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# Algebraic Relaxation Laws for Classical Particles in 1D Anharmonic Potentials

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Using extensive numerical analysis and exact calculations we show that the relaxation of a classical particle in 1D anharmonic potential landscapes with a leading quartic term follows a $1/t$ decay law at all temperatures, leading to a logarithmically increasing mean square displacement. For leading anharmonic terms of form $x^{2n}$ we find that the asymptotic relaxation is consistent with $1/t^{\phi}$, where $\phi = 1/(n-1)$ at all temperatures. We briefly comment on the possible implications of this result in the study of displacive structural transitions and in complex systems. [S0031-9007(96)01811-X]

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A variety of problems of considerable interest in physics is closely related to the behavior of a single classical particle relaxing in an anharmonic single or multiwell potential landscape while in thermal contact [1]. A detailed microscopic understanding of relaxation in 1D multiwell potentials could give important clues to the problems associated with thermally activated dynamics in the glass transition [2] and of relaxation in related complex systems [3].

In this Letter we show both numerically and analytically that the relaxation of any dynamical variable of a classical particle in a variety of anharmonic potentials follows a $1/t^{\phi}$ asymptotic decay law. This relaxation represents the loss of knowledge of the initial conditions of the anharmonic oscillator due to thermal effects. We find that $\phi$ is sensitive to the exponent of the *leading anharmonic term* in the potential. To our knowledge, these are the simplest systems for which a wide variety of slow algebraic decay is found. We conclude with a discussion of the possible implications of our findings.

We start with a classical particle in an anharmonic potential, $V_{\mathrm{anh}}(x)$ and consider several distinct forms for $V_{\mathrm{anh}}(x)$. Initially, we focus on potentials with leading *quartic* anharmonicity, perhaps the most common form of anharmonicity encountered in simple physical problems. These potentials are $V_{\mathrm{anh}}(x)$,

$$\text{(I)}\ \frac{A}{2}x^2 + \frac{B}{4}x^4 + Cx, \quad \text{(II)}\ \cosh(x), \quad \text{(III)}\ \cos(x). \tag{1}$$

Our objective is to study the time-dependent behavior of some chosen dynamical variable $\Psi(t)$ (e.g., position $[x(t)]$, velocity $[v(t)]$, etc.). We assume that the system is in thermal contact which may or may not lead to relaxation to equilibrium after the system has been subjected to an infinitesimal perturbation (i.e., no assumptions regarding ergodicity are made [4]). The study of the asymptotic behavior of such a relaxation process, after the perturbation has been removed, which can generally be characterized by the normalized relaxation function (RF) $\langle\Psi(t)\Psi(0)\rangle/\langle\Psi(0)^2\rangle$, where $\langle\cdots\rangle$ represents canonical ensemble averages, is the focus of this Letter.

Cases (I) and (II) in Eq. (1) describe systems in which the particle is spatially localized for all energies. To study the relaxation of the particle in (I) and (II) numerically, we integrate the equations of motion for each case at fixed total energy $E$ from some initial time $t$ to some final time $(t + \tau_E)$, where $\tau_E$ refers to the period of motion for the chosen $E$. $x(t)$, $v(t)$, and $a(t)$ (i.e., acceleration) and their corresponding microcanonical ensemble RF's are calculated and tabulated at 1024 equally spaced time intervals spanning the period $\tau_E$. The canonical ensemble RF is

  

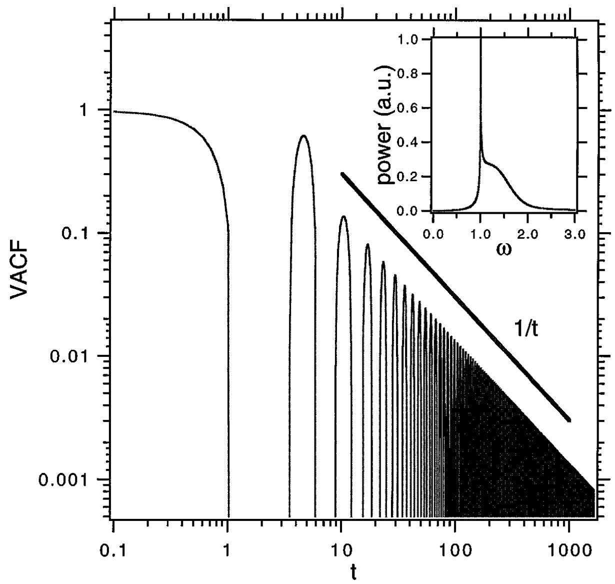


FIG. 1. Positive side of the velocity RF and corresponding power spectrum (inset) for the symmetric Duffing potential $V(x) = \frac{1}{2}x^2 + \frac{1}{4}x^4$ at $\beta = 1$.

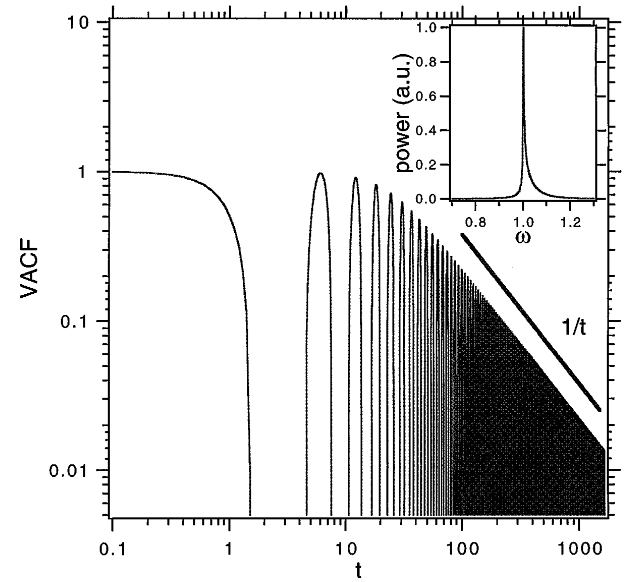


FIG. 2. Positive side of the velocity RF and corresponding power spectrum (inset) for the potential $V(x) = \cosh(x)$ at $\beta = 2.75$.

computed by first evaluating the microcanonical ensemble RF's at a number of different energies (typically, 2000) in the range $E_{\min} \leq E \leq E_{\max}$ and by then performing the integration over all the energies of the Boltzmann weighted microcanonical RF [5]. We used *unequal energy spacing* to ensure that the energy integral is correctly evaluated. The range of energies over which the microcanonical RF's are calculated is determined by the temperature of the system. We chose as the lower limit of integration an energy slightly higher than the potential minimum, typically, $E_{\min} = 5 \times 10^{-7}$, and, as the upper limit, $E_{\max}$ such that $\exp(-\beta E_{\max}) < 1 \times 10^{-11}$, where $\beta \equiv 1/kT$, $k$ is the Boltzmann constant, and $T$ is the temperature.

For the symmetric anharmonic single well, Case (I), with coefficients $\{A, B, C\} = \{1, 1, 0\}$, at $\beta \equiv 1/kT = 100$, the velocity RF can be numerically evaluated for times, $t \sim 2 \times 10^4$, yielding results that agree well with the exact asymptotic solution, which will be discussed below. Although it is more difficult to accurately calculate the RF's at long times for higher $T$'s, we still have been able to extend the solutions out sufficiently far so that it is possible to extract the asymptotic behavior. The velocity RF's (and related power spectra) are shown in Fig. 1 for the symmetric anharmonic single well at $\beta = 1$. Analysis of the results from the numerical calculations reveal that the RF's decay asymptotically as $-\frac{4\beta \sin(t)}{3t}$, i.e., a relaxation of form $1/t^{\phi}$, $\phi = 1$. Although we do not know of an analytic solution for the motion of a particle in a $\cosh(x)$ potential, numerical studies show that this potential also leads to a $1/t$ relaxation law at all $T$ as shown in Fig. 2.

Similar results have been obtained for the symmetric double well, Case (I), with the coefficients $\{A, B, C\} = \{-1, 1, 0\}$, and the asymmetric single well, Case (I) with $\{A, B\} = \{1, 1\}$, $C \neq 0$, i.e., with a linear field term. For the double well, the velocity RF and the corresponding spectrum is shown in Fig. 3 and has the asymptotic behavior $\frac{4\beta \sin(\sqrt{2}\, t)}{3t}$. To our knowledge, the asymmetric single well is not amenable to an exact solution. We find that the presence of a linear term strongly affects the RF at short times. However, the asymptotic behavior of the RF's, which sets in at a significantly later time in this spatially asymmetric potential, compared to the

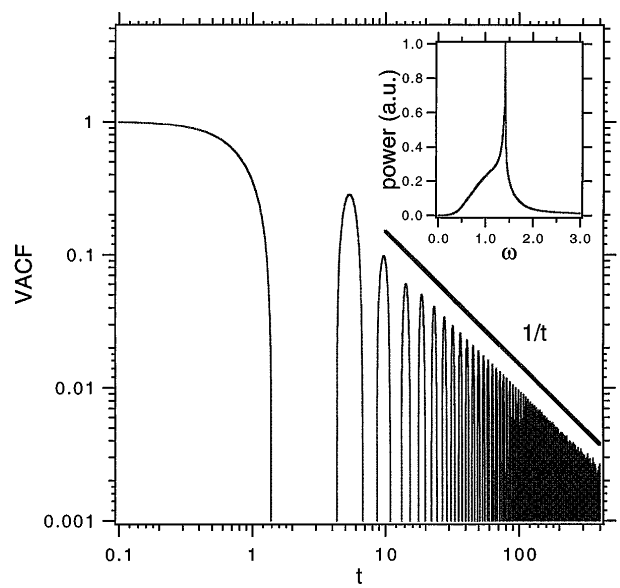


FIG. 3. Positive side of the velocity RF and corresponding power spectrum (inset) for the symmetric double-well potential $V(x) = -\frac{1}{2}x^2 + \frac{1}{4}x^4$ at $\beta = 1$ (barrier height in energy units is $1/4$).

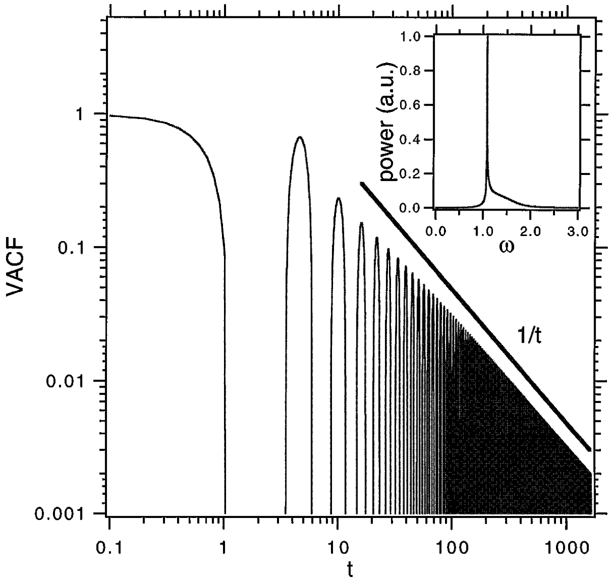


FIG. 4. Positive side of the velocity RF and corresponding power spectrum (inset) for the asymmetric Duffing potential $V(x) = -\frac{1}{4}x + \frac{1}{2}x^2 + \frac{1}{4}x^4$ at $\beta = 1$.

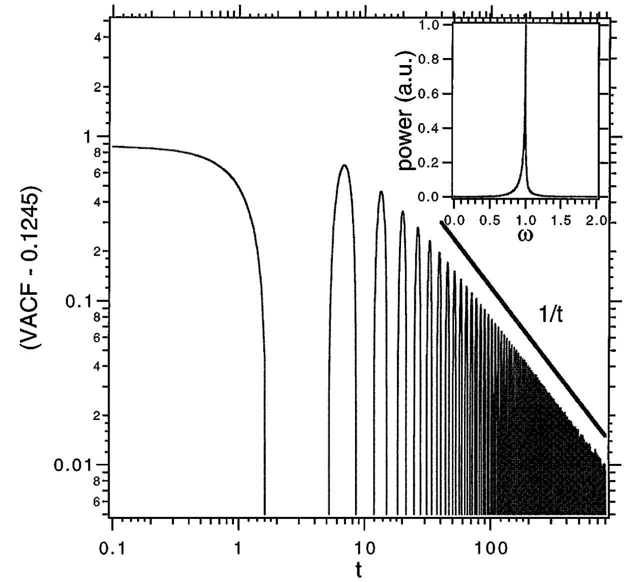


FIG. 5. Positive side of the velocity RF and corresponding power spectrum (inset) for the potential $V(x) = \cos(x)$ at $\beta = 1$. The velocity RF has been shifted so that the asymptotic value at $t = \infty$ is zero.

symmetric case, exhibits a robust $-\frac{4\beta\sin(t)}{3t}$ relaxation as shown in Fig. 4. Unlike the symmetric well and $\cosh(x)$ potentials, the position RF's for these two cases tend to a $T$ dependent constant $\Lambda_1(T)$ due to the fact that the potential minimum no longer lies at $x = 0$.

We now briefly focus on Case (III) in Eq. (1), which describes a system in which the particle becomes spatially delocalized at energies exceeding twice the amplitude of the corrugation potential. We have carried out numerical calculations in the manner sketched above. Since in the canonical ensemble there will always be contributions from energies for which the particle is no longer localized, the position RF will diverge, but the periodicity of the potential ensures that $v(t)$ and $a(t)$ will still be periodic leading to convergence of the corresponding RF's. The canonical RF's no longer tend to zero for Case (III), but the asymptotic behavior $1/t + \Lambda_2(T)$ is observed. The velocity RF for this potential is shown in Fig. 5.

The exact asymptotic analysis was accomplished as follows. We outline below the key steps in the calculations for Case (I) in Eq. (1). Let us set $\{A, B, C\} = \{1, r, 0\}$, with $r > 0$. The formal solution to the equation of motion is then given by [6]

$$x(t) = C \sum_{p=0}^{\infty} a_p \sin(2p + 1)\omega t\,, \tag{2}$$

where the leading terms of the constants $Ca_n$ are $Ca_0 = a$, $Ca_1 = (-ra^3/32)(1 - 21ra^2/32 + \ldots)$, ..., and the frequency $\omega = (1 + 3ra^2/4 + 3r^2a^4/128 + \ldots)^{1/2}$. In the above expressions, the variable $a$ is obtained as a function of $E$ by substituting the formal solutions for $x(t)$ and $v(t)$ into the Hamiltonian $p^2/2 + V_{\mathrm{anh}}$ yielding

$$a = (2E)^{1/2} - \frac{9E^{3/2}r}{2^{7/2}} \ldots. \tag{3}$$

A normalized microcanonical ensemble RF, say the velocity RF, is exactly obtained by substituting $v(t)$ obtained from Eq. (2) into the following equation for the velocity RF,

$$\frac{\int_{-\infty}^{\infty} v(t')v(t' + t)\,dt'}{\int_{-\infty}^{\infty} v(t')^2\,dt'} = \frac{\sum_{p=0}^{\infty} a_p^2(2p + 1)^2 \cos(2p + 1)\omega t}{\sum_{p=0}^{\infty} a_p^2(2p + 1)^2}\,. \tag{4}$$

It is difficult to carry out a closed form energy integral with the result of Eq. (4) above to obtain the canonical RF. We therefore focus on the nature of its asymptotic behavior and start by expressing $\omega$ in powers of $\gamma E$ (by substituting $a$ in the expression for $\omega$ above), where $\gamma$ is a system dependent constant $3r/4$. To leading order we obtain $\omega \simeq 1 + \gamma E$. For the moment let us ignore the terms with $p > 0$ and retain only the $p = 0$ term in the summation of Eq. (4). As we shall show later, the $p = 0$ term contributes to the slowest decay. Successively faster decays are contributed by the terms with increasing magnitude of $p$. We substitute Eq. (4) with the $p = 0$ term into the expression for the canonical RF and assume that at low enough temperatures the density of states is an energy independent constant. This gives

$$\frac{\int_0^\infty e^{-\beta E}\cos(1+\gamma E)t\,dE}{\int_0^\infty e^{-\beta E}\,dE} = \frac{\beta^2\cos(t) - \gamma\beta t\sin(t)}{\gamma^2 t^2 + \beta^2}, \tag{5}$$

which decays as $-\frac{\beta}{\gamma}\sin(t)/t$ for $\gamma t \gg \beta$. This, of course, is the behavior obtained from the numerical analysis reported above. The asymptotic functional form is that of $j_0(t)$, i.e., the zeroth order spherical Bessel function.

The result in Eq. (5), although originally derived to describe the asymptotic behavior of the velocity RF in the low $T$ limit, applies at all $T$'s. This can be shown easily by retaining higher order terms in $E$ in the expression for the RF at a fixed energy before substituting into the equation for the canonical RF. Keeping terms $p > 0$ in Eq. (4) leads directly to the appearance of powers of $E$ in the integrals while retaining higher order terms in the expansion for $\omega$ leads to trigonometric functions with arguments involving higher powers of $E$. This results in contributions to the canonical RF from integrals of the form $\int_0^\infty E^p e^{-\beta E}[\cos,\sin](\gamma t E)[\cos,\sin](c_2 t E^2)\cdots dE$ where the terms in square braces indicate that one or the other trigonometric function is chosen. Replacing the sin and cos functions containing arguments with powers of $E$ greater than one with their series expansions simply result in contributions from a sum of integrals of the form $\int_0^\infty t^l E^m e^{-\beta E}[\cos,\sin](\gamma t E)\,dE$, where all of the powers of $E$ have been collected in $E^m$, with $l$ and $m$ related by the inequality $m \geq l + 1$. In the long time limit, these integrals have the behavior that they tend either to $t^{l-m-1}$ or 0, depending on the choice of trigonometric function in the integrand and whether $m$ is even or odd. Since $m - l \geq 1$, all contributions to the velocity RF arising from retaining higher order terms in $E$ die off faster than $1/t$. In view of the formal similarities between this and the double-well problems, similar results can be derived for the double well [6]. In Case (III) the equation of motion is that of a pendulum [7]. The analysis is similar to the one above except for the issues mentioned earlier. This will be detailed elsewhere [8].

The $1/t$ behavior of the velocity RF leads to the result that the mean square displacement increases logarithmically as $t \to \infty$. This can be shown by relating the mean square displacement of the particle to the velocity RF as follows [9]: $\sigma^2(t) \equiv \langle [x(t) - x(0)]^2 \rangle = 2\int_0^t d\tau (t - \tau)\langle v(0)v(\tau)\rangle \propto 2t\ln(t) - 2t + \text{const.}$

Although as stated earlier, leading quartic anharmonicity is possibly more common than others, we have numerically probed relaxation in potentials of the form $\frac{1}{2}x^2 + \frac{1}{2n}x^{2n}$ for $n = 3, 4, 5$. To our knowledge, there are no simple closed form solutions to the equations of motion for these anharmonic potentials. Our analysis reveals that for $n = 3$, $\phi \simeq 0.45$, for $n = 4$, $\phi \simeq 0.32$, and for $n = 5$, $\phi \simeq 0.23$. These results strongly suggest that for arbitrary $n$, the asymptotic relaxation exponent follows the law $\phi = 1/(n-1)$ [8]. Thus, for arbitrary $n > 2$, the mean square displacement $\sigma^2(t) \sim t^{1+\frac{n-2}{n-1}}$ as $t \to \infty$. To our knowledge, these are the simplest Hamiltonian systems for which such a rich variety of slow algebraic decays have ever been reported.

The study presented above is relevant to a variety of problems of considerable interest in condensed matter physics. We briefly illustrate some of these connections below.

The Krumhansl-Schrieffer (KS) model [1] is described by the Hamiltonian $H = \sum_i \frac{m v_i^2}{2} + \sum_i (\frac{A u_i^2}{2} + \frac{B u_i^4}{4}) + \sum_{i>j} \frac{C_{ij}(u_i - u_j)^2}{2}$, with $A < 0$ and $B, C_{ij} > 0$. $u_i$ and $v_i$ are the displacement and velocity, respectively, of particle $i$. In the acoustic mode approximation, KS have shown that when well depths are less than the intersite energies, $H$ can be reduced to an effectively one-body problem in a continuum representation with $u_i = u_i(x)$, $v_i = v_i(x)$, $x = x_j = jl$, and $c_0$ equal to the velocity of low amplitude sound waves. The equation of motion is given as $\frac{d^2\eta}{ds^2} = \eta - \eta^3$, where $\eta \equiv u/u_0 = f(x - vt)/u_0$, $s \equiv (x - vt)\xi$, and $\xi^2 \equiv \frac{m(c_0^2 - v^2)}{|A|}$, with phase velocity $v$, and $u_0 \equiv \left(\frac{|A|}{B}\right)^{1/2}$. Our calculations prove that the relaxation in the KS system follows the $|1/t|$ relaxation law as $t \to \infty$, a general property which has not been previously noted. Perhaps the most striking consequence of this result is that particles in the KS model [1], in this continuum limit, possess a $t\ln t$ type mean square displacement, another new observation.

The dynamical behavior of the 2D Ising spin glass $Rb_2Cu_{1-x}Co_xF_4$ has been carefully probed recently by Dekker *et al.* [2]. They provide strong evidence that there exists a broad temperature range in which $q(t) \equiv \langle S_z(t)S_z(0)\rangle \sim \exp(-t/\tau_c)^{\beta'}$, where $\tau_c$ is the characteristic relaxation time and the exponent $\beta'$ is very small, being 0.06 at $T = 6.75$ K and increasing to a constant value 0.09 below 4 K. They also show that this behavior is consistent with a decay law of $t^{\alpha-1}$, where typically $0 < \alpha < 1$ with $(\alpha - 1) \sim -1$ in this particular system [[2], p. 11 249 below Eq. (11)]. If one can relate the dynamics in two-state systems with that in a double well, the connections between these results and ours may be established. Slow algebraic decay of dynamical density (and hence position) correlations is also observed via light scattering studies in the pregel phase of aqueous gelatin [3] and in a variety of other complex systems typically analyzed using mode coupling theories [10]. It is conceivable that our study may help develop some new insights to further clarify the existing analyses of these problems.

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