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Abstract.   The selective excitation of a set of frequencies in molecular dynamics simulations of complex nonlinear systems can be achieved via a series of quenches, properly spaced in time. The method, inspired by the temperature echo effect, is potentially useful in the study of the relaxation of large systems where exact normal mode analysis is numerically very demanding (glasses, polymers, biomolecules). We apply the method to the relaxation of a Lennard–Jones glass, taken as an example of a disordered nonlinear system.

1. Introduction

In this paper we present a method to prepare a microcanonical molecular dynamics (MD) systems in states characterized by a given set of frequencies, and its application in the study of relaxation of these states. The method was inspired by the temperature echo effect.

Temperature echo is observed in MD simulations of many body systems. If two quenches, in which all velocities are set to zero, are imposed in a constant energy MD simulation, then a spontaneous reduction in the temperature of the system is observed after the second quench, at a time equal to the interval between the quenches (see figure 1, where we show an example of temperature echo in a simulation of a Lennard–Jones mixture, described in section 3). The effect was originally found and investigated by Grest *et al* [1–4], in their study of Lennard–Jones computer glasses in the early 1980s. In 1993 Becker and Karplus [5] revived the temperature echo effect in MD simulations of proteins. A straightforward explanation of this phenomenon has been given [1]: before the first quench the system is equilibrated, so that the energy is equally shared by the normal modes and each normal mode gives the same contribution to the kinetic energy (i.e. temperature). At the time of the first quench all the phases are set to the same value. Then t_0, the time interval between quenches, selects those modes whose frequencies are near a multiple of π/t_0. These modes are the only ones which retain their kinetic energy, which is approximately zero at the time of the second quench; all other modes are damped. The temperature after the second quench is then dominated by the selected modes which have again zero kinetic energy after a time t_0, and this explains why at this time a negative peak is observed in the time course of the temperature of the system. In early studies and in the letter of Becker and Karplus [5] the temperature echo has been proposed as a tool to extract the density

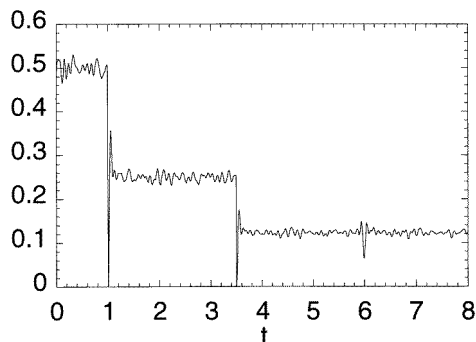§ To whom correspondence should be sent.

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Figure 1. Example of temperature echo in the microcanonical MD simulation of a Lennard–Jones mixture (see section 3). The graph shows, in arbitrary units, the kinetic energy as a function of reduced time t, from an arbitrary origin. At times $t = 0.0$ and $T = 3.5$ all the velocities are quenched to zero. The temperature echo is seen as a negative peak at $t = 6.0$. The reduced energy per particle in this run is $\epsilon = 10^{-3}$. Note that after each quench the kinetic energy is approximately halved.

of states, to select specific normal modes and to study anharmonicities in MD of complex systems, but, to our knowledge, it has not received further attention.

The method that we propose here is simple to implement and effective in the selective excitation of a set of frequencies in MD simulations of Hamiltonian nonlinear systems with many degrees of freedom. Of course, in all cases where normal mode analysis is straightforward, it is not necessary to have an alternative method of selective excitation of single modes. However, particularly in the study of protein dynamics, a complete normal mode analysis based on the diagonalization of the Hessian matrix is computationally very demanding, both in computer memory and in CPU time [6, 7]. Currently, there is much research devoted to the study and the construction of fast diagonalization algorithms for large proteins [8–10]. There is also numerical evidence that the relevant dynamics is dominated by a small subset of modes, generally of a low frequency [11, 12]. We think that our method could fit in this line of research, as an alternative to the determination of the full spectrum of normal modes through diagonalization procedures. This could be useful in the study of complex systems such as proteins, but also glasses and polymers.

In section 2 we illustrate, in detail, the method and its potentiality for the study of the relaxation in MD of Hamiltonian systems as a function of the energy density. In this paper, where we want to present the method, we have chosen, as a model of a nonlinear disordered system, a 500 particles Lennard–Jones glass, described in section 3, which is computationally not very demanding, but interesting to show the potentiality of the method. In section 4 we present some results. The conclusions are given in section 5.

2. The method

The original temperature echo as a tool to prepare a model system in an initial condition which corresponds to the excitation of a single mode has some drawbacks. First, to enhance the selection effect a long sequence of quenches is needed; but at each quench the system is cooled and, to keep the temperature constant, energy has to be fed into the system. Secondly, the choice of a given time interval between quenches, t_0, does not simply imply selection of a single mode; in fact, as already mentioned, after a sequence of quenches higher harmonics also survive, and not only the modes of the chosen angular frequency π/t_0. Thirdly, if the

proper frequencies of the system are close to each other then the simple selection of a given interval between subsequent quenches always implies selection of a group of frequencies around the desired one. In the following we show how to circumvent all these drawbacks.

Suppose to know x_0, a stable equilibrium configuration of the system. The potential energy is measured with respect to this equilibrium configuration, that is not necessarily that corresponding to the absolute minimum of the potential energy. The dynamics is started with random initial conditions about x_0. As explained in section 1, a kinetic energy quench is realized putting instantaneously all the velocities equal to zero, and leaving the positions unchanged. We will also use potential energy quenches, that are realized putting instantaneously all the positions equal to the equilibrium positions. A sequence of both kinds of quenches is required to select a given frequency without its harmonics. Moreover, it is possible to restore the total energy in the system by rescaling all the velocities immediately after the potential energy quenches, when the potential energy is zero. We do this each time that we perform a potential energy quench.

When energy is very low the time evolution of a system is very well described by the superposition of normal modes. In the following we consider simulations at very low energy; Q_i stands for a generic normal mode. Once the selection procedure is complete, the total energy of the system can be set to any chosen value via rescaling of the velocities.

2.1. Preparation of the system

It is convenient to perform the first quench when the phases of the normal modes are effectively random. This can be achieved by letting the system evolve for a sufficiently long thermalization time T_0. After this thermalization time, T_0, we begin our series of quenches to select a chosen frequency ω_0; we denote with t_0 the half period π/ω_0 of the corresponding mode. We remark that during the whole quenching procedure the integration time-step of the simulation is adapted so that the time intervals between two quenches are realized by an integer number of time-steps.

First, we perform a first series of quenches of the potential energy, separated by t_0. After this first series only the modes with frequency approximately equal to $n\omega_0$ (with n any integer) survive. This can be shown in the following way. After the first quench at time T_0 the evolution of each normal mode Q_i is given by:

$$Q_i(t) = A_i \sin[\omega_i(t - T_0)] \tag{1}$$

where ω_i is the the corresponding frequency and the amplitudes, A_i, are such that each mode has approximately the same energy. Equation (1) is valid for $T_0 < t < T_0 + t_0$. At time $T_0 + t_0$ a second quench is performed: this is equivalent to set all the Q_is to zero, and therefore the new amplitude of each mode is determined by the velocity of the mode at that time. Thus, after the second quench the dynamics of Q_i is given by:

$$Q_i(t) = C_1 A_i \cos(\omega_i t_0) \sin[\omega_i(t - T_0 - t_0)] \tag{2}$$

valid for $T_0 + t_0 < t < T_0 + 2t_0$. The constant, C_1, is introduced to take into account that, as previously explained, after each potential energy quench the total energy of the system is restored. It can be easily seen that after the pth quench the dynamics of Q_i is given by:

$$Q_i(t) = C_2 A_i \cos^{p-1}(\omega_i t_0) \sin[\omega_i(t - T_0 - (p-1)t_0)] \tag{3}$$

with another constant C_2. From equation (3) one can see that, since $t_0 \equiv \pi/\omega_0$, Q_i will be strongly damped if p is sufficiently large, unless $\omega_i \approx n\omega_0$, where n is any integer.

Next we perform other series of quenches to damp the multiples of ω_0. A very efficient way to damp the harmonics without affecting the selected fundamental frequency, is to alternate potential and kinetic energy quenches.

We first show how we can damp all the even multiples of ω_0. We perform alternated kinetic energy quenches and potential energy quenches; the time interval between two consecutive quenches is $\frac{1}{2}t_0$ (which is also the time between the last quench of the first series of potential energy quenches and the first quench of this series of alternated quenches).

Let us now, for convenience, denote with T_1 the time of the last quench of the first series: $T_1 \equiv T_0 + (p - 1)t_0$. After the first kinetic energy quench the dynamics of Q_i is given by:

$$Q_i(t) = C_2 A_i \cos^{p-1}(\omega_i t_0) \sin(\tfrac{1}{2}\omega_i t_0) \cos[\omega_i(t - T_1 - \tfrac{1}{2}t_0)] \tag{4}$$

valid for $T_1 + \frac{1}{2}t_0 < t < T_1 + t_0$; the factor C_2 is the same as that of equation (3) since after the kinetic energy quenches the total energy of the system is not restored. After the first potential energy quench we have instead:

$$Q_i(t) = -C_3 A_i \cos^{p-1}(\omega_i t_0) \sin^2(\tfrac{1}{2}\omega_i t_0) \sin[\omega_i(t - T_1 - t_0)] \tag{5}$$

valid for $T_1 + t_0 < t < T_1 + \frac{3}{2}t_0$. It is clear that after q kinetic energy and q potential energy quenches we have:

$$Q_i(t) = (-1)^q C_4 A_i \cos^{p-1}(\omega_i t_0) \sin^{2q}(\tfrac{1}{2}\omega_i t_0) \sin[\omega_i(t - T_1 - qt_0)]. \tag{6}$$

One can see that Q_i will be strongly damped unless $\omega_i \approx (2n + 1)\omega_0$, $n = 0, 1, 2, \ldots$.

In all our runs we have found that a q as low as 1 or 2 is sufficient for a complete suppression of the even frequencies. In fact, the quantity $\sin(\tfrac{1}{2}\omega_i t_0)$ in the equation above is very close to zero for the frequencies $\omega_i \approx 2n\omega_0$, $n = 0, 1, 2, \ldots$

Odd harmonics are damped in the following way. Analogously to the damping of the even multiples of ω_0, we perform alternated kinetic energy quenches and potential energy quenches; but now the time interval between quenches is $\frac{1}{3}t_0$. It can be seen that after r kinetic energy and r potential energy quenches we have (denoting $T_2 \equiv T_1 + qt_0$):

$$Q_i(t) = (-1)^q (-1)^r C_5 A_i \cos^{p-1}(\omega_i t_0) \sin^{2q}(\tfrac{1}{2}\omega_i t_0) \sin^{2r}(\tfrac{1}{3}\omega_i t_0) \sin[\omega_i(t - T_2 - rt_0)]. \tag{7}$$

Among the odd harmonics, after this last series of quenches the harmonics of the form $\omega_i \approx 3(2n + 1)\omega_0$, $n = 0, 1, 2, \ldots$ have been damped, as can be easily deduced from equation (7). Also in this case, a very small r (1 or 2) is sufficient.

The procedure continues performing, in principle, a series of quenches (always alternating kinetic and potential energy quenches) for each prime number. In practice, few such series will be needed, since the values of the proper frequencies of a system are bounded; in this work we have found that, for the frequencies that we have considered, we had to use no more than five series. The time interval between quenches, for the series associated with the prime number p, is taken as $(p - 1)t_0/2p$. This choice has prevailed on the more natural choice of a time interval equal to t_0/p, since it is more efficient in rejecting the harmonics without damping the fundamental.

At the end of the above procedure only the frequencies $\omega_i \approx \omega_0$ are excited. It is possible to eliminate the frequencies very close to the selected one by performing a new series of 'dilated' potential energy quenches, separated by a time nt_0, with n an integer > 1. In fact, the phase shift between the two close frequencies, ω_0 and $\omega_0 + \epsilon$, is larger after nt_0 than after t_0, increasing linearly with n. This makes the damping of $\omega_0 + \epsilon$ more efficient; we have found that with this last step we can excite only one frequency.

The above selection procedure is performed at low energy. After the last quench of the potential energy the system is left in the equilibrium configuration x_0, with a set of

velocities v_0, corresponding to the selected frequency. If a simulation is started from x_0 with a rescaled v_0, then one can study the dynamics at higher energy with only one mode initially excited.

2.1.1. Selection of two or more frequencies. It is possible to select initial conditions which correspond to the excitation of two or more frequencies. At low energy normal modes are uncoupled and superpositions of initial conditions imply superposition of the dynamics. Therefore, by summing the v_0s corresponding to different selected frequencies, (and by proper rescaling to set the energy), one can originate a dynamics in which only the chosen selected modes are initially present.

2.2. Relaxation and mode locking

One of the aims of the selection technique that we are presenting in this paper is the investigation of the degree of coupling of a particular mode or group of modes. Raising of the energy should induce an irreversible decay of the prepared state on shorter and shorter time scales, due to the coupling of the modes. To monitor the outflow of the energy from the initially selected mode(s) to the others, we use here a relaxation function which is a projection of the phase point of the system onto the vector(s) v_0 corresponding to the initially excited mode(s). In more detail, at each time-step of the run we collect the set of velocities $v(t)$ and of the displacements from the equilibrium positions $x(t) - x_0$. The relaxation function $d_i(t)$ associated with the ith initially excited mode, is defined by:

$$d_i(t) = B_i[\langle v(t)|\mathbf{M}|v_{0i}\rangle^2 + \langle (x(t) - x_0)|\mathbf{M}|v_{0i}\rangle^2 \omega_{0i}^2] \tag{8}$$

where B_i is a normalization factor such that $d_i(0) = 1$, ω_{0i} is the frequency of the ith initially selected mode, and v_{0i} the corresponding vector of initial velocities; the matrix $\mathbf{M}$ in the scalar products is the mass matrix of the system. In the absence of nonlinearity (i.e. of coupling), and therefore of decay, we would have $d_i(t) = 1$ for all t, since in that case it would be $\langle v(t)|\mathbf{M}|v_{0i}\rangle \propto \omega_{0i} \cos(\omega_{0i}t)$ and $\langle (x(t) - x_0)|\mathbf{M}|v_{0i}\rangle \propto \sin(\omega_{0i}t)$.

How the spreading of the energy lost by the initially excited modes affects the entire spectrum of the system can be studied in the following way. After the high energy trajectory has evolved for a certain time, one can go back to low energy (rescaling the velocities and the positions as explained below in section 4, where reference to figure 6 is made), damping back the coupling among the excited modes which are then locked. By performing a suitably long low-energy dynamics and by Fourier transform one can have information on which modes were excited by the high energy dynamics. Of course this rescaling back to low energy is not meaningful if during the high energy dynamics there is a structural rearrangement of the system, such that the dynamics evolves about a local minimum different from x_0. However, the function $d_i(t)$ defined above is able to show if such a jump has occurred (see figure 4 below).

3. The model

To test the applicability of the selection method we have chosen a widely studied computer glass: a mixture of two types of classical Lennard–Jones particles [13]. The two types of particles are labelled by A and B, both types have the same mass m. The interaction potential between particles of type α and β (with $\alpha, \beta \in \{A, B\}$) is given by: $V_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$. We have used reduced units with σ_{AA} as a unit of length, ε_{AA} as a unit of energy and m as a unit of mass; in reduced units time is

measured in units of $\tau = (m\sigma_{AA}^2/\varepsilon_{AA})^{1/2}$. For argon τ corresponds to 2.2 ps. In these units the parameters of our potential are: $\varepsilon_{AA} = \varepsilon_{AB} = \varepsilon_{BB} = 1$, $\sigma_{AA} = 1$, $\sigma_{BB} = 1.2$, and $\sigma_{AB} = (\sigma_{AA}+\sigma_{BB})/2 = 1.1$. The total number of particles, N, is 500, the sum of $N_A = 375$ and $N_B = 125$. The reduced density has been chosen to be $\rho\sigma_{AA}^3 \equiv \rho^* = N/V^* = 1.0$, that fixes the reduced volume to $V^* \equiv V/\sigma_{AA}^3 = 500$; the system is therefore enclosed in a cubic box of edge $500^{1/3}\sigma_{AA}$. Periodic boundary conditions have been enforced and the potential has been truncated and shifted at a cut-off distance of $2.5\sigma_{AA}$. Microcanonical MD trajectories have been generated via a bilateral symplectic integrator [14] which is simple, fast and precise. The time-step has been 0.005τ, except between quenches, when it has been properly adapted (see section 2). Starting from a well equilibrated high-energy initial condition in the liquid state the system has been cooled down via a schedule of rescalings in the velocities. At the end an amorphous state has been reached, as we have checked from the absence of diffusion and by an inspection of the various radial correlation functions $g_{\alpha\beta}(r)$. This Lennard–Jones glass is our system, characterized by one of its mechanically stable equilibrium configurations. We have chosen, for the low-energy selection procedure, an energy density (i.e. the total energy divided by the number of particles, in reduced units) of $\epsilon = 10^{-8}$. In this situation the normal modes are effectively uncoupled, as can be predicted from the values of the parameters of the potential energy of our system; besides, we have *a posteriori* checked this, looking at the $d_i(t)$ of the selected mode(s), that do not decay from 1.

4. Results

As we reported in section 2, our selection procedure can be divided into different stages: (i) a series of potential energy quenches which select a given frequency with all its harmonics; (ii) even and odd harmonics are rejected via subsequent series of alternated quenches: kinetic energy quenches, each one followed by a potential energy quench. In each series the quenches are separated by $\frac{1}{2}t_0$, $\frac{1}{3}t_0$, $\frac{2}{5}t_0$, $\frac{3}{7}t_0$, ...; (iii) final rejection of frequencies lying close to the selected ω_0 is obtained with a last series of 'dilated' potential energy quenches separated by nt_0, with n an integer > 1. In the following and in the figures, we will always use the reduced units, introduced in section 3.

We focus on the kinetic energy of the system, because it is the simplest collective observable, and it is proportional to the temperature of the system. The power spectrum of the kinetic energy, in a generic run at low energy, shows all the proper frequencies (actually this spectrum displays the double of each proper frequency, since the kinetic energy is given by the square of the velocities). In figure 2 we show the time courses of the kinetic energy (left column), and the corresponding power spectra (right column), recorded during the selection of a given frequency of the Lennard–Jones glass at $\epsilon = 10^{-8}$. The frequency chosen here, $\omega = 3.95$, is simply one of the many appearing in the low-energy spectrum of the system. In each row of the figure we show the kinetic energy after having performed the selection up to a given stage: in the top row we have the system after stage (i) described above; the spectrum is made of harmonics (note that the seventh harmonic near $\omega = 55$ is dominant). The frequency to be selected appears in the power spectrum of the kinetic energy as a small peak near 7.9, the double of $\omega = 3.95$. In the second row only odd harmonics are left. In the third row we show the kinetic energy of the system after we have completed stage (ii) above; in the power spectrum a group of frequencies is left; of these the less pronounced is that to be selected. After the last stage, based on a series of 'dilated' quenches, only the frequency $\omega = 7.9$ is present (bottom row).

After having illustrated a typical selection procedure, in the following we present a few applications of the method to outline its potentiality in the study of the relaxation of
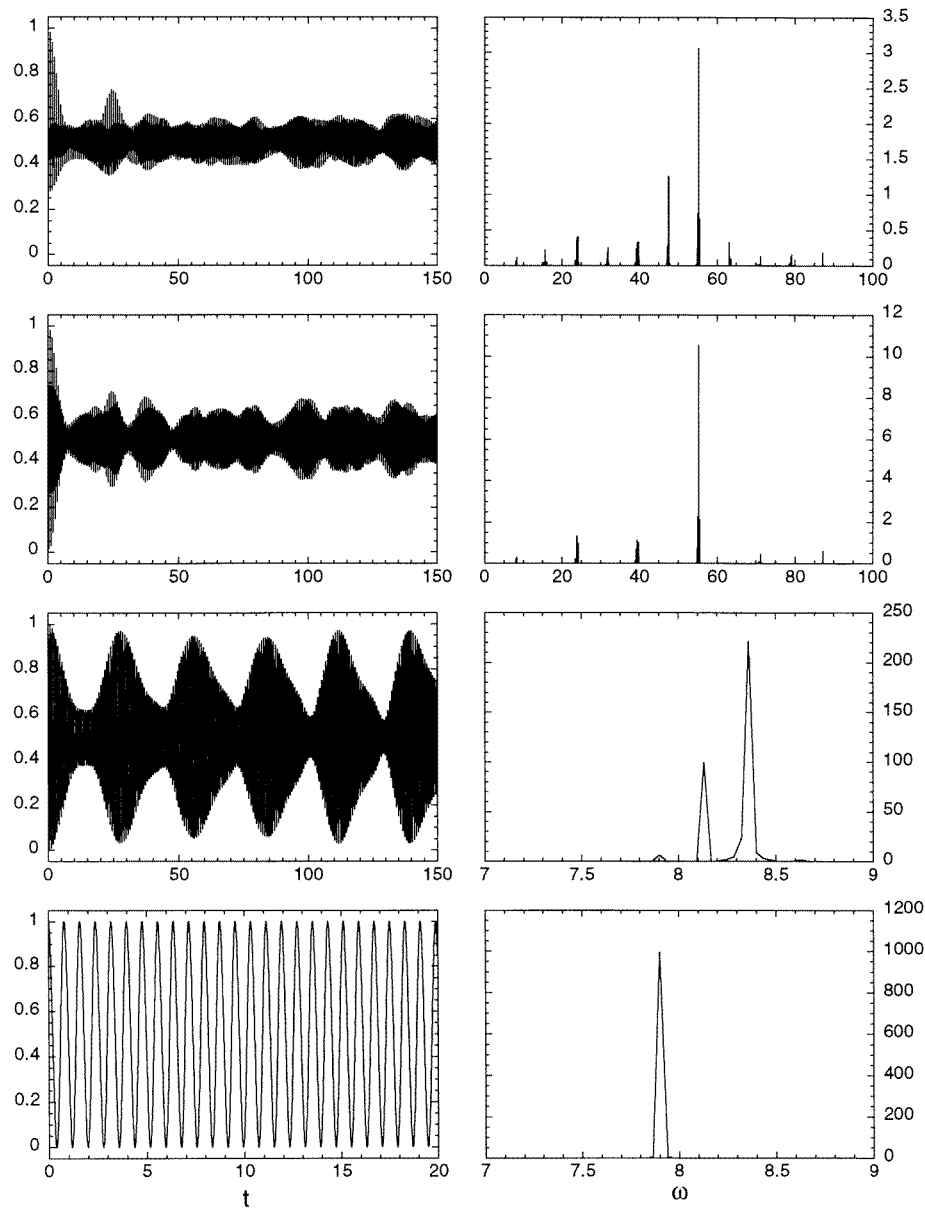
Figure 2. Normalized kinetic energy and the corresponding power spectra after various stages of the selection of a mode of frequency $\omega = 3.95$ (the frequency is doubled in the kinetic energy) in the Lennard–Jones mixture. First row: after a series of potential energy quenches; even and odd harmonics are present. Second row: after rejection of even harmonics. Third row: after rejection of odd harmonics; a group of three frequencies is left. That to be selected is the feeblest. Fourth row: after a last series of 'dilated' quenches; only $\omega = 7.9$ is left. Power spectra were computed via a standard FFT routine.

disordered dynamical systems.

In figures 3–5 we compare the decay of the initial state at different energies. Figure 3 refers to the mode with $\omega = 3.95$, the selection of which was illustrated in figure 2. On
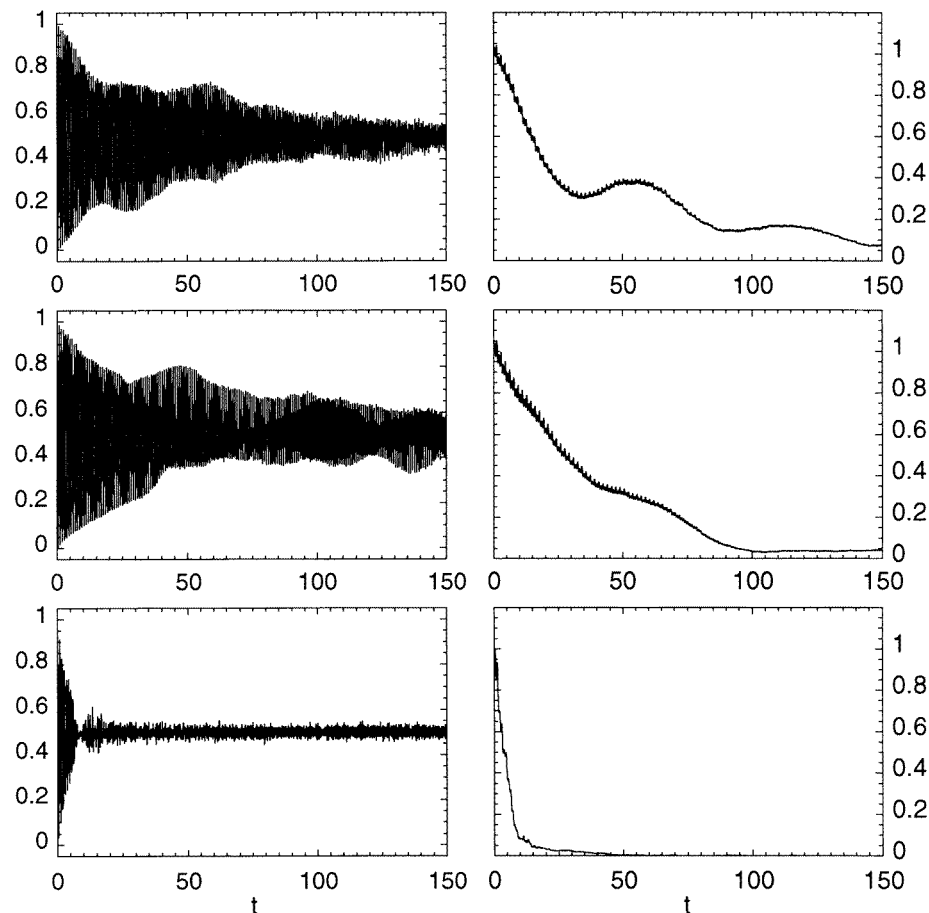
Figure 3. Decay of selected mode with $\omega = 3.95$ at different energy densities. On the left: normalized kinetic energy; on the right: relaxation function (see equation (8)) versus time. From top to bottom: $\epsilon = 10^{-4}$, 10^{-3}, 10^{-2}.

the left column we show the normalized kinetic energy and on the right the corresponding relaxation functions $d(t)$ (see equation (8); note that in the case of our Lennard–Jones system the mass matrix is the unit matrix). From top to bottom the graphs refer to the energy densities: $\epsilon = 10^{-4}$, 10^{-3} and 10^{-2}, respectively. At the higher energy density the memory of the initial state is rapidly lost; the relaxation function decays at zero after 40 time units. At the lower energies the decay of the relaxation function is more complex; apart from the slow oscillation which we do not discuss here, a fast and a slow component are present: the energy density affects both components. Let us remark that, near the kinetic glass transition temperature, the self-part of the density autocorrelation function has a similar behaviour to a fast 'β-relaxation', followed by a slower 'α-relaxation' [13]. Figure 4 is similar to figure 3, but refers to the mode with $\omega = 2.32$. This mode is less stable than the other; the decay of the relaxation function at the lower energy densities is comparatively faster. Moreover, at $\epsilon = 10^{-2}$ there is a jump in the relaxation function which is due to a structural rearrangement of the solid involving a group of particles jumping out from their initial positions, as we have checked by looking at the trajectory of the system.
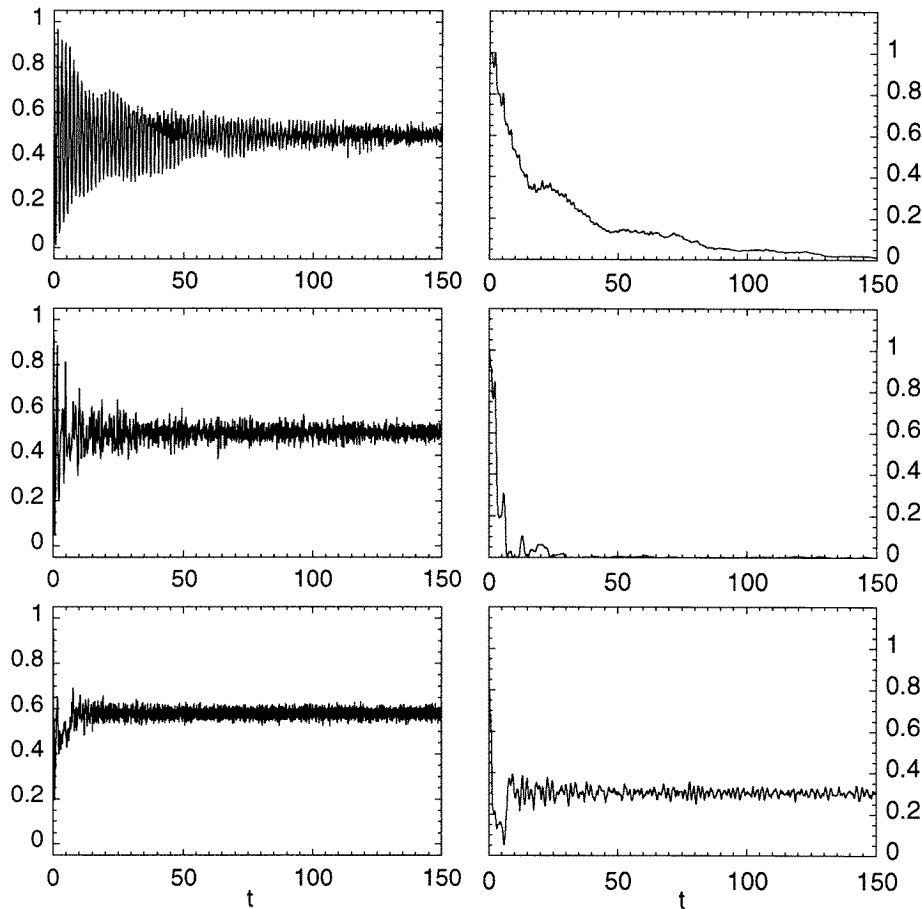
Figure 4. Decay of selected mode with $\omega = 2.32$. The energy densities are the same as in figure 3. From top to bottom: $\epsilon = 10^{-4}$, 10^{-3}, 10^{-2}. Note that the decay is faster than the decay for $\omega = 3.95$, at the higher energy density there is a jump in both kinetic energy and relaxation function due to a structural rearrangement of particles.

In figures 3 and 4 it is evident that, looking at the time course of the kinetic energy, one can, at least qualitatively, infer the behaviour of the relaxation function of the single excited mode. This is not the case when two or more selected modes are initially excited (see section 2.1.1). In this kind of dynamics the kinetic energy signal is affected by all the excited modes and it is useful to compute individual relaxation functions projecting the phase point onto the v_0 of each excited mode. In figure 5 we compare the relaxation functions of modes with $\omega = 2.32$ and $\omega = 15.91$ when singly excited (figures 5(*a*) and (*b*) respectively) and when superposed (figures 5(*c*) and (*d*) displaying individual relaxation functions) at an energy density of $\epsilon = 10^{-3}$. It is interesting to note that the slow decay of the high frequency mode is greatly influenced by the presence of the other while the fast decay of the low frequency mode is quite independent.

These results show that, combining our selection procedure with the analysis of the relaxation functions, it is possible to explore the relaxation behaviour of a given system as a function of both the energy density (i.e. the nonlinear coupling between modes) and the set of frequencies initially excited.
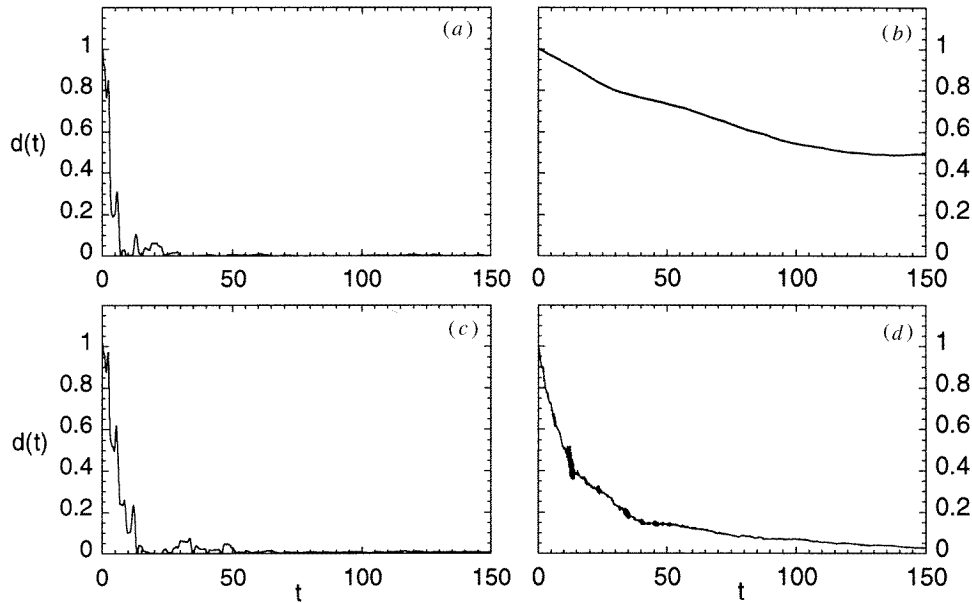
Figure 5. (*a*) Relaxation functions of a mode with $\omega = 2.32$ and (*b*) relaxation functions of a mode with $\omega = 15.91$, when singly excited. When both modes are excited the corresponding relaxation functions become (*c*) and (*d*). It is worth noting the change in the decay of $\omega = 15.91$ induced by the simultaneous excitation of $\omega = 2.32$.

In figure 6 we show an application of the technique of mode locking to have information on the spreading of energy from a single excited mode towards the other excitable frequencies in the system. Consider the simulation shown in the centre row of figure 4, in which the initial state is given by the excitation of the mode with $\omega = 2.32$ at an energy density of $\epsilon = 10^{-3}$. At six different times: $t_a = 2$, $t_b = 15$, $t_c = 30$, $t_d = 57$, $t_e = 112$ and $t_f = 167$, the velocities and the displacements from the equilibrium positions are recorded and then scaled back to give $\epsilon = 10^{-8}$. From these sets of initial conditions we have started six low energy MD runs. In figures 6(*a*)–(*f*) we show the power spectra of the kinetic energy in the different low energy runs. Each panel refers to the locking of the frequency spectrum at the subsequent times $t_a, \ldots, t_f$ in the run at $\epsilon = 10^{-3}$. It is evident that the spreading in frequency is due to the nonlinearity of the dynamics in the high energy run. With some refinements this mode locking procedure could be used to quantitatively study the frequency channels in the decay of a given initial state.

5. Conclusions

In this paper we have shown how to prepare a generic Hamiltonian system in states with selected frequencies initially excited. Via a simple rescaling of the velocities it is possible to study, at different energy densities, the effects of the nonlinearities on the relaxation of the prepared state. As an illustration we have shown the effectiveness and potentiality of the method on a computer Lennard–Jones glass, taken as an example of disordered system.

Selection of modes of a given frequency could also be achieved with a sufficiently long application of a periodic forcing on the system. A continuous cooling would be, in this case, necessary to avoid overheating. Besides we remark that with the forcing procedure
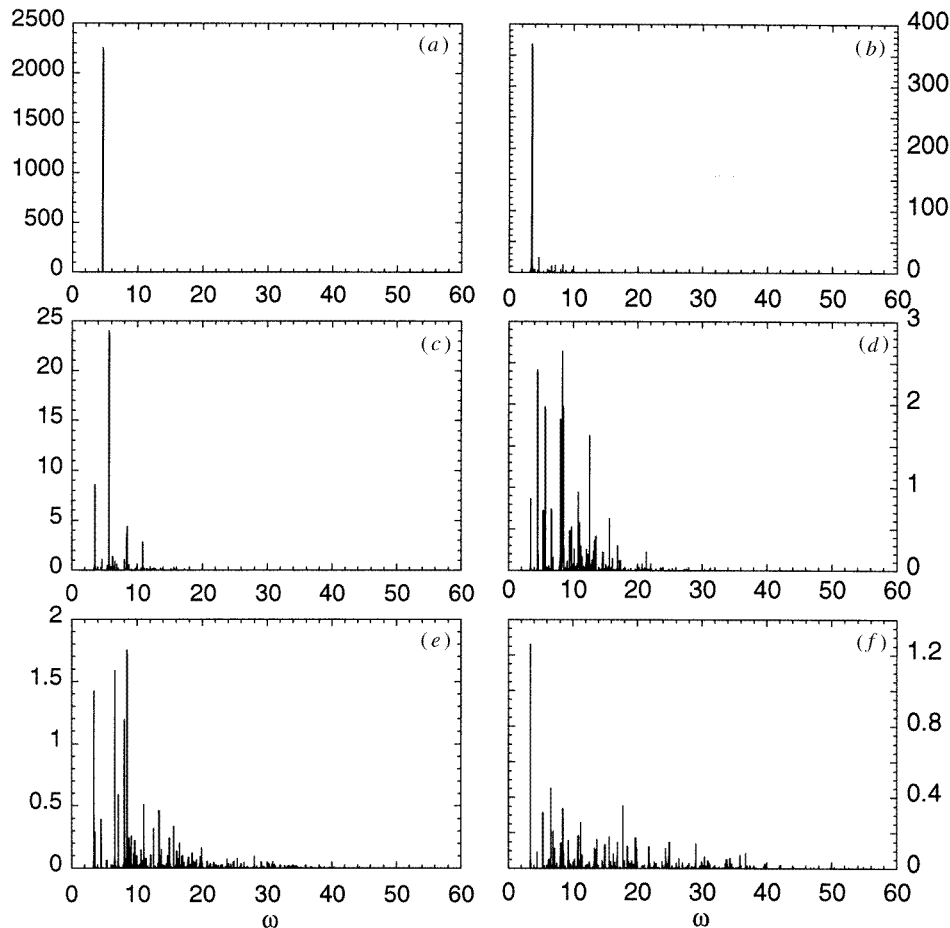
Figure 6. Power spectra of the kinetic energy in six low energy ($\epsilon = 10^{-8}$) MD runs. Each run started from rescaled initial conditions originally recorded at different times in a run at $\epsilon = 10^{-3}$ with only frequency $\omega = 2.32$ initially excited. See text for recording times.

the selection of the resonant frequency goes linearly with time, while in our quenching procedure it is exponential, as can be inferred from equation (3) (see also comments after equations (6) and (7)).

The study of the energy relaxation among normal modes has been extensively carried out on simple nonlinear lattices, where normal modes are readily computed (see, e.g. [15–17]). In these works the relaxation of the energy towards equipartition is numerically investigated on the basis of approximate analytical estimates [17], or on phenomenological approaches making use of the so-called spectral entropy [15, 16]. The effect of nonlinearity has also been studied through the decay of correlation functions of normal modes [18]; however, it is not obvious that a decaying correlation function gives information on the relaxation of the related normal modes [19]. The relaxation functions here, introduced in section 2, offer a direct way to evaluate the degree of coupling of selected modes.

The study of the dynamics in complex systems has concerned different aspects. In glasses or glass-forming liquids the attention has been concentrated on the dynamical signatures of the glass transition, based mainly on the so-called mode-coupling theory

(MCT) [20]. In this respect we notice that in [1] there was a proposal for the use of echo to determine the coupling between modes in glassy systems; in our work we believe to have followed that suggestion. In proteins the focus has been mainly on the characterization of normal modes, through their structural [6] and dynamical [8, 12] properties; however, also the effects of anharmonicities have been the subject of study [21–23].

From these last remarks we can conclude that the selection method presented in this paper could find a particularly relevant application in the study of models of glasses and of models for the dynamics of proteins and nucleic acids. Simulations in these fields are numerically intensive, requiring systems with many thousands of degrees of freedom.

Acknowledgments

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