Relaxation Kinetics of Nonlinear Systems Coupled to a Nonequilibrium Bath

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The nonexponential decay of a correlation function in physical, chemical, or biomolecular complex systems is often taken as explicit evidence for disorder. Here we show that even without disorder, nonexponential relaxation can arise through a coupling of the primary relaxations to the "invisible" relaxations of the rest of the system.

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In a number of poorly understood, strongly coupled systems, relaxation processes due to activation exhibit nonexponential time dependence. Often the relaxation function $\phi(t)$ of some initial excitation is well described by a Kohlrausch-Williams-Watts (KWW) law, $\phi(t) = \exp[-(\kappa_1 t)^{\beta}]$, or a power law, $\phi(t) = [1 + \kappa_2 t]^{-\eta}$. This is to be contrasted with the exponential time dependence of the majority of systems, which is in accord with the normal equilibrium activation rate theory. Here we construct a solvable microscopic model which exhibits nonexponential relaxation, and which is also reasonably well fitted over appropriate time scales by either a KWW or a power law. The simple, yet generic, form of this model allows us to explore the influence of an initial nonequilibrium excitation of the other degrees of freedom of a complex system on the relaxation of a specific quantity of interest.

Our analysis is based on the assumption that the dynamics in question can be divided into a homogeneous set of essentially nonlinear modes or mutually uncoupled relaxing species and into a vastly larger number of effectively linear "phonon" type modes. Here we study the case where the spectral density of the linear modes takes a particularly simple form. We will consider a one-dimensional scalar field theory, and take up the problem at the point where a particular nonlinear mode ψ_0 and a set of effectively linear modes ψ_k have been identified, and the system has been reduced to an effective Hamiltonian in these variables,

$$\begin{aligned}\mathcal{H} = {} & \tfrac{1}{2}\dot{\psi}_0^2 + U(\psi_0) + \mathcal{H}_{\mathcal{B}} + \tfrac{1}{2}\sum_k (\dot{\psi}_k^2 + \omega_k^2 \psi_k^2) \\ & + \mathcal{H}_{\mathrm{int}}(\mathcal{B}, \psi_0, \psi_k) - \epsilon V(\psi_0)\sum_k \psi_k \\ & + \delta\mathcal{H}_{\mathrm{int}}(\psi_k, \psi_{k'}) . \end{aligned} \tag{1}$$

The first two terms on the right-hand side (rhs) describe a nonlinear mode, which represents one of the primarily relaxing species in the system. $\mathcal{H}_{\mathcal{B}}$ is the Hamiltonian for the thermal bath. The fourth term describes the linear phonon modes with frequency spectrum $\{\omega_k\}$. The next two terms represent the coupling of the nonlinear and linear modes to the thermal bath and the coupling of the nonlinear mode to the linear modes, where ϵ is a coupling constant. The last term indicates the weak nonlinear phonon-phonon couplings, which we will neglect in what follows and treat heuristically later. Extensions of this approach to higher dimension (more nonlinear modes) are straightforward.

We consider a purely classical interpretation of $\mathcal{H}$. This method will be appropriate when the temperature is high enough, when $\hbar$ is small enough so that tunneling is unimportant, and when there are no quantum coherencies on the time scales of interest. The linear modes then obey the classical equations of motion

$$\ddot{\psi}_k + \nu\dot{\psi}_k + \omega_k^2\psi_k = \epsilon V[\psi_0(t)] + \xi_k(t) , \tag{2}$$

where ν is the dissipation coefficient of the thermal bath of the linear modes. The fluctuating term is Gaussian white noise with mean zero $\langle\xi(t)\rangle = 0$ and with correlation function $\langle\xi_k(t)\xi_k(s)\rangle = 2\nu kT\delta(t - s)$, given by the fluctuation-dissipation theorem, since the bath $\mathcal{B}$ is assumed to be in thermal equilibrium. Here we have assumed for simplicity purely Ohmic, frequency-independent dissipation of the phonon modes.

The evolution of the linear modes ψ_k is given by

$$\begin{aligned}\psi_k(t) = {} & \psi_k^s + A_k e^{-\nu t/2}\cos(\overline{\omega}_k t + \phi_k) \\ & + \frac{\epsilon}{\overline{\omega}_k}\int_0^t d\tau\, V[\psi_0(\tau)] e^{-\nu(t-\tau)/2}\sin\overline{\omega}_k(t - \tau) , \end{aligned} \tag{3}$$

where A_k and ϕ_k are the initial amplitudes and phases of the nonequilibrium excitations of the phonons. The first term represents the stationary solution for the ψ_k in the absence of the coupling to ψ_0, the second represents the memory effects, and the third represents the effect of the coupling to ψ_0.

The ψ_k^s must represent the stationary (long time) fluctuations of the variables ψ_k in the absence of the coupling to the subsystem. This term is composed of a superposition of oscillating terms $\psi_k^s(t) = \sum_k A_k^s\cos(\omega_k t + \phi_k^s)$, with random phases ϕ_k^s and amplitudes distributed in proportion to the Gibbs distribution $P(A_k^s) = N^{-1}\exp[-\omega_k^2(A_k^s)^2/2kT]$. We will assume that the

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interaction of the nonlinear modes with the thermal bath is Ohmic, and that the frequency spectrum of the linear modes is semicontinuous with a frequency density $\rho(\omega)$ of the Debye type,

$$\rho(\omega) = \begin{cases} 3\omega^2/2\omega_c^3, & |\omega| \le \omega_c\,, \\ 0, & |\omega| > \omega_c\,, \end{cases} \tag{4}$$

which is regularized by a cutoff at high frequency ω_c that is assumed to be larger than any typical frequency of the nonlinear mode. In general, the spectrum will not be of this very simple type, and the dissipation will generally be retarded [1]. As was shown in [2], the effects discussed here have a microscopic thermodynamic interpretation in terms of the excess physical information (negentropy) in the phonon bath. This interpretation and the effect remains qualitatively unchanged when the spectrum is more complicated.

The equation for the gross variable ψ_0 is

$$\ddot{\psi}_0 + \gamma_b\dot{\psi}_0 + U'(\psi_0) = \xi_b(t) + \epsilon V'(\psi_0)\sum_k \psi_k\,, \tag{5}$$

where $\langle\xi_b(t)\rangle = 0$, and $\langle\xi_b(t)\xi_b(s)\rangle = 2\gamma_b kT\,\delta(t - s)$. Making use of Eqs. (3) and (4) and integrating by parts, we obtain a nonlinear Langevin equation for ψ_0,

$$\ddot{\psi}_0 + \Gamma(\psi_0)\dot{\psi}_0 + \tilde{U}'(\psi_0) = \xi_b(t) + V'(\psi_0)\xi_p(t)\,, \tag{6}$$

where γ_b and γ_p are the dissipation coefficients due to the thermal bath and the phonons on the nonlinear modes. Note the distinction between the latter, and the dissipation on the phonon modes due to the external bath ν. In addition $\Gamma(\psi_0) = \gamma_b + \gamma_p[V'(\psi_0)]^2$, and $\xi_p(t)$ is a Gaussian noise with $\langle\xi_p(t)\rangle = 0$ and an energy density (proportional to the power spectrum)

$$\begin{aligned} u(\omega, s) &= \frac{1}{4\gamma_p}\int_{-\infty}^{\infty} d\tau\,\langle\xi_p(s)\xi_p(s + \tau)\rangle e^{i\omega\tau} \\ &= kT/2 + e^{-\nu s/2}[u(\omega, 0) - kT/2], \end{aligned} \tag{7}$$

where s is a slow time variable. The last term describes just the effects of the damping of the linear modes by the thermal bath. We have made the assumption that $\xi_p(t)$ is effectively stationary on the fast time scale of τ_c, the correlation time of the noise, so that the fast and slow time scales are well separated. The properties of ξ_p now depend explicitly on the nonequilibrium state of the phonons through $u(\omega, t)$, the energy density distribution at time t. In addition, the "bare" potential is now dressed by the oscillator bath, $\tilde{U}(\psi_0) = U(\psi_0) - (\omega_c/\pi)\gamma_p V^2(\psi_0)$. We have assumed a random distribution of initial phases of the oscillators, which ensures that the noise is Gaussian. We assume γ_p is small.

Equation (7) *is a nonequilibrium fluctuation-dissipation relation.* It relates the properties of the fluctuating term $\xi_p(t)$ to the coupling constant γ_p (the friction coefficient of the phonon bath on the nonlinear modes) and the instantaneous nonequilibrium distribution of the phonon modes. While there is a vast literature on projection techniques [3], where the last step is the assumption of an equilibrium distribution of the bath modes, there seem to have been little or no work treating explicitly the kinetics of systems coupled to a bath which itself is not in equilibrium, particularly the case where the bath is not even in quasithermal equilibrium. Perhaps this is due to the formidable nature of the non-Markovian kinetics which arises in such cases, but near enough to equilibrium that relaxation functions can be calculated explicitly even for the case of an arbitrary perturbation of the bath, as we will presently show. Thus, instead of simply treating the relaxation of a few nonlinear degrees of freedom coupled to an equilibrium bath, we are calculating *the effect of the relaxation of the rest of a semi-infinite dimensional nonequilibrium system on the degrees of freedom of interest.*

For the purposes of this paper we will only consider the overdamped (γ_b, large) case in the limit where γ_p is small. In this case the γ_p dependent terms which arise (due to the ψ_0-dependent noise) when the overdamped limit is taken [4] can be neglected and

$$\Gamma(\psi_0)\dot{\psi}_0 + \tilde{U}'(\psi_0) = \xi_b(t) + V'(\psi_0)\xi_p(t)\,. \tag{8}$$

The picture we have in mind is that the system is perturbed by some external shock at time $s = 0$. This shock has the effect of exciting the nonlinear mode into the metastable state $S1$ (picture in Fig. 1) and also of exciting the linear modes into a nonequilibrium state. Here we assume that the effect of ψ_0 on the ψ_k is small enough to be neglected.

Equation (8) resembles the heuristic fluctuating barrier model of Stein *et al.* [5], which was also an attempt to understand some aspect of nonexponential relaxation. The fluctuating barrier models have their spiritual roots in the pioneering work of Landauer [6]. The coupling energy $V(\psi_0)$ of the nonlinear mode to the phonons is in fact the fluctuating part of the barrier. However, our equation is derived from microscopic considerations rather than

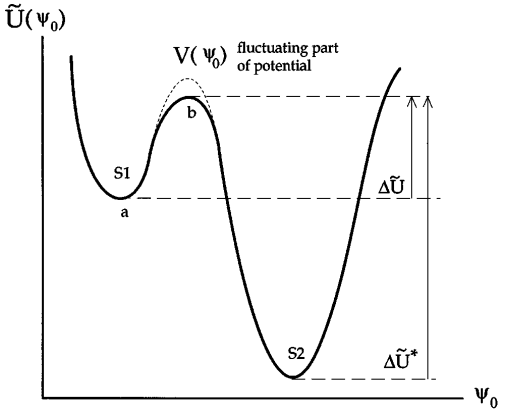

FIG. 1. Typical dressed effective potential $\tilde{U}(\psi_0)$ of the nonlinear mode ψ_0. The fluctuating part of the potential is indicated schematically.

heuristic ones. In order to maintain self-consistency of the formulation in terms of a Langevin equation, it is necessary that the friction be spatially varying $\Gamma(\psi_0)$ [7]. The analysis presented here reveals in a clear way the origin of interesting effects in these models: They arise only in cases where the system which produces the fluctuations is not in thermal equilibrium. The fluctuating part of the potential is indicated schematically in Fig. 1. The shape of $V(\psi_0)$ will of course have generally a more complicated form than the one pictured here.

The noise variables, $\xi_b(t)$ and $\xi_p(t)$, are mutually uncorrelated $\langle \xi_b(t)\xi_p(t)\rangle = 0$, and the probabilities of various processes can be calculated via path integration over the joint probability density functional

$$\mathcal{P}(s)[\xi_p, \xi_b] \propto \exp\left[-\int \mathcal{L}(s)d\tau\right].$$

$$\mathcal{L}(s) = \frac{1}{4\gamma_b kT}\,\xi_b^2(\tau) + \tfrac{1}{2}\xi_p(\tau)\hat{F}(s)\xi_p(\tau), \tag{9}$$

subject to the constraint of Eq. (8) and the boundary conditions of the process of interest. As shown in [8], the operator $\hat{F}(s)$ is obtained via the substitution $\omega \rightarrow -id/dt$ in $F(\omega, s) = 1/4\gamma_p u(\omega, s)$.

This path integral formulation [Eqs. (8) and (9)] represents a complete formal description of the dynamics of the nonlinear modes. Equations (8) and (9) are the description of a *non-Markovian system.* While there exists a rather large literature in which the non-Markovian effects of noise are incorporated within Markovian descriptions (such as the Fokker-Planck equation) via the inclusion of "auxiliary dimensions" or virtual particles [9], we do not make use directly of such techniques here. These techniques are most useful when noise has a simple power spectrum (such as Ornstein-Uhlenbeck noise), which allows for a small set of auxiliary dimensions. Because of the arbitrary shape of the power spectrum in the present case, there will generally be *no finite dimensional auxiliary description.* This will manifest itself in the fact that the $F(\omega)$ has no finite polynomial expansion in ω^2, and the operator $\hat{F}$ will have an infinite number of terms of increasingly high order in d^2/dt^2. Near equilibrium, when the bandwidth of the energy spectrum $u(\omega)$ greatly exceeds the reciprocal relaxation time of the system $t_r^{-1} = \tilde{U}''(a)/\gamma_b$, the magnitude of these terms decreases rapidly, and the stochastic instanton trajectories and the corresponding activation energies to logarithmic accuracy can be obtained via an extension of the variational approach used in [8].

Since we have already assumed separation of fast and slow noise time scales this implies that the escape time, which for practical purpose is t_r [as distinct from the average activation time $1/W(s)$], is much faster than the slow relaxation time scale of the noise. In this case we obtain dressed activation rates $W(t) = \exp[\delta R(t)/kT]W_0$, where W_0 is the equilibrium (Kramers) activation rate and

$$\delta R(t) = \kappa_1\left(\frac{2u(0,t)}{kT} - 1\right) + \kappa_2\left(\frac{u''(0,t)}{\gamma_p kT}\right), \tag{10}$$

$$\kappa_1 = \left(\frac{\gamma_p}{\gamma_b}\right)\int_a^b \tilde{U}'[V']^2 dx, \tag{11}$$

$$\kappa_2 = \left(\frac{\gamma_p}{\gamma_b}\right)^2\int_a^b \tilde{U}'[V'\tilde{U}'' + V''\tilde{U}']^2 dx, \tag{12}$$

where $\kappa_{1,2} \geq 0$. Near equilibrium, $\delta R(t)$ is small with respect to $\Delta\tilde{U}$, and we have kept only terms of lowest order in γ_p/γ_b in $\kappa_{1,2}$. $R(t)$ has been calculated to logarithmic accuracy, and we have ignored terms in the prefactor proportional to τ_c and kT, and the contributions of higher order than d^2/dt^2 in the Lagrangian. A systematic evaluation of these small corrections is possible but does not contribute any useful understanding to the present problem in proportion to the increasing effort required to obtain them.

The first term in Eq. (10) is the effect of quasithermal excitations at low frequency. The second term represents the effects of a nonuniformity of the low-frequency nonequilibrium excitations of the phonons, which gives rise to time correlation in ξ_p. Near equilibrium both terms contribute, but typically they decay at different characteristic rates. The quasithermal excitations decay on time scales of $1/\gamma$, the relaxation time of the phonons to thermal equilibrium. The second term will decay on time scales of the intraphonon energy equipartition, which can occur in a number of ways. The smallness of higher order terms and the typical separation of time scales of the relaxation processes give rise to a particularly generic form for the relaxation function $\phi(t)$.

The relaxation function $\phi(t)$ can be viewed as the probability for a system to be in state $S1$ a time t after the system has been prepared in state $S1$ (where $\Delta\tilde{U} \ll \Delta\tilde{U}^*$, as pictured in Fig. 1). Alternatively, $\phi(t)$ can be regarded as the evolution of the correlation function of the initial state, which is given in terms of the time-dependent activation rate $W(t)$ by $\ln\phi(t) = -\int_0^t W(s)ds$. When the phonons are in equilibrium [$u(\omega) = kT/2$ and $\delta R(t) = 0$], Arrhenius activation rates and exponential relaxation are naturally recovered.

The phonon-phonon coupling which we have initially neglected can lead to "spectral diffusion," that is, a conservative redistribution of the energy due to weak nonlinear couplings between phonons. The simplest example of this can be described by the energy diffusion equation

$$\partial_t\overline{u} = D\partial_\omega^2\overline{u} - \nu\overline{u}/2, \tag{13}$$

where $u = \overline{u} + kT/2$, and the last term is a consequence of the effects of dissipation of energy into the thermal bath as described by Eq. (7). The initial disturbance in the frequency domain spreads outward like a shock through the system and is eventually dissipated. More complicated models such a solitonic ones for the propagation

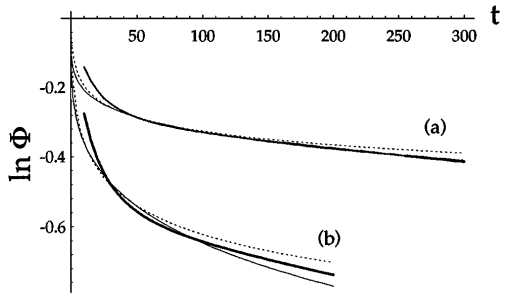

FIG. 2. The theoretical relaxation function $\phi(t)$ (bold lines) for long time, and fits to the KWW law (thin lines) and the power law (dashed lines), where (a) $a = 4$, $\nu = 0.045$, $\beta = 0.2$, $\kappa_1 = 0.048$, $\eta = 0.27$, $\kappa_2 = 2$ and (b) $a = 3.9$, $\nu = 0.048$, $\beta = 0.255$, $\kappa_1 = 0.0025$, $\eta = 0.123$, $\kappa_2 = 2.95$.

of energy through the frequency domain are possible. Additionally, one could start with a model for the spread of energy in the spatial domain, and then transform to the frequency domain.

For an arbitrary initial distribution of energy $u(\omega, 0)$, and provided we are near thermal equilibrium $[2u(\omega, 0) - kT]/kT \ll 1$, it is possible to show by means of a simple Fourier analysis of Eq. (13) that Eq. (10) can be expressed in the form $\delta R(t) = (c_0 a_0/2)e^{-\nu t/2} + \sum_{n=1}^{\infty} c_n a_n e^{-\lambda_n t}$, where $c_n = 2\kappa_1/kT - \kappa_2 n^2\pi^2/\omega_c^2\gamma_p kT$ with $\lambda_n = \nu/2 + Dn^2\pi^2/\omega_c^2$, and $a_n = (1/\omega_c)\int_{-\omega_c}^{\omega_c} \overline{u}(\omega, 0) \times \cos(n\pi\omega/\omega_c)d\omega$.

At very short $t \ll 1/\nu, \omega_c^2/d\pi^2$ and very long times $t \gg 1/\nu$, there are natural crossovers to pure exponential relaxation, and at intermediate time the relaxation can be fitted by the KWW or power law. Regardless of the initial distribution, for time scales $t > \omega_c^2/4D\pi^2$, $\delta R(t)$ takes the form $\delta R(t) = \exp(-\nu t/2)[a + b\exp(-ct)]$, where usually $|b| < |c|$. The signs of a and b are given by the signs of $u(0, t) - kT/2$ and $u''(0, t)$, respectively, which is a manifestation of the fact that these two quantities measure the negentropic source/sink in the bath as shown in [2]. It is important to point out that while $\delta R(t)$ is small with respect to the main contribution to the activation energy $\delta\tilde{U}$, it is not small in comparison to kT and can change the activation rate substantially.

For times longer than the intraphonon relaxation time, $\delta R(t) = a\exp(-\nu t/2)$, and for even longer times, $\tau > 1/\nu$, there will be a crossover to exponential decay, $R(t) \approx 0$. This gives rise to a two-parameter family of relaxation functions which have the same qualitative features, and are modestly well fitted by either a power law or a stretched exponential as shown in Fig. 2. Our results differ from the power law and the stretched exponential as little as the two differ from each other.

Here we have discussed only the near-equilibrium case, where the variational solutions for the escape paths are smooth. The treatment in terms of instantons can be extended to cases farther from equilibrium [8,10]. In this case these solutions generically possess topological singularities as a parameter is varied [8,11], which can give rise to sudden changes in behavior such as observed in [12]. Once the singularities (which are global features of nonequilibrium systems [11]) set in, the perturbative approach exemplified by Eq. (10) must break down suddenly. This breakdown is of interest in itself as the onset of a nonequilibrium kinetic phase transition (as opposed to the spatial symmetry breaking transition discussed in [12]). A physically observable consequence of this spontaneous kinetic symmetry breaking would be that $W(t)$ may possess kinks, or sudden shifts from one regime of behavior, as the escape trajectory suddenly shifts from a family with the broken symmetry to the symmetric trajectory as the relaxation occurs.

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