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Interaction of a relaxing system with a dynamical environment

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It is shown that nonlinear interactions with a dynamical environment are able to transform the microscopic trajectories of a relaxing system to evolve as a time-dependent multiplicative process. When averaged over an ensemble of such trajectories, a nonexponential response with a scaled relaxation time is generated. Similar features have been observed for dispersive transport and relaxation in experiments and simulations of interacting constituents in condensed matter. This new class of statistical-mechanical systems is illustrated using a Hamiltonian-driven damped Fermi accelerator and an asymmetrically damped stadium billiard.

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There has been a considerable recent growth of research activities concerned with relaxation and transport in condensed-matter systems, such as amorphous and porous materials, glass-forming viscous liquids, vitreous ionic conductors, and entangled polymer melts [1]. The approach to equilibrium is generally characterized by (a) time-dependent linear responses such as dispersive transport and nonexponential correlation functions, and by (b) anomalous dependence of the transport or relaxation time on a number of experimental variables. It is believed these features are due both to the effects of dynamical interactions between the relevant degrees of freedom and to the effects of the static disorder of the material. This has led to numerous recent theoretical and numerical investigations of model systems which contain dynamical interactions or disorder. For example, recent large-scale computer simulations of glass-forming polymers [2,3] and liquids [4], ionically conducting lattices [5], and entangled polymer chains [6] explicitly contain both nonlinear interactions (e.g., Lennard-Jones, hard-core, Coulomb, etc.) with the relaxing degrees of freedom and thermal bath effects. The results of these simulations are able to reproduce features (a) and (b) as observed in experimental data. These observed features of both experiments and numerical computations are concisely summarized by a macroscopic description and interpretation of relaxation developed by Ngai and co-workers [7–11], often designated as the "coupling model." It has been found from both experiments and simulation that the relaxation of the individual constituents becomes slowed down after a time scale t_c, mainly due to the dynamical interactions, and must then be described by nonexponential response functions [feature (a)] with characteristic scaled rate parameters [feature (b)]. These observations can be efficiently and accurately parametrized by the equations of the coupling model [see Eqs. (3) and (4) below]. The repeated success of this description of both experiments and simulations provides evidence that the essential features of relaxation in these systems are determined mainly by the effects of dynamical interactions involving the relaxing degrees of freedom, with static material disorder often playing a secondary role.

However, it has been difficult to understand in detail how these observed features emerge in the simulations of these complicated interacting statistical-mechanical systems from the properties of dynamically interacting degrees of freedom and statistical mechanics. It would therefore be useful to isolate specific dynamical and statistical-mechanical mechanisms that can exhibit similar properties and yet can be analyzed in detail. A number of mechanisms for the modification of transport and relaxation by static disorder or dynamical effects have been studied in simple models [12–16]. These models contain mechanisms for nonexponential relaxation [feature (a)] and provide insight into the statistical mechanics of complex systems. In addition, there are the mode-coupling theories [17] that provide macroscopic scaling relations among the α, β, and other relaxation regimes. However, there are no microscopic models that also explain the relation between the observed relaxation time and the microscopic relaxation time [feature (b), Eq. (4) below], which is essential to describing the systems of interest here [1–11]. In this paper, we analyze a class of systems in which thermally relaxing degrees of freedom are interacting nonlinearly with a dynamical environment at the microscopic level. The macroscopic response is found to contain the essential features (a) and (b) observed in the simulations and experiments, as summarized by the coupling model equations, and also provides insight into how these features emerge from the microscopic trajectories. Two simple examples are analyzed which contain the ingredients found more generally in this class of systems.

It has long been known that the phase-space trajectories for Hamiltonians with nonlinear interactions can exhibit classical chaos at long times. However, it is now also known that the evolution in time of such trajectories (for a large class of chaotic Hamiltonians) is comprised of segments of smooth motion for finite intervals of time corresponding to approximate invariants of the motion, sequentially interrupted in time by sudden jumps to other approximate invariants [18–23]. For example, the route to chaos in the dynamics of two ions in a radio-frequency trap has been experimentally found to be due to ion-ion collisions in which stable single-particle-like motion is occasionally interrupted by jumps to new orbits caused by the nonlinear Coulomb interaction during close encounters [18]. Theoretical and numerical studies [19–23] have found that, for a large class of nonintegrable Hamil-

tonians with a variety of nonlinear potentials, there exist approximate invariants of motion that break down and become singular only in very *localized* regions (not necessarily confined to a point) of phase space. These regions act as "scattering centers" in the phase space that interrupt the otherwise smooth trajectories corresponding to the approximate invariants. The curvature of the potential-energy surface is negative along a line perpendicular to the flow near these centers so that subsequent motion is very sensitive to initial conditions there. This causes the trajectory to make a transition to a new approximate invariant, which survives until the next scattering center is encountered. The result of many such encounters of a trajectory with scattering centers results in deterministic chaos at long times.

We demonstrate here that such encounters also have implications for statistical-mechanical systems in which some of the degrees of freedom are damped by coupling to a thermal bath. Figure 1 shows two simple examples of such systems. Figure 1(a) consists of a Brownian point particle moving in a one-dimensional box along the y direction. The Brownian particle collides elastically with a fixed hard wall at one end and has elastic hard-core collisions with an undamped (i.e., Hamiltonian) harmonic oscillator at the other end. The Brownian particle and the harmonic oscillator both have unit point mass. This is analogous to the famous Fermi accelerator [24], except the oscillating wall here is a Hamiltonian oscillator instead of being externally forced and the particle undergoes Brownian instead of free motion between collisions. Figure 1(b) shows the even simpler example of a point particle moving in a stadium-shaped billiard where motion in the y direction is Brownian and motion in the x direction is free for times between elastic collisions with the boundary. If the Brownian damping and thermal fluctuations were temporarily turned off, the particle momentum in the y direction, P_y, in each of these examples would be conserved between collisions. However, the magnitude of P_y is abruptly changed at each collision with the environment [i.e., the oscillator in Fig. 1(a) or the curved end of the stadium in Fig. 1(b)]. In the absence of damping, both examples can exhibit chaos at long times due to sequential interruptions in time of the approximate invariant of the motion, P_y, due to the hard-core scattering events. These two examples with hard-core interactions thus contain the features found more generally [18–23] for the sequentially interrupted evolution of trajectories in nonintegrable Hamiltonians, but are simple enough to be analyzed in detail. If the Brownian damping and thermal fluctuations are now turned back on, the particle in both the Hamiltonian-driven damped Fermi accelerator of Fig. 1(a) and the asymmetrically damped stadium billiard of Fig. 1(b) obeys the simple Langevin equation, $dP_y/dt=-\gamma P_y+F(t)$, during the time intervals between collisions, where $F(t)$ represents Gaussian white noise; i.e., $\langle F(t)F(0)\rangle=2\gamma kT\delta(t)$.

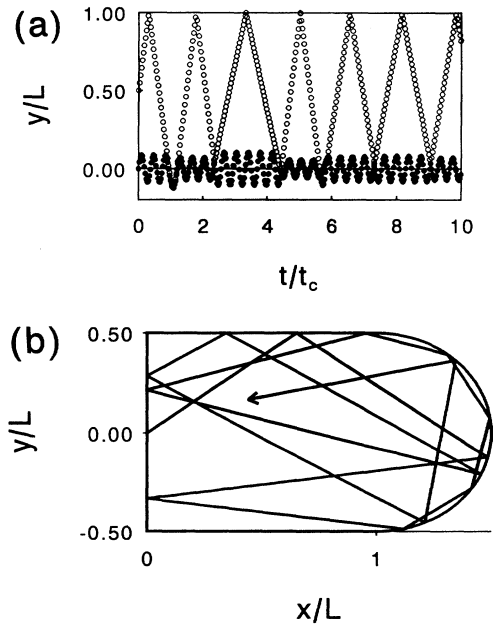

FIG. 1. (a) Brownian particle in a box with a harmonically oscillating wall. (b) Particle in a stadium billiard with Brownian y motion and free x motion. The Brownian fluctuations are not visible in the initial behavior of the trajectories shown here because the average initial particle energy is $500kT$.

If t_1 is the time of the first collision with the environment, the solution for $P_y(t)$ during this initial time interval is the same as for Brownian motion in a one-dimensional box with rigid walls [25]. For example, the energy of the particle, $E_y=P_y^2/2$, thermally averaged over an ensemble of trajectories will initially decay toward equilibrium as an exponential, $\phi(t)=\exp(-2\gamma t)$ for $t<t_c$, where $t_c=\langle t_1\rangle$ is the average time of the first collision. However, subsequent collisions with the environment will modify the solutions for $P_y(t)$. If the environmental degree of freedom initially has an energy comparable to the Brownian particle, the collisions will repeatedly cause significant changes in the particle energy during its time evolution. The value of the particle energy for a single trajectory as a function of time will thus have a very tortuous appearance. However, the properties of these trajectories can be shown to be described simply in terms of *time-dependent* multiplicative processes. And averages over ensembles of such trajectories exhibit smooth behavior and are consistent with the observed features (a) and (b).

The microscopic trajectories for the models of Fig. 1 can be analyzed most directly from the discrete mapping of the coordinates and momenta from one collision with the environment to the next. Although the exact mappings for these systems can be studied, and the exact systems will be discussed below, let us first consider a simplified version of the mappings for these models in which the particle exchanges momentum during a collision with the environment, but always at the same fixed position [e.g, $y=0$ for Fig. 1(a) and $x=x_c$ for Fig. 1(b)]. This is analogous to the simplified Ulam map for the standard Fermi accelerator [24]. We will ignore thermal fluctuations for these simplified maps so that the energy decays toward zero instead of $kT/2$. These simplified maps contain the essential features of the exact models but simplify the discussion considerably. If the phase of

the dynamical environment changes rapidly between collisions, it can be approximated as being random. For the simplified maps, there is no phase dependence for the position at each collision and an average over the random phase can be done directly. This results in a map for the particle energy for $t > t_1$, at each collision with the dynamical environment, for the Hamiltonian-driven damped Fermi accelerator of Fig. 1(a):

$$E_y(i+1)=[E_y(i)+E_y(i-1)\exp(-2\gamma\Delta_{i-1})]/2 , \quad (1)$$

and for the asymmetrically damped stadium billiard of Fig. 1(b):

$$E_y(i+1)=E_y(i)[1+\exp(-2\gamma\Delta_i)]/2 , \quad (2)$$

where the collisions take place at times t_i and the interval between collisions, $\Delta_i = t_{i+1} - t_i$, is determined self-consistently by the dynamics of each model. In Eq. (1), the oscillator energy is given by $E_{\rm osc}(i)=2E_y(i+1)$, and in Eq. (2), the energy for the x motion is given by $E_x(i)=E_y(i)$. These maps take the form of averages of a damped and an undamped term because the damped Brownian particle exchanges energy with the undamped environment. The Δ_i will change with time, increasing on average, as the Brownian particle slows, because it takes longer to return to the oscillator or curved stadium wall. Equations (1) and (2) thus take the form of *time-dependent* multiplicative processes that clearly must decay slower than $\exp(-2\gamma t)$ (which is the decay had there been no interaction with the dynamical environment). The nature of this nonexponential decay is most clearly seen in the average behavior of the trajectories.

Numerical solutions of the *exact* equations of motion of the two models for the decay of the energy of the Brownian particle averaged over a Gaussian ensemble of initial momenta and over thermal noise are shown in Figs. 2 and 3. In these examples, the initial energies of the Brownian particle and the dynamical environment were chosen to be equal and the Brownian damping constant γ was chosen small enough so that many collisions would occur before equilibrium with the thermal bath was attained. As seen in Figs. 2 and 3, the effect of the environmental collisions is to transform an initial exponential decay of the energy for $t < t_c$, with the relaxation time $\tau_0 \equiv 1/(2\gamma)$, to a nonexponential decay with a larger relaxation time τ. Here t_c is the average time of first collision. For $t > t_c$, the decay function undergoes a brief transient and then settles down to a smooth nonexponential function that, in these examples, can be approximated by a stretched exponential with a scaled relaxation time as shown by the solid lines in Figs. 2 and 3. The normalized time-dependent decay can be parametrized approximately as

$$\phi(t)=\begin{cases}\exp[-t/\tau_0], & t<t_c \quad (3a)\\ \exp[-(t/\tau)^{1-n}] , & t>t_c \quad (3b)\end{cases}$$

$$\tau=\tau_0[1-n)(\tau_0/t_c)^n]^{1/1-n} . \quad (4)$$

The values of the stretching exponent n in Eqs. (3b) and (4) generally depend on the strength and frequency of the environmental interactions [26]. For the particular

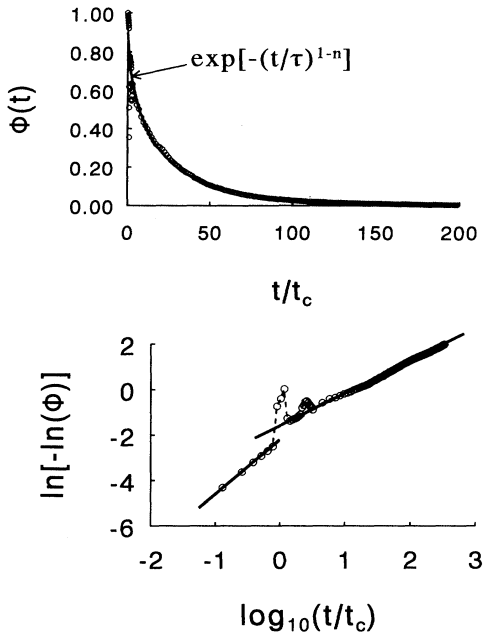

FIG. 2. Normalized energy decay of the Brownian particle in the accelerator of Fig. 1(a) showing the transition from exponential to stretched exponential. Average of 10^4 trajectories with $y(0)/L=0.5$, $y_{\rm osc}(0)/L=0$, a Gaussian distribution of $P_y(0)$ and $P_{\rm osc}(0)$ with average of unity and variance of 0.01; $L=10$, $\tau_0/t_c=9.7$, oscillator frequency $\omega t_c=15.4$, and $kT/2=\langle E_y(0)\rangle/1000$. Solid lines: fits to Eqs. (3) and (4) with $n=0.33$.

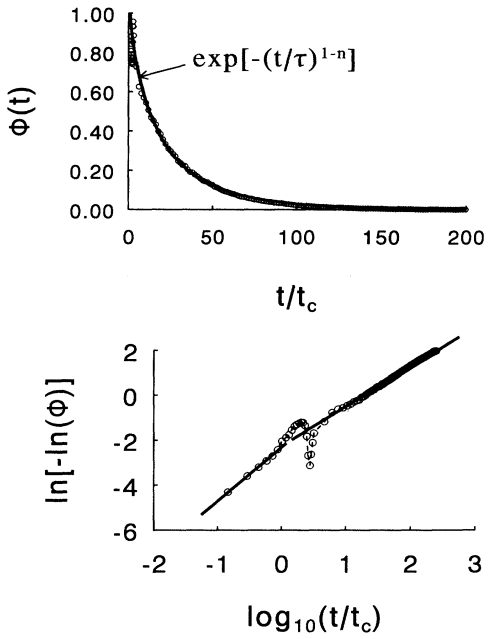

FIG. 3. Normalized energy decay of the Brownian motion in the stadium of Fig. 1(b) showing the transition from exponential to stretched exponential. Average of 10^4 trajectories with $y(0)/L=0$, $x(0)/L=0$, a Gaussian distribution of $P_y(0)$ and $P_x(0)$ with average of unity and variance of 0.01; $L=10$ $\tau_0/t_c=11.0$, and $kT/2=\langle E_y(0)\rangle/1000$. Solid lines: fits to Eqs. (3) and (4) with $n=0.27$.

parameters chosen in these illustrations, the values are found to be $n \simeq 0.33$ for the accelerator and $n \simeq 0.27$ for the billiard. The approximate parametrization in Eqs. (3) and (4) are the equations of the coupling model of Ngai and co-workers [7–11]. These have been found to accurately and concisely describe the macroscopic relaxation for many physical systems with interacting constituents both from experiments [1,7–9] and from computer simulations [9–11] of glasses, polymers, and ionic conductors [2–6]. The scaling relation for the τ of the stretched exponential in Eq. (4) can be understood [7–9] if it is assumed that the rates, $W = -\phi^{-1} d\phi/dt$, for the exponential, Eq. (3a), and the stretched exponential, Eqs. (3b), match smoothly at $t = t_c$. This is the case for the models in Figs. 2 and 3, and Eq. (4) for the scaling of the Brownian relaxation time τ_0 to the nonexponential relaxation time τ is obeyed. Although progress has been made in interpreting Eqs. (3) and (4) [7–9], there has been no derivation from fundamental principles. However, as shown here, this behavior is exhibited by relaxing systems nonlinearly interacting with a dynamical environment (which can be undamped or weakly damped) as a result of encounters with phase-space *scattering centers*. The time scale t_c will be generally well defined in this class of systems because the scattering centers are quite localized in phase space [18–23]. The microscopic dynamics takes the form of an interrupted evolution in time described by a time-dependent multiplicative process. The average over many trajectories results in a response similar to the observed macroscopic behavior. It is known that macroscopic linear-response behavior is compatible with microscopic nonlinear interactions [27]. The simplified maps of Eqs. (1) and (2) also give behavior similar to Figs. 2 and 3 when averaged over an ensemble of trajectoreis, although the exact solutions more closely approximate the stretched exponential.

The macroscopic features can be seen to emerge from the microscopic trajectories due to two interrelated properties of this class of systems (in the regime of random phase): (i) the time interval Δ_i between encounters with a phase-space scattering center is *time-dependent* (increasing on average) [28], and (ii) each such encounter has a probability of changing the state of the system. If (i) is obeyed but not (ii), the energy decays as a simple exponential with the Langevin relaxation time $\tau_0 = 1/(2\gamma)$ for all times. If (ii) is obeyed but not (i), then the decay will still be an exponential on average but with a larger modified relaxation time. For example, if $\Delta_i = \Delta_1 = \text{const}$ for all collisions, then the simplified map of Eq. (2) gives a simple exponential but with $\tau \simeq 2\tau_0$ (if $\Delta_1/\tau_0 \ll 1$). With both (i) and (ii), the relaxation following the initial environmental interaction is both nonexponential and must have a scaled relaxation time. If the nonexponential decay can be approximated by a stretched exponential, then Eqs. (3) and (4) will provide an accurate description of the average *macroscopic* behavior of these systems. The microscopic time-dependent multiplicative processes resulting from interactions with a dynamical environment can be described more generally by a scattering theory for the propagator of the interacting system in terms of the noninteracting propagator, the probability of encountering the next scattering center, and the state transition operator due to the scattering [26].

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