initio work on Xe_2 dimer.

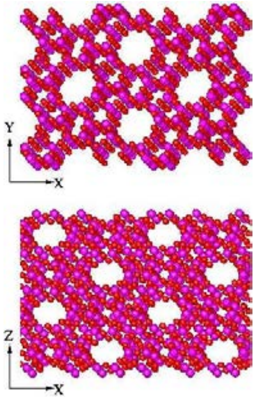
Grand canonical Monte Carlo simulations of molecules in zeolites has been carried out by G. B. Woods and J. S. Rowlinson, J. Chem. Soc. Faraday Trans. 2 85,765 (1989). The distributions of Xe atoms within the zeolite afforded by the grand canonical simulations will provide the instantaneous Xe chemical shifts for each Xe in the system. Those in the cavity with n Xe atoms will contribute to the average chemical shift for the Xe_n peak. Thereby, the GCMC simulations will provide the prediction of the entire Xe spectrum: where the peaks are, the relative intensity of each peak, the position of the overhead gas peak, each spectrum as a function of temperature for a given sample with fixed number of moles of zeolite and fixed number of moles of Xe.

The simulation results should provide a firm basis for assignment of the observed peaks. If indeed the peaks observed by Samant et al. correspond to one, two, three, etc. Xe atoms within a cage, we may consider as a first approximation that the Xe_1 peak is a measure of the Xe NMR response arising from interaction with the cage atoms. The simulations will discover whether the cage gives the same contribution to the chemical shift in every case. The simulations will also find how large is the contribution arising from Xe-Xe interactions in Xe_2, Xe_3, Xe_4, Xe_5, etc. which can be compared with the experimental incremental shifts from peak to peak.

(b) Interpret the temperature and pressure dependence of the adsorption of Xe in zeolite NaA

The measured temperature dependence of the spectra will provide a rigorous check of the simulations, since no parameters are changed in comparing the results from one temperature to another, with all the detail as described above.

(c) Generalize lessons learned from the model system to more general open network systems with various morphology



I propose to measure the adsorption of Xe in open network zeolites such as NaY, which have cavities with larger openings than in NaA thereby permitting the Xe to freely explore a large number of cavities in the NMR time scale. The single peak observed is an average over many cavities with various occupancies. From the understanding gained in the above studies, a prediction of the average chemical shift as a function of temperature and overhead Xe pressure can be had, given the known crystalline structure of the chosen zeolites. Comparison of predictions from simulations with our experiments in various open network crystalline zeolites will permit general interpretation of adsorption of Xe in these types of porous solids. Changing the morphology in the simulation box can yield predictions that will permit interpretation of Xe spectra with changing morphology.

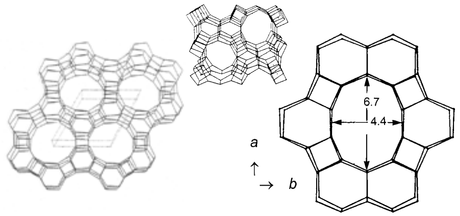
Project 2 Studies of the anisotropy of the average tensor of Xe in cages and one-dimensional channels in order to develop a new tool for detailed understanding of intra-crystalline molecular diffusion of various types.

It may be possible to measure the anisotropy of the chemical shift tensor in cages and one-dimensional channels. If we consider the Xe running along a channel, unable to move in all three directions isotropically, then the NMR spectrum will reflect the component of the tensor along the magnetic field direction, for a given orientation of the channel axis with respect to the magnetic field. For a large number of crystals, the distribution of orientations will provide the relative intensity at each tensor component, thereby tracing out what is called a powder pattern, showing as singularities the two or three unique tensor components. If the Xe is unable to exchange between channels at different orientations, i.e., unable to sample several crystallites, then the anisotropy of the chemical shift tensor may be observed. This more detailed information about the Xe chemical shift will be determined by the structure of the channel, the diameter of the channel, the ellipticity of its cross-section, etc. By studying the line shapes, it may be possible to develop a new tool for studying nanochannels in sold materials. Again, the approach is to do experimental and theoretical studies in crystalline systems with well-known structures and then use the gained understanding to make predictions for the general case of more complex materials.
The standard method for studying diffusion of molecules through porous materials is by pulsed field gradient (pfg) NMR methods. When the crystals are big, then the measurements can be dominated by

diffusion within the crystal. When the crystals are small, then diffusion between crystallites can dominate the measured diffusion. Therefore, pfg studies do not necessarily give correct diffusivities. I intend to measure intra-crystalline diffusion by a completely new way.

(a) Observe the occupancies of pores and channels as a function of temperature and pressure for uniform cages and channels

Ripmeester has observed powder pattern line shapes which seemed to indicate that Xe atoms trapped inside cages can report on the symmetry of the cage structure. Ripmeester, J. A.; Ratcliffe, C. I.; Tse, J. S. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3731.



SSZ-24

ALPO4-11

I propose to study the Xe NMR spectra for sealed samples of Xe in crystalline zeolite SSZ-24 which has a one-dimensional channel structure and then to consider other systems with channels having elliptical cross sections such as ALPO4-11. Again, studies at different mole ratios of Xe to zeolite and variable temperature will be done for a comprehensive comparison with simulations.

(b) Molecular simulations toward developing the anisotropy tool

As a completely new approach we propose a dimer tensor model. In other words, a Xe atom in a particular position in a channel, can be thought of as having the instantaneous Xe chemical shift tensor which is a sum of contributions from all the Xe-wall atom pairs. The Xe-Ar chemical shift tensor and the Xe-Ne chemical shift tensor is calculated as a function of internuclear distance. An SSZ-24 nanochannel exposes Xe to the O atoms which form the silicate units. If I replace the channel atoms with Ar atoms (or Ne atoms) in the simulations, then I can use the sum of calculated dimer tensors Xe-Ar over all Xe-Ar directions and distances to find the instantaneous Xe chemical shift tensor. Considering the distribution of orientations will yield the line shapes. This permits not only the development of the anisotropy tool, but also investigation of the effect of the electronic structure of the wall atoms (Ar or Ne) on the observed line shape.

(c) Measure and interpret cavity-to-cavity hopping activated diffusion process in networked channels

One of the advantages of the individually observed well-separated peaks for Xe_n in zeolite NaA is that it will be possible to selectively invert the magnetization of one peak at a time and observe the decay/build-up of intensity of the target peak and all the other peaks as a function of time. This is known as a magnetization transfer experiment. By observing and analyzing the time-evolution curves (for all the possible experiments using different samples with various occupancies) I can find the individual rate constants for Xe leaving a cage containing 4Xe by jumping to an adjacent cage with 6 Xe atoms, for example. The combination of all these rate constants provide the diffusion coefficient for intra-crystalline diffusion, and should lead to the correct equilibrium distribution of Xe among the cages that is revealed by the relative peak intensities. This will be a more detailed observation of diffusion than has ever been done.

(d) Generate rules of thumb to characterize various types of diffusion based on relative sizes of sorbate molecular species relative to pore sizes and shapes and relate these to enthalpies of adsorption.

Molecular dynamics simulations studies using idealized pores of variable diameters can be used to form general rules about diffusion. Various parameters can be used to explore, effects of enthalpies of adsorption can be explored by using Ne or Ar atoms as constituent atoms of the zeolite structure and using appropriate potential parameters for the Xe-Ar or Xe-Ne interactions. Various known zeolite structures may be used in the simulations to explore factors such as relative sizes of sorbate and pore openings.

Project 3 Temperature and pressure studies of competitive adsorption of a mixture of gases in open network zeolites

For heterogeneous catalysis applications and for separations, reactants and products coexist within the porous solid catalyst so it is important to understand competitive adsorption.

(a) Competitive adsorption of Xe and CH_4 in zeolite NaA

The Xe in zeolite NaA system provides a unique opportunity to study competitive adsorption at the most fundamental level. Because the individual peaks identify those n Xe atoms cohabiting a cage, the relative intensity of this peak permits the determination of the distribution of the first component, Xe. Then, the distribution of the second component into the cavities occupied by n Xe atoms is reflected by the incremental chemical shift of the Xe_n peak in the mixture relative to the Xe_n peak in the pure xenon sample. I propose to investigate competitive adsorption in this fundamental way: At a given temperature, for a given overall pressure of the bulk gas mixture and the mole fractions of the components in the gas phase, the average number of CH_4 molecules in the same cage as n Xe atoms is directly measurable from this incremental shift. We know this from the understanding of the dependence of the intermolecular chemical shift on the number of close neighbor atoms. Grand canonical Monte Carlo simulations will permit the determination of the average number of other molecules visiting the n Xe atoms in the cage. Comparison of simulations against the NMR measurements will verify this proposition. M. W. Maddox and J. S. Rowlinson, J. Chem. Soc., Faraday Trans. **9**, 3619 (1993) provides an example of GCMC of gas mixtures in open framework zeolites. We modify our pure Xe simulations code for Xe in zeolite NaA accordingly.

A characterization of competitive adsorption at this level of detail has never been possible before. It will be interesting to compare trends in binary mixture cage occupancies as a function bulk gas composition and temperature for various other gases such as CO_2, Ar, N_2, etc. in addition to CH_4. How will the number of Xe atoms in a cage affect the average number of the other molecules in it? How will this change with mole fraction in the overhead gas? So many questions can be investigated, now that we have the possibility of direct measurements of distributions of both components.

As in the other projects, combining simulations with experiments in well chosen systems permit more detailed answers than is otherwise possible.

(b) Competitive adsorption of Xe and CH_4 in open network zeolites

The physical insight and trends discovered in the above experiments will provide understanding in the extension of our mixture studies from zeolite NaA to open network zeolites where only a fully averaged peak is observed, and GCMC simulations will be verified against experiments. My previous studies in mixtures of gases provide the composition of the bulk gas from the chemical shift of the bulk gas peak.

(c) Generalize lessons learned in model system studies to competitive adsorption of a mixture of gases in open network zeolites as a function of temperature, pressure and composition of fluid phase.

By doing simulations in model systems such as zeolite architectures composed of Ne or Ar atoms, we can explore the general trends one would find for competitive adsorption in open network zeolites.

SUMMARY

In this research program, we expect to provide a fundamental characterization of adsorption, competitive adsorption, and intra-crystalline diffusion using the exquisitely sensitive Xe NMR chemical shift in specifically chosen architectural types of nanoporous solid systems. We will do experiments in systems specifically chosen to provide experimental information of unprecedented detail so that grand canonical Monte Carlo simulations can be adequately tested. Having passed the test in type A systems, simulations and experiments will provide physical insight in those more complex systems with open networks or different morphology where only highly averaged data can be obtained.