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Intramolecular Vibrational Relaxation Seen as Expansion in Phase Space. 4. Generic Relaxation Laws for a Spectroscopic Clump Profile

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We examine the volume of phase space sampled by a nonstationary wave packet when the spectral function consists of a single clump or of a series of them. The relaxation laws are expressed in terms of reduced time variables τ, whose definition involves either the average density of states (for a single clump) or appropriately weighted average densities of states (when the spectrum consists of many clumps). Introducing reasonable approximations, very simple generic relaxation laws are derived for the ratio $N(\tau)/N_\infty$, which measures the fraction of available phase space that has been sampled by time τ. Under certain assumptions, these laws are found to depend neither on the number nor on the individual features (shapes and widths) of the clumps. However, they strongly depend on the nature (regular or chaotic) of the underlying dynamics. When the dynamics is regular, the relaxation law is expressed in terms of τ^{-1}, whereas the corresponding equation in the chaotic limit is slightly more complicated and involves terms in τ^{-2} and τ^{-2} ln τ. Phase space is thus explored according to essentially different relaxation laws in the regular and chaotic limits, the difference being appreciable during the entire relaxation. These laws reflect in the time domain the difference in the distribution of nearest-neighbor level spacings observed in the energy domain (Poisson or Wigner statistics).

I. Introduction

The aim of the present article is to contribute to the study of intramolecular dynamics taking place in a vibrationally excited isolated molecule, thus studied under collision-free conditions. The process by which vibrational energy is redistributed, denoted IVR for short, has been extensively studied by a large variety of approaches that all make use of the time-dependent picture of spectroscopy.[1−4] There exists a fascinating connection between intramolecular dynamics and spectroscopy, based on the fact that the Fourier transform of an optical spectrum $I(E)$ generates an autocorrelation function $C(t)$. When properly studied (e.g., when applied to homogeneously broadened spectra), this function can provide information on the relaxation process in the time domain.[5−13] We are especially interested here in the case of congested molecular spectra, measured at high energies, where detailed assignment in terms of traditional quantum numbers is impossible because the density of states is very high and the amplitude of the nuclear motions very large. In that case, the characteristics of the classical dynamics that underlies the relaxation process are known to appear in the energy domain. For example, on the basis of the frequency distribution of nearest-neighbor energy spacings, two limits can be defined:[5,6,10,14−22] regular dynamics, which leads to a Poisson distribution for adjacent spacings, and chaotic dynamics, which implies a Wigner distribution for nearest-neighbor energy spacings (i.e., an absence of zero spacings). The purpose of this article is to use this dichotomy to uncover some generic differences in the time domain between the dynamics of intramolecular vibrational energy redistribution in the two limiting cases.

To contribute to this problem, we concentrate on a typical spectral profile that seems to be of fairly general occurrence. At low energy resolution, the profile $I(E)$ consists of a number of peaks, each of which is found, at higher resolution, to be a clump of numerous narrow lines.[10,16,23−27] For example, in the stimulated emission pumping spectrum of acetylene in the 27 900 cm^{-1} energy region,[16] a typical clump is 1 or 2 cm^{-1} wide and consists of 50−100 narrow lines. This structure derives from the fact that, as a result of the Franck−Condon principle, the oscillator strength is spread over a small number of vibrational modes (bright states) that interact with a quasi-continuum of so-called dark states. A clump structure corresponds to an intermediate situation in which previously good quantum numbers have lost their value and is thus intermediate between the regular and chaotic limits. For such a spectral profile, how does phase space exploration proceed?

In previous articles of this series,[7−10] we have studied the time behavior of the quantum measure $N(t)$ initially introduced by Stechel and Heller.[5,6] This quantity measures the effective number of phase-space cells visited by the system during the relaxation process up to time t. Accepting that the spectrum can be described by a continuous function (i.e., replacing summations over discrete Franck−Condon factors by integrations over energy), we could show[10] that the function $N(t)$

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approaches its limiting value N_∞ as $-1/t$ in the regular case and as $-\ln t/t^2$ when the dynamics is chaotic. This result is general, but requires further clarification on an important point. It might be suspected that the differences in the asymptotic behaviors are detectable only at very long times, i.e., when the relaxation process is nearly completed. In such a case, the derived result would be of academic interest only.

However, by studying the *fraction* of phase space that has been sampled by time t (rather than its absolute magnitude), and by expressing the relaxation laws in terms of suitable reduced dimensionless time variables, we show here that a distinction between regular and chaotic dynamics can be established in the time domain where relaxation effectively takes place and not only in the limit of extremely long times. Furthermore, under certain assumptions, the derived relaxation laws are found to be generic. By this we mean that they do not depend on the number and individual features (shapes and widths) of the clumps but depend only on the nature of the underlying dynamics.

The paper is organized as follows. Section II describes the continuous model for the spectrum. In section III, we consider the relaxation of a single clump of levels. Different symmetric and asymmetric spectral profiles are studied, and generic relaxation laws are derived, both in the regular and in the chaotic limits. In the chaotic case, a reasonable approximation for the distribution function of all energy spacings is introduced. The relaxation laws are shown not to depend on the details of the spectral profile when appropriate dimensionless reduced time variables are adopted. Section IV deals with a spectrum that consists of a series of individual clumps. An averaging procedure over the clumps is proposed, which leads to the same generic relaxation laws as in section III with suitably modified parameters. Concluding remarks are presented in section V.

II. Continuous Model

Consider an optical spectrum $I(E)$ generated by a pure initial state (i.e., homogeneously broadened). The function $I(E)$ is required to be normalized, i.e., for an electronic spectrum,

$$\int_{-\infty}^{+\infty} I(E)\,\mathrm{d}E = \sum_k p_k = 1 \tag{2.1}$$

where the quantities p_k are Franck−Condon factors. Its Fourier transform generates an autocorrelation function $C(t)$ from which we wish to extract information in the time domain.

$$C(t) = \int_{-\infty}^{+\infty} I(E)\,\exp(-\mathrm{i}Et/\hbar)\,\mathrm{d}E \tag{2.2}$$

Different measures have been proposed to evaluate the volume of phase space available to a nonstationary wave packet in the infinite time limit or, equivalently, the effective number of quantum states that significantly contribute to the dynamics. These definitions can be grouped in a general formula[28−30]

$$N_{\mathrm{eff}} = (\sum_k \mathrm{p}_k^{1+\beta})^{-1/\beta} \tag{2.3}$$

where β is an arbitrary parameter. Stechel and Heller[5,6] advocate the choice $\beta = 1$, which defines the so-called inverse participation ratio. Alternatively, the limit $\beta \to 0$ generates the entropic measure of phase space which, as shown by Levine et al.,[25,26,31,32] has a more fundamental significance. Here, however, we adopt Heller's measure, which leads to simple and tractable equations. In that formalism, the number of phase space cells sampled as a function of time is denoted as $N(t)$.[6] Several previous studies[7,10−13] have shown the advantages of using the measure $N(t)$ instead of the survival probability $|C(t)|^2$ in the derivation of generic patterns of behavior. The function $N(t)$ has been shown[7,10] to increase from an initial value of 1 at $t = 0$ to a final value N_∞ according to the law

$$N(t)^{-1} = N_\infty^{-1} + 2S(t) \tag{2.4}$$

with

$$N_\infty^{-1} = \sum_k \mathrm{p}_k^2 \tag{2.5}$$

$$\begin{aligned} S(t) &= \sum_{k=1} p_k \sum_{n=k+1} p_n [\sin(\omega_{nk}t/2\hbar)/(\omega_{nk}t/2\hbar)]^2 \\ &\equiv \sum_{k=1} p_k \sum_{n=k+1} p_n\, \mathrm{sinc}^2(\omega_{nk}t/2\hbar) \end{aligned} \tag{2.6}$$

$$\omega_{nk} = E_n - E_k \tag{2.7}$$

Our analysis of phase space sampling is based on the mathematical properties of eqs 2.4−2.7 and, in particular, on the properties of the sinc function. This function was first derived by Heller.[6] He smoothed the spectral profile $I(E)$ and defined an envelope $I_T(E)$ as the result of the integration of the autocorrelation function between times $-T$ and $+T$. Heller noted the arbitrary nature of the procedure. However, we showed[7] that a sinc^2 function arises quite naturally by associating a measure to the density operator of an average distribution represented by a statistical ensemble in which the weights of the different states are determined by the dynamics of the system. It may also be mentioned that asymptotic laws were found not to be modified if the sinc^2 function is averaged over, i.e., is replaced by a Lorentzian decrease.[10]

Thus, eqs 2.4−2.7 are an exact quantum mechanical result if two assumptions are accepted: (i) the inverse participation ratio is a reliable measure of phase space sampling and (ii) the underlying spectrum is a line spectrum.

Very short times will be henceforth disregarded: they correspond to large energy gaps, i.e., to the interclump relaxation, and have no relevance to the problem dealt with here. As shown in a previous paper of this series,[10] when the spectrum is congested, i.e., when the energy gaps ω_{nk} are small, it is advantageous to replace the discrete summations by integrations over the continuous variables E and ω. The individual Franck−Condon factors p_k are replaced by a continuous function $p(E)$ such that $I(E) = p(E)\,D(E)$, where $D(E)$ is the density of states. Equation 2.5 then becomes

$$N_\infty^{-1} = \int_{-\infty}^{+\infty} [p(E)]^2 D(E)\,\mathrm{d}E = \int_{-\infty}^{+\infty} \frac{[I(E)]^2}{D(E)}\,\mathrm{d}E \tag{2.8}$$

Furthermore, it is profitable to take into account the statistical theory of energy levels.[14,15,17,18] The usual energy gaps ω are replaced by rescaled dimensionless quantities ϖ defined as

$$\varpi \equiv G(E+\omega) - G(E) \tag{2.9}$$

where $G(E)$ is the dimensionless integrated density of states, i.e.,

$$G(E) = \int_0^E D(E')\,\mathrm{d}E' \tag{2.10}$$

The procedure leads to[10]

$$S(t) = \int_0^{+\infty} g(\omega)\ \mathrm{sinc}^2(\omega t/2\hbar)\ \mathrm{d}\omega \qquad (2.11)$$

where

$$g(\omega) = \int_{-\infty}^{+\infty} I(E)I(E+\omega)D_{\varpi}[\varpi(\omega,E)]\ \mathrm{d}E \qquad (2.12)$$

The dimensionless function $D_{\varpi}[\varpi(\omega,E)]$ represents the density of all rescaled energy spacings (and not only the nearest-neighbor spacings). Finally, we also consider a simplified version of this function, which has already been studied in the literature[19,21,22]

$$q(\omega) = \int_{-\infty}^{+\infty} I(E)I(E+\omega)\ \mathrm{d}E \qquad (2.13)$$

III. Relaxation of a Single Clump

A. General Equations. Consider a spectral profile $I(E)$ restricted to a single clump of states. The clump may possibly have an internal structure (e.g., may possibly exhibit several maxima) but must obey two mathematical requirements. First, the intensity vanishes at both ends of its profile. Second, the clump has to be sufficiently narrow for its density of states $D(E)$ to be taken as a constant, denoted D. In such a case, the rescaled frequencies are simply given by

$$\varpi = D\omega \qquad (3.1)$$

Within each clump, the reduced variable ϖ no longer depends on E but on ω alone.

An important role will be played by the width of the clump, which is defined as follows:

$$\mu \equiv q(0)^{-1} = \left(\int_{-\infty}^{+\infty} [I(E)]^2\ \mathrm{d}E\right)^{-1} \qquad (3.2)$$

This can be justified by noting that if the density D is constant within the width of the clump, then (2.8) and (3.2) lead to

$$\mu = N_{\infty}/D \qquad (3.3)$$

which shows that the quantity μ has the dimension of energy and can be interpreted as the effective width of the clump.

B. Models. Different functions were examined to parametrize the shape of the overall clump envelope. Two symmetric bell-shaped functions were considered first: an inverted parabola $I(E) = 0.75(b^2 - E^2)/b^3$ (with $-b \le E \le b$) and a Gaussian function $I(E) = \exp(-E^2/b^2)/b\sqrt{\pi}$. Then, to examine asymmetric profiles, we turned to the functions $I(E) = E^n \exp(-E/b)/(b^{n+1}n!)$, where $0 \le E \le \infty$ and where the exponent n is allowed to vary between 0 and 10. Next, we tried two functions presenting a double maximum, viz., $I(E) = E^2 \exp(-|E|/b)/4b^3$, as well as the sum of two inverted parabolas of different widths. Finally, we considered a spectroscopic profile exhibiting $2n + 1$ regular maxima, i.e., the function $I(E) = 2\cos^2(E/b)/(2n+1)b\pi$ [with $-(2n+1)\pi b/2 \le E \le (2n+1)\pi b/2$]. In all of these examples, the parameter b has the dimension of an energy and is simply related to the width of the clump μ.

C. Regular Dynamics. It has been shown earlier[10] that in the regular case the relaxation proceeds according to a general asymptotic law given by

$$S_{\mathrm{reg}}(t) = \pi\hbar g(0)/t \qquad (t \to \infty) \qquad (3.4)$$

To proceed further, we note that the distribution function D_{ϖ} is equal to a constant,[14,15] which we denote K_{reg}, and which can be determined from the normalization condition $N(0) = 1$. In the Appendix, K_{reg} is shown to be equal to $1 - 1/N_{\infty}$. Since the continuous model implies a large number of levels, the term $1/N_{\infty}$ will henceforth be everywhere neglected with respect to 1 and K_{reg} will be simply replaced by one. From (2.12), (3.2), and (3.4), one has

$$S_{\mathrm{reg}}(t) = \pi\hbar/\mu t \qquad (3.5)$$

This result remains true even if the clump displays two or more maxima, provided only that the density of states can be assumed to remain constant within the energy range spanned by the clump.

If the efficiency of phase space sampling is to be assessed, the most interesting part of the relaxation law concerns the long-time behavior of the function $S_{\mathrm{reg}}(t)$. The value of N_{∞} for a typical clump is, e.g., of the order of 100. Let T be the time such that S is reduced to the very small value $S_{\mathrm{reg}}(T) = S_{\mathrm{reg}}(0)/N_{\infty} = 0.5/N_{\infty}$. From (2.4), it follows that $N_{\mathrm{reg}}(T) = 0.5N_{\infty}$. Thus, by a time T such that $S_{\mathrm{reg}}(T)$ is considerably reduced with respect to its initial value and reaches its asymptotic behavior, $N_{\mathrm{reg}}(T)$ has reached only half of its final value. Therefore, the simple asymptotic law (3.5) can be expected to reproduce adequately the behavior of $N(t)$ in the dynamically interesting time range. Substituting (3.3) and (3.5) into (2.4) leads to

$$\left[\frac{N(t)}{N_{\infty}}\right]_{\mathrm{reg}} = \left(1 + \frac{2\pi\hbar D}{t}\right)^{-1} \qquad (3.6)$$

Note that it is more instructive to examine the ratio $N(t)/N_{\infty}$ rather than the absolute value $N(t)$. The ratio gives direct information on the stage of the relaxation. Furthermore, measuring the time in terms of the reduced variable

$$\tau = t/2\pi\hbar D \qquad (3.7)$$

provides a very simple law

$$[N(\tau)/N_{\infty}]_{\mathrm{reg}} = (1 + 1/\tau)^{-1} \qquad (3.8)$$

Results for the different model spectra are given in Figure 1.

D. Time Scales. Note the difference in the time scales of the two parts of Figure 1. Although the difference between the individual models and the approximation expressed by eq 3.5 is very conspicuous for the functions $S_{\mathrm{reg}}(t)$ examined in the short-time range, it is no longer noticeable on the plot of the functions representing $N_{\mathrm{reg}}(t)$ during the period of time necessary for complete relaxation. The important point is that $S_{\mathrm{reg}}(t)$ reaches its asymptotic behavior much faster than $N_{\mathrm{reg}}(t)$. Therefore, when N_{∞} is large, the leading term of the asymptotic expression of $S_{\mathrm{reg}}(t)$ suffices to derive an expression of $N_{\mathrm{reg}}(t)$ valid everywhere except at short times.

Heller introduced the concept of break time, defined as the time after which no new region of phase space can be visited.[6] He recognized the approximate nature of this concept and proposed for it the value $2\pi\hbar D$, which corresponds to $\tau = 1$, thus to $N/N_{\infty} = 0.5$ and $S = 1/2N_{\infty}$. Therefore, an interesting part of the relaxation law takes place at times larger than the break time (in practice between $\tau = 1$ and, e.g., $\tau \approx 30$). How can this be understood? Two remarks can be made. First, the density of states D provides information on average energy gaps. The break time would be better defined[5,7] as $2\pi\hbar/\delta$, with δ equal to the smallest energy gap between two optically active levels and not to the average quantity D^{-1}. As a result, the relaxation

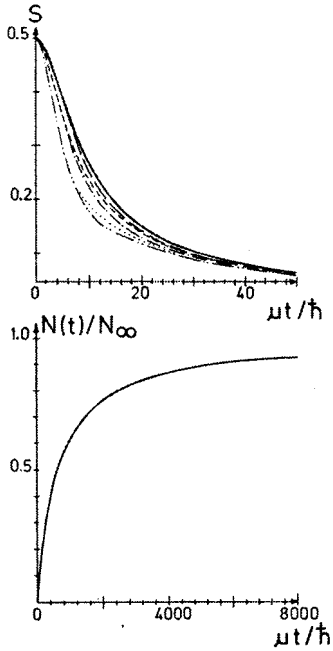

Figure 1. Upper part: behavior of the function $S(t)$ in reduced time units $\mu t/\hbar$ for the regular case. The broken lines represent the exact results for the various clump profiles enumerated in section III.B. The solid line is the approximation provided by (3.5). Lower part: Fraction of sampled phase space as a function of $\mu t/\hbar$. The exact results for all of the spectral profiles and for (3.5) are indistinguishable.

can be expected to end at values of τ larger than 1. Second, the break time is a qualitative concept corresponding to the first zero of the sinc^2 function. However, for a given energy splitting, the sinc^2 function does not die out after its first zero, but decreases asymptotically as t^{-2} on the average, thus giving rise to dynamics after the break time.

Short-time behavior is also strongly influenced by the systematic effects studied by Wolynes and by Gruebele concerning energy flow in a phase space of reduced dimensionality.[3,4,33−35] In an effort to capture the generic features of IVR, these authors have developed the logical idea that transitions between states that are close to each other in quantum space occur more readily than those between distant states. Furthermore, vibrational coupling constants have been shown to be characterized by scaling properties. As a result, energy is expected to flow along specific pathways, especially during the initial stages of the relaxation. This model has received experimental confirmation.[4] The corresponding regime, denoted "correlated intermediate time scale dynamics", ends at the time at which $|C(t)|^2$ fluctuates about its average N_∞^{-1}, i.e., at $\tau = 1$, in reduced units. The short-time regime is of course of extreme importance if one aims at controlling molecular reactivity.[4] However, our purpose is to estimate the efficiency of spontaneous IVR and, therefore, we concentrate on the $\tau > 1$ time scale.

In summary, it makes sense to study the dynamics after the break time. The essential result derived in section III.C is that, in that range, the fraction of phase space that has been sampled by time t depends in practice only on the density of states of the clump, independently of its structure (i.e., shape, width, and spectral moments).

E. Chaotic Dynamics. Heller also pointed out that the break time is probably better defined for a Wigner surmise due to the mutual repulsion of energy levels.[6] He argued that, as a result of that repulsion, $N(t)$ must approach its final value more rapidly in chaotic than in regular systems. We now try to quantify Heller's conjectures.

The exact distribution function $D_\varpi(\varpi)$ valid for all of the rescaled spacings is not known in the chaotic case. However, its qualitative behavior is quite simple.[14,15] For small values of the rescaled spacings, it coincides with a Wigner nearest-neighbor distribution. Thus, at the origin, the function is equal to zero with a slope equal to $\pi/2$. For larger values of ϖ, it tends to a constant value K_{chaos}, as in the regular case. The value of the constant K_{chaos} is determined by the condition $N(0) = 1$. As shown in the Appendix, it can be safely taken equal to 1. Thus, a reasonable approximation for D_ϖ is given by the following piecewise defined function:

$$D_\varpi(\varpi) = \begin{cases} \pi\varpi/2 & \varpi \le 2/\pi \\ 1 & \varpi \ge 2/\pi \end{cases} \tag{3.9}$$

From (2.11), (2.12), (2.13), and (3.1), one has

$$S_{\text{chaos}}(t) = S_{\text{reg}}(t) - S_{\text{a}}(t) + S_{\text{b}}(t)$$

with

$$S_{\text{reg}}(t) = \int_0^\infty q(\omega)\ \text{sinc}^2(\omega t/2\hbar)\ \text{d}\omega$$

$$S_{\text{a}}(t) = \int_0^{2/\pi D} q(\omega)\ \text{sinc}^2(\omega t/2\hbar)\ \text{d}\omega$$

$$S_{\text{b}}(t) = \int_0^{2/\pi D} (\pi D\omega/2) q(\omega)\ \text{sinc}^2(\omega t/2\hbar)\ \text{d}\omega$$

The function $S_{\text{reg}}(t)$ has been calculated in section III.C. Its asymptotic behavior is given by (3.5). To calculate the integrals $S_{\text{a}}(t)$ and $S_{\text{b}}(t)$, new variables are introduced: $z = \mu t/\hbar$ and $x = \omega/\mu$. Taking (3.3) into account, one gets

$$S_{\text{a}}(t) = \mu \int_0^{2/\pi N_\infty} q(\mu x)\ \text{sinc}^2(xz/2)\ \text{d}x$$

and

$$S_{\text{b}}(t) = (\pi\mu N_\infty/2) \int_0^{2/\pi N_\infty} x q(\mu x)\ \text{sinc}^2(xz/2)\ \text{d}x$$

The upper bound of these integrals is so small that a Taylor expansion of the integrand limited to its first term (i.e., replacing q(μx) by $q(0)$) suffices to give a result that cannot be distinguished from that of an exact calculation. (This can be understood as follows. From its definition [(2.13)], $q(\omega)$ is a bell-shaped function whose width is approximately twice as large as the width of the clump. A small value of x implies a value of ω small with respect to this width.) This approximation (which was extensively checked by numerical calculations) leads to

$$S_{\text{a}}(t) = \int_0^{2/\pi N_\infty} \text{sinc}^2(xz/2)\ \text{d}x$$

$$= (2/z)\ \text{Si}(2z/\pi N_\infty) + (\pi N_\infty/z^2)[\cos(2z/\pi N_\infty) - 1]$$

and

$$S_{\text{b}} = (\pi N_\infty/z^2)[\ln(2z/\pi N_\infty) + \gamma - \text{Ci}(2z/\pi N_\infty)]$$

where Si and Ci are the sine and cosine integrals and γ is Euler's constant.

Altogether, one arrives at the following expression

$$S_{\text{chaos}}(t) = (\pi N_\infty/z^2)[\ln(2z/\pi N_\infty) + \gamma + 1] \tag{3.10}$$

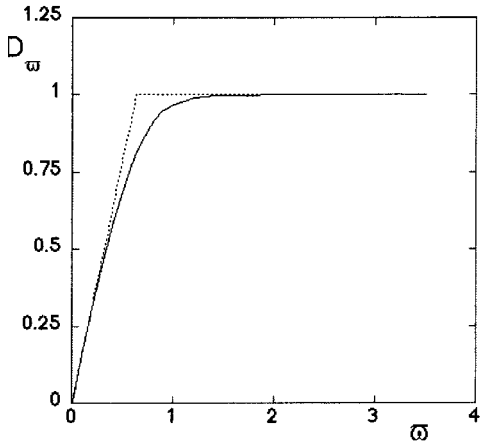

Figure 2. Solid line: distribution function for rescaled energy spacings in the chaotic case. Dashed line: piecewise defined linear approximation [(3.9)]. The slope at the origin is equal to $\pi/2$.

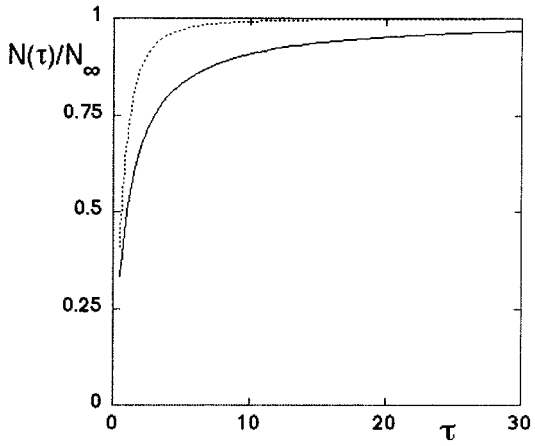

Figure 3. Fraction of sampled phase space in the single-clump case as a function of the reduced parameter $\tau = t/2\pi\hbar D$: (solid line) regular dynamics; (broken line) chaotic limit.

The leading term in (3.10) is $z^{-2} \ln z$, in agreement with our previous result.[10] However, numerical studies show that this term dominates the expansion only when the relaxation is nearly completed. Therefore, the use of the whole eq 3.10, involving both the z^{-2} and $z^{-2} \ln z$ terms is necessary to get the correct result in the physically interesting domain. This remark turns out to have important consequences in the many-clump case studied in the next section.

It is again advantageous to measure the time in terms of the reduced variable τ defined in (3.7). Using this variable and (3.10), (2.4) can be rewritten in the form

$$\left[\frac{N(\tau)}{N_\infty}\right]_{\text{chaos}} = \left\{1 + \left(\frac{1}{2\pi\tau^2}\right)[\ln(4\tau) + \gamma + 1]\right\}^{-1} \qquad (3.11)$$

This result can be compared with (3.8), derived for the regular case. In both cases, the fraction of sampled phase space is found to depend only on the density of states of the clump, irrespective of its shape and width. The appropriate reduced time variable to be used is the same in both regimes, i.e., $\tau = t/2\pi\hbar D$. Therefore, both laws can be plotted on the same diagram, as has been done in Figure 3, which thus clearly displays that regular and chaotic dynamics are characterized by a different behavior in the physically interesting time domain.

We note that, as pointed out by Heller, the concept of break time becomes more useful in the chaotic case, because small splittings are discriminated against. As a result, the value $\tau = 1$ is more closely related to the last stages of the relaxation.

IV. Averaging over Many Clumps

If the whole spectrum consists of a long series of not too dissimilar clumps, then the overall relaxation law is intuitively expected to result from some kind of an average over the behavior of each individual clump. However, the exact nature of the averaging procedure is not immediately obvious.

A clump structure is characterized by the fact that the normalized spectral profile $I(E)$ splits into a sequence of nonintersecting unnormalized functions $i_k(E)$

$$I(E) = \sum_k i_k(E) \qquad (4.1)$$

It is more convenient to rewrite (4.1) in terms of normalized clump functions $I_k(E)$

$$I(E) = \sum_k a_k I_k(E) \qquad (4.2)$$

with weighting coefficients a_k equal to

$$a_k = \int_{\Omega_k} i_k(E)\, \mathrm{d}E \qquad (4.3)$$

where Ω_k is the energy range where $i_k(E)$ or $I_k(E)$ are different from zero. The coefficients a_k are thus normalized according to $\Sigma a_k = 1$.

The existence of a clump structure implies that the relaxation process is characterized by more than one time scale.[10,23−27] Equation 2.6 clearly shows that the terms that make up $S(t)$ gradually fade away as time goes on. The larger the frequency ω_{nk}, the faster its contribution vanishes. It is therefore advantageous to split the summation and to group the large interclump energy gaps in a term $S_1(t)$ that corresponds to a fast interclump relaxation process, whereas small intraclump frequencies build up a second contribution, denoted $S_2(t)$, that is responsible for the long-time relaxation.[10] In other words, $S_1(t)$ has already reduced to a negligible value when intraclump relaxation takes place. As already said, the present work is not concerned with the short time scale. Therefore, $S(t)$ has to be equated with $S_2(t)$. Equation 2.4 then can be rewritten in the form

$$\frac{N(t)}{N_\infty} = [1 + 2N_\infty S_2(t)]^{-1} \qquad (4.4)$$

In the long-time limit, $S_2(t)$ splits into a sum of contributions $S_{2k}(t)$. Each term is associated with a particular clump and has an expression derived in section III.

$$S_2(t) = \sum_k a_k{}^2 S_{2k}(t) \qquad (4.5)$$

We now show that it is possible to derive a suitable averaging procedure that casts (4.4), with a function $S_2(t)$ defined by (4.5), in the form found for the single-clump spectrum. First, we substitute (4.2) and (3.2) into (2.8) and note that profiles corresponding to different indices do not overlap. This leads to the following expression for N_∞

$$N_\infty{}^{-1} = \sum_k a_k{}^2 \int_{\Omega_k} \frac{[I_k(E)]^2}{D_k}\, \mathrm{d}E = \sum_k \frac{a_k{}^2}{\mu_k D_k} \qquad (4.6)$$

Next, we introduce three kinds of weighted means of the intraclump densities of states that will appear in the following developments. The weighting coefficients are defined as

$$c_k = \frac{a_k^2/\mu_k}{\sum_k a_k^2/\mu_k} \tag{4.7}$$

The first one is the weighted arithmetic mean

$$\langle D\rangle_{\text{arith}} = \sum_k c_k D_k \tag{4.8}$$

The second one is the weighted harmonic mean

$$\langle D\rangle_{\text{harm}} = \frac{\sum_k \frac{a_k^2}{\mu_k}}{\sum_k \frac{a_k^2}{\mu_k}\frac{1}{D_k}} \tag{4.9}$$

Third, strange as it may seem, we also define $\langle D\rangle$ as the geometric mean of the weighted arithmetic and harmonic means of the average densities of states of the various clumps.

$$\langle D\rangle = \sqrt{\langle D\rangle_{\text{arith}}\langle D\rangle_{\text{harm}}} = \left[\frac{\sum_k c_k D_k}{\sum_k c_k/D_k}\right]^{1/2} \tag{4.10}$$

Equation 4.6 can then be rewritten in the form

$$N_\infty = \frac{\langle D\rangle_{\text{harm}}}{\sum_k \left(\frac{a_k^2}{\mu_k}\right)} \tag{4.11}$$

A. Regular Case. Let us first consider the regular case. Substituting (3.5) into (4.5), one has

$$S_2(t) = \left(\frac{\pi\hbar}{t}\right)\sum_k \frac{a_k^2}{\mu_k} \tag{4.12}$$

From (4.11), the product $N_\infty S_2(t)$ that appears in (4.4) becomes

$$N_\infty S_2(t) = \left(\frac{\pi\hbar}{t}\right)\langle D\rangle_{\text{harm}} \tag{4.13}$$

Then, (4.4) becomes

$$\left[\frac{N(t)}{N_\infty}\right]_{\text{reg}} = \left[1 + \frac{2\pi\hbar\langle D\rangle_{\text{harm}}}{t}\right]^{-1} \tag{4.14}$$

Introducing a reduced time variable similar to that defined in (3.7)

$$\tau' = t/2\pi\hbar\langle D\rangle_{\text{harm}} \tag{4.15}$$

leads to an extremely simple relaxation law valid for the regular case:

$$\left[\frac{N(\tau')}{N_\infty}\right]_{\text{reg}} = \left(1 + \frac{1}{\tau'}\right)^{-1} \tag{4.16}$$

Thus, a suitable definition of the average density of states is seen to make (4.14) and (4.16) identical to those obtained for the single clump case [(3.6) and (3.8)].

B. Chaotic Case. The situation is more complicated in the chaotic case, where two terms ($t^{-2}\ln t$ and t^{-2}) are necessary to generate a satisfactory relaxation law for an individual clump [(3.11)]. Reducing the expansion of $S_{2k}(t)$ to $t^{-2}\ln t$ gives good results at extremely long times only.

Substituting (3.3), (3.10), (4.5), (4.7), and (4.11), into (4.4) leads to

$$\left[\frac{N(\tau)}{N_\infty}\right]_{\text{chaos}} = \left\{1 + \frac{2\pi\hbar^2}{t^2}\langle D\rangle_{\text{harm}}\sum_k c_k D_k\left[\ln\left(\frac{2t}{\pi\hbar D_k}\right) + \gamma + 1\right]\right\}^{-1} \tag{4.17}$$

In the chaotic case, it turns out advantageous to define the reduced time variable as

$$\tau = t/(2\pi\hbar\langle D\rangle) \tag{4.18}$$

This leads to

$$\left[\frac{N(\tau)}{N_\infty}\right]_{\text{chaos}} = \left\{1 + \left(\frac{1}{2\pi\tau^2}\right)[\ln(4\tau) + \gamma + 1] - \left(\frac{1}{2\pi\tau^2}\right)\left(\frac{\langle D\rangle_{\text{harm}}}{\langle D\rangle_{\text{arith}}}\right)^{1/2}\sum_k c_k\left(\frac{D_k}{\langle D\rangle}\right)\ln\left(\frac{D_k}{\langle D\rangle}\right)\right\}^{-1} \tag{4.19}$$

Comparing (3.11) and (4.19), the relaxation law valid for a many-clump spectrum is seen to differ from that pertaining to a single clump by an additional term. To estimate the role of the last term, we calculate it for a simplified model defined by the following assumptions.

(i) The number of clumps is large enough to replace the summation over the peaks by an integration over the energy.

(ii) Note that the quantities μ_k, a_k, and thus the weighting coefficients c_k are random variables because there is no systematic trend in the widths and intensities of the clumps. Therefore, the corrective term will be averaged over all possible spectral profiles within the energy range $E_1 \le E \le E_2$, which amounts to taking the weighting coefficients c_k all equal.

(iii) However, in contradistinction to the coefficients c_k, the densities of states D_k increase rapidly with the energy and thus as a function of the index k. A simple solution can be obtained if this increase is parametrized by an exponential law:

$$D(E) = A\exp(\alpha E) \tag{4.20}$$

This procedure leads to

$$\langle D\rangle_{\text{arith}} = \frac{1}{E_2 - E_1}\int_{E_1}^{E_2} D(E)\,\mathrm{d}E = \frac{D(E_2) - D(E_1)}{\alpha(E_2 - E_1)} \tag{4.21}$$

$$\langle D\rangle_{\text{harm}} = \left[\frac{1}{E_2 - E_1}\int_{E_1}^{E_2}\frac{\mathrm{d}E}{D(E)}\right]^{-1} = \frac{\alpha(E_2 - E_1)\,D(E_1)\,D(E_2)}{D(E_2) - D(E_1)} \tag{4.22}$$

$$\langle D\rangle \equiv \sqrt{\langle D\rangle_{\text{arith}}\langle D\rangle_{\text{harm}}} = \sqrt{D(E_1)\,D(E_2)} \tag{4.23}$$

The corrective term

$$\left(\frac{\langle D\rangle_{\text{harm}}}{\langle D\rangle_{\text{arith}}}\right)^{1/2}\left[\sum_k c_k\left(\frac{D_k}{\langle D\rangle}\right)\ln\left(\frac{D_k}{\langle D\rangle}\right)\right]$$

then becomes

$$\frac{1}{E_2-E_1}\sqrt{\frac{\langle D\rangle_{\text{harm}}}{\langle D\rangle_{\text{arith}}}}\int_{E_1}^{E_2}\frac{D(E)}{\langle D\rangle}\ln\left[\frac{D(E)}{\langle D\rangle}\right]\mathrm{d}E = \frac{1}{2}\left(\frac{\rho+1}{\rho-1}\right)\ln\rho - 1 \quad (4.24)$$

with

$$\rho \equiv \frac{D(E_2)}{D(E_1)} \quad (4.25)$$

To summarize, the correct expression for the many-clump case is given by (4.19). The evaluation of this expression requires a detailed analysis of the spectrum. If that information is not available, then a much simpler expression, based on assumptions i−iii can be used:

$$\left[\frac{N(\tau)}{N_\infty}\right]_{\text{chaos}} = \left\{1+\left(\frac{1}{2\pi\tau^2}\right)[\ln(4\tau)+\gamma+1] - \left(\frac{1}{2\pi\tau^2}\right)\left[\frac{1}{2}\left(\frac{\rho+1}{\rho-1}\right)\ln\rho - 1\right]\right\}^{-1} \quad (4.26)$$

Note that the physically interesting range of the relaxation corresponds to $\tau \geq 1$. Therefore, when $\rho \leq 10$, the second term of the right-hand side of (4.26) can be neglected with an accuracy better than 10%. Thus, when the densities of the first and last clumps of the spectrum do not differ by several orders of magnitude, the relaxation law simplifies to

$$\left[\frac{N(\tau)}{N_\infty}\right]_{\text{chaos}} = \left\{1+\left(\frac{1}{2\pi\tau^2}\right)[\ln(4\tau)+\gamma+1]\right\}^{-1} \quad (4.27)$$

Comparing with (3.11), the relaxation law for the many- and single-clump cases are seen to coincide with a suitable choice of $\langle D\rangle$.

C. Regular Case Again. To compare regular and chaotic dynamics, the relaxation laws have to be expressed in terms of the same time variable. Equations 4.14 and 4.16 describe the regular case in terms of the harmonic mean $\langle D\rangle_{\text{harm}}$ and of the associated reduced time variable τ' [(4.15)]. It is thus necessary to recast them in terms of the reduced time variable τ [(4.18)] appropriate to the more complicated chaotic limit.

$$\left[\frac{N(\tau)}{N_\infty}\right]_{\text{reg}} = \left[1+\frac{1}{\tau}\sqrt{\frac{\langle D\rangle_{\text{harm}}}{\langle D\rangle_{\text{arith}}}}\right]^{-1} \quad (4.28)$$

This equation can be seen as the many-clump generalization of (3.8), because in the single-clump case (4.28) reduces to (3.8).

Here again, if a detailed analysis of the spectrum is not available, a much simpler expression, based on assumptions i−iii can be used:

$$\left[\frac{N(\tau)}{N_\infty}\right]_{\text{reg}} = \left[1+\frac{1}{\tau}\frac{\ln\rho}{\rho^{1/2}-\rho^{-1/2}}\right]^{-1} \quad (4.29)$$

V. Generic Relaxation Law in Reduced Units

Equations 4.16 (or eq 4.28) and 4.19 provide simple relaxation laws that are independent of the shapes of the clumps and of their number. They remain valid even if the spectrum is characterized by a rich variety of shapes and widths. Of course, our averaging procedure makes sense only provided that the dynamical regime does not switch from regular to chaotic as the energy increases.

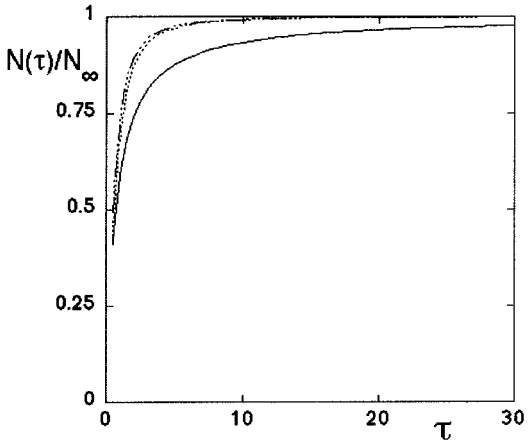

Figure 4. Fraction of sampled phase space in the many-clump case as a function of the reduced parameter $\tau = t/2\pi\hbar D$: (solid line) regular dynamics; (broken line) chaotic situation. Parameter $\rho = 20$ [ρ = ratio of the densities of states of the last and first clumps; see (4.25)]. To show the influence of ρ, the fraction $[N(\tau)/N_\infty]_{\text{chaos}}$ is also reported for $\rho = 0$ (thin dotted line).

The origin of the simplicity of the regular case with respect to the chaotic limit lies in the number of terms to be retained in the expansion of $S(t)$. For the regular case, a single term in t^{-1} suffices for nearly the entire time range (i.e., excluding very short times only). By contrast, in the chaotic limit, the relaxation law that has to be averaged contains two terms, viz., t^{-2} and t^{-2} ln t. Each one requires a different average over the characteristics of the individual clumps.

In principle, (4.16), (4.28), and (4.19) require a detailed analysis of the spectrum. If that information is not available, then the much simpler expressions (4.26) and (4.29) can be proposed. They are expressed in terms of the same reduced time variable τ [(4.18)], and involve parameters $\langle D\rangle$ and ρ that are simply related to the densities of states of the first and last clumps of the spectrum [(4.23) and (4.25)].

However, (4.26) and (4.29) are based on assumptions i−iii. One should be aware of the fact that, as a result of assumption ii, they provide a correction that has been averaged over all possibilities; i.e., they describe an average situation. Thus, they propose generic relaxation laws; i.e., they provide a reference against which particular cases are to be examined.

Particularly interesting is the result that both kinds of dynamics, regular and chaotic, obey generic (i.e., model independent) laws expressed in terms of the same reduced time variable τ. Equations 4.19 and 4.28, or eqs 4.26 and 4.29, are thus directly comparable. The latter two can be plotted on the same diagram, as has been done in Figure 4, where the relaxation laws of the regular and chaotic limits are compared. A value of $\rho = 20$ has been adopted, which means that the density of the last clump is assumed to be 20 times higher than that of the first clump. Apart from showing that the influence of the averaging procedure over many clumps is hardly noticeable in this case, Figure 4 demonstrates that phase space is not explored at the same rate in the regular and chaotic limits. The difference in behavior remains appreciable during the entire relaxation. Equations 4.26 and 4.29 (or more fundamentally eqs 4.16, 4.28 and 4.19) express in the time domain the difference in the

distribution of nearest-neighbor level spacings observed in the energy domain.

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Appendix. Density of Rescaled Energy Spacings

At time $t = 0$, the number of sampled phase space cells is required to be equal to 1, i.e., $N(0) = 1$. Hence, from (2.4), it follows that

$$S(0) = 0.5(1 - 1/N_\infty) \tag{A.1}$$

Consider first the regular case. Then, the rescaled density $D_\varpi(\omega)$ is a constant, so that (2.12) transforms into

$$g(\omega) = K_{\text{reg}}\int_{-\infty}^{+\infty} I(E)\, I(E+\omega)\, \mathrm{d}E = K_{\text{reg}} q(\omega) \tag{A.2}$$

with $q(\omega)$ defined by (2.13). From (2.11),

$$S(0) = K_{\text{reg}}\int_{-\infty}^{+\infty} \mathrm{d}E \int_0^{+\infty} \mathrm{d}\omega\, I(E)\, I(E+\omega) = K_{\text{reg}}\int_0^{+\infty} q(\omega)\, \mathrm{d}\omega \tag{A.3}$$

The double integral can be evaluated as follows. Squaring (1.2), one gets

$$\int_{-\infty}^{+\infty} \mathrm{d}E_1 \int_{-\infty}^{+\infty} \mathrm{d}E_2\, I(E_1)\, I(E_2) = 1 \tag{A.4}$$

Adopting as new integration variables $E = E_1$ and $\omega = E_2 - E_1$, and noting that the integrand is invariant with respect to the interchange of E_1 and E_2 and hence is now an even function of the new variable ω, leads to

$$2\int_{-\infty}^{+\infty} \mathrm{d}E \int_0^{+\infty} \mathrm{d}\omega\, I(E)\, I(E+\omega) = 2\int_0^{+\infty} q(\omega)\, \mathrm{d}\omega = 1 \tag{A.5}$$

Comparing with (A.1) and (A.3), one obtains

$$K_{\text{reg}} = 2S(0) = 1 - 1/N_\infty \tag{A.6}$$

Thus, in practice, K_{reg} is extremely close to 1.

The sensitivity of $N(t)$ to an approximation on K_{reg} can be studied as follows. From (2.4), (2.11), and (A.6), the correct number of phase space cells sampled at time t is given by

$$N(t) = [N_\infty{}^{-1} + 2(1 - N_\infty{}^{-1})s(t)]^{-1} \tag{A.7}$$

where $s(t)$ is defined as

$$s(t) \equiv \int_0^{+\infty} q(\omega)[\sin(\omega t/2\hbar)/(\omega t/2\hbar)]^2\, \mathrm{d}\omega \tag{A.8}$$

whereas the approximation which consists of admitting $K_{\text{reg}} = 1$ leads to

$$N_{\text{app}}(t) = [N_\infty{}^{-1} + 2s(t)]^{-1} \tag{A.9}$$

The error associated with this approximation is thus given by the difference

$$\Delta N(t) = N(t) - N_{\text{app}}(t) = \frac{2N_\infty s(t)}{[1 + 2N_\infty s(t)][1 + 2N_\infty s(t) - 2s(t)]} \tag{A.10}$$

This expression admits a maximum when $s(t) = 0.5[N_\infty{}^2 - N_\infty]^{-1/2}$ equal to

$$\Delta N_{\max} = {}^1/_4 + ({}^1/_8 N_\infty) + ({}^5/_{64} N_\infty{}^2) + \ldots \tag{A.11}$$

An error of one-fourth of a phase space cell in the evaluation of the total volume is entirely negligible.

The chaotic case, K_{chaos}, is dealt with in a similar way.

References and Notes

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