Molecular reaction dynamics looks toward the next century: Understanding complex systems

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Abstract: Chemical reaction dynamics is making increasing contact with 'real' chemistry: examination of more elaborate reaction mechanisms typical of organic chemistry, the study of chemical reactions where the medium plays an active role (as is often the case in solution and on surfaces) and the ability to mimic systems of biochemical complexity are all of current interest. Much of our early conceptual understanding was acquired by the study of isolated, simple chemical exchange reactions in which one bond is broken and another bond is formed, in concert. A central feature in these reactions is the high selectivity which can be achieved by the choice of initial conditions and the considerable specificity of the resulting products. These themes do carry over to the world of more complex systems. Applications discussed include four center reactions, activated chemical reactions in solution, in clusters and on surfaces and photochemical processes. Surprisal analysis, long used to characterize the selectivity and specificity in simple reactions, is equally applicable here and the dynamical origin for the approach is discussed. The primary conclusion is that at the dawn of the new millennium, chemical reaction dynamics is ready to make inroads into the world of reactions of realistic complexity.

Much of our early conceptual understanding of reaction dynamics (1) was acquired by the study of isolated, simple chemical exchange reactions in which one bond is broken and another bond is formed, in concert. A central feature in these reactions is the high selectivity which can be achieved by the choice of initial conditions and the considerable specificity of the resulting products. Familiar examples (1) include the specificity of energy disposal of exoergic reactions (which gave rise to chemical lasers) or the quite anisotropic distribution of the reaction products in space. More recently similar results were observed in dissociation and/or elimination reactions following photochemical activation. I argue that these themes carry over to the world of more complex reactions (2) (additions, isomerization, substitution) of the kind that are employed in the synthesis of new compounds. Lasers (1,3,4) are an already available tool to selectively provide the required free energy of activation, if needed, on the same time scale as that of the chemical event itself (4-7). Laser control [e.g., (8)] and other modes for ultra fast activation [e.g., (9)] are being explored. Traditionally, the progress in dynamics has been achieved by a synergetic experimental-theoretical approach where the questions which were being raised by new experimental capabilities stimulated the development of theoretical tools. In a complementary fashion, suggestions by the theory as to hitherto unexplored effects were addressed by new experimental designs. The rapid growth in both experimental and theoretical capabilities is currently resulting in a progress that is somewhat less coordinated. There is just so much that

one can do that experimentalists and theorists alike are right now busy pushing ahead the limits of their respective crafts. It is safe to argue that when this evolutionary stage is over, the two cultures will converge in a new understanding of dynamics of many atom systems.

What drives the current evolution? Overall, is the general trend in chemistry (certainly motivated by systems of biochemical importance but equally so by material science, catalysis etc.) toward the understanding of weaker interactions. This is sometimes known as 'supramolecular' chemistry (10). The bridges between dynamics and such problems as molecular recognition are already being built (11). Other examples are the dynamics of clusters of molecules (12), held together by weaker than chemical forces. Experiments and theory of such finite systems (13) are likely to provide for us an understanding of the role of the solvent during the barrier crossing in activated chemical reactions. The reason is that the barrier crossing act is fast, so fast that the reactive system has no time to explore the long range structure of its environment (14). This is also the reason why an elementary reaction in solution can exhibit the same selectivity in initial conditions and specificity in final conditions that we have come to recognize as typical in the gas phase.

For the theoretician, the new freedom is brought about by the availability of powerful workstations. These provide a benchtop capability to follow the individual motion of a large number (hundreds or even thousands) of atoms. Figure 1 is an illustration of this capability for the 'burning of air' (9).
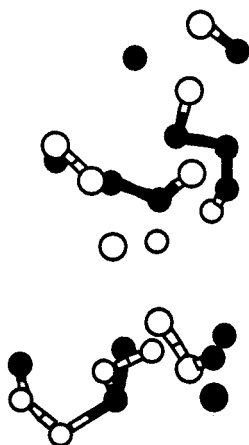

Fig. 1 An ultra fast heating of a cluster containing both N_2 and O_2 molecules upon impact at a surface (9). Shown is the instantaneous configuration of 14 N atoms (dark) and 14 O atoms (light) 50 fsec after a cluster of 7 N_2 and 7 O_2 molecules embedded in 97 Ne atoms impacts a surface at a velocity of 20 Mach. The potential used allows for all 125 atoms of the cluster to interact with one another and with the atoms of the surface. In addition, each atom-atom chemical interaction is influenced by the presence or absence of other open shell atoms nearby.

The well recognized limitation of the molecular dynamics (MD) approach (15) is that the results are only as realistic as the assumed forces which are used as an input to generate the motion of the atoms. A less obvious point is that the very strength of the method is also its greatest weakness. It generates so much detailed information that the essence can get lost. I return to this point below.

A major technological innovation that opens up the possibility of novel experiments is the availability of reliable solid state (e.g., TiSapphire) lasers which provide ultra short pulses over much of the spectral range which is of chemical interest (6). This brings about the practical possibility of exciting molecules in a time interval which is short compared to a vibrational period. The result is the creation of an electronically excited molecule where the nuclei are confined to the, typically quite localized, Franck-Condon region. Such a state is non stationary and will evolve in time. This is unlike the more familiar continuous-wave (cw) excitation which creates a stationary but delocalized state. The time evolution of a state prepared by ultra fast excitation can be experimentally demonstrated (5,7,16) and figure 2 shows the principle of one such experiment (16) and the theoretical simulation (17) of the results, for an iodine molecule immersed in a rare gas solvent. The optical excitation lasts for about 60 fsec and the dissociation is induced by the solvent
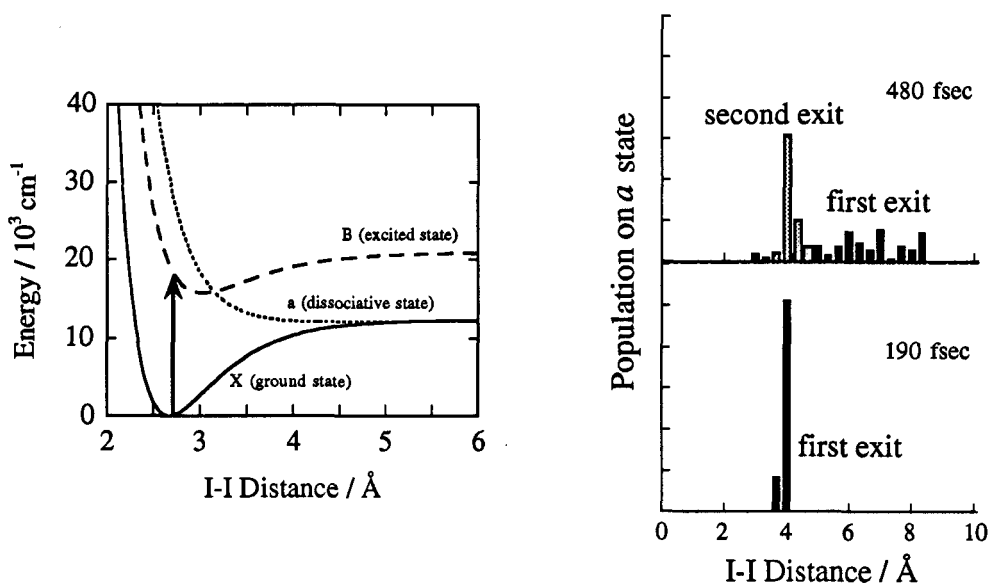
Fig. 2 Left: The ground (X, full line), excited (B, dashed line) and dissociative [$a1_g(^3\Pi)$, dotted line] electronic state potentials of the iodine molecule. The arrow indicates the electronic excitation. The initial excited wave packet is located in the Franck-Condon region near to the inner classical turning point of the B state. The transition from the B to the a state is forbidden by symmetry in the isolated molecule but becomes allowed when the molecule is placed in a solvent. Right: Histograms of the $a1_g(^3\Pi)$ population vs. the iodine-iodine separation at 2 time points. Shown are the first two exits for such points in time that the dissociative population has reached an average intramolecular separation of ~4 Å. [This distance is about the upper limit of the experimental probing window (16)]. The localized nature of the dissociative population is a direct result of the vibrational localization on the parent B state, as an exit to the a state occurs only when there is population in the curve crossing region.

The methodology used in (17) overcomes an important limitation of current MD methods namely that they are limited to a motion on one electronic state. In a problem of the type discussed in fig. 2, where the system can make a transition from a bound to a dissociative state, it is clearly necessary to allow for different dynamics on the different electronic states. In other words, what one needs are methods capable of handling both the intrastate and the interstate dynamics (18). Quantum mechanical wave packet methods (19) are, in this sense, a very useful tool but they are currently limited to systems with very few degrees of freedom and the point about the iodine dissociation is that it is induced by the solvent surrounding the molecule. A traditional route to systems of many particles is a self consistent field in which each degree of freedom moves in the average field of all the others (20). However, for many problems of interest there are strong correlations which requires configuration interaction . Extension of such methods to the electronic multistate problems are in progress.

Another important limitation of current MD methods is that of the conservation of zero point energy. [See (21) and references therein]. In a many atom system the total quantum mechanical zero point energy can be quite high and, in classical mechanics, this energy is available to the system. Additional sources of reviews of current methodologies are (22-24).

Two central problems remain. One is that one needs the potential which governs the motion. In many atom systems even if the motion is confined to the ground electronic state, this potential is a function of the spatial configuration of all the atoms. It is therefore a function of many variables so its analytical form is far from obvious nor do we necessarily want to know it everywhere. Indeed, we really only want it at each point along the actual trajectory of the system (so that the forces can be computed and thereby the next point to which the system will move to can be determined). Such an approach has been implemented (25) and applied to many atom systems and an extension to a multi-electronic state dynamics will be important.

The other central problem in a many atom system is that of the wealth of detail which is provided by the dynamics. One knows that, from one point of view, this detail is definitely necessary since it is the nature of typical many body systems that the dynamics is quite chaotic. What this means is that any loss of precision is rapidly (i.e., exponentially) propagated. Indeed, this is the most serious problem in the actual computation of the dynamics. If one really wants to compute a trajectory of the system, one needs an extremely stable method of numerical integration. The resulting time step is then so small that only very short propagations are practical as otherwise the accumulated computer round off error becomes too high.

There are those who adopt a 'practical' attitude which is that it does not matter if one is on 'the' correct trajectory as long as one is propagating 'some' trajectory. [The technical backing for this point is known as the 'shadowing' theorem. See (26) and references therein.] The difference between 'the' and 'some' trajectory is in terms of back integration. The correct trajectory will integrate backward in time to its initial conditions, as it, in principle, should. Some trajectory is a solution of the dynamics. Such a solution need not integrate back to the initial conditions which were specified. The proponents of the 'some' approach argue that as long as it is a solution, it does not matter. It does not even matter if, during a long integration, a numerical trajectory hops several (or even many) times between possible solutions. Not all MD practitioners care to have this point aired in public. Here I wish to argue that if a pragmatic point is useful, we should ask 'why'; Why do we have the luxury of not carefully caring that what we compute is the one unique trajectory that corresponds to our choice of initial conditions? (I hasten to add that my students and I do take a purist attitude and when we compute a trajectory, it is 'the' trajectory.)

The answer to the problem lies, I believe, in that a single classical trajectory is never the answer to a dynamical question. There are two reasons. One is a reason of principle. To mimic quantal initial conditions it is necessary to generate an entire ensemble of trajectories, each with somewhat different initial conditions. Then one needs to average over these initial conditions. Now comes a wonderful technical point [and a tribute to Stan Ulam (27) who, as far as I know, was the first to realize it]. The number of initial conditions that one needs to sample is independent of the number of atoms in the system. It takes just as many initial conditions to mimic the ensemble for an atom-diatom collision as for a cluster collision with hundreds of atoms. The one important role of the number of computed trajectories does play is in determining the numerical accuracy of the sampling. But this is essentially independent of the number of degrees of freedom (as long as it is not unrealistically small). In more technical terms, to answer a simple question the number of trajectories that needs to be computed is independent of the complexity of the system. Hence, to generate an ensemble average it may not matter that the final set of trajectories does not quite correspond to what we think their initial conditions are. It may matter, if the actual trajectories correspond to a different ensemble than what we have in mind. This may be alleviated by the second reason for averaging over initial conditions. It is that experiments seldom begin with a well defined quantum state. This is particularly so for a typical many atom system. So, in practice, one needs to average over a wider ensemble. (Remember the wonderful theorem of Mr. Ulam: The need to sample a bigger set of initial conditions does not require running more trajectories.) In other words, the less specific is the preparation of the initial state, the less one needs to really worry. A related but not equivalent point is that if the trajectory is ergodic (i.e., it samples all of the available phase space) then one need not worry about the choice of initial conditions (28).

I do not take these considerations as a license not to compute the correct trajectory in an MD simulation. I do take them as showing that unless one really wants a complete dynamical description, one is over computing. In other words, if all I want to know is if a reaction did or did not take place, the precise knowledge of where all the atoms of the system are, is not needed.

Figure 3 uses a four center electrocyclic reaction (29) to illustrate the sensitivity to initial conditions. There are two, simple, yes/no questions. One is did or did not the impact result in ring closure, cf. fig. 3. The other is, provided a reaction did take place, what is the branching fraction (i.e., the fraction of trajectories that reacted) in a concerted way (both new bond distances contracting together) vs. a sequential way (one new bond contracts first.) The reaction shown in fig. 3 is the isomerization of norbornadiene to quadricyclane (see inset in the figure) induced by an impact of a rare gas cluster containing one norbornadiene molecule on a surface (9). The only difference between the two trajectories shown is in the initial conditions of the surface atoms (due to their thermal motion which is at a temperature of 50 K).
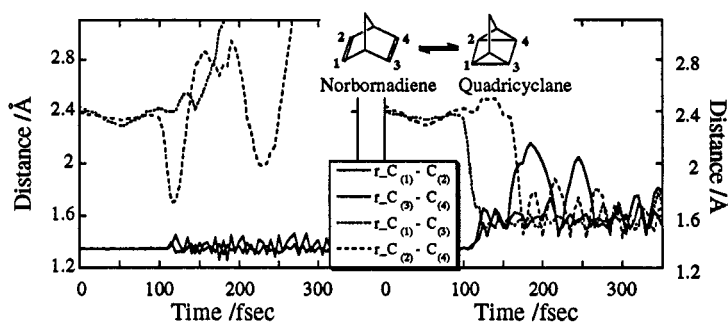

Fig. 3 Sequential (right) vs. a non reactive four center ring closure in the isomerization of norbornadiene to quadricyclane, inset. The two new C-C bond distances and the two bonds that start as the C=C bonds of norbornadiene are shown vs. time in fsec. The two trajectories shown correspond to exactly the same initial conditions for the Ar_{125} cluster. They differ only in the initial conditions for the surface at which the cluster impacts. In a concerted mechanism the two new bonds contract simultaneously.

How can one make practical use of these observations? For some time I have advocated the use of information theory. [For more details: Introductory discussion in (1) and (3). Surprisal analysis in (23), applications to spectra in (24) and (30), a recent prediction of a phase transition induced by cluster impact in (31)]. What this approach seeks to do is to use the minimal dynamical input that is necessary to account for the dynamical observations of interest. The point being that one very rarely has the experimental resolution to probe the individual final quantum states. The information measured is much more coarse grained.

The Monte-Carlo theorem of Stan Ulam tells us that to generate reproducible results for such coarse grained questions one needs to compute a number of trajectories that is independent of the complexity of the system. Much of the details of the initial conditions is therefore necessarily irrelevant to computing the final answer. Of course, with a finite number of trajectories one only obtains the final answer with a finite accuracy. But to within this accuracy, two sets of computations employing, say, 100 trajectories each, for, say an impact of a cluster containing 125 atoms (as in fig. 1) will yield the same result. This is so even though the number of computed trajectories is smaller than the number of degrees of freedom. (Just the cluster itself has $750 = 6$ degrees of freedom per atom $\cdot$ 125 atoms.) It will clearly not be possible for the individual trajectories in the two computations to look alike, yet a coarse grained result of interest would be the same, to within the statistical error. Point one is, therefore, that *to get reproducible results I do not need much of the initial detail that must go into the actual MD computation.* This is central to my argument. To

perform an actual MD simulation, each computed trajectory must be specified by 750 initial conditions. Yet the same practical result can be obtained from two different samples of only 100 trajectories each, note a.

The second point depends on the nature of the dynamics. Say we begin with a limiting case of truly ergodic trajectories. Then I really do not need to compute the actual trajectories. I would get the very same result if I simply postulate that my final set of trajectories is the set of all possible trajectories (where by 'possible' I mean that they conserve energy, etc.) Information theory starts from this limit which we refer to as the 'prior' distribution (1,3,23).

The prior distribution is the limiting situation when computing the dynamics will not provide any constraints on the final answer. I must emphasize that while this limit can never be the case, it is a very practical tool. The resolution of the apparent paradox is, as already emphasized, in the nature of the question asked. If I ask for the position and velocities of all atoms at the end of the trajectory, the so called, distribution in phase space, then there is no choice but to accurately compute the trajectory, whether the dynamics is nearly ergodic or not. The reason is that these variables must be highly correlated in order to ensure that, upon time reversal, the trajectory does integrate back to its starting point. Yet one can not ask for such a detailed information because it is more than quantum mechanics allows us, in principle, to measure. Even an ideal experiment can only resolve finite 'cells' in phase space ($\equiv$ the space of final positions and momenta.) Even for an isolated atom-diatom collision, studied in a molecular beam configuration we are not quite yet at such a level of resolution and for a complex system the size of a typical cell that can be measured is very much larger than the theoretical limit [e.g.,(31)]. For such measurements, the Monte Carlo theorem tells us that the detailed fate of an individual trajectory is not required.

The prior distribution is often not what is observed and there can be extreme deviations from it (1,3,23). By our terminology this means that the dynamics do impose constraints on what can happen. How can one explicitly impose such constraints without a full dynamical computation? At this point I appeal again to the reproducibility of the results of interest as insured by the Monte Carlo theorem. The very reproducibility implies that much of the computed detail is not relevant to the results of interest. What one therefore seeks is the crudest possible division into cells in phase space that is consistent with the given values of the constraints. This distribution is known as one 'of maximal entropy'.

There are two ways to implement this program. One is to directly discuss the distribution of final states. This is known as 'surprisal analysis'. In this, simpler, procedure one does not ask how this distribution came about. Instead one seeks the coarsest or 'most statistical' ($\equiv$ of maximal entropy) distribution of final states, *subject to constraints*. The last proviso is, of course, essential. If no constraints are imposed, one will obtain as an answer the prior distribution. It is the constraints that generate a distribution which contains just that minimal dynamical detail as necessary to generate the answers of interest. Few, simple, and physically obvious constraints are often sufficient (1,3,23) to account for even extreme deviations from the prior distribution.

The distribution generated by surprisal analysis is meant to reproduce the results of actual interest. A typical example being the distribution of products vibrational energy which is of interest say for chemical laser action (3). The distribution is not meant to reproduce the fully detailed distribution in classical phase space, which, as already noted, has a to be a highly correlated and complicated distribution.

The other mode of application, known as 'surprisal synthesis' is the more fundamental one. It starts from the distribution of initial conditions $\equiv$ the distribution in the initial phase space. As I argued, most of the details of this distribution are irrelevant for obtaining a reproducible final distribution of interest. (Again, the

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Note a. I should note one technical qualification. The statistical error will depend on the nature of the question which in a simple way one can describe as 'into how many bins do I sort the answer'. Did a reaction take place is two bins (yes or no). How many NO molecules were formed is eight bins (from none up to seven). For a given number of trajectories, the statistical error will be higher in the latter.

caveat, all initial details are essential if what is needed is the final distribution of ultimate resolution.) One therefore seeks that most coarse grained initial distribution which is sufficient to get reproducible results for the final distribution. Here too, the most coarse grained initial distribution is obtained as one of maximal entropy subject to constraints. We now have an initial distribution, but what we need is the final distribution. This requires an appeal to the dynamics. One needs a way to phrase the dynamics so as to take advantage of the conclusion that, apart from the constraints, all other details about the initial state are irrelevant for our purpose. Here comes the final theorem that I will appeal to: *In both classical and quantum mechanics, an initial distribution of maximal entropy remains a distribution of maximal entropy throughout its time propagation.* The theorem is exact (32). It therefore follows that in order to know the final distribution (which, by the theorem, is guaranteed to be one of maximal entropy) it is sufficient to propagate the constraints and we have shown analytical examples of how this can be implemented (32).

One can also identify constraints on the basis of physical considerations. One reason for selectivity is that different motions often have different time scales (18). E.g., for a chemical barrier crossing event in solution, it is found that in non associated solvents it is the motion along the reaction coordinate that is typically faster than the response of the solvent (14). Figure 4 shows the frequency range of the barrier crossing for a symmetric atom exchange reaction relative to the range of frequencies which a typical rare gas solvent can provide. (Negative values of ω^2 are due to unstable motions.) It is evident from the plot that activation by the solvent occurs primarily at the foothills of the barrier to reaction, as is verified by the MD simulations.
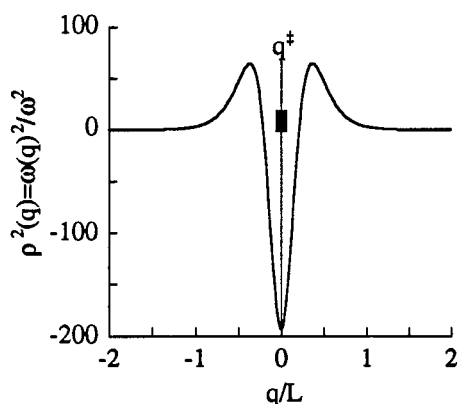

Fig. 4 The (squared) frequency of the motion along the reaction coordinate q for a symmetric atom exchange reaction. L is the range of the chemical barrier region and the frequency is shown in units of the mean frequency of the unperturbed solvent. The range of frequencies in the solvent is indicated as a solid bar. The negative values for the solvent correspond to unstable solvent modes.

The propagation in phase space can also be probed in the frequency domain via the vibrational overtone spectra of polyatomic molecules (30,33). The separation of time scales can be demonstrated in this fashion and is useful in representing such spectra by the maximal entropy method (30). Further details can be found in two recent tutorial reviews in refs. 23 and 24.

An exact dynamical description requires keeping track of each and every atom in the system. For many problems of chemical interest this represents an enormous detail. Experimentalists and theorists both know that, for the kind of questions that they ask, one can obtain reproducible results without the need to specify the initial conditions with such precision. MD simulations mimic this by performing the exact dynamics first and then coarse graining the result to the required level. Here I discussed a complementary point of view, where the averaging is carried out first, retaining only as much details as necessary to generate a reproducible result at the desired level of resolution.

ACKNOWLEDGMENT

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