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MONTE CARLO EXPERIMENTS IN GAS KINETICS

82111

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MASTER

Ever since the 1926 revolution in physics, it has been known that chemistry is a closed science. All chemical phenomena can now in principle be deduced from physical law. In the years immediately following this discovery, such deductions were in fact made for all phenomena for which solution of the physical equations is relatively easy.

However, most chemical problems are not relatively easy to relate to physical law. This is why chemistry, although closed, is far from terminated. The challenge remains of explaining molecular properties which are certainly connected ultimately to physics, but in such complicated ways as to defy understanding. The task of nevertheless understanding them is the one which absorbs the energy and ingenuity of the present-day chemist.

The impact of digital computers on this area of effort is bound to be large. Before their appearance, molecular properties which could be studied directly on the basis of physical law were few. They were ones whose definition implies the absence of atomic motion -- for example, the lengths of chemical bonds in simple compounds. Even the most uncomplicated of dynamic situations, the transformation of one chemical species to another in the gas phase, was practically intractable. These simple reactions can be profitably discussed using classical as well as the newer quantum mechanics. But even the classical description had to be severely simplified if recognizable conclusions were to be reached.

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The availability of computers has greatly increased our ability to calculate static properties of molecules, and it has brought some of the dynamic processes within range of detailed mathematical study. The situation in the latter case is especially interesting. Some of our knowledge of rates and other dynamic properties of gas reactions comes from experiment. Some of it is embodied in theoretical work based on hypothetical molecules with simplified physical properties ("models"). The subfield concerned with all this, called gas kinetics, thus overlaps a line of demarcation. On one side of this line chemistry is studied primarily by means of laboratory experiment; on the other, by interpretation of physical law. Because of its borderline position, gas kinetics is unusually susceptible to clarification by computer study -- using the computer not as an ultra-high-speed adding machine, but as an experimental tool in itself.

Such a computational experiment might involve solving the physical equations for a particular theoretical model, to see whether its detailed properties really conform to what people have always assumed. Or, one might wish to simulate an imaginary experiment which cannot be carried out in the laboratory, but which would be very informative if it could. These are only the two most obvious possibilities; several others exist, as will be shown.

At first sight, simulation of gas reactions in order to learn something about them presents staggering difficulties. Any reaction worthy of attention involves at least three atoms, and they are not at rest. They may have a variety of relative positions and velocities. If some of them

are combined into a molecule, the molecule may vibrate and rotate. To scan through all the possible combinations of atomic positions and motions, calculating and later averaging some property of the reaction, is impossible even for a computer. The hideous complexity of this task can only be sidestepped by the use of Monte Carlo methods.

An everyday Monte Carlo procedure which has much in common with that used for molecules is the public opinion poll. Suppose one wishes to know who will next be elected president, and by what margin. An exact answer can only be obtained by holding an election. But perhaps an approximate prediction, good within some probable tolerance, is acceptable. If so, it can be secured by sampling the intentions of a relatively small number of voters. It is necessary to ensure that this sample is not too small for the desired tolerance. Also, it is very important that the voters be chosen by a strictly random method, so that they represent the electorate in an unbiased way. Failure of these precautions has been known to lead to embarrassment.

In the same way, one avoids considering all the possible configurations of molecules, by picking out representative ones at random. One then tries to study enough of them to make the main features of their behavior evident. It is clear that an element of luck is involved -- hence the name of the procedure. Even if the sample is a strictly random one, there will be fluctuations away from the properties being sought. The reason is the same one that causes an honest coin being tossed 100 times seldom to yield exactly 50 heads. In the molecular problem, there is always a chance that a larger-than-usual fluctuation will lead to a false conclusion,

or obscure a real one. The results therefore have to be interpreted very circumspectly.

In this article two applications of the Monte Carlo technique to problems of gas kinetics are described. These applications are of contrasting character.

* * * *

In a reaction between two chemical species, a large amount of energy is often released. The simplest such reaction may be symbolized

A, B and C represent three atoms, not necessarily all different. The energy of the reaction might appear as relative velocity of departure of the products AB and C, or as internal energy (rotation and vibration) of AB, or both. The exact way it is divided up has long been of interest to kineticists. It has been suspected of containing information about the interatomic forces involved in the reaction. These interatomic forces are not very well known, and their theoretical calculation is extremely difficult. Acquisition of experimental evidence on their nature would greatly improve our understanding of kinetic processes.

The partition of product energy may be experimentally studied in several ways (see Figure 1). In the flash spectroscopy method, pioneered by R. G. W. Norrish at Cambridge University, atoms are produced by the action on molecules of an intense burst of light. A few microseconds later a second light pulse occurs. In the meantime the original atoms have reacted with molecules to produce molecular products, whose spectrum

is observed by means of the second flash. The state of vibrational energization of these products can be determined in this way. (See "Flash Photolysis," by L. I. Grossweiner, Scientific American, May 1960.) Other studies have involved the injection of atoms into a rapidly moving stream of gas, and observation downstream of product vibrational energy. Finally, in a remarkable series of experiments started at the University of California and continuing at Harvard, D. R. Herschbach and his co-workers have used crossed beams of atoms and molecules to find both the disposition of energy of reaction and the distribution of directions in space taken by the departing products.

The evidence gained from this group of experiments has been contradictory and hard to interpret. Sometimes much, sometimes little energy appears as vibration of the product molecules. Attempts to predict the amount from the properties of the reacting molecules have not been very successful.

We decided, at Los Alamos, to try to compute some order into this somewhat chaotic situation. (My co-worker in this part of the project has been Normand C. Blais.) There was available a digital computer, STRETCH, whose speed and precision would allow us to study many hypothetical examples of this kind of reaction. The array of such reactions provided by nature contains large gaps across which it is difficult to interpolate experimental behavior. We thought that by filling in these gaps with imaginary reactions we might gain a comprehensive viewpoint from which generalizations could be made.

In an individual reaction event of this kind, varying amounts of vibration and rotation of BC might at first be present. The approach

velocity of A and BC is a variable, as is the distance by which they would miss one another if they continued in their initial directions. There are still other details which have to be specified. We first arranged to be able to choose representative reaction events, by picking values of the foregoing quantities at random out of the biased distributions in which they naturally occur (see Figure 2). This is a moderately complex process. Often the fastest method is to have the computer choose values at random, and then use them or not according to the outcome of a game of chance. In this game, which the computer plays with a list of random numbers rather than a set of dice, the odds for a particular value are adjusted so that it will "win" in just the correct number of instances.

Once the starting conditions are chosen, the ensuing reaction can be followed by well-known numerical methods. The classical equations of motion are solved approximately for very short time intervals, and the trajectories of the atoms traced out step by small step. At the end of the reaction the energy and the angle of departure of each product are determined. Then another random set of starting conditions is chosen and its subsequent motion calculated. The procedure is repeated until the accumulated results begin to make sense.

It was not evident in advance that distributions of product angle and energy obtained in this way would have convincing significance for real reactions. We therefore began by simulating the best laboratory experiment that had until then been done. Agreement between this and the computed results was taken as a prerequisite to the study we ultimately wished to make.

The process we chose to imitate was

This reaction (in which it is permissible to think of the methyl group, CH_3 , as a single particle) has been studied extensively by Herschbach et al in a molecular beam environment. Over 80% of the available energy is known to appear as vibration and rotation of the product, potassium iodide. The most probable recoil directions of KI and CH_3 have been determined. We chose this reaction largely because both these results can be computed; there is thus more information with which to compare computations than in a flash or flow experiment.

The results of the comparison were entirely satisfactory. The assumed set of interatomic forces which gave agreement with Herschbach's product energy distribution turned out to be of a character generally believed reasonable for this kind of reaction. The angles of recoil of the products, computed and experimental, were in agreement regardless of what interatomic forces were assumed. In addition, much experimentally unavailable information on the nature of the trajectories was gathered.

It was therefore permissible to continue. An orderly array of fictitious reactions, having various combinations of atomic masses, interatomic forces, and energies of reaction, was studied. Altogether 50 example reactions were considered, with about 200 events for each.

At first the computed results were as confusing as the experimental ones. However, after a while it became apparent that only three kinds of answer were possible. Most reactions had a product angle distribution of a characteristic kind, similar to that for $K + CH_3I$, but a few had a particular type of anomalous one (see Figure 3). Similarly, most distributions of product vibration energy were peaked near a value corresponding to all the energy of reaction, as in $K + CH_3I$; a few were not (see Figure 4).

The two anomalies never occurred together.

The strange distributions of product angle are easily explainable. A molecular collision such as we were studying involves both energy and angular momentum. Both have to be conserved, and if reaction occurs both are involved in any rotational motion the product molecule AB might have. The normal kind of angle distribution shown in Figure 3 also implies a certain way of distributing the angular momentum between the rotation of AB and that of the three atoms as a group. Anomalous angle distributions occur when these requirements cannot be simultaneously reconciled with the amount of energy available from the reaction. In these circumstances something has to give way, and since it cannot be the conservation laws it must be the form of the angle distribution. A simple pencil-and-paper calculation, involving the masses of the atoms, the temperature, and the lengths of the chemical bonds in the molecules, infallibly predicts whether or not the angle distributions will be normal.

It has long been an article of faith among kineticists that the normal kind of product energy distribution, in Figure 4, goes with the kind of interatomic forces thought to be reasonable for $K + CH_3I$ and most other reactions. In these the reactants are supposed to attract strongly and the products repel weakly. The opposite kind, with weak reactant attraction and strong product repulsion, has been assumed to be associated with the anomalous variety of product energy distribution.

The Monte Carlo calculations confirmed this for many reactions, but some specific exceptions have to be made. The second kind of forces mentioned above leads to much more unpredictable results than the first. The position

of the maximum in the vibration energy distribution varies with things to which it is insensitive in the other case. This variation sometimes leads to a normal energy distribution for abnormal forces. More important, in every case where the mass of A was much less than that of B or C, an anomalous energy distribution was obtained even though the forces were of the first kind. This corresponds with the experimental observation that hydrogen atom reactions are unexpectedly unlikely to lead to vibrationally energized products.

In summary, it was possible (at a cost of 130 hours computing time) to sort out and list for the first time the factors that determine the outcome of the experiments on $A + BC$. Reasoning empirically from this list, one can predict what kind of energy and angle distributions might be expected from a given laboratory experiment, and one can indicate what experiments might be especially interesting. And the possibility has appeared on the horizon of using a combination of computations and laboratory experiments to determine, at last, what the interatomic forces actually are.

* * * *

The problem of unimolecular reaction rates is in several ways unlike the one just discussed. It is a much older problem, having been near the center of attention of gas kinetics for more than forty years. During that time much theoretical work based on simple models has been done. Experiments in this area are difficult, and even now only a few really useful ones exist. Because of this, computer studies are apt to be aimed more at testing the validity of theoretical models than at collating experimental results.

The simplest unimolecular reaction which displays all the properties characteristic of this class of processes again involves three atoms.

Symbolically,

This kind of reaction, fragmentation of a single molecule, has been so intensively studied mainly because of its relatively uncomplicated nature. Until its rate can be explained, there is little hope of quantitatively predicting the properties of the more complex multistep processes in which molecules often engage.

Only a highly condensed sketch can be given of how the ideas of the last forty years have led up to today's principal unanswered question. At the end of the 1920's it was understood, as a result of the work of F. A. Lindemann and C. N. Hinshelwood in England and O. K. Rice, H. C. Ramsperger and L. S. Kassel in the United States, that two overlapping processes are involved in unimolecular reactions. The ABC molecule has to acquire enough energy to break one of its bonds, and then accumulate it in the bond which is to break. The first step is regulated by the frequency of collision of ABC with other molecules in the gas. The rate of the second is a property of the vibrational motions of energized ABC.

A molecule has several vibration frequencies, corresponding to different possible relative motions of the atoms. They can be determined by infrared spectroscopy; but in the 1920's this had not been extensively done, so the early theoretical models of unimolecular reactions had to be very simple. All the frequencies were given the same arbitrary value, and an approximate statement was made about the migration of energy among

the corresponding modes of vibration. This led to a rate of energization of the breakable bond, which was then compared with that of collisions. The resulting theory persisted almost unchanged for twenty years.

By 1950 so much information had been gathered by spectroscopists that almost every kinetically interesting molecule had known vibrational properties. It was time to inject this knowledge into the theory of their reaction rates. One of the attempts to do this is largely the work of R. A. Marcus of Brooklyn Polytechnic Institute. His theory is an extension of the earlier one of Rice, Ramsperger and Kassel; the initials RRKM are commonly used to identify it. Identification is necessary because an alternative, and at first contradictory, theory has been provided by the mathematician N. B. Slater of the University of Hull.

The Slater theory contains both an improved mathematical formulation of the interaction of collisions with vibrational motion, and a specific recommendation on how the known vibrational properties of molecules ought to be taken into account. It is nowadays doubtful on various grounds whether the second of these can be maintained. The first, however, led Slater to notice and vigorously point out an untested assumption present in all theories of unimolecular reactions.

This assumption, the truth of which is the crucial question addressed by our computer experiments, can be approached as follows. Consider two molecules with the same energy (enough for reaction) but with different atomic positions and velocities. Is there any way to tell from these positions and velocities which molecule will react first? Slater correctly observed that everyone till then had implicitly assumed there was not. This is called the random lifetime assumption. It implies that a fair

game could be constructed in which one bets on which molecule, in a gas of identically energized ones, will first succeed in coming apart. If the random lifetime assumption is untrue -- if the game can be beaten -- then the RRKM theory cannot be accepted.

Few of the theoretical considerations touched on above can be studied directly by experiment. The possibility of resolving some of the difficulties by computation occurred to many people. The first computer studies of the trajectories of atoms during any kind of reaction had been published in 1958 by F. T. Wall, L. A. Hiller, Jr., and J. Mazur of the University of Illinois. Similar investigations, specifically concerned with unimolecular reactions, began in several laboratories. The first results, those of E. Thiele and D. J. Wilson of the University of Rochester, appeared in 1961.

Much was learned from these studies. They illuminated the nature of molecular motion. They confirmed the growing experimental suspicion that the RRKM method of dealing with molecular vibrations was preferable to that of Slater. (Later, this view was still more strongly reinforced by our work.) But because they dealt with isolated reaction events, they gave no indication of whether the random lifetime assumption was tenable. Only Monte Carlo calculations of distributions of molecular lifetimes could do that.

At Los Alamos we considered this problem so important that we began planning our attack on it in early 1960, a full year before the STRETCH was delivered to us. Our work would clearly consist of selection of representative molecules, following their motion by solution of the classical equations, and finding how much time elapsed before they reacted.

In contrast with the first problem described in this article, we were much more certain what the interatomic forces are. The compensating disadvantage is that very few randomly chosen molecules react unimolecularly in a sufficiently short time, so that enormous numbers of them have to be considered. Selection of the representative molecules is also much more difficult than in the other instance. The probabilities of initial atomic positions and velocities all depend on one another, and the game of chance involved in their selection has to be played in a geometry of many dimensions. This caused us some trepidation about our ability to solve the overall problem. But by the time STRETCH arrived a method had been evolved of finding representative molecules in a time no longer than that required to compute their subsequent motion.

In the course of the next two years 200 hours of computing time were expended on calculation of lifetimes of energized triatomic molecules. The resulting distributions of lifetimes for various model molecules contain 30,000 reaction events, but there were ten times as many trajectories that did not lead to reaction. The basic step of solving the classical equations of motion over a short time interval was repeated 10^8 times. Our procedure for selection of starting conditions, which gains speed by sacrificing economy of random number input, consumed more than 10^{11} random digits. These all had to be manufactured by STRETCH.

This large effort led to some pleasant results, although at first they seemed disastrous. The random lifetime assumption was confirmed for a large number of hypothetical molecules. But there was a group of molecular models that persistently refused to conform to it. (Randomness

implies a definite shape for the computed distributions; see Figure 5.)

The conditions for nonconformity were somewhat obscure, but it was evident that a sufficient--not necessary--one was the occurrence of widely separated vibration frequencies. This is a potentially disturbing observation, since it implicates the hydrocarbon molecules with which much of the laboratory experimentation has been concerned.

Having characterized the lifetime distributions as well as we could, and also verified that the RRKM theory is numerically accurate whenever the random lifetime assumption is true, we were in a position to reconsider the theory of unimolecular reaction rates. In a short time it was found possible to devise a theoretical model that predicts whether a particular molecule will have a random lifetime distribution or not. Why was this not done years before? Because a variety of plausible models are possible, and until the Monte Carlo results were available a choice could not be made among them. We could ^{not apply our theoretical treatment to real molecules until we could} demonstrate that it explained the computed results.

Our conclusions about real molecules are simple to state. They are: Departure from the random lifetime approximation is not general. Badly behaved lifetime distributions will occur for only a few molecules--among them the ones for which the computations were done--and then only under very special experimental conditions. No experiment in which they would be expected has ever been carried out. We can therefore endorse the RRKM theory without reservation for all reactions to which it has as yet been applied. On the other hand, it is not impossible to produce in the laboratory the conditions for which the RRKM theory fails, so we can also suggest some experiments that should have novel and interesting results.

* * * *

These two studies have been described in some detail to illustrate the variety of ways computational experiments may interact with, and draw together, theory and laboratory experiment. In our work they have elicited details which, in laboratory chemical processes, are averaged into inaccessibility because of the large numbers of molecules present. They have been used to introduce organization into a set of experimental observations, so that the combined results might be subjected to theoretical speculation or used in predicting the outcome of other experiments. They have suggested numerous experiments whose special interest might not otherwise have occurred to us. We have been able to test theoretical models of chemical processes, leaving some of them in a better state of justification than before. New theoretical work has been suggested by the calculations, and the means of verifying its accuracy provided. No doubt many other possibilities exist. Certainly many other problems of chemistry are susceptible to this still rather unfamiliar kind of attack. Thus far only a few areas in kinetics and statistical mechanics (see "Molecular Motions," by B. J. Alder and T. E. Wainwright, Scientific American, October 1959) have been marked as targets.

An interesting aspect of these computational experiments, besides their versatility, is the way in which they unexpectedly inject a human element back into an experimental science that is becoming largely one of instrumentation. To anyone familiar with the way a computer problem is most often solved--formulation in an artificial language, translation into a program by the machine itself, and automatic operation of the program in the formulator's absence--this may seem a preposterous statement. The

fact is that computational experiments cannot be conducted in this manner. The complexity of this kind of scientific problem always exceeds the ability of the computer to solve it. Any failure to use the computer at maximum efficiency is directly reflected in the quality of the answers. For this reason it is necessary to operate the problem under the direct and continuous supervision of a human who is familiar with both the physical process being simulated and the details of the computer program (so that artificial programming languages are ruled out). Any unusual or unexpected result--and there are a great many in a research problem--has to be detected promptly, translated into physics, and used as the basis of a spot revision of the strategy of the calculation. The success of this process depends heavily upon the intuition and tactical skill of the operator. In our case, even though correct decisions were not invariably taken, hundreds of hours of computing were saved by this kind of man-machine interaction. Without it many of our results would have been out of reach.

Computational experiments, then, furnish a useful and also entertaining method of arriving at new physical insights. They will eventually become of widespread importance as a supplement to, and often on equal terms with, laboratory experiment and theory.

SUGGESTED ILLUSTRATIONS

1. (Top) Flash photolysis experiment. A atoms, produced from AA molecules by the initial flash (left), react with BC. Vibrationally energized AB can be detected a short time later with a second flash (right). (Center) Flow experiment. Vibrationally energized AB can be observed downstream from the junction of streams of A atoms and BC molecules. (Bottom) Molecular beam experiment. Products AB and C emerge, with varying energies and at various angles, from the intersection of beams of A and BC. A movable detector is used to determine the scattering pattern.

2. The small graphs show the relative probabilities of various values of parameters involved in a collision between A and BC. The "impact parameter," b , is the distance by which A would miss BC if there were no forces between them.

NORMAL

ANOMALOUS

3. Distributions of the computed angle of emission of C, measured from the approach line of A. Normally C is ejected mostly forward (left); in some cases this is inconsistent with angular momentum conservation, and a different result is obtained (right).

NORMAL

ANOMALOUS

4. Distributions of the computed vibration energy of AB. Q is the total energy available; if it exceeds the vibration energy, the excess becomes kinetic energy of separation of AB and C. Unusual interatomic forces, or very small mass of A, produce the anomalous type of distribution.

RANDOM

NONRANDOM

5. Computed distributions of elapsed time before reaction, for randomly chosen molecules of the same energy. A random distribution of lifetimes would have the descending exponential shape shown by the dashed curves--the same as describe a radioactive decay process. The distribution on the left is random within the fluctuation level of the Monte Carlo procedure. The one on the right is not.