Fractional behavior in nonergodic reaction processes of isomerization

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We present numerical evidence of fractional behavior in reactions for a prototype model of three-degree-of-freedom isomerization. The survival probability in the well exhibits two distinct ranges of time scales: one where it decreases with a power law, and the other where it decreases exponentially. Trajectories corresponding to power law decays exhibit $1/f$ spectra and subdiffusion in action space, and those with exponential decays exhibit Lorentzian spectra and normal diffusion. The existence of these two types of behavior is explained on the basis of nonergodicity in the network of nonlinear resonances (Arnold web) in the well, and connection between the saddle and the Arnold web. Implications of the fractional dynamics are discussed in terms of Maxwell’s demon in molecules.

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The time development of complex systems often deviates from what we expect based on the conventional statistical laws [1]: relaxation processes exhibit power law decays and diffusion processes differ from the Brownian type. Moreover, power spectra show a $1/f$ dependence on frequency. Research areas involving such fractional behavior extend from fields of physics such as amorphous semiconductors [2], fluid mechanics [3], and Hamiltonian systems [4,5], to biophysics where long-time memories and anomalous diffusion are observed for a variety of biomolecules [6–8]. Fractional behavior is of interest also in econophysics [9] where prices in stock markets, for example, show anomalous fluctuation. The origins of such fractional behavior are attributed to the existence of hierarchical structures and/or the impossibility of separating characteristic time scales. These lead to breakdown of the underlying assumptions of the central limit theorem, giving rise to deviation from normal diffusive behavior. Thus, fractional behavior is expected to be ubiquitous in a wide range of fields involving complex systems.

Considering the possibility of fractional behavior in reaction processes opens a new frontier beyond the conventional ideas of the statistical reaction theory. In the conventional theory, reaction processes are supposed to be normal diffusive motions [10]. This idea is based on the assumption that the characteristic time scale for the reaction is much longer than that for trajectories to lose their memories. Then, reaction processes are regarded as being composed of many erratic dynamical motions, leading to Brownian type of diffusion. However, recent studies on reaction processes cast doubt on this assumption. For example, $1/f$ spectra are found in simulations of water clusters [11,12], and power law decays are observed in correlations of vibrational dephasing [13]. These studies indicate that the basic assumptions of the statistical reaction theory should be reexamined.

In particular, fractional behavior in reaction processes presents the possibility of Maxwell’s demon in molecules. This idea is based on recent studies where Maxwell’s demon is discussed in terms of fractional behavior in Hamiltonian dynamics [14]. An important aspect of these studies is that the problem of Maxwell’s demon is treated from a purely dynamical point of view without assuming the existence of a heat bath. The demon is conventionally supposed to work under thermal fluctuations [15,16]. Then, the only possibility for the demon is to wait for rare fluctuations [17]. However, if fractional behavior exists at molecular levels, the demon can utilize long-lasting memories inherent in anomalous fluctuations for sorting out molecules [18]. Thus, the existence of fractional behavior provides new resources with which Maxwell’s demon can work. On the other hand, decays of the exponential type lead to fast recovery of equilibrium, where Maxwell’s demon cannot operate. Therefore, studies of fractional behavior in reactions offer a new arena where possibility of information processing by molecules is considered.

However, dynamical approach to the demon has been limited to billiards and low-dimensional maps [5], although $1/f$ spectra have been found in systems of many degrees of freedom (DOFs) [4,11,12]. In this approach, it is supposed that fractional behavior is caused by “sticky regions” near tori and cantori, creating a hierarchy of dynamical barriers [19]. However, it is not obvious whether the same mechanism works in systems of more than two DOFs, since the dimension of tori is not sufficient to constitute dynamical barriers. Therefore, fractional behavior in systems of more than two DOFs presents a new problem in nonlinear physics. In particular, no studies exist where fractional behavior is found for Hamiltonian systems describing reaction processes. This leads us to seek fractional behavior in Hamiltonian systems which are relevant to molecules. This will support more realistic arguments about Maxwell’s demon in reactions.

Hamiltonian systems describing reaction processes have potential minima and saddles. Minima correspond to stable configurations of molecules, and saddles correspond to configurations which lie between stable ones. Locally near minima and saddles, a perturbative approach is possible as follows. Around minima, the normal form theory offers a
method to represent the Hamiltonian in terms of nonlinear vibrational modes [19]. The normal form breaks down at locations in phase space where nonlinear resonances takes place, and enhanced energy transfer occurs among these modes. In general, nonlinear resonances constitute a network in action space (Arnold web), and resonance overlap causes global chaos [20]. Thus, characteristics of the Arnold web are important for intramolecular vibrational-energy redistribution [21–23]. In particular, nonuniformity of the Arnold web and distribution of resonance overlap are crucial for fractional behavior.

As for saddles, the normal form theory has been recently developed based on geometric structures in phase space called normally hyperbolic invariant manifolds (NHIMs) [24–26]. The theory offers a sound foundation for the concept of transition states in systems of many DOFs in general. Moreover, reaction processes can be well described by the theory at least near saddles [27]. The theory can be applied to reactions ranging from atomic, molecular [25,28,29], and cluster physics [30,31] to even celestial mechanics [32]. In the search for fractional behavior in Hamiltonian systems describing reactions, global aspects should be taken into account; that is, dynamics near saddles and around minima, and how they are connected [33]. Thus, we need to combine the results obtained by applying the normal form theory locally near saddles and minima.

In this Rapid Communication, we present numerical evidence of fractional behavior in a model Hamiltonian system of three degrees of freedom (3DOF) describing reaction dynamics. We show that the fractional behavior results from nonuniformity of the Arnold web and the connection between the web and the NHIM around the saddle.

The model Hamiltonian corresponds to a 3DOF system with a double-well potential. The process of going over the saddle is regarded as an isomerization reaction taking place with nonergodic dynamics in the well,

\[ H = H_0 + H_1, \]

\[ H_0 = \frac{p_1^2}{2} - \frac{\lambda^2 q_1^2}{2} + bq_1^4 + \sum_{i=2}^{3} \left( \frac{p_i^2}{2} + \omega_i^2 q_i^2 + bq_i^4 \right), \]

\[ H_1 = e^{-(q_1 - 1)^2/\sigma^2} \left[ C_1 q_1 q_2^2 q_3^2 + C_2 (q_1 - 1)^2 (q_2^2 + q_3^2) \right]. \]  

(1)

Here \( q_1 \) is the reaction coordinate, and \( q_i \ (i = 2, 3) \) are the bath coordinates. The values of the frequencies are \( \omega_1 = 1.02, \omega_2 = 0.94, \) and \( \omega_3 = 1.04. \) The frequency \( \omega_1 = \lambda/\sqrt{2} \) is the unperturbed frequency at the bottom of the well at \( q_1 = 1. \) We choose the coupling function and the parameters \( (\sigma = 0.5, q_1 = 0.1, q_2 = 0.9, \) and \( b = 0.5 \) so that the interactions among the modes take place more in the well than near the saddle. This is valid for energy values slightly above the saddle energy [30]. In the well, \( H_0 \) consists of nonlinear oscillators with actions \( J_i \ (i = 1, 2, 3), \) which are described by elliptic functions. Their nonlinear frequencies are given by \( \omega_i = \partial H_0 / \partial J_i \ (i = 1, 2, 3). \) Then, the following primary resonances exist: \( \bar{\omega}_1 = \bar{\omega}_2, \bar{\omega}_1 = \bar{\omega}_3, \) and \( \bar{\omega}_2 = \bar{\omega}_3. \)

Initial conditions are chosen to be uniformly distributed on the unstable manifold of the NHIM near the saddle with energy value \( E = 0.1, \) while the potential energy at the saddle and the minimum is 0 and \( -0.125, \) respectively. Then the residence time \( t_r \) inside the well is estimated for each trajectory in unit of the period

\[ t_r = \frac{1}{2\pi\sqrt{\omega_1}}. \]

By adding the number of trajectories with their residence times from \( t_r \) to infinity, we obtain the number of trajectories which remain in the well at the residence time \( t_r \). The ratio of this quantity to the total number of the trajectories gives the survival probability \( P(t_r). \) In Fig. 1, \( P(t_r) \) shows two distinct time scales: up to about 100 cycles, \( P(t_r) \) decays as \( t_r^{-0.83}, \) and, for longer time scales, \( P(t_r) \) decays as \( \exp(-0.0015t_r) \) (the dashed lines), respectively.

What is the origin of the coexistence of the two distinct time scales in \( P(t_r) \)? This results from the nonuniformity feature of the underlying Arnold web, as shown in Fig. 2. Here, the average location is plotted for each trajectory in action space. The location is estimated each time the trajectory crosses a surface of section \( (q_1 = 1 \) with \( p_1 > 0), \) and their average is taken over the residence time. In Fig. 2, the different colors represent trajectories exhibiting power law [orange (gray)] and exponential [blue (black)] decays, respect-
A representative trajectory (light green curve) corresponding to exponential decay behavior and the primary resonances are also displayed for comparison.

In Fig. 2, we can see that blue (black) and orange (gray) points are distributed in different regions in action space. This suggests that dynamical structures exist which prevent trajectories from exploring the whole phase space. While blue (black) points are spread around the resonance junctions, orange (gray) points lie away from the resonance junctions. Note that resonance overlap takes place near junctions leading to fully chaotic motions. Thus, while trajectories corresponding to blue (black) points experience fully chaotic regions, those corresponding to orange (gray) points do not. These features do not change qualitatively when the energy is changed moderately.

How do trajectories behave when they wander away from fully chaotic regions? Figure 3 shows diffusivity in action space and the Fourier spectrum of the autocorrelation of $J_1$ for trajectories exhibiting power law decays. The diffusivity in action space is defined by

$$\sigma_1(t,t_0) = \langle [J_1(t) - J_1(t_0)]^2 \rangle,$$

where the mean square displacement of $J_1(t)$ at time $t$ is averaged over an ensemble of trajectories. The ensemble is composed of trajectories whose residence times are equal to a chosen value (60 cycles in Fig. 3). Here, trajectories showing power law decays exhibit subdiffusion in action space with $1/f$ spectra. This implies that they experience hierarchical structures. To the contrary, trajectories showing exponential decays exhibit Lorentzian spectra [34]. Thus, the coexistence of dynamically distinct regions brings about the difference in $P(t)$. How do trajectories leaving from (approaching) the saddle land on (depart from) the Arnold web? In other words, what is the connection between the web in the well and the NHIM around the saddle? Figure 4 shows how the local diffusivity $\sigma_1(t,t_0)$ varies as trajectories wander around in the web. The averages are taken over trajectories showing exponential decays of $P(t)$. Here, the variation of diffusivity is shown for three $t_0$ corresponding to three different regions on the Arnold web, just after landing on the web, just before departing from it, and a region intermediate between these, respectively. In the inset of Fig. 4, the power $p$ of the local diffusivity $\sigma_1(t,t_0) = (t-t_0)^p$ is shown as a function of $t_0$. This indicates that trajectories of exponential decays travel through regions of different statistical nature: subdiffusion (just after landing on the web) $\rightarrow$ normal diffusion (moving about the web) $\rightarrow$ subdiffusion (just before departing from the web at $t_f$). Moreover, local Fourier spectra correspondingly change as $1/f \rightarrow$ Lorentzian $\rightarrow 1/f$ [34]. This indicates that trajectories leaving the saddle first visit regions remote from the resonance junctions and exhibit subdiffusion. Some migrate into regions near the junctions yielding local ergodicity while the others go back to the saddle directly showing power law decays. Those showing local ergodicity migrate back again into subdiffusive regions before returning to the saddle. It takes a longer time to find a way out of the locally ergodic regions. Thus, they have longer residence times than those of power law decays.

In this Rapid Communication, fractional behavior is shown for a 3DOF Hamiltonian system describing a prototype isomerization reaction. This fractional behavior is analyzed in terms of the coexistence of distinct dynamical regions on the Arnold web, and how these regions are connected with the NHIM. Note that similar fractional behavior has recently been found in isomerization of HCN [34]. Hierarchical structures have also been observed experimentally or numerically in other real molecules, e.g., spectra of stimulated emission pumping for acetylene [35,36], and potential energy fluctuation in liquid water [12].

Based on our results, we propose the possibility of a Maxwell’s demon system in molecules: The Maxwell’s demon system is composed of two chambers, and a nonequilibrium distribution is maintained between the two chambers for a
fairly long time [5]. Suppose a system has a double-well potential with the property that the survival probability within each well exhibits power law decays with different powers, and it takes a long time to establish equilibrium within each well exhibits power law decays with different powers, and it takes a long time to establish equilibrium between the two. This is a molecular version of the system studied in [14]. Moreover, a dynamical ratchet could be constructed by connecting in sequence wells with nonuniform Arnold webs (for a ratchet, see [37]). How fractional behavior in classical and quantum dynamics corresponds is also important [38,39]. The larger the number of degrees of freedom, the more likely they will correspond [40]. We will discuss this elsewhere.

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