

On correlation functions and the onset of chaotic motion^{a)}

M. L. Koszykowski

Sandia National Laboratories, Livermore, California 94550

D. W. Noid

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37870

M. Tabor^{b)} and R. A. Marcus

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

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A variety of correlation functions computed over a microcanonical ensemble for the Hénon–Heiles system are investigated. We find the general trend is that of a gradual change to some form of decaying behavior as the motion becomes predominantly chaotic. The decay of a mode energy correlation function indicates a time scale for intramolecular energy redistribution.

I. INTRODUCTION

In unimolecular reactions, in chemical activation experiments, and in infrared multiphoton dissociation a bond or group of bonds is vibrationally excited, by collision in the first case, by a chemical reaction in the second, and by an infrared laser in the third. The rate of energy transfer to other bonds is a matter of much current interest. It is often assumed at high energies, in a statistical theory such as RRKM, that this energy relaxes intramolecularly in a time short compared with the mean time for the subsequent dissociation or isomerization of the molecule. In the present paper we investigate classical mechanical mode energy relaxation, both in the so-called stochastic and quasi-periodic regimes. These regimes in modern nonlinear dynamics are briefly described first.

Hamiltonian systems are classified as integrable or nonintegrable, the former being relatively rare and including (but not limited to) those solvable by separation of variables. Integrable Hamiltonian systems of N degrees of freedom are systems with N first integrals. For such systems, all the trajectories in $2N$ -dimensional phase space are actually confined to N -dimensional manifolds, referred to as invariant tori, imbedded in the $(2N-1)$ -dimensional energy shell. The KAM theorem¹ tells us that for a sufficiently weak nonintegrable perturbation most tori are still preserved. However, as the perturbation strength is increased, more and more tori are destroyed and the trajectories start to explore the energy shell in a chaotic manner. (The term “stochastic” is sometimes used in this context to imply a chaotic, randomlike behavior—the motion is still, of course, deterministic.)

Numerical studies of some simple Hamiltonian systems^{2,3} show that there is, in fact a rather rapid, although not sharp, transition from predominantly integrable motion to predominantly chaotic motion. These results have led to the notion of a critical energy, or

perturbation strength, that marks this transition. A number of criteria for predicting this quantity have been proposed³ and among these is one due to Mo⁴ that is based on the use of the generalized Langevin equation formalism. A particular correlation function is assumed there to change from oscillatory to diverging behavior at the critical energy, and quite good agreement was obtained with the observed behavior of a number of simple systems. Here we examine a number of correlation functions and, although the behavior is not always easy to characterize, the general trend is that of a gradual change to some form of decaying behavior as the motion becomes predominantly stochastic, rather than a relatively sharp transition. We also study a mode energy correlation function that provides information on the time scales for intramolecular energy transfer processes.

II. GENERALIZED LANGEVIN EQUATION AND CORRELATION FUNCTIONS

For a Hamiltonian system the motion of some associated dynamical variable $a(t)$ is given by Liouville's equation

$$\frac{d}{dt} a(t) = iL a(t), \quad (2.1)$$

where iL is the Liouville operator of that system. This motion can also be described by a generalized Langevin equation⁵

$$\frac{d}{dt} a(t) = i\Omega a(t) - \int_0^t d\tau K(\tau) a(t-\tau) + F(t), \quad (2.2)$$

provided the proper choice of the frequency Ω , the memory function $K(\tau)$, and random force $F(t)$ is made. The correlation function of $a(t)$ is defined as

$$C(t) = \langle a(0)^*, a(t) \rangle, \quad (2.3)$$

where the asterisk denotes complex conjugate and the brackets denote an inner product that depends on the ensemble chosen. $C(t)$ is related to the memory function by the equation

^{a)}Contribution No. 6159.

^{b)}Present address: La Jolla Institute, La Jolla, Calif. 92037.

$$\frac{d}{dt} C(t) = i\Omega C(t) - \int_0^t d\tau K(t-\tau)C(\tau). \quad (2.4)$$

When $K(\tau)$ is taken to be a delta function and the frequency Ω set to zero, the generalized Langevin equation reduces to the familiar equation for Brownian motion.

In this case the correlation function exhibits a pure exponential decay characteristic of a Gaussian Markov process.⁶ The introduction of certain projection operators⁵ enables the systematic and random parts of $a(t)$ to be separated and one can then deduce the form of the random force $F(t)$ and the memory function $K(t)$. The frequency Ω is related to the initial time derivative of the correlation function; in what follows we shall take it to be zero. This is the usual case.⁵

The Laplace transform of Eq. (2.4) yields the simple relationship

$$\tilde{C}(s) = \frac{1}{s + \tilde{K}(s)}, \quad (2.5)$$

where the tildes denote the transformed functions and s is the Laplace transform space variable. Mori^{7,8} has shown that $\tilde{K}(s)$ can be represented in the form of a continued fraction involving functions of the moments of the Liouville operator, i.e., of quantities of the form $Y_n = \langle (iL)^n a, (iL)^n a \rangle$. Substitution of that form of $\tilde{K}(s)$ into Eq. (2.5) gives a similar continued fraction representation for $\tilde{C}(s)$. A finite order truncation of this representation leads to an expansion of $C(t)$ of the form

$$C(t) = \sum_i c_i \cos(\Omega_i t), \quad (2.6)$$

where the c_i are constant coefficients and the frequencies Ω_i are fairly complicated functions of the moments of the Liouville operator; they should in no way be confused with the classical frequencies of the motion.

In the work of Mo,⁴ the dynamical variable

$$a(t) = \sum_{i=1}^N (p_i^2 + q_i^2) \quad (2.7)$$

was used, being taken to represent the distance of a phase point (on a given trajectory) from the origin. The correlation function of $da(t)/dt$, cast in a form analogous to Eq. (2.6), was investigated. It was deduced that the frequencies Ω_i became complex, leading to a change from oscillatory to diverging behavior, at energies in quite good agreement with the observed "critical energy." An analysis of Mo's method is given by Tabor.³

In analyzing the behavior of correlation functions the choice of inner product, i.e., ensemble average, is crucial. This choice is motivated by physical considerations. For example, in the case of integrable motion the trajectories lie on tori and any dynamical variable can be expressed as a Fourier series of the form

$$a(t) = \sum_{\mathbf{m}} a_{\mathbf{m}} \exp[i(\mathbf{m} \cdot \boldsymbol{\omega} t + \delta)] \quad (2.8)$$

where the $a_{\mathbf{m}}$ are certain coefficients [labeled by the integers $\mathbf{m} = (m_1 \dots m_N)$], $\boldsymbol{\omega} = (\omega_1 \dots \omega_N)$ the vector of classical frequencies associated with a given torus, and $\delta = (\delta_1 \dots \delta_N)$ a set of arbitrary initial phases. For a certain class of line-shape functions^{9,10} we have used the

family of trajectories lying on a particular torus as the ensemble. This results in the correlation function taking the simple form

$$C(t) = \langle a(0)^* a(t) \rangle_{\text{torus}} = \sum_{\mathbf{m}} |a_{\mathbf{m}}|^2 e^{i\mathbf{m} \cdot \boldsymbol{\omega} t}. \quad (2.9)$$

In the case of the frequencies ω_i being incommensurable, it may be shown that the orbits cover the torus ergodically.¹¹ We then take the ensemble average to equal the time average; i.e., Eq. (2.9) can be computed with a single trajectory.⁹

However, if we choose the microcanonical ensemble (a suitable choice of ensemble for studying energy randomization in unimolecular reactions), then for integrable motion $C(t)$ can no longer take the simple form of Eq. (2.9). Rather, it will correspond to contributions of the form of Eq. (2.9) averaged over all tori. The result will be some nontrivial behavior oscillating about the mean value $\langle [a(0)]^2 \rangle$. Typically the frequencies vary slightly from torus to torus and so each line in the power spectrum of $C(t)$ [as given by Eq. (2.9)] will now become a band.

In the chaotic regime, the majority of trajectories are no longer confined to tori but explore most of the energy shell. However, the behavior of the correlation function in this regime can be entirely different from its behavior in the integrable regime even when one also uses the microcanonical ensemble. A characteristic of the chaotic regime is the (exponential) divergence of nearby trajectories.¹ This then means that the correlation between them decreases and hence the microcanonical ensemble averaged correlation function must decay, albeit in an oscillatory manner, with increasing time. This is quite easy to see since

$$C(0) = \langle a(0)^* a(0) \rangle = \langle [a(0)]^2 \rangle \quad (2.10)$$

and

$$C(\infty) = \langle a(0)^* a(\infty) \rangle = \langle a(0) \rangle \langle a(\infty) \rangle = \langle a(0) \rangle^2. \quad (2.11)$$

Since mean square is greater than square mean, $C(t)$ must decay as t approaches infinity. Note that we have only been able to obtain the decomposition [Eq. (2.11)] by assuming that the motion is stochastic (in the strict sense of the word) and hence $a(0)$ and $a(\infty)$ are uncorrelated. We cannot do this when $a(t)$ is multiply periodic. Generally speaking, in the chaotic regime, we cannot assume that the trajectories are ergodic over the whole energy shell. Hence the ensemble average must be obtained by averaging over many trajectories rather than from the time average of a single trajectory.

III. RESULTS

In order to illustrate these ideas we have performed a numerical investigation of correlation functions of the well-known Hénon-Heiles system

$$H = \frac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2) + q_1 q_2 - \frac{1}{3} q_1^3. \quad (3.1)$$

We first study the correlation function investigated by Mo, i.e., the (normalized correlation function of $\dot{a}(t)$, where the dot denotes the time derivative,

$$D(t) = \frac{\langle \dot{a}(0)^* \dot{a}(t) \rangle}{\langle \dot{a}(0)^* \dot{a}(0) \rangle}, \quad (3.2)$$

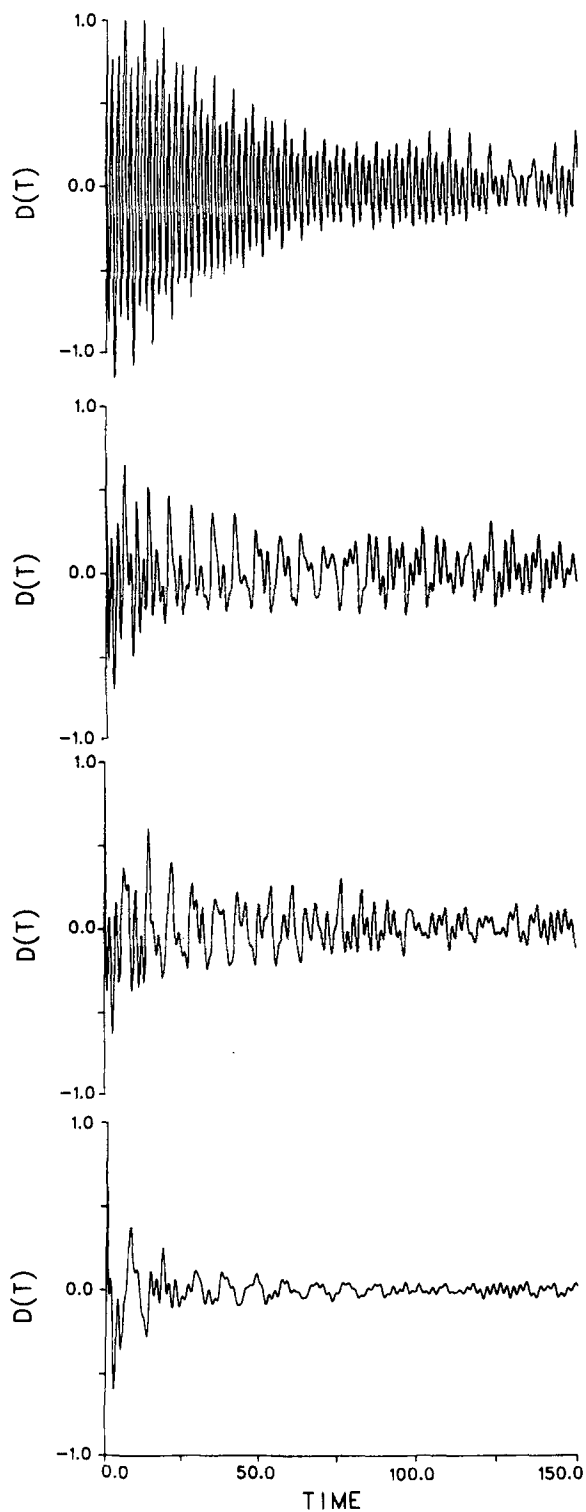


FIG. 1. Normalized auto correlation function $D(T)$ [Eq. (3.2)] computed at energies (from top to bottom) 0.0367, 0.1167, 0.1367, and 0.1667.

and where the dynamical variable $a(t)$ is

$$a(t) = \sum_{i=1}^2 ([p_i(t)]^2 + [q_i(t)]^2). \quad (3.3)$$

The ensemble is the (normalized) microcanonical ensemble, i.e., for any function $f(p, q)$ the brackets denote

$$\langle f(p, q) \rangle = \frac{\int dp \int dq f(p, q) \delta(E - H(p, q))}{\int dp \int dq \delta(E - H(p, q))}. \quad (3.4)$$

The $2N$ dimensional integrals are reduced to $(2N - 1)$ -dimensional integrals over the surface of constant energy $E = H(p, q)$.¹²

In Fig. 1 we show $D(t)$ computed at a series of energies ranging from motion near the bottom of the potential right up to near dissociation ($E = 0.1667$).¹³ At the lowest energies, where the motion is predominantly integrable, $D(t)$ shows a regular oscillatory structure within a modulating envelope. As the energy is increased the oscillations become more and more irregular and at $E = 0.1667$, where the motion is almost entirely chaotic there is a clearly decaying envelope to the oscillations. The change in behavior as the motion changes from predominantly regular to predominantly chaotic can be seen more clearly by examining $D(t)$ computed over a longer time scale. Examples are shown in Fig. 2. Here the difference between the periodic envelope of oscillations at low energies and the decaying envelope at high energies is quite clear.

We have also investigated the correlation function of $a(t)$ [as given by Eq. (3.3)], i.e., the function

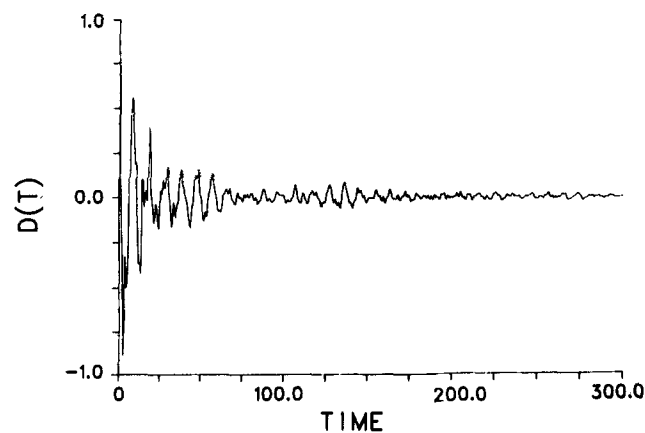
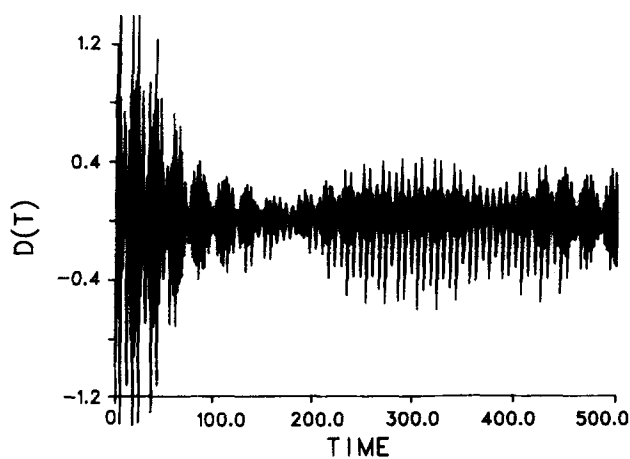


FIG. 2. $D(T)$ computed for longer times at energies 0.0067 (top) and 0.1667.

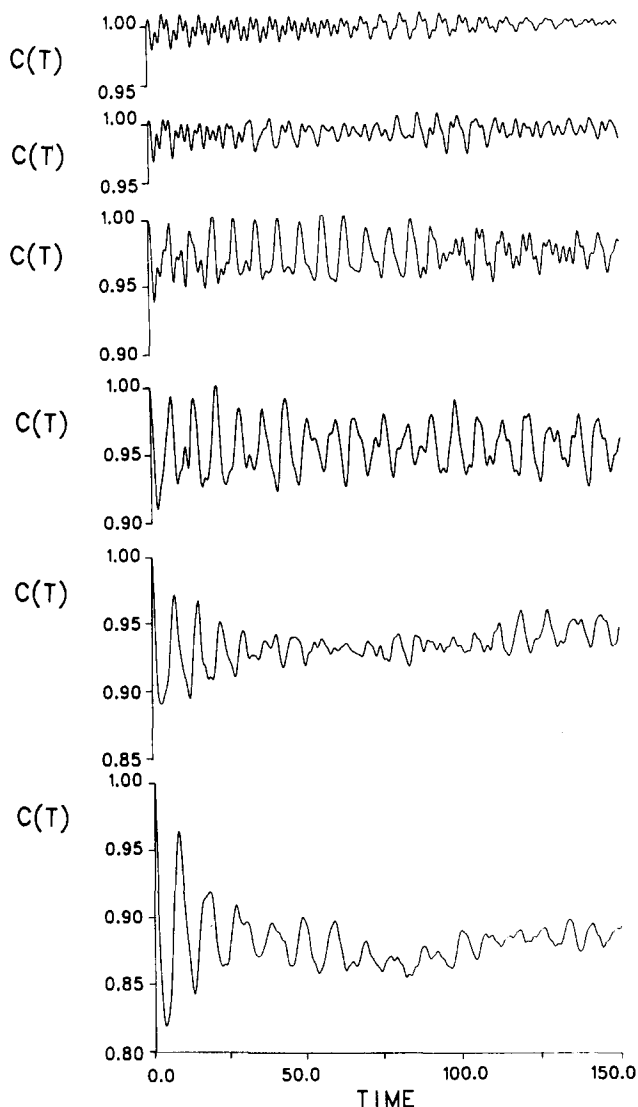


FIG. 3. Normalized auto correlation functions $C(T)$ [Eq. (3.5)] computed at energies (from top to bottom) 0.0367, 0.0767, 0.1167, 0.1367, 0.1567, and 0.1667.

$$C(t) = \frac{\langle a(0)^*, a(t) \rangle}{\langle a(0)^*, a(0) \rangle} . \quad (3.5)$$

In Fig. 3 we show $C(t)$ computed at some of the same energies used in Fig. 1 for $D(t)$. Now the change in behavior is much clearer. In the predominantly integrable regime, $C(t)$ displays a somewhat regular oscillatory structure about a constant mean. As the motion changes to predominantly chaotic at higher energies, a clearly decaying behavior sets in. For both $C(t)$ and $D(t)$ the change in behavior is gradual, and it would be difficult to determine a "critical energy" from their behavior. Our results suggest that Mo's method, as it now stands, has a questionable basis, since there is no clear break in behavior from oscillatory to exponential at the critical energy (0.112).

In Fig. 4 we show the scaled first moment of the Liouville operator (iL); i.e.,

$$Y_1 = \langle (iLa)^*, (iLa) \rangle / \pi^2 E_0^4 , \quad (3.6)$$

[where a is again given by Eq. (3.3)—but time indepen-

dent of course] at a series of energies.¹⁴ It displays, as must all other moments Y_n , a smooth dependence on energy. This smooth behavior simply reflects the increasing volume of accessible phase space with increasing energy. The scaled moments agree with those calculated⁴ by perturbation theory to about 15%.

Finally, we look at the correlation function of a physically more useful quantity, namely, an individual mode energy

$$a(t) = \frac{1}{2} \langle [p_1(t)]^2 + [q_1(t)]^2 \rangle . \quad (3.7)$$

The behavior of the corresponding $C(t)$ is shown in Fig. 5. The general trend is not easy to characterize, but there is again a clear change from a smooth periodic structure to a (rapidly) decaying behavior in the predominantly chaotic regime. The equipartition value of $C(t)$ is approximately 3/4. In the Appendix, we use a simple model to demonstrate that such a value is to be expected.

To model this correlation function we have introduced the following form for the memory function $\bar{K}(s)$:

$$\frac{1}{\bar{K}(s)+s} = \frac{a}{s} + \frac{f}{s+c} + \frac{b(s+c)}{(s+c)^2 + \omega_1^2} + \frac{ds}{s^2 + \omega_2^2} . \quad (3.8)$$

From Eq. (2.5) one finds that this function corresponds to a correlation function of the form

$$C(t) = a + (b \cos \omega_1 t + f) e^{-ct} + d \cos \omega_2 t . \quad (3.9)$$

Since $C(t)$ equals unity at $t=0$, f can be expressed in terms of a , b , c , and d . This correlation function has several oscillatory terms, some overall decay, and an average value at long times (a).

Using the following values for the constants in the chaotic regime: $a=0.74$, $b=0.13$, $c=0.1$, $d=0.01$ (and so $f=0.11$), $\omega_1=0.78$, $\omega_2=0.84$, and using for the constants in the quasi-periodic regime: $a=0.88$, $b=0.11$, $c=0$, $d=0.01$ (and so $f=0$), $\omega_1=0.05$, $\omega_2=1.05$, a comparison is given in Fig. 6 with two of the mode energy correlation functions of Fig. 5 in the range $0 \leq t \leq 75$. The fact that a has its equilibrium value ($\sim \frac{3}{4}$) in the chaotic case is reasonable.

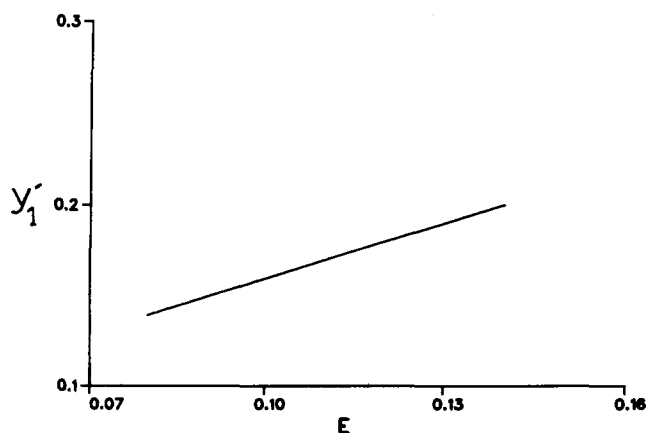


FIG. 4. Scaled first moment of the Liouville operator as a function of energy [Eq. (3.6)].

From the correlation function one can estimate a relaxation time for mode energy decay. In the case of unimolecular reactions, this would correspond to the time for significant intramolecular redistribution of energy in the isolated high energy molecules. Here we see a relaxation time varying from 20–30 vibrational

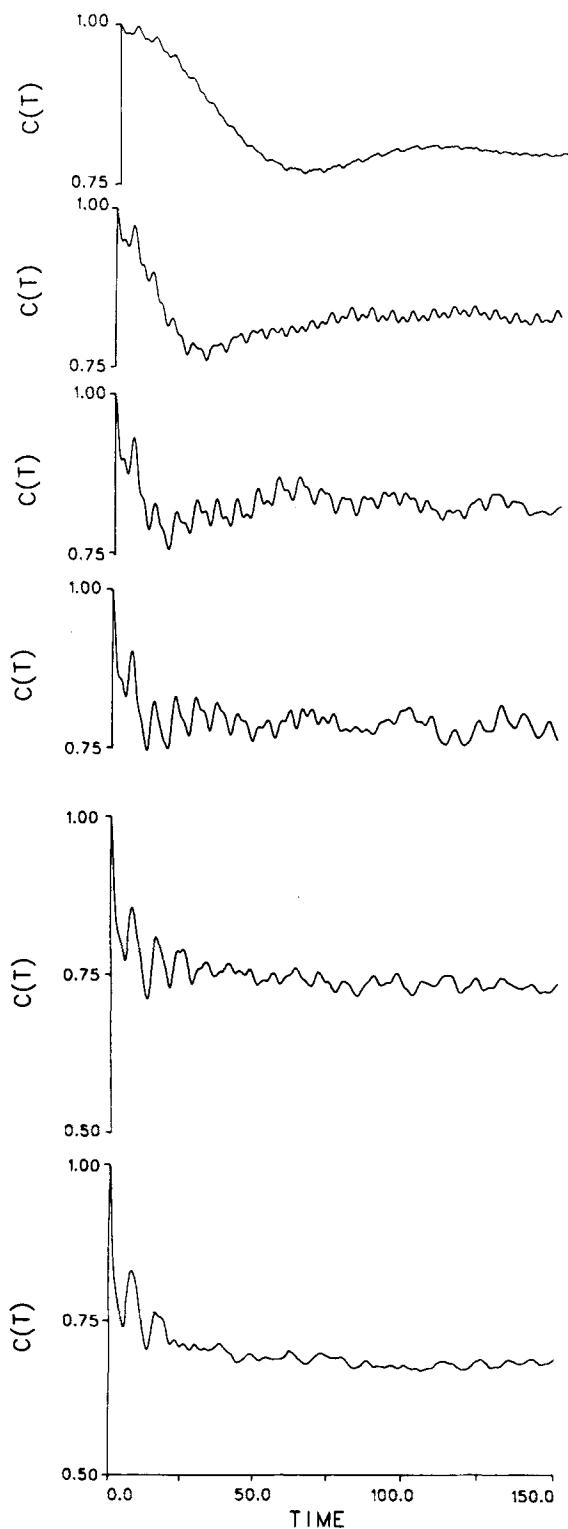


FIG. 5. Normalized mode energy autocorrelation functions corresponding to the energies of Fig. 3.

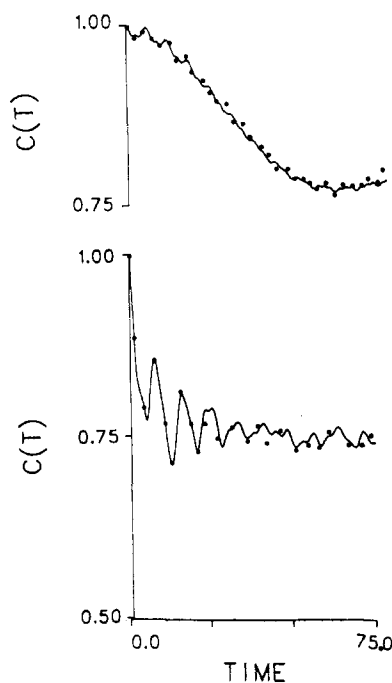


FIG. 6. Comparison of two of the results in Fig. 5 ($E = 0.0367$ and 0.1567) (dots in the present figure) with Eq. (3.9) (smooth curve in the present figure) using the constants cited in the text.

periods at low energy to 1–5 vibrational periods at high energy. In other computations¹⁵ and experiments¹⁶ this relaxation time has been found to be of the order of a picosecond. Finally, we remark that the relaxation time we deduce from the correlation function pertains to a rate of energy diffusion. This contrasts with other work¹⁷ where the time scale is deduced from a K -entropy-like quantity that is related to a dephasing time scale.¹⁸

IV. CONCLUSIONS

We have demonstrated that a variety of correlation functions, computed for the Hénon–Heiles system over a microcanonical ensemble, show a gradual change to some form of (oscillatory) decaying behavior as the motion becomes predominantly chaotic. The decay of a mode energy correlation function indicates a time scale for intramolecular energy redistribution of the order of a few vibrational periods in the chaotic regime. However, it should be pointed out that once a system becomes sufficiently large, correlation functions will decay independently of the underlying dynamics. As an example of this, we cite the study of the momentum autocorrelation function of a mass defect in a linear chain by Cukier *et al.*¹⁹ Thus, although the motion is entirely integrable, they were able to observe an almost pure exponential decay for a mass defect ratio of 0.1 in a chain of 50 particles. The multiply periodic trajectories of a sufficiently large integrable system generate a “randomness” comparable to that of the chaotic trajectories of a smaller, nonintegrable, system.

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APPENDIX

The "equipartition" value of the normalized autocorrelation function is simply given by

$$C(\infty) = \frac{\langle a(0)^* a(\infty) \rangle}{\langle a(0)^* a(0) \rangle} = \frac{\langle [a(0)]^2 \rangle}{\langle [a(0)]^2 \rangle}. \quad (\text{A1})$$

For the case of the mode energy correlation function for the Hénon-Heiles system, we may obtain a crude estimate of $C(\infty)$ by evaluating the mean square to square mean ratio of the mode energy in the absence of the intermode coupling.

For a pair of uncoupled oscillators, the Hamiltonian takes, in action angle variables, the simple form

$$H = I_1 \omega_1 + I_2 \omega_2. \quad (\text{A2})$$

The normalization integral is simply

$$\Gamma = \int d\theta \int dI \delta(E - H(I)) = (2\pi)^2 \int dI \delta(E - H(I)) \\ = \frac{(2\pi)^2 E}{\omega_1 \omega_2}. \quad (\text{A3})$$

The individual mode energy is just $I_1 \omega_1$; hence

$$\langle (\omega_1 I_1)^2 \rangle = \omega_1^2 \int d\theta dI \frac{I_1^2 \delta(E - H(I))}{\Gamma} \\ = (2\pi)^2 \frac{1}{3} \left(\frac{E^3}{\omega_1 \omega_2} \right) / (2\pi)^2 \left(\frac{E}{\omega_1 \omega_2} \right) = \frac{1}{3} E^2. \quad (\text{A4})$$

The mean value is just

$$\langle \omega_1 I_1 \rangle = \omega_1 \int d\theta \int dI \frac{I_1 \delta(E - H(I))}{\Gamma} \\ = (2\pi)^2 \frac{1}{2} \left(\frac{E^2}{\omega_1 \omega_2} \right) / (2\pi)^2 \left(\frac{E}{\omega_1 \omega_2} \right) = \frac{1}{2} E. \quad (\text{A5})$$

Hence the equipartition value is simply

$$C(\infty) = \frac{\langle (\omega_1 I_1)^2 \rangle}{\langle (\omega_1 I_1) \rangle^2} = \frac{\frac{1}{3} E^2}{\left(\frac{1}{2} E \right)^2} = \frac{3}{4}. \quad (\text{A6})$$

- ¹J. Ford, "The Statistical Mechanics of Analytical Dynamics" in *Fundamental Problems in Statistical Mechanics, II*, edited by X. Cohen, (North-Holland, Amsterdam, 1975), pp. 215-55.
- ²M. Henon and C. Heiles, *Astrophys. J.* **69**, 73 (1964); B. Barbanis, *ibid.* **71**, 415 (1968).
- ³These methods have been reviewed by M. Tabor in "The Onset of Chaotic Motion in Dynamical Systems," *Adv. Chem. Phys.* (to be published). See also P. Brumer "Intramolecular Energy Transfer: Theories for the Onset of Statistical Behavior," *Adv. Chem. Phys.* (to be published).
- ⁴K. C. Mo, *Physica* **57**, 455 (1972); A. Lonke and R. Caboz, *ibid.* **99A**, 350 (1979).
- ⁵R. Zwanzig, in *Lectures in Theoretical Physics, Boulder 1960*, edited by Britten, Downs, and Downs (Interscience, New York, 1960).
- ⁶M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.* **17**, 323 (1945).
- ⁷H. Mori, *Prog. Theor. Phys. (Kyoto)* **33**, 423 (1965).
- ⁸B. J. Berne, *Time-Dependent Properties of Condensed Media*, Vol. VII B in *Physical Chemistry: An Advanced Treatise*, edited by D. Henderson (Academic, New York, 1971).
- ⁹D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *J. Chem. Phys.* **67**, 404 (1977).
- ¹⁰D. W. Noid, M. L. Koszykowski, M. Tabor, and R. A. Marcus, *J. Chem. Phys.* **72**, 6169 (1980).
- ¹¹V. I. Arnol'd and A. Avez, *Ergodic Problems of Classical Mechanics* (Benjamin, New York, 1968).
- ¹²Writing dp_1 as $dH/(\partial H/\partial p_1)$ and integrating over H one obtains $\int f \dots \int f(\partial H/\partial p_1)^{-1} dq_1 \dots dq_N dp_2 \dots dp_N$, with p_1 determined from $H = E$ at the given energy. The sum is over the two branches (+ and -) of p_1 .
- ¹³To obtain the results in Figs. 1-3 and 5, initial conditions for integrating Hamilton's equations were chosen from a microcanonical ensemble, randomly in $q_1 \dots q_N p_2 \dots p_N$ space using the weighting factor in Ref. 12 to evaluate the expression there. Typically, several hundred trajectories were used. Hamilton's equations were integrated using the program ODE by L. F. Shampine for each initial condition.
- ¹⁴To obtain the results in Fig. 4 the integrand given by Eqs. (3.6) and (3.4) was evaluated, using the integral in Ref. 12; 10 to 12 million points were used (program MNTRL).
- ¹⁵D. L. Bunker, *J. Chem. Phys.* **37**, 393 (1962); **40**, 1946 (1964). W. L. Hase, in *Dynamics of Molecular Collisions, Part I*, edited by W. H. Miller (Plenum, New York, 1976), Chap. 3, and references cited therein.
- ¹⁶J. D. Rynbrandt and B. S. Rabinovitch, *J. Phys. Chem.* **75**, 2164 (1971).
- ¹⁷K. D. Hansel, *J. Chem. Phys.* **70**, 1830 (1979).
- ¹⁸G. M. Zaslavski and B. V. Chirikov, *Sov. Phys. Usp.* **14**, 549 (1972).
- ¹⁹R. J. Cukier, K. E. Shuler, and J. D. Weeks, *J. Stat. Phys.* **5**, 99 (1972).