Fractals in atomic and molecular collisions

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Fractal geometry describes many irregular forms in nature, such as geographical features, as well as complex shapes that describe chemical, among other, phenomena. Fractal patterns occur in shapes associated with atomic and molecular collision processes, including collinear reactive and nonreactive and rotationally inelastic processes, molecule–surface collisions and interparticle diffusion.

'When Krishna opened his mouth, mother Yasoda looked inside and saw outer space spreading before her in all directions, with all its stars and planets. She saw the oceans.... And in the midst of everything, Yasoda also saw herself taking little Krishna on her lap.' Included in this ancient description[1] is the concept of self-similarity, which has become identified with fractals[2] in recent times. Fractals are a mathematical tool useful in describing irregular shapes. In addition to having a self-similar pattern repeating itself endlessly, a fractal set would have a scale-invariant property called fractal dimension (D_F), which is bounded by the topological (D_T) and Euclidean (D_E) dimensions: $D_T \leq D_F \leq D_E$. While there are several examples of fractals cited in the literature perhaps the simplest is the Cantor set illustrated in Figure 1. If we consider the length in A divided into three equal parts and the middle one left out as in B, the logarithmic ratio of the occupied to the total length is given by $\ln 2/\ln 3$. Each sublength can be further subdivided into three portions, once again leaving the middle one out. Such a subdivision can be carried out *ad infinitum*, but the characteristic property

$$D_F = \ln 2/\ln 3 = \ln 2^2/\ln 3^2 = \cdots = \ln 2^n/\ln 3^n, \quad (1)$$

where n is the generation number, remains the same. Objects like ferns, cauliflower, roots (branching) and Kondapally toys (these are wooden dolls; if you open one, you find a smaller but identical-looking doll inside; when you open that one you find yet another smaller but identical-looking doll; and so on) are examples that we come across in everyday life. Popular descriptions of fractals are plenty in the literature (for example, see ref. 3). Earlier in this journal, Chowdhury[4] discussed the significance of fractals in the study of proteins. In this article I illustrate the occurrence of fractals in atomic and molecular collisions.

In any dynamical problem, the output can be considered to be functionally dependent on the input. Sometimes the dependence would be *regular* and sometimes *irregular*. The former refers to the fact that for a small change in the input there would be a predictable change in the output, while in the latter case a small change in the initial condition leads to an unpredictable (but reproducible) dramatic change in the final condition. The latter behaviour is also termed *chaotic*[5] and is characterized by a positive value for the Lyapunov characteristic exponent (LCE)

$$\lambda = (1/N) \ln(\Delta O/\Delta I), \quad (2)$$

where O and I represent the output and the input respectively and N is the number of time steps used in the dynamical evolution. It is worth emphasizing that what we are referring to is *deterministic chaos*, as opposed to complete randomness. Buried in this disorder is an order that manifests itself in the form of fractals when the dynamical outcome is viewed as a function of some appropriate (input) control parameter. As a matter of fact, the existence of fractals can be used as a characteristic of chaos in scattering systems[6].

Collinear inelastic collisions

One of the simplest collision problems we could consider involves an atom (A) and a diatomic species (BC) interacting with each other along a straight line. The state of the diatomic species before and after the collision could be characterized in terms of its vibrational action—the classical analogue of the quantum number—,n_i and n_f respectively. At a fixed

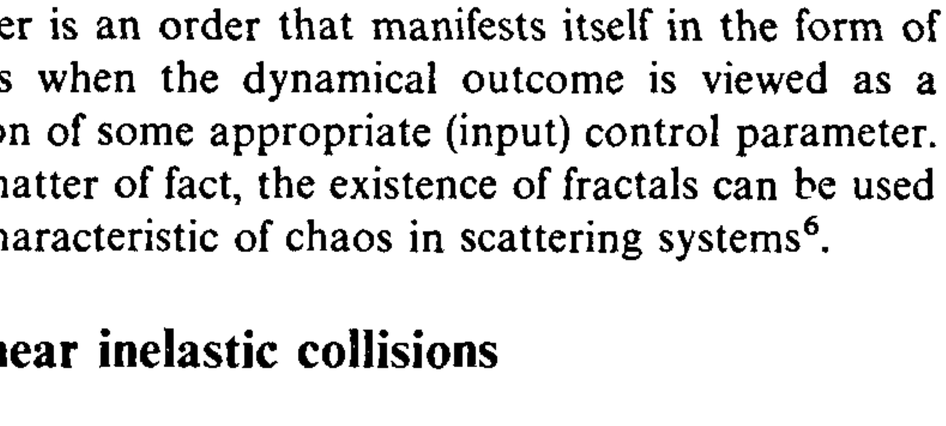

Figure 1. Illustration of a 2/3 Cantor set and its fractal dimension.

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relative translational energy (E_{tr}) between the reactants, for a chosen initial separation between the atom and the diatomic species the only variable remaining to be specified for full characterization of the collision problem is the initial vibrational phase ϕ_i of the diatomic species. For a 'direct collision, the dependence of n_f on ϕ_i is depicted schematically in Figure 2. In the quasiclassical trajectory approach[7], the inelastic transition probability $P_{n_i \to n_f}$ is given by the ratio of the number of trajectories lying in the range $(n_f - \frac{1}{2}) \leq n_f \leq (n_f + \frac{1}{2})$ to the total number computed in the range $\phi_i = 0 - 2\pi$. In the semiclassical S-matrix theory[8], $P_{n_i \to n_f}$ is computed in terms of $(\delta n_f / \delta \phi_i)_j$ for the jth stationary or 'root' trajectories which connect the states n_i and n_f:

$$P_{n_i \to n_f} = |\Sigma 2\pi i \hbar (\delta n_f / \delta \phi_i)_j^{-1/2} \exp(i \hbar^{-1} \Phi_j)|^2,$$

where Φ_j is the phase for the jth root trajectory. For a variety of 'real' systems the dependence of n_f on ϕ_i is partly regular and partly irregular, as shown in Figure 3,*a* for collinear $He + H_2^+$ ($n_i = 0$) collisions at $E_{tr} = 0.5$ eV on an *ab initio* surface. The trajectories in the irregular region were used to be referred to as 'chattering' and were shown to involve long-lived complexes; in current parlance their behaviour would be described as chaotic (see above).

While investigating the collinear collision of an atom with a Morse oscillator through exponential interaction, Gottdiener[9] showed that the chattering region in n_f-versus-ϕ_i plots revealed additional structures on increased resolution along ϕ_i and that a characteristic array of parabolas repeated itself endlessly. More recently, Noid *et al.*[10] showed that, for the interaction of a He atom with an I_2 molecule in a T-shaped geometry, the action–angle plot contained an irregular region revealing a self-similar pattern of 'icicles' repeating itself with additional fine combing of the ϕ_i axis; they also showed that the 'icicles'

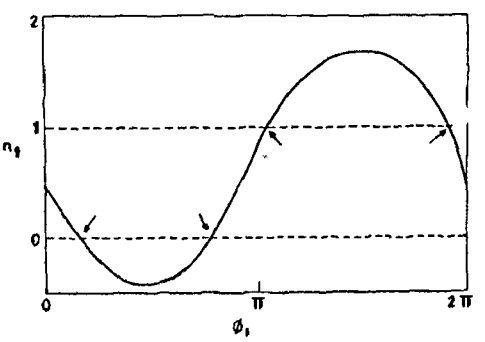

Figure 2. Schematic representation of the n_f-versus-ϕ_i plot for a collinear atom diatom system undergoing only 'direct' collisions. The root trajectories corresponding to $n_f = 0$ and $n_f = 1$ are indicated by arrows.

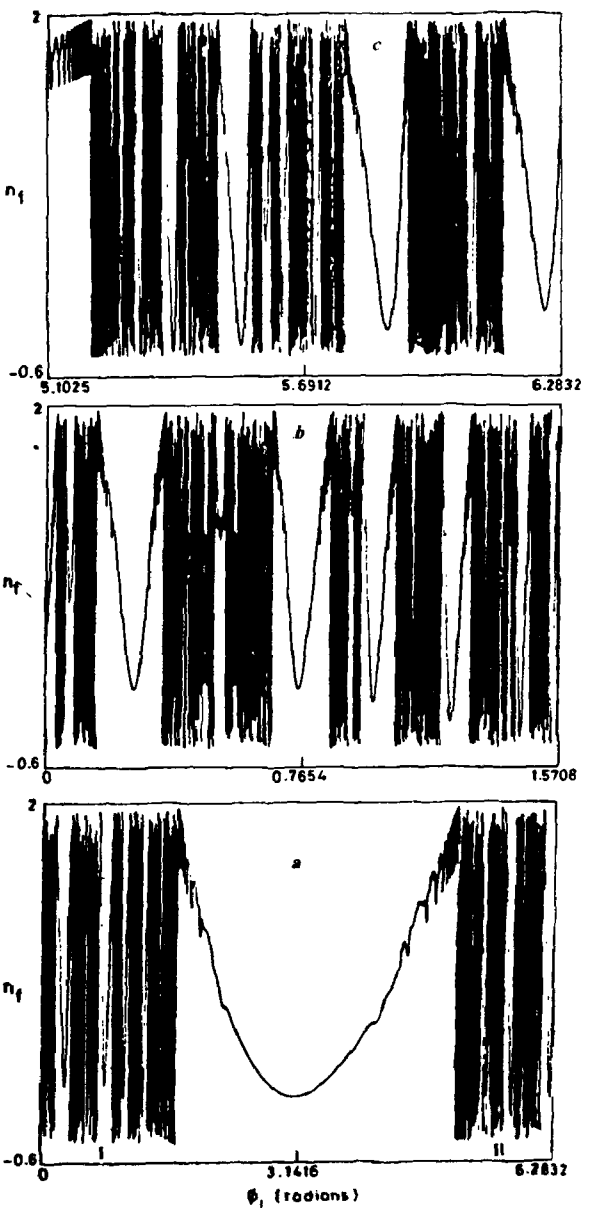

Figure 3. *a*, Action–angle plot obtained from 8000 trajectories for collinear $He + H_2^+ (n_i = 0)$ collisions on an *ab initio* surface at $E_{tr} = 0.5$ eV. Resolution along the ϕ axis has been increased by a factor of 10 for the irregular regions I and II in *b* and *c* respectively.

constituted a fractal set with a D_F close to but less than 2.0 when viewed in a two-dimensional phase space.

We have also found[11] that on increased resolution along ϕ_i, both chattering regions I and II in Figure 3,*a* revealed additional parabolas, as shown in Figure 3, *b* and *c*. It is amazing that even the 'wiggles' in the parabolas are reproduced in the self-replication. In conformity with the findings of earlier workers we have

also found the trajectories in the regular region to be direct (short-lived) and those in the irregular region to be indirect (long-lived) or involving multiple collisions. As expected, LCE is negative for the former and positive for the latter type of trajectories.

Collinear reactive collisions

For systems in which the exchange reaction is possible, the $n_f(\phi_i)$ curve would normally consist of two parts, the reactive (R) and the nonreactive (NR). The corresponding state-to-state transition probabilities would be computed from Φ_j and $(\delta n_f/\delta \phi_i)_j$ for the root trajectories in the R and NR bands respectively. As early as 1971, Rankin and Miller[12] had shown that there were a continuous reactive band and a chattering region in which the collisional outcome was nearly statistical. While investigating dynamical resonances in (H, H_2) collisions, Stine and Marcus[13] showed: 'between the reactive and the nonreactive branch is a region in which the atoms execute multiple collisions. Between two reactive and nonreactive branches we have found that there is another reactive-nonreactive branch, each branch containing two stationary phase points. Between each of these is still another branch and so on.' They found that while the reaction probability P^R computed from the zero-order branch varied monotonically with E_{tr}, inclusion of the contribution from the trajectories in the first- and second-order branches resulted in a nearly quantitative reproduction of the reactive scattering resonance, thus establishing a one-to-one correspondence between fractals and quantal resonances. There have been other reports (see, for example, ref. 14) that confirm such a correlation. In studies involving collinear (He, H_2^+) collisions we have found[11] that the shoulders of the R band reveal additional structures on expansion along the ϕ_i axis, suggesting that an exact semiclassical calculation[8] would include contributions from several generations of 'root' trajectories. It is clear from equation (3) that the resulting P^R would have positive as well as negative contributions from the different root trajectories. Therefore one can anticipate that P^R would vary non-monotonically and that there could be resonances. Indeed, our quantum calculations[15] confirm such an expectation and show that the (He, H_2^+) collisions are rich in reactive scattering resonances.

Rotationally inelastic collisions

While investigating the rotationally inelastic rigid rotor HF($J_i=0$)-Li collisions at zero impact parameter ($b=0$) we had noticed[16] that the final rotational action J_f—the classical equivalent of the rotational quantum number—varied smoothly for certain ranges of the relative orientation θ_i between the atom and the diatomic molecule, and that it varied erratically for certain other ranges of θ_i. An examination[17] of the irregular region revealed additional structures with increase in resolution along the θ_i axis. Particularly with a 10^5-fold increase in resolution, the self-similar pattern that repeated itself became apparent. This would be called a *statistical fractal* in contrast to a fractal like the Cantor set wherein the repetition is *exact*. The functional dependence of J_f on θ_i is reflected in plots of collision time as well as the scattering angle χ as a function of θ_i. To examine if the 'fractals' could be 'observed' in three-dimensional collisions we varied b_i systematically and found that there were indeed regular and irregular regions in $J_f(b_i)$ and $\chi(b_i)$ plots. But it is not clear whether these patterns would survive θ_i and b_i averaging and thus be amenable to observation. Polanyi and Wolf[18] had observed a similar behaviour in rotationally inelastic collisions between a rigid rotor and a rigid surface and pointed out that the rotational rainbows (which could be observed) would get quenched as a consequence.

Molecule–surface collisions

There has been considerable effort made in the last decade or so to understand the dynamics of gas–surface interactions to the same extent that has become possible for the gas phase. For example, Gadzuk[19] has investigated I_2–W collisions and pointed out how under certain conditions the trajectories were simple and under certain other conditions quite complicated. To understand the dynamics fully, we plotted n_f versus ϕ_i for I_2 ($n_i=0$)–W collisions at $E_{tr}=0.25$ eV for a constrained parallel approach of the diatomic molecule to the rigid surface. The $n_f(\phi_i)$ plot revealed[20] additional structures with increase in resolution along the ϕ_i axis for almost the entire range (0–2π) of ϕ_i possible, implying that the scattering was mostly irregular. That means, for such systems, the chances of observing the chaotic behaviour experimentally are high.

For an H_2–M model potential with a barrier of 1 eV for dissociative chemisorption, we found[21] that there were clear-cut D (dissociative) and N (non-dissociative) bands, as illustrated in Figure 4,*a*. But a closer examination revealed that the switch-over region contained alternating D and N bands. It can be stated in general that, whenever the dissociation probability is nonzero but less than unity, there would be D and N bands and the switch-over region would contain fractal singularities. Duff and Truhlar[22] had earlier pointed out for collinear atom–diatom collisions that, whenever the exchange channel was open and $0 \leq P^R \leq 1$, there would be R and NR bands with a chattering region in between. Pechukas and Pollak[23] pointed out that in such a situation there would be

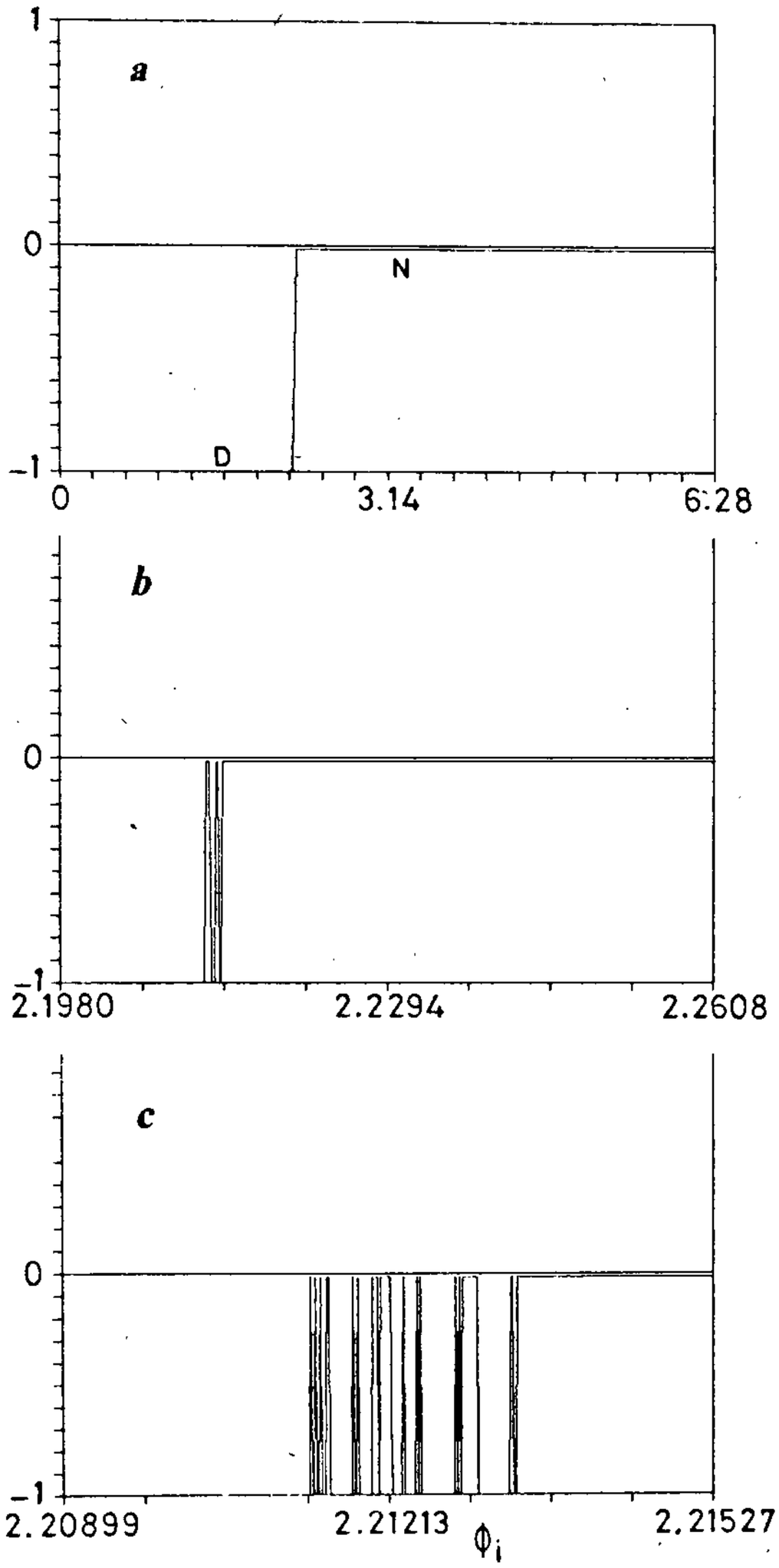

Figure 4. *a*, Action–angle plot for H_2 ($n_i = 0$)–surface collisions on a model potential-energy surface at $E_{tr} = 0.517$ eV obtained from 200 trajectories. Results with a magnification of 2×10^2 and 2×10^3 along the ϕ_i axis are illustrated in *b* and *c* respectively. Dissociative trajectories have been assigned an n_f value of -1.

trajectories that would be trapped forever—unable to make up their mind to come out in either channel. Indeed, we find that, in the case of molecule–surface collisions also, there are trapped trajectories in the switch-over region.

Interparticle diffusion

To understand the dynamics of H diffusion in a lattice, we have considered a model[24] in which an H atom is allowed to diffuse towards another H atom held stationary at the centre of a four-fold symmetric potential field with the four 'hills' corresponding to four rigid lattice atoms. While most of the trajectories for different initial conditions are simply reflected there are a number of them that traverse through the 'canal' and a small fraction of them that undergo multiple collisions and are long-lived. In addition to plotting the scattering angle χ and lifetime τ as a function of the impact parameter Y, which revealed fractal patterns, we have also plotted the position of the trajectories at equal intervals of time in the (X, Y) space and found a very interesting pattern, illustrated in Figure 5. There are interesting focusing and defocusing effects. In addition to the aesthetically pleasing spiral patterns and vortices, the figure shows that the configuration space is not uniformly filled. The implications for interparticle-diffusion observables remain to be understood.

Meaning of the fractal dimension

So far we have focused our attention on discerning fractal patterns that could, in principle, be characterized by a fractal dimension, a scale-invariant property Unfortunately there does not seem to be any unique definition of D_F (ref. 5). Often one computes the capacity dimension D_{ca}, which is identical to the Hausdorff (or fractal) dimension for fractals like the Cantor set. For scattering systems, D_{ca} can be computed by counting the number N_ε of square boxes

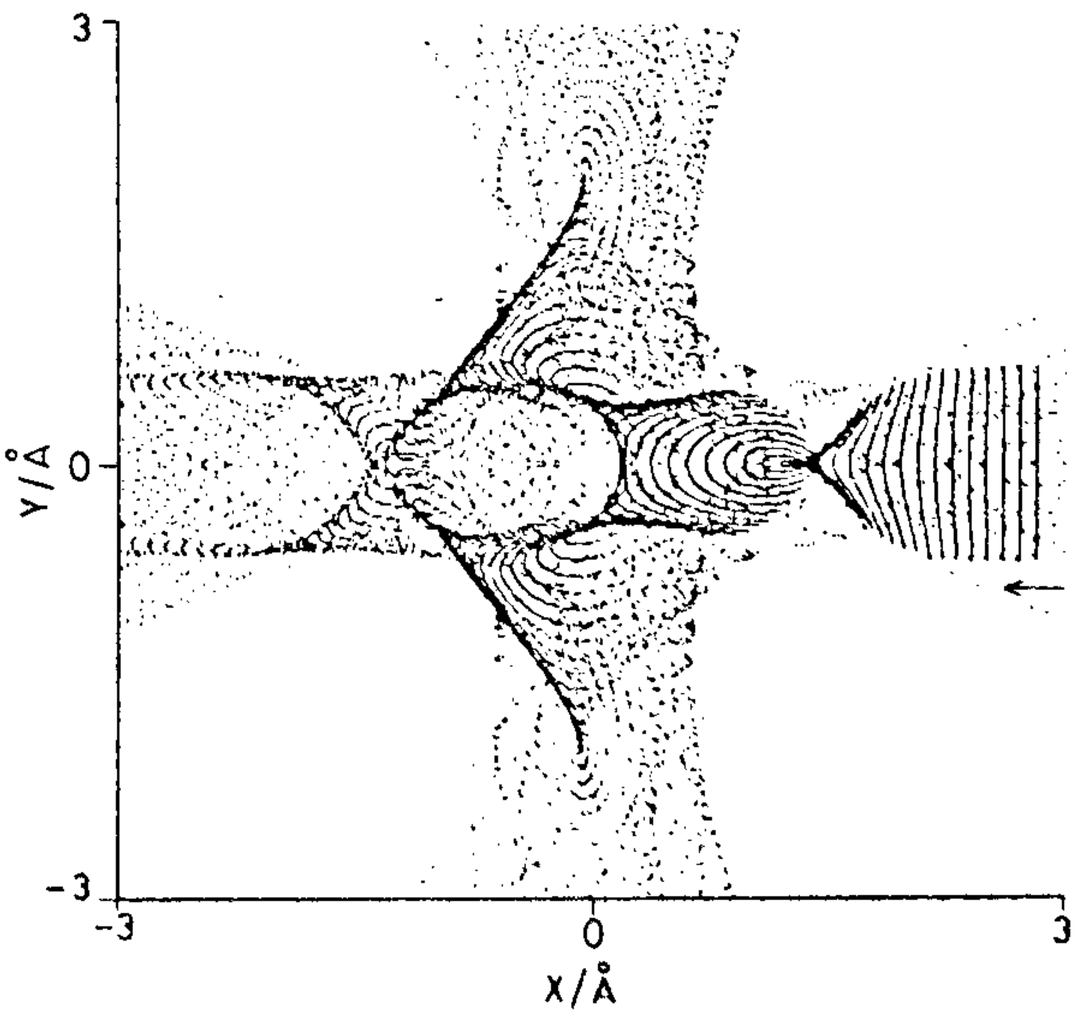

Figure 5. Propagation of a family of trajectories corresponding to the motion of one H atom towards another, from right to left as indicated by the arrow.

of length ε actually visited by the trajectories as follows:

$$D_{ca} = \lim_{\varepsilon \to 0} [\ln N_\varepsilon / \ln (1/\varepsilon)]. \quad (4)$$

A plot of $\ln N_\varepsilon$ versus $\ln(1/\varepsilon)$ yields a straight line with a slope D_{ca} for not-too-large and not-too-small values of ε. An alternative approach is to compute the correlation dimension D_{co} defined as

$$D_{co} = \lim_{r \to 0} [\ln C(r) / \ln r], \quad (5)$$

where $C(r)$ is the correlation function giving the average fraction of points lying within a radius r from a point. If N is the total number of points and $P(r)$ the number of points with a separation not more than r,

$$C(r) = P(r)/N^2. \quad (6)$$

For the $He-H_2^+$ collisions discussed above, D_{ca} and D_{co} differ from each other: 1.68 ± 0.03 and 1.33 ± 0.02 respectively. The reason is that the former ignores the variation in the density of points while the latter includes them. There are other ways of computing fractal dimension but I shall not go into all of them here. I only wish to emphasize that what is important is not the absolute value of D_F but the fact that it is not an integer and is less than the Euclidean dimension. It is worth adding that it plays a role somewhat analogous to that of the surprisal parameter in a surprisal analysis[25] used in compacting large volumes of state-to-state rate constant/cross-section data. Singh and Chattaraj[26] tried to relate the dynamics to the structure by computing the 'observables' in a study of scattering from a fractal lattice. But a clear picture of the relation between structure and dynamics in this context is yet to emerge.

Concluding remarks

Atomic and molecular collisions in general exhibit regular as well as irregular scattering, the fraction of each in the global behaviour being dependent on the nature of the potential-energy surface, mass combination of the collision partners, energy conditions, etc. As a matter of fact, two almost 'identical-looking' potential-energy surfaces have been known to yield two different dynamical behaviours: on one the scattering is completely regular and on the other it is regular for a range of ϕ_i and irregular for the remaining values of ϕ_i (ref. 27). Since it has become possible recently to study chemical events in the femtosecond time domain[28], it is possible, in principle, to control the vibrational phase for the reactants, which in turn means that we could choose between regular and irregular scattering, thus paving the way to controlling chemical reactions.

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