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Computational Chemistry in Argonne’s Reactor Analysis Division

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ABSTRACT

Roughly 3 years ago work on Argonne's Integral Fast Reactor ("IFR") was terminated and at that time, ANL funding was redirected to a number of alternative programs. One such alternative was waste management and, since disposal of spent fuel from ANL's EBR-II reactor presents some special problems, this seemed an appropriate area for ANL work. Methods for the treatment and disposal of spent fuel (particularly from EBR-II but also from other sources) are now under very active investigation at ANL. The very large waste form development program is mainly experimental at this point, but within the Reactor Analysis ("RA") Division a small computational chemistry program is underway, designed to supplement the experimental program. One of the most popular proposals for the treatment of much of our high-level wastes is vitrification. As noted below, this approach has serious drawbacks for EBR-II spent fuel. ANL has proposed, instead, that spent fuel first be pretreated by a special metallurgical process which produces, as waste, chloride salts of the various fission products; these salts would then be adsorbed in zeolite A, which is subsequently bonded with glass to produce a waste form suitable for disposal. So far it has been the main mission of RA's computational chemistry program to study the process by which leaching occurs when the glass-bonded zeolite waste form is exposed to water. It is the purpose of this paper to describe RA's computational chemistry program, to discuss the computational techniques involved in such a program, and in general to familiarize the M. and C. Division with a computational area which is probably unfamiliar to most of its member.

I. BACKGROUND

The role of Argonne's Reactor Analysis ("RA") Division has been, historically, the development of nuclear reactors (especially fast reactors) and of neutronics computational methods. Needless to say, DOE funds for such activities have been very scarce for some time. When Argonne's IFR program terminated, the laboratory's focus shifted from fast reactor development to other fields, including the problems of spent fuel disposal which now consume a lot of DOE's money and attention. One of the most popular proposals for high-level waste disposal is encasement of the waste in glass, deposition of the vitrified waste in steel containers and, finally, disposal of these containers in a permanent repository. For Argonne's spent fuel this disposal plan has some special problems. Fuel for ANL's fast reactor, EBR-II, contains sodium which must be removed before disposal, i.e. the fuel must be processed in one way or another before it can be permanently stored. ANL has proposed that the necessary preprocessing be accomplished by electrometallurgical equipment which is very much the same as that developed for reprocessing IFR fuel. But the IFR electorefiner produces, in one of its output streams, chloride salts of the fission products in the fuel, along with chloride salts of the potassium and lithium used in the electrometallurgical process itself. Unfortunately chloride ions can't be contained very well in glass. As an alternative ANL has proposed that the chloride salts be injected into zeolite A, which would then be compacted into a zeolite-glass composite at fairly high temperature and pressure. Here we won't go into complications one encounters in the process of compaction, or discuss other alternatives also now under consideration. Suffice it to say that zeolite A has three attractive features as an immobilization matrix for ANL spent fuel. First, it appears to be at least as leach-resistant as glass. Secondly, it tends (by ion exchange) to adsorb fission products selectively from the output stream of the electrometallurgical preprocessor and, finally, it contains a lot of vacant space accessible for waste-storage. Most of ANL's work on this sort of composite waste form has, so far, been experimental. There is, in fact, a lot of experimental work that has to be done before a final waste form can be deemed acceptable, and chosen as ANL's waste form candidate. But it isn't possible to extrapolate from results of short-term experiments, to reliable conclusions about the waste form's long-term behavior, without a good understanding of its internal microscopic processes. Such an understanding can only be attained through a blending of experiment, computation and theoretical analysis. In view of RA's long experience in the invention and perfection of computational and analytic methods, it was concluded that it would be appropriate for us to get involved in the theoretical and computational aspects of waste form development, via the methods of computational chemistry.
But it's not our purpose here to discuss breakthroughs in computational chemistry. What we want to do is to describe the problems, methods and tools one encounters in what is, for most of us in the M. and C. Division, a new and unfamiliar field. In the development of a glass-zeolite waste form there is no shortage of difficult, interesting problems. Two of the most important problems are easy to state (though not nearly as easy to solve) namely, the problem of getting the salt wastes into the zeolite and, then of preventing it from getting back out. For various reasons we choose to start with the second, i.e. to try to understand leaching from zeolite A.

Zeolite A is a synthetic crystalline material with a cubic unit cell about 24.6 Angstroms on a side. The "frame" of the crystal is a structure composed of 96 aluminums, 96 silicons and 384 oxygens, with each Al and each Si located at the center of a tetrahedron of O's. Because the valence of aluminum is only three, (i.e. not four like the valence of silicon) the frame has one unit of negative charge for each Al. This charge on the frame must be compensated by the charges of positive ions ("cations") which are built into the crystal when it is constructed, or ions later exchanged for the original cations. The zeolite is microporous in that it contains vacancies ("cages") large enough to hold several small atoms or ions, or even a small molecule. These cages are of two types, both roughly spherical, with dimensions of 8.8 and 12.3 Angstroms respectively. The larger ("alpha") cage is bounded by a surface made up of "4-rings", "6-rings" and "8-rings", i.e. polygons of 4, 6 and 8 sides. At each corner of these polygons is an Al or Si, with Al's and Si's alternating around the ring. Roughly at the center of each side is an O. The smaller ("beta") cages are bounded by 6-rings and 4-rings, both smaller than the 8-rings just by virtue of the fact that they have fewer sides. Beta cages adjoin alpha cages, which are also directly connected to other alpha cages via 8-rings. In addition beta and alpha cages are interconnected by smaller, cubical, cages bounded by 4-rings. These cubical cages can contain small ions, but are usually empty. Fission-product ions are injected into the zeolite by ion exchange into zeolite preloaded with LiCl and KCl. This ion exchange process is carried out at fairly high temperatures, ~700 degrees K, at which the ions are relatively mobile within the crystal lattice. As the loaded zeolite cools the ions become less mobile until, at about room temperature, they are effectively trapped in the zeolite cages. The trapping is due to two different effects. It is partly steric: i.e. partly due to the limited size of the openings through which the ions would have to move. It is also partly electrical, in that some of the ions are very tightly trapped in deep electrostatic potential wells.

Unfortunately the trapping isn't perfect and the ions aren't totally immobilized. They do leach from the zeolite when it is immersed in water. The leaching mechanism seems to be different from the leaching mechanism in glass but the leach-rates in several-day leach tests from both are roughly the same, roughly a fraction of a gram per day per square meter of outer surface.

Leaching in glass is largely due to the corrosion of the glass surface by the surrounding water. In water the exposed glass surface turns to a kind of clay which no longer can confine the adsorbed spent fuel. Mechanisms for leaching in zeolite A have not yet been clearly identified but, to some large extent, in this case leaching seems to be due to the diffusion of ions to the surface of the crystal, induced primarily by concentration gradients. As we'll point out below, however, diffusion along concentration gradients can't be the whole story.

II. LEACHING FROM A MACROSCOPIC POINT OF VIEW

We will assume here that leaching is, basically, a diffusive process, i.e. that ions diffuse through the zeolite-glass log and, on reaching its surface, are removed by the surrounding water. There is evidence, though perhaps not conclusive evidence, that this is true. Ions left to diffuse through an infinite glass-zeolite composite would diffuse at different rates, governed by their sizes and charges, and conceivably by chemical properties; but they must leach from the log in such a way as to leave it almost charge-neutral. It's conceivable that the ions move in neutral pairs or clumps, but if they aren't bound chemically it's difficult to see why this would happen. And generally, in fact, the cations and anions considered here are very different in electronegativity, so that the bonds between them are largely electrical. Thus it seems plausible that the overall neutrality of the log will be maintained by small electric fields, established within it as ions of different species move slightly apart. It's easy to set up the equations which would govern such a process.

Define a diffusion current, \( I_D^i \), for ion species \( i \), such that

\[
I_D^i = -D^i \nabla (q^i c^i),
\]

where \( q^i \) is the charge on an ion of that species and \( c^i \) is its concentration. Further, suppose that ions of each species drift in the
electric field, $E$, with velocity $v^i_E$,

$$v^i_E = E \cdot q^i \cdot \mu^i_E,$$

(2)

where $\mu^i_E$ is the mobility of species $i$ in the field $E$. Then

$$I^i_E = q^i \cdot v^i_E \cdot c^i, \quad I^i = I^i_D + I^i_E,$$

(3)

$$q^i \cdot c^i = \nabla \cdot D^i \cdot \nabla (q^i \cdot c^i) + \nabla \cdot (v^i_E \cdot q^i \cdot c^i)$$

(4)

Further

$$\nabla \cdot E = \sum_i q^i \cdot c^i / e,$$

(5)

where $e$ is the dielectric constant of the zeolite glass composite, assumed here to be constant.

If we assume that a) there is no special obstacle to the escape of ions just inside the log, and b) that the concentration of ions vanishes in the water just outside the log then, at the surface of the log, the concentrations, $c^i$, vanish. It is possible, however, that some sort of structural irregularity at the surface does impede the penetration of ions, in which case

$$c^i + b^i \cdot \partial c^i / \partial \tau = 0$$

(6)

where $b^i$ is a constant to be determined. It should be noted that the above equations also seem applicable to charge-exchange.

Eqs.(4) can be differenced very much like standard advection equations in fluid dynamics, but do present some special difficulties. In fluid dynamics it's quite common to treat the advection velocity explicitly i.e., for example, to take it from the preceding timestep. Here that's not permissible. Eqs.(4) are very stiff, in that very small changes in the concentrations can give rise to enormous electric fields. Therefore in differencing these equations the electric field must be treated semi-implicitly. This means that, in Eq.(4), one must linearize the advection term (now quadratic in the concentrations) and then solve the resulting matrix-difference equations, now no longer tridiagonal; or one might, as well, use any standard stiff ODE solver to solve the time dependent matrix equation which results from space-differencing Eqs.(4) and (5).

III. LEACHING FROM A MICROSCOPIC POINT OF VIEW

The structure of a glass-zeolite log, which surely will be very complicated, is not known in any detail. In fact even the composition of such a log is uncertain, since it's possible that water would flow into it through a system of microcracks. Parameters in the macroscopic equations might be obtained, in some situations, by fitting to known leaching rates, but it should be understood that all the parameters really must be treated as time- and position-dependent. It seems clear that we are far from the point where we might predict the long-term behavior of the log as a whole, and that we must first focus on a small piece of the leaching problem. As a first goal we've chosen to learn as much as possible about ionic mobility in a perfect zeolite A lattice. It is hoped that, ultimately, insight gained through the study of ionic mobility, viewed at an atomistic level, will help us determine the parameters in the above macroscopic equations.

A. MD Structure Calculations

Before undertaking to study ionic mobility it is necessary to be satisfied that one can calculate the equilibrium structure of simple zeolite A crystals, containing only charge compensating cations and no adsorbed (or "occluded") salts. Many different tools are available for such calculations. The tool we find most useful is molecular dynamics ("MD")\(^4\). An MD calculation starts from a classical model of a system of particles, in which the particles interact through a simple set of hypothetical forces. These represent, for example, chemical bonding forces: repulsion of electron clouds as they get too close together; Van der Waals forces that attract electron clouds as they polarize each other, etc. The necessary classical interaction potentials are constructed by a combination of techniques. For example for a small molecule, one containing many features of a larger system, one may solve the quantum mechanical equations for the electron-cloud distribution (by "ab initio" calculations). Then features of this solution
may be incorporated into the classical model used to treat the larger system. In addition the strengths of hypothetical bonding potentials will often be adjusted so that vibration frequencies for the classical system will match observed infrared frequencies as closely as possible. One must then run many tests to see whether the model potentials are "transferrable", i.e. whether they give reasonable results for other systems containing the same chemical bonds. In our MD calculations we have simply adopted the potentials in the extensive literature on zeolites. Given classical potentials, it isn't difficult to construct the classical trajectories for all particles in the system, or for all those which are taken to be moveable in the simulation. This may be done by any stable and reasonably accurate scheme for the numerical integration of Newton's laws of motion. Of these one of the simplest and oldest is the "Verlet algorithm", accurate to second order in the timestep-size. This algorithm is still useful, though many other more accurate schemes are currently invoked in MD codes.

After the system is tracked, from some starting configuration through an initial transient period, the particles will, if all goes well, move as they do in the real system. In a crystal this means that all or most will oscillate around their equilibrium positions. The computed equilibrium locations can then be compared with particle locations reconstructed by X-Ray crystallography, or by other spectroscopic methods.

Our initial MD calculations were run without occluded ions. Here we won't discuss results of these initial computations in detail, except to say that they did give reasonably good agreement with experimentally determined structures in the literature. Some of their special features do, however, seem to merit further comment.

We find that, as is well known, the charge compensating cations tend to sit near the centers of 6- and 8- rings. But in a unit cell there aren't enough of these rings to accommodate all the charge-compensating cations. In fact 8 cations per unit cell are, essentially, homeless. Some of these wander in the neighborhood of the small cubic cages that connect beta cages. What is interesting about these homeless cations is that, in their wanderings, they are able to move from one cage to another while the rest of the cations sit in traps. Thus there is some possibility that these will prove to be the most mobile of the cations, those responsible for ionic diffusion. That such diffusion does occur is known experimentally. Results similar to ours have been found by other researchers in their MD calculations.

But it is clear from many MD computations, that ionic diffusion in zeolite A is much too slow a process to be observed directly via MD. Timesteps in MD calculations must be reasonably small compared to the time between ionic "collisions", where a collision is defined as any abrupt change in a particle's velocity. Thus the allowable timestep-size isn't likely to increase by large factors simply through an improvement in time-differencing. In our MD calculations, as in many others, this timestep size is about $10^{-15}$ seconds, and this limit on the timestep-size is certainly one of the most serious weaknesses in direct simulation techniques. Many macroscopic phenomena occur much too slowly to be observed in MD simulations. What alternative methods are available then?

B. Potential Surfaces

Useful insight into the location of migration paths can sometimes be gained from an examination of potential surfaces. Consider a case where LiCl and KCl salt clusters are occluded in zeolite. Suppose, for example, we want to know how difficult it would be for a chloride ion to traverse a 6- or 8-ring. In Figs. 1 and 2 we've plotted the potential of a chloride ion, as a function of position, in the force-field produced by all other particles of the system. The figures show potential surfaces across a 6-ring and an 8-ring. One finds that the minimum potential barrier, $V$, across a 6-ring is $-100 \text{kT}$ if the ring is empty, or $-1000 \text{kT}$ if it's occupied, while the barrier across an 8-ring is only $-10 \text{kT}$. Since the probability that a particle will cross a barrier is proportional to $\exp(-V/kT)$, it will be seen that 6-rings are nearly impenetrable for chloride ions, while 8-rings can be crossed much more easily.

The relative immobility of chloride ions has been observed in MD calculations, at 700 degrees K, in configurations including occluded KCl. One finds that, if the KCl is placed initially in beta cages, then the K⁺ ions will redistribute themselves among all cages, while the Cl⁻ ions will remain in the beta cages where they were placed. Correspondingly if the KCl is placed in alpha cages the potassium ions will redistribute themselves while the chloride ions will not.

From all that has been said one can expect that few chloride ions will get into beta cages when the zeolite is loaded, and that most will go into alpha cages. By the same arguments one is led conclude that containment in sodalite should be much more
effective than in zeolite since sodalite is made up exclusively of beta cages; as noted earlier, the surface of a beta cage consists only of six-rings and the much smaller 4-rings.

Are all these conclusions correct? Unfortunately, at this point the relevant experimental information is inconclusive. But in any case what one can learn just from an examination of potential surfaces is very limited. Implicitly it has been assumed above that, as a chloride ion moves across a ring, all other ions are stationary. But it may be more likely that an ion will penetrate a ring as a result of a rare accidental combination of the motions of several ions. Further, the factor \( \exp(-\frac{V}{kT}) \) is, roughly, the probability that an ion will cross a barrier once it gets there; to calculate the crossing rate one still needs to know how often the ion reaches the barrier. A much more powerful method for computing the occurrence rates of rare events is transition state theory ("TST",\(^1\)). This is a method developed originally for the computation of very slow chemical-reaction rates, and now used to compute slow reaction rates for many different sorts of processes governed by statistical mechanics.

C. Transition State Theory

It's the basic purpose of TST to determine the rate at which a system will move from one equilibrium state (or more accurately one quasi-equilibrium state) to another, particularly in cases where the transition rate is slow. In the space available here we won't attempt to derive the TST expression for this transition rate in any of its versions. Instead we only want to sketch the computations commonly involved in TST in its simplest form, discussing the underlying rationale only very superficially.

If the transition rate from one state to another is very slow, then TST assumes that there must be a high potential barrier between the states. This means that, if we were to transform the particle configuration continuously from one equilibrium configuration to another, we would always pass through at least one configuration where the system's net potential energy would be very high. Further, the fastest transition would correspond to that transformation which leads the system over the lowest pass through the potential barrier. In a system with two degrees of freedom one can see intuitively that such a pass will be a saddle point, and this turns out to be true in general. Technically a saddle point is a point where the Hessian matrix, \( H \), has one negative eigenvalue, while all the other eigenvalues are positive. By definition

\[
H_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}
\]

where \( V \) is the potential and the \( x_i \) are Cartesian coordinates for all the degrees of freedom.

Generally we are interested in that path (the "reaction path") which takes the system from one given equilibrium state to another, barely surmounting the lowest saddle point. Often this path is taken to be the zero-velocity path, a path constructed under the assumption that the velocity is always zero\(^9\). If such a path is traced, from the saddlepoint, in both descending directions, it will always connect equilibrium states. Further, if the lowest saddle point between the given states is much lower than all others, and if the positive eigenvalues are all large enough, then the saddle point determines the transition rate.

The "transition state" for a transition between the equilibria A and B is the particle configuration just at the saddlepoint on the reaction path. In any state of the system the square roots of the eigenvalues of the Hessian are the normal-mode frequencies\(^10\), the oscillation frequencies of the system in that state. In the equilibrium states all the eigenvalues are real and the frequencies are positive; on the other hand, by definition one eigenvalue is negative in the transition state, and one frequency is imaginary. It turns out that this imaginary frequency determines the rate at which the system goes through the transition state. If it is assumed that the motion of the system is a combination of simple harmonic motions (i.e. that particle deviations from equilibrium positions are very small) one finds that the number of transitions per second, per unit cell, from state A to state B, is given by the expression

\[
R = \frac{1}{2\pi} \prod_{m=1}^{N} v_m^A \exp \left[ -\frac{E_s - E_A}{kT} \right] \prod_{m=1}^{N-1} v_m^B
\]

Here \( N \) is the number of degrees of freedom in the unit cell; the \( v_m^A \) are the vibration frequencies in state A; the \( v_m^B \) are the \((N-1)\) real frequencies at the saddlepoint; and, finally, \( E_s \) and \( E_A \) are, respectively, the energies at the saddlepoint and at the equilibrium site, A.
D. Determination of Diffusion Coefficients

Given this transition rate, it is still not trivial to make the connection we need between the microscopic and macroscopic behavior of the system. To do this we need to track the diffusive motions of particles over distances substantially larger than a unit-cell-width. This is commonly done via "dynamic Monte Carlo" (11), a method somewhat similar to time-dependent Monte Carlo in neutronics. To implement dynamic Monte Carlo so as to simulate diffusion in a crystal lattice one might proceed as follows. 1) Identify a particle which is expected to migrate diffusively. 2) Locate the equilibrium sites for this particle throughout the lattice. 3) Calculate the probability that an equilibrium site is vacant. 4) Calculate the rate at which the mobile particle will jump from any equilibrium site to any "nearby" empty site. "Nearby" might mean, here, within the same or the adjacent unit cell. 5) Implement a Monte Carlo which, given jumping rates, will simulate a particle's long-range migration, keeping track of its position as a function of time. 6) Estimate the self-diffusion coefficient, D(self), from the Einstein relation

\[ D(\text{self}) = \lim_{t \to \infty} \left\{ \frac{\ell^2}{6t} \right\} , \]

where \( t \) is the elapsed time, and \( \ell \) is the crow's-flight distance traveled during that time. Here \( D(\text{self}) \) is the diffusion coefficient for diffusion of an ion through the lattice in the absence of any concentration gradient. From \( D(\text{self}) \) one can calculate the diffusion coefficient for multi-component diffusion in the presence of gradients.

Obviously, to compute diffusion coefficients by all the steps outlined above would be a major undertaking. On the other hand, predicting the behavior of buried wastes over thousands of years will require very large advances in our understanding of material behavior. It seems very rash to assume that such advances can be achieved quickly and without the commitment of substantial effort. More likely the monitoring and analysis of waste form behavior will require ongoing long-term research.

References

Figure 1

Minimum barrier

PotEnergy/avg KE

-7000 -6000 -5000 -4000 -3000 -2000 -1000 0 1000

-2 -1.5 -1 -0.5 0 0.5 1 1.5 2

z'  y'

'../normal_plane/test.27'

-357

-1.38e+03

-2.41e+03

-3.56e+03

-4.46e+03

-5.48e+03
Figure 2