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Stochastic localization

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In this paper we address the phenomenon we call ''stochastic localization,'' within which we include a number of interrelated characteristics exhibited by soft anharmonic oscillators in thermal equilbrium. Principal among these characteristics are a tendency for soft oscillators to spend more time at higher energies than comparable harmonic oscillators, and for high-energy fluctuations in soft oscillators to persist longer than lower-energy fluctuations, leading to a tendency for energy fluctuations to be organized into ''bursts'' separated by intervals of relative quiet. [S1063-651X(96)01110-5]

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I. INTRODUCTION

The localization of energy in time, that is, the enhanced persistence and/or anomalously frequent occurrence of high-energy states, is one factor in promoting chemical or physical processes that require epithermal energies for their initiation. Another important factor may be the spatial localization of energy in otherwise homogeneous extended systems. Either of these distinct effects may be more prominent than the other in a particular instance, and they may be correlated to varying degrees depending on ambient conditions [1].

It is well known that a wide variety of translationally invariant, anharmonic systems are capable of supporting long-lived, localized excitations under appropriate conditions. Among these are systems modeled by completely integrable nonlinear wave equations that support robust, spatially coherent, infinite-lived localized excitations known as ''solitons'' [2–8]. The beauty and potential power of the soliton concept has motivated a substantial volume of research on solitons and anharmonic models of diverse types. There are well-known examples of soliton behavior sufficiently well understood to be the basis of practical devices, the best known, perhaps, being the soliton laser pulses used to transmit information through long optical fibers [9]. On the other hand, there are examples of solitonlike behavior for which attempts at experimental observation and control have been more equivocal; among these are molecular-scale solitons that arise from a number of theoretical models of solids and macromolecules [10,11].

One of the central difficulties plaguing the attempted observation of molecular solitons both in laboratory experiment and numerical simulation is the generally uncooperative nature of thermal fluctuations at finite temperatures. There are several distinct aspects to this difficulty: (1) The problem of ''soliton stability''; that is, the fact that few situations of practical interest approach a degree of idealization consistent with the existence of infinite-lived excitations such as solitons. A particular challenge in this regard is arriving at a meaningful and quantitative characterization of a ''lifetime'' that may be attributed to solitonlike initial conditions. (2) The fact that in many cases of practical interest the relevant circumstance is not a solitonlike initial condition, but the long-time, unhappy equilibrium in which any solitonlike excitations that *may* be present have been thoroughly abused by ravages of the heat bath. (3) The fact that most experimental techniques available for probing soliton structure are indirect and nondiscriminating in the sense that bulk properties of materials are probed; thus, most measurements average signals over substantial volumes of space from coherent and incoherent motions simultaneously, presenting serious challenges to ''deconvolution.'' (4) The latter experimental difficulty has a counterpart in theoretical analysis; that of discriminating a coherent ''nonlinear signal,'' such as a possible solitonlike component, from the incoherent ''nonlinear noise'' that may account for a large fraction of the energy in an anharmonic system.

We approach the general problem of anharmonic energy localization from the noisy side; that is, we look first to ensembles of uncoupled anharmonic oscillators to determine characteristics of the intrinsic noise with which any coherent structure must coexist in thermal equilibrium. Later, we consider arrays of weakly coupled oscillators and analyze the nature of the spatial coherence that results from direct interactions between oscillators. It may be useful to consider Secs. II and III of this paper as being addressed to such arrays of oscillators in the limit of vanishing coupling; in such a limit, spatial averaging reduces to ensemble averaging.

In this paper we focus our attention on fluctuations of the local energy density of an oscillator system in both space and time. We focus on the energy density rather than more direct mechanical coordinates such as oscillator amplitudes for several reasons: (1) the energy density determines the range of mechanical amplitudes; (2) the energy density is an intrinsically *slow* variable relative to mechanical amplitudes, permitting slow dynamics to be observed without the use of averaging; (3) the energy density is subject to thermodynamic constraint.

We are concerned primarily with systems of ‘‘soft’’ oscillators, a soft oscillation being one whose period increases with increasing amplitude; the periods of ‘‘hard’’ oscillations, on the other hand, decrease with increasing amplitude. The soft or hard nature of an oscillation is reflected as well in the structure of its phase space; the volume of phase space $\Gamma(E)$ included by the surface of constant total energy E of a soft (hard) oscillation increases more (less) rapidly than in the harmonic case. It is important to note that not all oscillators can be labeled definitively as ‘‘soft’’ or ‘‘hard’’; e.g., though the period of an oscillation may increase with amplitude at low amplitudes, this trend may reverse itself any number of times at higher amplitudes. Thus the characterization of an oscillation as ‘‘soft’’ or ‘‘hard’’ generally is limited to a specific range of amplitude. A *strictly* soft oscillation would be one whose period increases monotonically with amplitude, or in terms of phase space volume, one for which $d\Gamma(E)/dE$ increases monotonically with total energy.

A more practical approach is to characterize an oscillation as soft or hard depending on the *leading* anharmonic behavior at low amplitude. This is not only convenient, but it reflects the circumstance most commonly encountered in practice. It is this characterization that we shall employ throughout this paper, taking care that the temperatures considered justify restricting our attention to this low-amplitude regime.

For simplicity, we confine our explicit examples to symmetric potentials, but the same arguments apply to asymmetric potentials such as the Morse or Lennard-Jones [12]. Moreover, though much of the argument we present holds for potentials exhibiting multiple relative minima, we focus our discussion on potentials having unique, nondegenerate global minima and approximate these by monostable potentials at low temperatures.

II. THERMODYNAMICS

Consider a single oscillator described by the Hamiltonian

$$H\{\dot{x},x\}=\frac{\dot{x}^2}{2}+V(x), \tag{1}$$

in which $V(x)$ is a bound potential. For notational convenience, we set the mass m and low-amplitude frequency ω_0 of the oscillator to unity, and complete the scaling to dimensionless quantities by choosing the length scale to be the amplitude x_c characterizing the onset of softening or hardening of the potential. The energy scale in these terms is $m\omega_0^2x_c^2$. For such systems, the generalized equipartition theorem [13] reads

$$\left\langle \dot{x}\frac{\partial H}{\partial \dot{x}}\right\rangle=\left\langle x\frac{\partial H}{\partial x}\right\rangle=k_BT, \tag{2}$$

where $\langle\cdots\rangle$ indicates the ensemble average and T is the temperature. This implies that

$$\langle E\rangle=\langle H\rangle=k_BT+\langle\Lambda\rangle, \tag{3}$$

where

$$\Lambda(x)=V(x)-\tfrac{1}{2}xV'(x) \tag{4}$$

is an auxiliary function containing *no* quadratic terms; though $\Lambda(x)$ is not equal to the anharmonic part of $V(x)$, it is the vehicle through which the anharmonicity of the potential enters our calculations. We shall see below that $\langle\Lambda\rangle$ is generally positive for soft potentials, indicating that the equilibrium expectation value of the total energy of a soft anharmonic oscillator exceeds that of a harmonic oscillator at a given temperature. This qualitative conclusion does not depend on the frequency of the harmonic oscillator used for comparison, nor on the degree of freedom underlying the vibration, since all harmonic oscillators in equilibrium at the same temperature share the same energy expectation value. Consequently, we may conclude that any soft anharmonic oscillator will equilibrate to an average energy higher than that of any harmonic oscillator at the same temperature.

The magnitude of this excess is not necessarily large, of course. Clearly, the magnitude of this disparity increases with the strength of the anharmonicity, but for the same value of the anharmonicity the expected value of the higher moments (e.g., $\langle x^4\rangle$) will be larger in comparable oscillators having lower frequencies at low amplitude. This suggests that we may expect anharmonicity-driven concentrations of energy to be most pronounced among the lowest-lying vibrational modes of a complex system.

We make use of the notion of a ‘‘comparable harmonic oscillator’’ as a standard to use in discriminating deviations from harmonic behavior. This hypothetical harmonic oscillator is understood to exist in the same degree of freedom as the anharmonic oscillator in question, and its potential is understood to be the parabola that osculates the anharmonic potential at its global minimum. In such comparisons, quantities associated with *soft* anharmonic oscillators are decorated with tildes (e.g., $\widetilde{V}$), while harmonic reference quantities are decorated with zeros (e.g., V_0) to indicate that the anharmonicity has been set to zero.

It follows from considering either the behavior of the oscillator potential or the included phase space volume $\Gamma(E)$ that the partition function

$$Q=\int\int e^{-[(1/2)p^2+V(x)]/k_BT}dp\,dx \tag{5}$$

of a soft anharmonic oscillator is greater than the partition function of a comparable harmonic oscillator, at least at low temperatures ($\widetilde{Q}>Q_0$). Consequently, the free energy

$$A=\langle E\rangle-TS=-k_BT\ln Q \tag{6}$$

of the soft anharmonic oscillator is lower ($\widetilde{A}<A_0$), and (using the equipartition result) the entropy and heat capacity higher ($\widetilde{S}>S_0$, $\widetilde{C}_v>C_v^0$) than in a comparable harmonic oscillator.

From such considerations we may draw some conclusions regarding energy fluctuations. The variance of the total energy in thermal equilibrium is related to the heat capacity by the relation

$$\langle\Delta E^2\rangle=k_BT^2C_v\,. \tag{7}$$

In view of the equipartition theorem, we may conclude that the normalized variance of the total energy of a single harmonic oscillator at thermal equilibrium is equal to unity

$$\frac{\langle \Delta E_0^2\rangle}{\langle E_0\rangle^2}=1. \tag{8}$$

On the other hand, the normalized energy variance for our anharmonic oscillator is given by

$$\frac{\langle \Delta E^2\rangle}{\langle E\rangle^2}=\frac{k_BT^2C_v}{\langle E\rangle^2}. \tag{9}$$

We can use the relation

$$C_v=\frac{\partial\langle E\rangle}{\partial T} \tag{10}$$

to compute the heat capacity. We have then

$$\frac{\partial\langle E\rangle}{\partial T}=k_B+\frac{\partial\langle \Lambda\rangle}{\partial T}. \tag{11}$$

To complete the computation, we note that

$$\langle \Lambda\rangle=Q^{-1}\int\int \Lambda(x)e^{-[(1/2)p^2+V(x)]/k_BT}dp\,dx, \tag{12}$$

so that the differentiation of $\langle \Lambda\rangle$ with respect to temperature involves two contributions, one involving $\langle V\Lambda\rangle$ arising from the differentiation of the integral written explicitly above, and one involving $\langle \Lambda\rangle\langle V\rangle$ arising from the differentiation of the normalization Q^{-1}; thus

$$\frac{\partial\langle \Lambda\rangle}{\partial T}=\frac{1}{k_BT^2}(\langle V\Lambda\rangle-\langle \Lambda\rangle\langle V\rangle). \tag{13}$$

Substituting these expressions into our formula for the energy fluctuations, we get

$$\frac{\langle \Delta E^2\rangle}{\langle E\rangle^2}=\frac{1+\frac{1}{k_B^2T^2}(\langle V\Lambda\rangle-\langle \Lambda\rangle\langle V\rangle)}{\left(1+\frac{1}{k_BT}\langle \Lambda\rangle\right)^2}. \tag{14}$$

This quantity may be greater or less than unity, depending on the nature of the potential (e.g., whether hard or soft) and the temperature.

To make this more concrete, consider the example of a bound, anharmonic oscillation in a potential whose Taylor expansion at small amplitudes begins

$$\widetilde{V}(x)=\frac{1}{2}x^2-\frac{\epsilon}{4}x^4+R\{\epsilon,x\}, \tag{15}$$

where $\epsilon>0$. This potential is harmonic at small amplitudes and softens initially as a quartic potential. The remainder $R\{\epsilon,x\}$ is understood to vanish relative to the exhibited terms as either ϵ or x goes to zero; however, consistent with the physical meaning of $V(x)$ as a bound potential, $R\{\epsilon,x\}$ is understood to dominate positively for any positive ϵ when x is sufficiently large. We concentrate on the small-ϵ, small-T regime, where, for the specific calculations we perform, it is sufficient to expand quantities to leading order in ϵ, such that

$$\langle \widetilde{E}\rangle\approx k_BT+\frac{\epsilon}{4}\langle x^4\rangle, \tag{16}$$

$$\frac{\langle \Delta\widetilde{E}^2\rangle}{\langle \widetilde{E}\rangle^2}\approx\left(1+\frac{\epsilon}{4k_B}\frac{\partial\langle x^4\rangle}{\partial T}\right)\left(1+\frac{\epsilon}{4k_B}\frac{\langle x^4\rangle}{T}\right)^{-2}. \tag{17}$$

Expanding the partition function in orders of the anharmonicity parameter ϵ, we may compute $\langle x^4\rangle$ approximately as

$$\langle x^4\rangle\approx\langle x^4\rangle_0+\frac{\epsilon}{4k_BT}[\langle x^8\rangle_0-\langle x^4\rangle_0^2], \tag{18}$$

$$\approx 3(k_BT)^2+24\epsilon(k_BT)^3, \tag{19}$$

in which the zero subscript indicates the thermal expectation value in the absence of anharmonicity. From this one may show that the normalized energy variance is greater than unity in the soft anharmonic case,

$$\frac{\langle \Delta\widetilde{E}^2\rangle}{\langle \widetilde{E}\rangle^2}\approx 1+\frac{87}{16}\epsilon^2k_B^2T^2>1. \tag{20}$$

This indicates that relative to harmonic oscillators, the energy fluctuations of soft anharmonic oscillators are marked by an increased preponderance of high-energy fluctuations.

We can elaborate on this characterization by considering an example for which the entire energy distribution can be determined and not just its low moments.

The partition function of a simple, monostable oscillator such as we considered above may be written

$$Q=\int_0^\infty e^{-\beta E}d\Gamma(E), \tag{21}$$

in which $\Gamma(E)$ is the phase space volume as discussed in the Introduction. The probability density for finding the energy E in a particular observation at thermal equilibrium is given by

$$p(E)=\frac{e^{-\beta E}}{Q}\frac{d\Gamma(E)}{dE}. \tag{22}$$

A harmonic oscillator is characterized by a $\Gamma(E)\propto E$, while a soft (hard) oscillator is characterized by a $\Gamma(E)$ that increases more rapidly (slowly) than a simple linear dependence on E [14]. As a specific example, consider the piecewise linear $\Gamma(E)$

$$\Gamma(E)=\gamma[E+\epsilon(E-E_c)\theta(E-E_c)], \tag{23}$$

in which $\theta(u)$ is the unit step function, $\gamma\times 1$ expresses the rate at which phase space volume increases with respect to energy at *low* amplitudes, and $\gamma(1+\epsilon)$ expresses the corresponding rate above the energy E_c. Thus, the *onset* of the soft anharmonicity is characterized by the energy scale E_c, and the *strength* of the anharmonicity is characterized by $\epsilon \in (0,\infty)$ for soft anharmonicity and $\epsilon \in [-1,0)$ for hard anharmonicity.

The partition function and mean energy are given by

$$Q = \frac{\gamma}{\beta}[1+\epsilon e^{-\beta E_c}], \tag{24}$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta}\ln Q = \beta^{-1} + \frac{\epsilon e^{-\beta E_c}}{1+\epsilon e^{-\beta E_c}} E_c . \tag{25}$$

The probability density is given by

$$p(E) = \frac{\beta[1+\epsilon\theta(E-E_c)]e^{-\beta E}}{1+\epsilon e^{-\beta E_c}}. \tag{26}$$

The probability density for a harmonic oscillator ($\epsilon = 0$) is simply the normalized exponential $p_0(E) = \beta e^{-\beta E}$. The probability density $\tilde{p}(E)$ for the soft anharmonic oscillator, on the other hand, is piecewise exponential with the property that $\tilde{p}(E) < p_0(E)$ below E_c and $\tilde{p}(E) > p_0(E)$ above E_c.

It is worth noting, perhaps, that although soft anharmonicity is responsible for an increase in the mean energy $\langle E \rangle$ and a spreading of the energy distribution to higher energies consistent with the notion of a ‘‘hot’’ oscillator, the energy distribution of a soft oscillator differs from that of a harmonic oscillator *qualitatively* as well as *quantitatively*. To illustrate these qualitative differences, consider the artifice of a comparable harmonic oscillator *overheated* to a temperature $T^* > T$ chosen such that the harmonic and anharmonic oscillators have the same mean energies. The probability density $p_0^*(E)$ for the energy in this overheated harmonic oscillator is a normalized exponential, just like $p_0(E)$, but decreases more slowly with increasing energy.

At low energies $p_0(E) > p_0^*(E), \tilde{p}(E)$, with the relationship between $p_0^*(E)$ and $\tilde{p}(E)$ being determined by the temperature; e.g., at higher temperatures $p_0^*(E) > \tilde{p}(E)$, such that the soft anharmonic oscillator experiences fewer low-energy fluctuations than even the overheated harmonic oscillator. At high energies $p_0^*(E) > \tilde{p}(E) > p_0(E)$, reflecting the fact that the exponential high-energy tails of the probability densities for both the harmonic and soft anharmonic oscillators are controlled by the ambient temperature T and thus fall off more rapidly with increasing temperature. The typical circumstance at intermediate temperatures is characterized by $\tilde{p}(E) > p_0(E), p_0^*(E)$. In terms of the specific phase space measure $\Gamma(E)$ employed in our example, the strength of the anharmonicity as measured by ϵ indicates *how much* energy redistribution occurs, while the energy scale E_c indicates *where* the redistributed energy *goes*.

Thus, although the notion of overheating can account for (1) an anomalous increase in the mean energy, (2) a relative decrease in the probability of low-energy fluctuations, and (3) a relative increase in the probability of high-energy fluctuations, the actual reshaping of the energy distribution due to soft anharmonicity differs in significant respects; namely, a soft oscillator experiences *fewer* high-energy fluctuations, *more* intermediate-energy fluctuations, and may experience *more or fewer* low-energy fluctuations than does a comparable harmonic oscillator having the same mean energy.

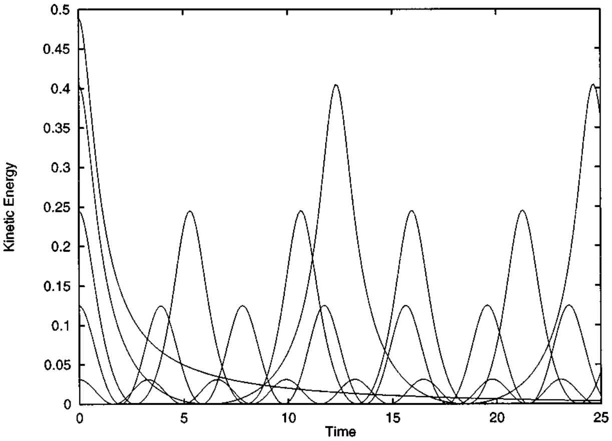

FIG. 1. Kinetic energy of free oscillations in the potential (27) for initial conditions $x(0)=0$, $\dot{x}(0)=0.25,0.5,0.7,0.9,0.99$, in order of increasing total energy. Elapsed time for all traces is approximately four harmonic oscillator periods.

III. DUTY CYCLE AND DISSIPATION

The duty cycle of an oscillation is the ratio of the fractions of a cycle that the oscillator spends in two essentially exclusive states; for example, a square wave may be ‘‘on’’ for one third of a cycle and ‘‘off’’ for two thirds, for a duty cycle of 1:2. For our purposes, it is useful to consider as exclusive states the conditions that the energy of an oscillation reside (a) primarily in the kinetic form or (b) primarily in the potential form. For harmonic oscillators, the energy spends equal times in the two forms, for a duty cycle of 1:1. For soft anharmonic oscillators, the period of oscillation is greater than that of the reference harmonic oscillator, and most of this increase is accounted for by a lengthening of the time that the energy spends in the potential form. This leads to a duty cycle of $1:1+\eta$, where η is a measure of the lengthening of the period due to anharmonicity.

For use in concrete examples, we consider the symmetric soft potential

$$V(x) = \frac{1}{2}\,\frac{x^2+\alpha x^4}{1+x^2}. \tag{27}$$

For the immediate example, we set $\alpha = 0$, such that the potential is harmonic with unit frequency at low amplitudes, and saturates to a constant at high amplitudes. The nature of this oscillator’s duty cycle can be shown by comparing the time traces of the kinetic energy for ‘‘kicked’’ initial conditions $x(0)=0$, $\dot{x}(0) \in (0,1)$ (See Fig. 1).

The duty cycle affords a dynamical understanding of the equipartition results obtained earlier. Since the kinetic energy of both harmonic and anharmonic oscillators is a quadratic degree of freedom, the equipartition theorem requires that both harmonic and anharmonic oscillators have the same average kinetic energy. However, since the energy of soft anharmonic oscillators spends relatively more time in the potential form than is the case for harmonic oscillators, the *equality* of the average kinetic energies forces an *inequality* of the average total energies such that the greater average energy is found in the soft anharmonic oscillator.

The duty cycle also allows some conclusions to be drawn regarding dissipation. Using the Langevin approach, for example, one may model the dynamics of an oscillator in contact with a heat bath by the equation of motion

$$\ddot{x} = -\frac{\partial V}{\partial x} - \gamma \dot{x} + f(t), \tag{28}$$

in which γ represents the dissipation and $f(t)$ is a zero-centered stochastic force. This implies that energy drains from the oscillator according to

$$\dot{E} = -2\gamma(E_{\mathrm{kin}}) + \dot{x} f(t), \tag{29}$$

where E_{kin} is the kinetic energy. Note that the oscillator potential $V(x)$ does not appear explicitly in the latter equation, so that the relationship among the displayed quantities is valid for *any* oscillator. Since the kinetic energy is positive definite, the first term on the right-hand side is strictly dissipative; the noise term, on the other hand, may either increase or decrease the total energy depending on the net sign of the fluctuation and the instantaneous velocity. For bound oscillations such as we consider, the kinetic term is ''on'' only half of the time (harmonic potential) or less (soft potential). Moreover, though the fluctuation can be either a source or a sink of energy, the fact that the fluctuation is weighted by the velocity causes this term also to have greater impact during the ''kinetic'' phase of oscillation. Thus, regardless of potential type, the energy drains nonuniformly in time, and primarily during that fraction of the cycle in which the energy resides mainly in the kinetic form. Since soft anharmonicity lengthens the time that an oscillator's energy resides in the potential form, extending the phase of *least* dissipation, we may conclude that softened oscillations decay more slowly than corresponding harmonic oscillations. Since the low amplitude oscillations of a soft oscillator are quite harmonic, we may conclude as well that low-amplitude oscillations of a soft oscillator decay more rapidly than do high amplitude oscillations in the *same* oscillator. This phenomenon is illustrated in Fig. 2. This relative persistence of high-energy fluctuations is quite *unlike* the behavior of a harmonic oscillator, in which oscillations of all amplitudes decay at the same rate.

These observations allow us to conclude that the time trace of the total energy of a soft anharmonic oscillator in thermal equilibrium is, in a sense, *more organized* than that of a comparable harmonic oscillator under the same conditions, despite the fact noted previously that the entropy of such a soft oscillation is greater than that of a comparable harmonic oscillation.

The nature of this organization is illustrated schematically in Fig. 3 using the previously introduced artifice of a comparable harmonic oscillator overheated to a temperature T^*, such that the mean energy of the harmonic oscillator at T^* is equal to the mean energy of the soft oscillator at T.

Since the overheated harmonic oscillator has the same mean energy as the soft oscillator, the areas under the time traces of the total energy in these two oscillators are equal. The first panel of Fig. 3 offers a schematic representation of the energy time trace of the overheated harmonic oscillator. The time trace shown in the second panel of Fig. 3 consists of exactly the same energy excursions heuristically *rearranged* so as to reflect the relative persistence of high-energy fluctuations found to characterize soft oscillations. The essential point of this illustration is that the rearrangement of energy excursions that is required to reflect the relative persistence of high-energy fluctuations *necessarily* results in an increased persistence of low-energy fluctuations as well.

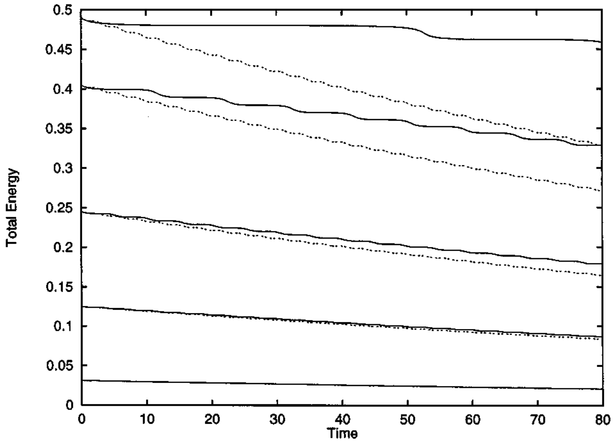

FIG. 2. Total energy of oscillations decaying freely according to Eq. (28) for a small value of the damping constant γ. Solid curves computed using the soft potential (27); dashed curves computed using the corresponding unit-frequency harmonic potential. Initial data for all curves are the same as in Fig. 1. All harmonic oscillations (dashed curves) decay at the same rate regardless of initial energy, while oscillations in the soft potential (solid curves) decay more slowly at higher energies. Elapsed time for all traces is approximately 13 harmonic oscillator periods.

This bunching of energy fluctuations into bursts separated by intervals of relative quiet is one aspect of the anharmonic effect we call ''stochastic localization.'' This bunching phenomenon is distinct from the reshaping of the energy probability density discussed at the end of the last section. Were we to refine the second panel of Fig. 3 to include that redistribution effect, we would have to reduce the height of some of the larger fluctuations and increase the height of some of the smaller fluctuations keeping the average energy across the time record fixed, reflecting the increased probability of midrange fluctuations relative to the extremes.

The quality of persistence that figures centrally in the concept of stochastic localization can be measured quantitatively using time correlation functions. We have made such measurements in the course of Langevin simulations of both harmonic and soft oscillations under identical conditions. In each case the total energy $E(t)$ in the oscillator was monitored as a function of time and used to construct the correlator

$$C(\tau) = \frac{\overline{E(t)E(t+\tau)}}{\overline{E(t)}^2}, \tag{30}$$

in which the overbar indicates the time average. Results typical of such calculations are shown in Fig. 4, which clearly show the markedly increased persistence of energy fluctuations in soft oscillations relative to comparable harmonic oscillations under identical conditions.

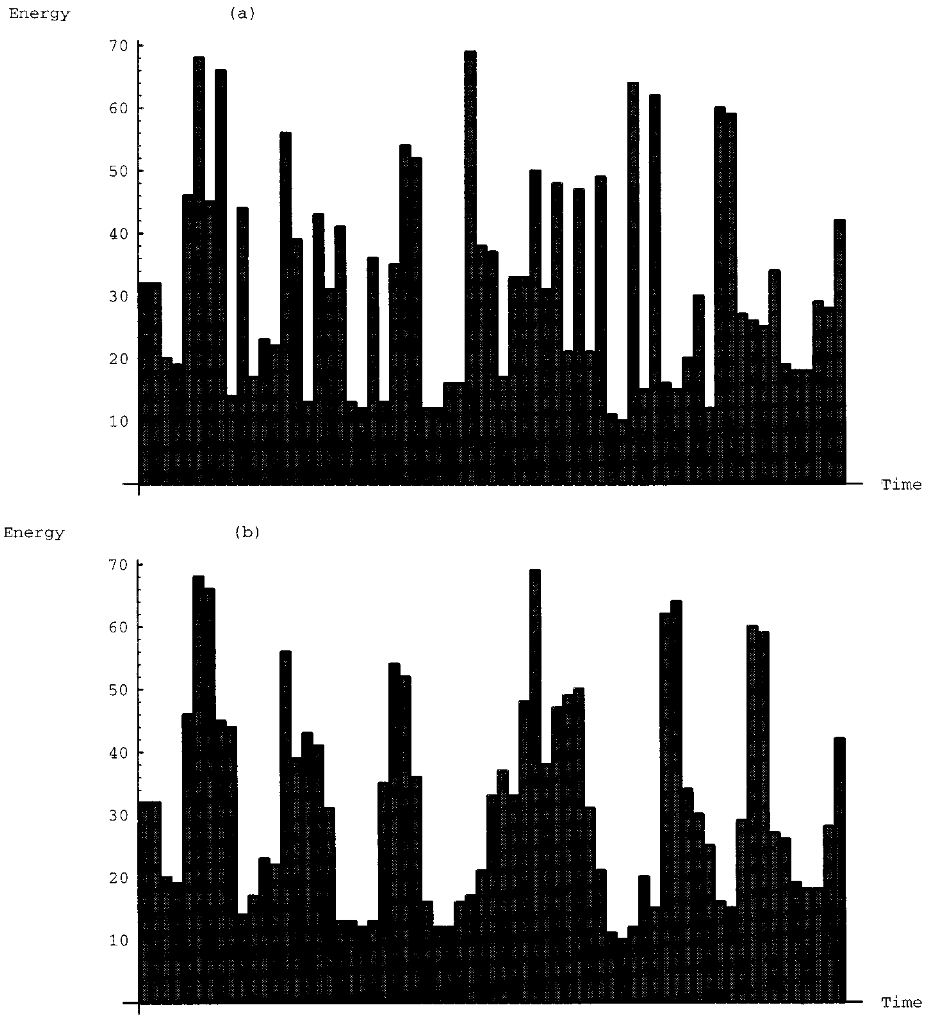

FIG. 3. Left panel: Schematic representation of the energy time trace in a harmonic oscillator *overheated* to T^* as discussed in the text. Right panel: The *same* set of energy excursions heuristically reordered to reflect the persistence of high-energy fluctuations in a soft anharmonic oscillator at T. As a schematic representation only, energy and time scales are arbitrary.

IV. SPATIAL COHERENCE

The previous sections have addressed the dynamics and thermodynamics of single oscillators in contact with a heat bath. In many cases, however, what is of primary interest is not individual oscillators, but collections of coupled oscillators arrayed in specific configurations; e.g., as in vibrational networks and lattices.

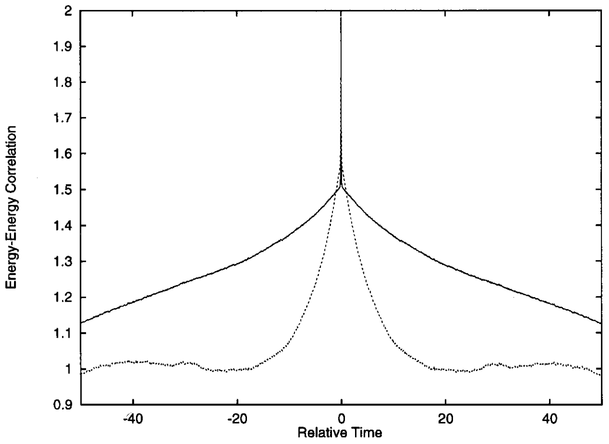

FIG. 4. Time correlation functions computed by Langevin simulation at intermediate temperature. Dotted line: $C(\tau)$, computed for the unit-frequency harmonic oscillator using potential (27) with $\alpha=1.0$. Solid line: $C(\tau)$, computed using the potential (27) with $\alpha=0.2$.

The generalization from single oscillators to collections of *decoupled* oscillators is straightforward, and therefore omitted, except to observe that through the equivalence of time and ensemble averages, increased variability of the energy of a single oscillator in *time* as found in the case of soft oscillations implies a corresponding increase in the variability of the energy density across the ensemble. In the absence of any mechanical coupling between oscillators, we may *not* expect this increased variability to be manifested in spatial localization *per se*. However, the increased variability of the energy must be present in equilibrium averages, implying that although arrays of decoupled soft oscillators cannot display any collective behavior, the energy distribution across arrays of such oscillators must display increased *inhomogeneity* relative to arrays of comparable harmonic oscillators under the same conditions.

This influence of anharmonicity upon the spatial inhomogeneity of the energy density originates from exactly the same physical mechanisms and thermodynamic considerations as discussed in the preceding section, and may be properly considered to be part of the same phenomenon of *stochastic localization*, though in the absence of any coupling between distinct oscillators there can be none of the organization one might otherwise associate with the notion of localization.

Spatial organization of the energy density requires mechanical couplings that allow spatially distinct oscillators to interact directly, and through such interactions establish spatial coherence. The most elementary interaction between neighboring oscillators is the harmonic one giving rise to the propagation of energy through space; e.g.,

$$H\{\dot{x},x\}=\sum_{n}\left[\tfrac{1}{2}\dot{x}_n^2+\tfrac{1}{2}c^2(x_n-x_{n-1})^2+V(x_n)\right]. \qquad (31)$$

In the absence of an on-site potential $V(x)$, this describes acoustic vibrations in which c is the speed of sound in units of the lattice constant. The effect of the nearest-neighbor interaction is to drive neighboring oscillators toward the same phase, and thus to establish coherence on the smallest spatial scale. Dynamically, this local drive toward spatial coherence has the effect of dispersing any localized energy distribution, since such a distribution constitutes a *deviation* from perfect alignment. Thus the main dynamical consequence of building spatial coherence in vibrational systems is *dispersion*.

Thus we have the tendency of soft anharmonicity to increase inhomogeneity, and the tendency of a drive toward spatial coherence to lead to the dispersion of energy. Since these opposing tendencies coexist in the same dynamical system, it is reasonable to expect optimal solutions to achieve some degree of balance between them. Indeed this is the case, and it is this physical need to balance anharmonic focusing against dispersion that gives rise to solitary waves, and their idealization in the concept of the soliton [2–6].

The value of the dispersion parameter c plays a central role in deciding the nature of the ultimate self-consistent state in the absence of thermal flucuations; large values tend to result in broad solitary waves spanning many lattice sites, and small values tend to result in compact localized vibrations that may be ‘‘pinned’’ to particular lattice sites [8]. The illustrations to follow use the value $c=0.5$, which besides being ‘‘intermediate’’ [the allowed range is $c\in(0,1)$], is motivated by consideration of the actual dispersion relations of low-lying librations in certain organic molecular crystals [11].

As in other aspects of our analysis, the energy density proves to be a useful discriminator of overall dynamical behavior. In light of the coupling between oscillators, however, we must expand our notion of a local energy to include the contribution from the nearest-neighbor restoring forces giving rise to dispersion. Thus we define

$$E_n=\tfrac{1}{2}\dot{x}_n^2+\tfrac{1}{4}c^2[(x_{n+1}-x_n)^2+(x_n-x_{n-1})^2]+V(x_n), \qquad (32)$$

$$E=\sum_{n} E_n, \qquad (33)$$

wherein E is now the total energy of the entire system of oscillators. With this definition, all of the energy is captured in local functions E_n that can be meaningfully analyzed and visualized.

For simulating anharmonic lattices at finite temperature, we use $H\{\dot{x},x\}$ with the potential (27). Typical outtakes from thermal equilibrium simulations of both harmonic and anharmonic systems showing the time evolution of the energy density are presented in Fig. 5.

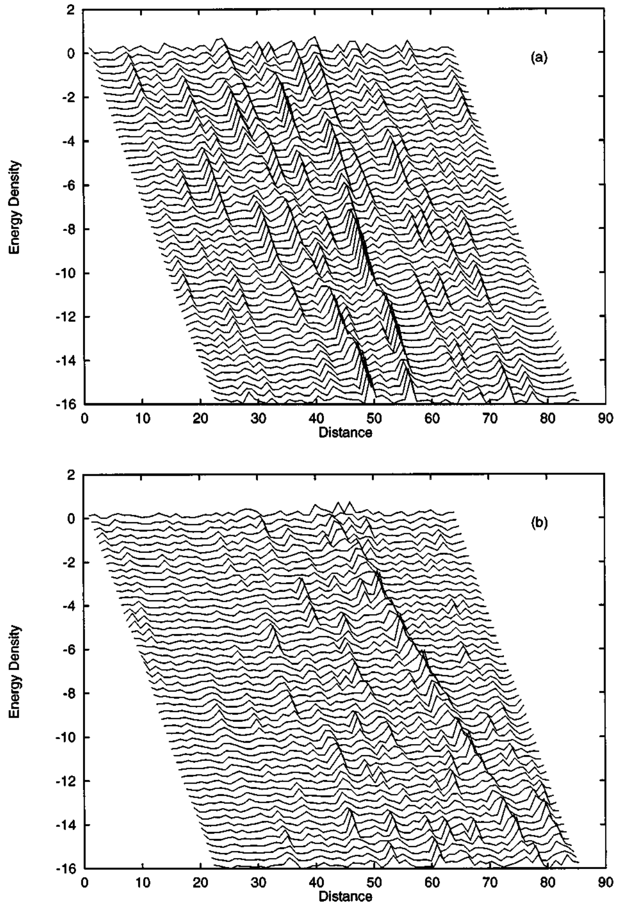

FIG. 5. Time dependence of the energy density in a chain of oscillators evolving according to (31) for $c=0.5$. (a) the harmonic case, $\alpha=1$; (b) the most anharmonic case, $\alpha=0$. Vertical axis represents energy in dimensionless units; horizontal axis represents distance along the chain of 64 sites; time increases from top to bottom and is represented by the incremental offset of successive ‘‘strobes.’’ Overall time elapsed from top to bottom is 8 harmonic periods, with the strobe interval corresponding to approximately two radians.

To obtain these results, we used Langevin terms as in Eq. (28), following Heun’s method [15,16]. Each simulation began with a warm-up phase, during which the system was warmed to the desired temperature from a zero-temperature initial state. Measurement began only after thermal equilibrium diagnostics fell within required tolerances. These particular runs were engineered such that both the harmonic and anharmonic systems had the same temperature; that is, both evolved with the same mean kinetic energy per oscillator equal to $\frac{1}{2}\widetilde{V}(\infty)$, which in our units is 0.25. The rms amplitudes of oscillators in the harmonic (anharmonic) system was less (greater) than the amplitude threshold x_c, which in our units is 1.0. It is important to note that unlike the situation in Figs. 1 and 2, the initial data for the harmonic and anharmonic records shown are *not* the same; since harmonic and anharmonic systems thermalize differently, it is not possible to make such direct comparisons. Instead, care has been taken to assure that the records shown are *characteristic* of

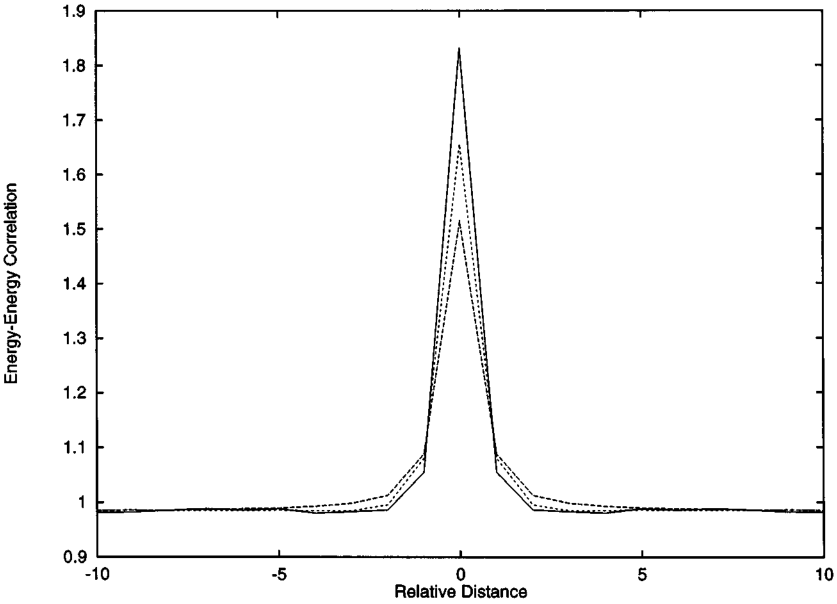

FIG. 6. Energy-energy correlation function C_n as defined in (34). From top to bottom, center: Solid, $\alpha=1.0$, (harmonic). Dotted, $\alpha=0.2$, (anharmonic). Dashed, $\alpha=0.0$, (saturated, maximum anharmonicity for this potential). All results are from Langevin simulations for $c=0.5$ under equivalent equilibrium conditions at intermediate temperatures.

the typical energy landscape of both systems.

The outstanding characteristic of these simulations is that the difference between the harmonic and anharmonic simulations is *not* dramatic; it is difficult with the naked eye and a common vocabulary to characterize the differences in texture. One may say that the energy density in the anharmonic simulation is generally more smooth, and marked by a smaller number of high-energy excursions that are generally more broad in space; i.e., the anharmonic simulation displays more spatial coherence.

A more quantitative characterization can be made using the space correlation function

$$C_n=N\frac{\langle \Sigma_m E_m(t)E_{m+n}(t)\rangle}{\langle \Sigma_m E_m(t)\rangle^2}, \tag{34}$$

in which $\langle \cdots \rangle$ indicates the ensemble average, or, as implemented in the Langevin simulation, a mixed time and ensemble average over large space-time records.

In the absence of *any* spatial coherence, C_n should consist of a central spike above a uniform background; i.e., $C_n \sim a\delta_{n0}+b$. It is deviation from this form, primarily the broadening of the central spike, that indicates the presence of nontrivial spatial coherence. The result of computing the space correlation function for the two scenarios of Fig. 5 are shown in Fig. 6.

Clearly, the presence of nontrivial dispersion ($c\neq 0$) causes a broadening of C_n indicative of nontrivial spatial coherence. Other conditions being equal, it is clear as well that under the conditions simulated in Fig. 5, increasing the ''softness'' of the oscillator potential *increases* the amount of spatial coherence. This is consistent with our qualitative characterization of Fig. 5, but has the benefit of being subject to quantitative measurement.

Those familiar with the study of solitons may find that our simulations and quantitative characterization leave a nagging question unanswered; namely, is the obvious ''ridge'' in Fig. 5(b) a *soliton*? While we do not expect our Langevin model to support true infinite-lived solitons, the energy excursion in question does have some of the characteristic features of a soliton; it shows significant temporal persistence and appears to retain its integrity while meandering somewhat in space. This suggests that the ''ridge'' might be interpreted as a solitonlike object [7,8], arising from balancing of anharmonic and dispersive forces. In a blind comparison, however, one might be inclined to characterize the strictly harmonic simulation illustrated in Fig. 5(a) as being more ''solitonlike,'' since the high-energy excursions in that space-time record are in some respects more discrete and more ''ballistic'' in their propagation, traits commonly attributed to solitons; that ballistic appearance, however, is due to the weak dispersion characteristic of Klein-Gordon equations in the parameter range studied and not any anharmonic effect. Since the word ''soliton'' carries with it far greater implications than we have been able to substantiate thus far, we are reluctant to make such an assignment. A more complete analysis of the thermal behavior of soft, low-lying, dispersive librations in certain organic molecular crystals will be presented elsewhere [17].

V. CONCLUSION

In this paper we have addressed the phenomenon we call ''stochastic localization,'' within which we include a number of characteristics exhibited by soft anharmonic oscillators in thermal equilbrium. Principal among these characteristics are a tendency for soft oscillators to spend more time at higher energies than comparable harmonic oscillators, and for high-energy fluctuations in soft oscillators to persist longer than lower-energy fluctuations, leading to a tendency for energy fluctuations to be organized into ''bursts'' separated by intervals of relative quiet. These characteristics of stochastic localization can be traced to the entropic drive of a system in thermal equilibrium to sample the ''extra'' phase space rendered accessible by the softening of the vibrational potential, and to the lengthening of the duty cycle of softened vibrations that decreases the effectiveness of dissipation at higher energies.

These characteristics of soft oscillators in thermal equilibrium are distinct from the spatial localization characteristic of solitons. In general terms, solitonlike order follows from a minimization of the mechanical energy that brings dispersion and anharmonic focusing into balance. Stochastic localization, on the other hand, depends on the promoting effects of the entropy. In thermal equilibrium, the minimization of the free energy $E-TS$ has the effect of balancing solitonlike order *against* stochastic localization.

Thermal equilibrium in vibrational systems is inhospitable to solitonlike excitations in the sense that it is typically difficult to resolve well-defined, long-lived vibrational excitations. The leading causes of this difficulty are that (1) the ''substance'' of which any such excitation is made is thermal energy that is not conserved except in a statistical sense, being subject to loss through dissipation and being regenerated only stochastically, (2) solitons are low-entropy states that exact a significant free-energy cost at elevated temperatures, and (3) in order to achieve mean energies sufficiently high to allow a significant penetration of the anharmonic regime, the temperature must be significant as well, such that whatever thermally generated solitons *may* appear are vulnerable to (1) and (2). Soft anharmonic vibrations in thermal equilibrium thusly execute a Sisyphean dance, perpetually driving thermal fluctuations toward a solitonlike order, only to see that growing order continuously degraded by never-ending waves of randomizing fluctuations.

Stochastic localization may be thought of as the constellation of dynamic and thermodynamic correlations that depend on the existence of soft anharmonicity, but do *not* depend on existence of spatial coherence. Stochastic localization thus describes the properties of the background against which solitons must be resolved in any practical circumstance.

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