One-dimensional arrays of oscillators: Energy localization in thermal equilibrium

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All systems in thermal equilibrium exhibit a spatially variable energy landscape due to thermal fluctuations. Thus at any instant there is naturally a thermodynamically driven localization of energy in parts of the system relative to other parts of the system. The specific characteristics of the spatial landscape such as, for example, the energy variance, depend on the thermodynamic properties of the system and vary from one system to another. The temporal persistence of a given energy landscape, that is, the way in which energy fluctuations (high or low) decay toward the thermal mean, depends on the dynamical features of the system. We discuss the spatial and temporal characteristics of spontaneous energy localization in 1D anharmonic chains in thermal equilibrium. © *1999 American Institute of Physics.* [S0021-9606(99)51628-0]

I. INTRODUCTION

The pioneering work of Fermi, Pasta, and Ulam[1] demonstrated that a periodic lattice of coupled nonlinear oscillators is not ergodic, and that energy in such a lattice may never be distributed uniformly. A great deal of work has followed that classic paper trying to understand how energy is distributed in discrete nonlinear systems.[2–7] Specifically, the possibility of spontaneous energy localization in perfect anharmonic lattices has been a subject of intense interest.[8–13] The existence of solitons and more generally of breathers and other energy-focusing mechanisms, and the stationarity or periodic recurrence or even slow relaxation of such spatially localized excitations, are viewed as nonlinear phenomena with important consequences in many physical systems.[10,14,15]

The interest in the distribution and motion of energy in perfect arrays arises in part because localized energy in these systems may be *mobile*, in contrast with systems where energy localization occurs through disorder. The interest also arises because such arrays may themselves serve as models for a heat bath for other systems connected to them.[16] Albeit in different contexts, ''perfect'' arrays serving as energy storage and transfer assemblies for chemical or photochemical processes are not uncommon.[17,18]

The study of anharmonic chains and of higher-dimensional discrete arrays has been less than systematic, certainly an inevitable consequence of the breadth and mathematical difficulty of the subject. Some studies (including the work of Fermi, Pasta, and Ulam) deal with microcanonical arrays. Here one observes the way in which a given constant amount of energy distributes itself among the elements of the array. The notion of ''temperature'' usually does not enter in these discussions, although such an association could be made if the energy is randomly distributed. Other studies of anharmonic chains (far more limited in number) deal with systems subject to external noise and other external forces. The questions of interest here involve the ways in which noise can enhance (as in noise-enhanced signal propagation)[15] or even totally modify (as in noise-induced phase transitions)[19] the properties of the nonlinear array. Even more limited has been the study of systems that are in thermal contact with one or more external heat baths maintained at a constant temperature.[10,12] Here the questions usually revolve around the robustness against thermal fluctuations of stationary or quasistationary solutions of the microcanonical problem. In both microcanonical and canonical systems, some work concentrates on stationary states or long-time behavior or equilibrium properties of the array, while other work deals with transport properties or with the approach to equilibrium. Furthermore, there is variation in the portion of the potential where the nonlinearity resides. Thus, in some cases the elements of the array are themselves nonlinear while in others it is the coupling between elements that is nonlinear (and, on occasion, both are nonlinear).

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Within this broad setting, our interest in this paper focuses on one-dimensional arrays of classical oscillators in *thermal equilibrium*.[12] An understanding of thermal equilibrium properties and the effects of nonlinearities on these properties is a prerequisite to the perhaps more interesting analysis of the nonequilibrium behavior of anharmonic lattices in the presence of thermal fluctuations and the approach to equilibrium in such systems. In particular, here we deal with the case of ''diagonal anharmonicity,'' that is, the nonlinearity in our model is inherent within each oscillator in the array (representing, for example, intramolecular interactions), while the connections between oscillators (representing, for example, intermolecular interactions) are ordinary linear springs. The anharmonicity may be soft or hard. We explore the conditions that lead to spontaneous energy localization in one or a few of the oscillators in the array, and the time it takes for a given energy landscape to change to a different landscape. One could undertake a parallel study in systems with anharmonic interactions between oscillators (''off-diagonal'' anharmonicity). We address such systems in subsequent work.[20]

The energy landscape is determined by the local potential of each oscillator, and by the channels of energy exchange in and out of each of the oscillators. The couplings between oscillators provide one such exchange channel, and the coupling of the array with the heat bath provides the other. We shall see that different arrays (soft, hard) behave very differently in response to these channels. We broadly anticipate our conclusions by revealing that (i) persistent energy localization occurs in arrays of weakly coupled soft oscillators even when strongly coupled to a heat bath (while such localization is absent in the hard chain); (ii) persistent localization occurs in strongly coupled hard arrays provided they are weakly coupled to a heat bath (while such localization is absent in the soft chain); (iii) quasidispersionless mobility of localized energy requires off-diagonal anharmonicity.

These remarks point to the fact that our analysis of anharmonic chains in thermal equilibrium could start from two ''opposite'' viewpoints. On the one hand, we might start by analyzing uncoupled oscillators in thermal equilibrium and then proceed to investigate what happens if we couple these oscillators to one another. This approach focuses on the entropic localization mechanism[12] and the way in which the coupling between the oscillators eventually degrades it. On the other hand, we might start with a coupled isolated chain, focus on energetic localization mechanisms in such a chain,[7] and then proceed to investigate the ways in which thermal fluctuations and dissipation affect such local structures. Since we are explicitly interested in localization in the presence of thermal fluctuations, and since entropic effects have received far less attention than energetic ones, we choose to follow the former approach.

No matter the sequence of our queries, since here our interest lies mainly in understanding energy localization in a nonlinear discrete array in *thermal equilibrium* and the way in which thermal effects depend on system parameters, we pose our questions as follows:

(a) How is the energy distributed in an equilibrium nonlinear chain at any given instant of time, and how does this distribution depend on the anharmonicity? In other words, can one talk about *spontaneous energy localization* in thermal equilibrium, and, if so, what are the mechanisms that lead to it?

(b) How do local energy fluctuations in such an equilibrium array relax in a given oscillator? Are there circumstances in the equilibrium system wherein a given oscillator remains at a high level of excitation for a long time?

(c) Can local high-energy fluctuations move in some nondispersive fashion along the array? In other words, can an array in thermal equilibrium transmit long-lived high-energy fluctuations (if indeed they exist) from one region of the array to another without too much energy loss to dispersion?

The answers to these questions have not been found analytically, and are for that reason most clearly presented in comparative fashion. Starting with an ensemble of uncoupled oscillators at thermal equilibrium, one knows exactly the behavior of a *single harmonic oscillator* and can say a great deal about the behavior of a *single anharmonic oscillator* from general thermodynamic considerations. Thus, for instance, the mean energy of a single harmonic oscillator in thermal equilibrium at temperature T is $E=k_BT$ ($k_B=$ Boltzmann's constant). This energy is on average divided equally between kinetic and potential (a partition that enters importantly in questions concerning landscape persistence). A simple virial analysis immediately shows that a soft anharmonic oscillator in thermal equilibrium has energy *greater* than k_BT while a hard anharmonic oscillator has energy *smaller* than k_BT. Both share the property of the harmonic oscillator that the average kinetic energy is $k_BT/2$, but their average potential energies differ. One also knows exactly the energy fluctuations in a harmonic oscillator: the energy variance σ^2 is equal to $k_B^2T^2$, and the ratio of σ to E is therefore independent of temperature. The energy fluctuations are easily determined to be greater in a soft oscillator and smaller in a hard oscillator. From these facts one can arrive at rather definitive qualitative conclusions regarding the distribution and persistence of energy in ensembles of single oscillators and the effects of the anharmonicities on these features.[12]

The situation becomes more complicated when such oscillators are connected to one another. Not only can the oscillators now exchange energy with the heat bath, but there are also coupling channels whereby oscillators can exchange energy with one another. The interplay of these various energy exchange channels and the effects of anharmonicity on this interplay are some of the issues to be addressed in this work.

This paper is organized as follows. In Sec. II we introduce our model and notation. We fix some of the parameter values and briefly discuss the numerical methods used in our simulations. Here we introduce the hard, harmonic, and soft local potentials to be compared. In Sec. III we review and illustrate previous results for uncoupled oscillators in thermal equilibrium so as to establish the background for the coupled systems. The phenomenon of ''entropic localization,'' whereby ensembles of single thermalized soft oscillators localize and retain energy more effectively than harmonic or

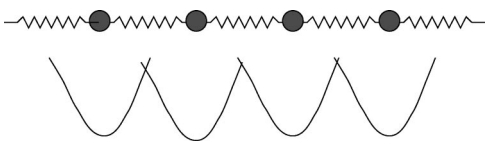

FIG. 1. Illustration of the 1D chain considered in this work. Each oscillator in the chain experiences an on-site potential and is harmonically bound to its nearest-neighbors.

hard oscillators, is recalled. In Sec. IV we explore the consequences of coupling our oscillators. In Sec. V we briefly address the mobility of energy fluctuations in our systems. Finally, Sec. VI summarizes our findings and anticipates further studies.

II. THE MODEL AND NUMERICAL METHODS

Our system is a one-dimensional chain of N identical unit-mass oscillators labeled $i=1,2,\ldots,N$ with harmonic nearest-neighbor interactions and on-site potentials $V(x_i)$ that may be hard, harmonic, or soft. Here x_i is the displacement of oscillator i from its equilibrium position, with associated momentum p_i. We assume periodic boundary conditions. The Hamiltonian of the system is

$$H=\sum_{i=1}^{N}\left(\frac{p_i^2}{2m}+\frac{1}{2}k(x_i-x_{i+1})^2+V(x_i)\right), \tag{1}$$

where k is the intermolecular force constant. Figure 1 is a schematic of the model.

To represent the thermalization of our chain the model is further expanded to include the Langevin prescription for coupling a system to a heat bath at temperature T via fluctuating and dissipative terms. The stochastic equations of motion for the chain are then given by the Langevin equations

$$\ddot{x}_i=-k(2x_i-x_{i+1}-x_{i-1})-\gamma\dot{x}_i-\frac{dV(x_i)}{dx_i}+\eta_i(t), \tag{2}$$

where a dot represents a derivative with respect to time. The $\eta_i(t)$ are mutually uncorrelated zero-centered Gaussian δ-correlated fluctuations that satisfy the fluctuation–dissipation relation:

$$\langle\eta_i(t)\rangle=0,\quad \langle\eta_i(t)\,\eta_j(t')\rangle=2\gamma k_BT\delta_{ij}\delta(t-t'). \tag{3}$$

Since we are interested in assessing the effects of anharmonicities on energy localization, we start by specifying the on-site potentials to be used in our analysis:

$$\begin{aligned}V_0(x)&=\tfrac{1}{2}x^2\\ V_s(x)&=|x|-\ln(1+|x|)\\ V_h(x)&=\tfrac{1}{2}x^2+\tfrac{1}{2}x^4.\end{aligned} \tag{4}$$

The subscript 0 stands for the harmonic case, s for the soft and h for the hard. At small amplitudes the three potentials are harmonic with a unit natural frequency. Figure 2 shows the potentials and associated forces.

We end this section with a brief description of the numerical methods used in our simulations throughout this paper. The numerical integration of the stochastic equations for all our simulations is performed using the second-order Heun's method (which is equivalent to a second-order Runge–Kutta integration).[21,22] We use a time step $\Delta t=0.005$. The number of oscillators in our simulations ranges between 100 and 1000 and is indicated in each figure as appropriate. In each simulation the system is initially allowed to relax for enough iterations to insure thermal equilibrium, after which we take our ''measurements.'' In all of our subsequent energy landscape representations we have used the same sequence of random numbers to generate the thermal fluctuations.

III. PROPERTIES OF UNCOUPLED OSCILLATORS: ENTROPIC LOCALIZATION

In order to understand the equilibrium properties of a chain of oscillators it is useful to first review the behavior of single (uncoupled) oscillators described by the potentials in Eq. (4).

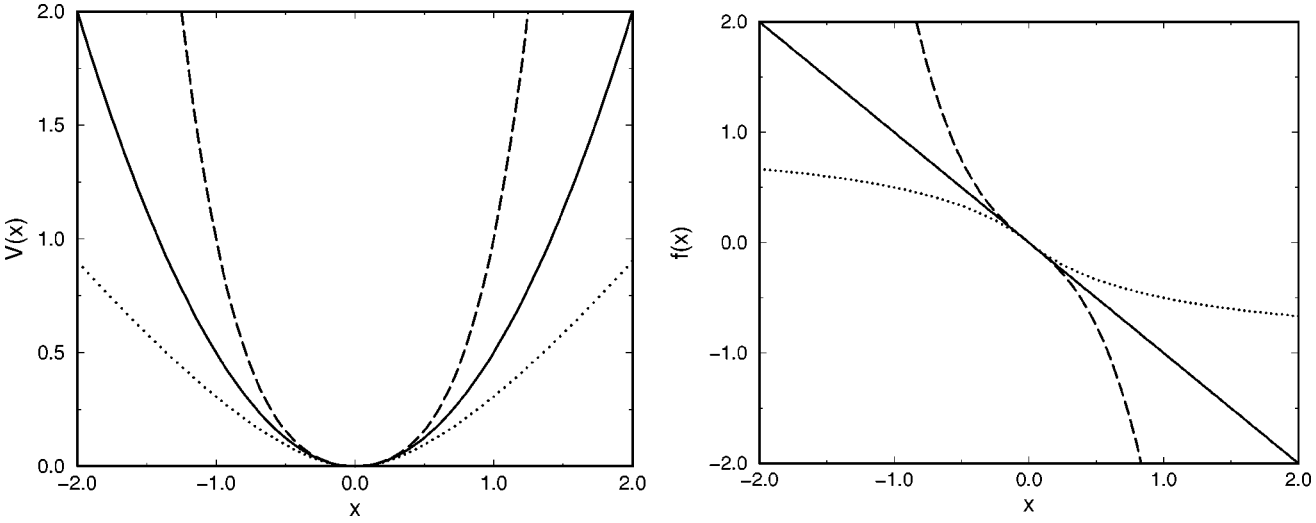

FIG. 2. Left panel: the on-site potentials defined in Eq. (4). Right panel: the associated forces. Solid lines: harmonic potential, $V_0(x)$. Dotted lines: soft anharmonic potential, $V_s(x)$. Dashed lines: hard anharmonic potential, $V_h(x)$.

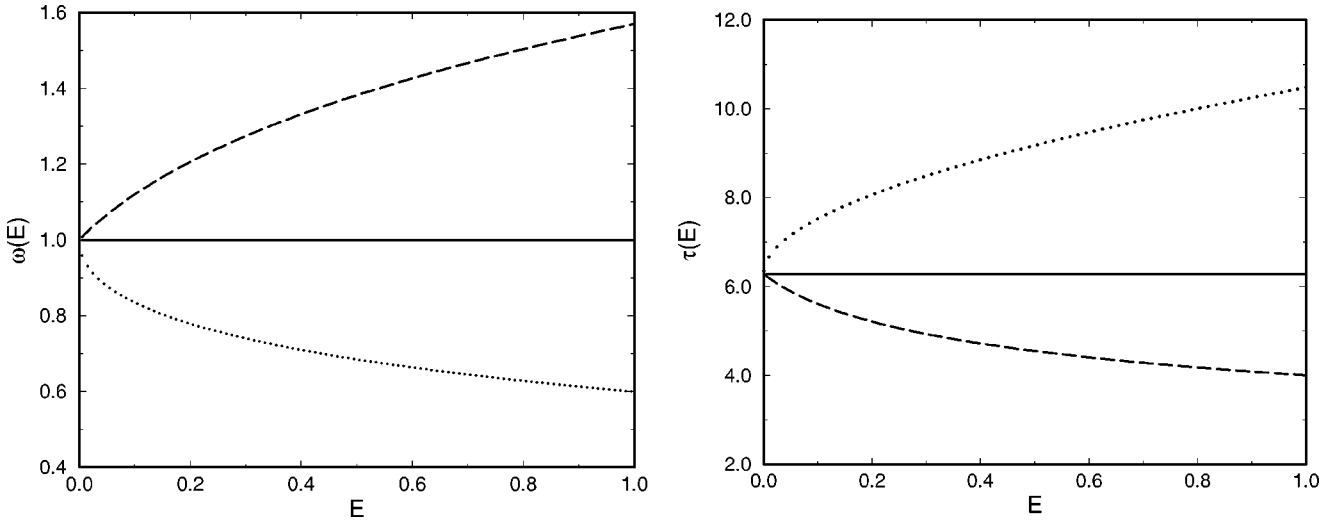

FIG. 3. Oscillation characteristics of single isolated oscillators. Left panel: frequency as a function of the oscillator energy for the potentials in Eq. (4). Right panel: oscillation periods for single oscillators. Solid lines: harmonic oscillator. Dotted lines: soft anharmonic oscillator. Dashed lines: hard anharmonic oscillator.

Suppose first that our oscillator is *isolated*. The salient features of anharmonic oscillators are that (i) they oscillate with different frequencies at different energies, and (ii) the density of states changes with changing energy. In particular, hard potentials are associated with increasing frequencies of oscillation and sparser densities of states with increasing amplitude (energy); on the other hand, in soft potentials the oscillation frequency decreases and the density of states increases with increasing amplitude.

To get a sense, useful for later analysis, of these and associated oscillator characteristics, we present several figures that show various distinct features of our three types of oscillators. Figure 3 shows the frequencies $\omega(E)$ of *isolated single* oscillators as a function of increasing energy E (which in turn corresponds to increasing amplitude). This frequency is evaluated directly by solving the equation of motion $dx/dt = \pm\sqrt{2[E-V(x)]}$ over one period of oscillation at energy E:

$$\omega(E) = \pi\left(\int_{-x_{\max}}^{x_{\max}} \frac{dx}{\sqrt{2[E-V(x)]}}\right)^{-1}. \tag{5}$$

The amplitude of oscillation $x_{\max}$ at a given energy can be found by solving for the positive root of $V(x)=E$. The harmonic oscillator has a single frequency at unity. The soft and hard oscillators oscillate at unit frequency at low amplitudes (energies) because we have chosen all the oscillators to coincide there, but with increasing amplitude the hard oscillator frequencies increase and those of the soft oscillator decrease. In Fig. 3 we also show the period of oscillations $\tau(E) = 2\pi/\omega(E)$. The period increases with increasing energy for the soft oscillator, remains constant for the harmonic oscillator, and decreases with energy for a hard oscillator. This behavior will figure prominently in our subsequent analysis of energy localization.

Next we consider these same single oscillators, but now each connected to a heat bath at temperature T via Langevin terms. The left panel of Fig. 4 shows the normalized energy distribution $P(E)$ vs E for the three cases. This distribution is given by

$$P(E) = \frac{e^{-E/k_BT}\tau(E)}{\int_0^\infty dE\, e^{-E/k_BT}\tau(E)} \tag{6}$$

(the density of states is proportional to the period of oscillations). The figure supports our introductory comments: firstly, that the average energy of the soft oscillators is greater than that of the harmonic oscillators, whose average energy is in turn greater than that of the hard oscillators; secondly, that the energy fluctuations are smallest in the hard oscillator and largest in the soft oscillator. Thus in equilibrium we find at any instant that there is a greater variability of energy in an ensemble of single soft oscillators than in one of harmonic or hard oscillators. The right panel of Fig. 4 shows the average period of oscillation $\tau(k_BT)$ for a thermalized distribution:

$$\tau(k_BT) \equiv \int_0^\infty dE\ \tau(E)P(E). \tag{7}$$

Consonant with the energy dependence of $\tau(E)$, the average period of the soft oscillator increases with temperature, that of the harmonic oscillator is independent of temperature, and that of the hard oscillator decreases with temperature.

The features just discussed are also visible in the energy landscape rendition shown in Fig. 5. Along the horizontal direction in each panel lies an ensemble of 100 independent thermalized oscillators and the vertical upward progression shows how these oscillators evolve with time in the equilibrium system. Here and in all our energy landscape figures the y axis covers 120 time units, the same units shown on time axes throughout the paper. Each oscillator is connected to a heat bath. The gray scale represents the energy – an oscillator of higher energy is darker in this portrayal.

The first thing to note is that along any horizontal line (i.e., at any given time) the soft landscape is darker and grainier than the harmonic, and the lightest and least grainy is the hard oscillator landscape. This reflects the fact that the

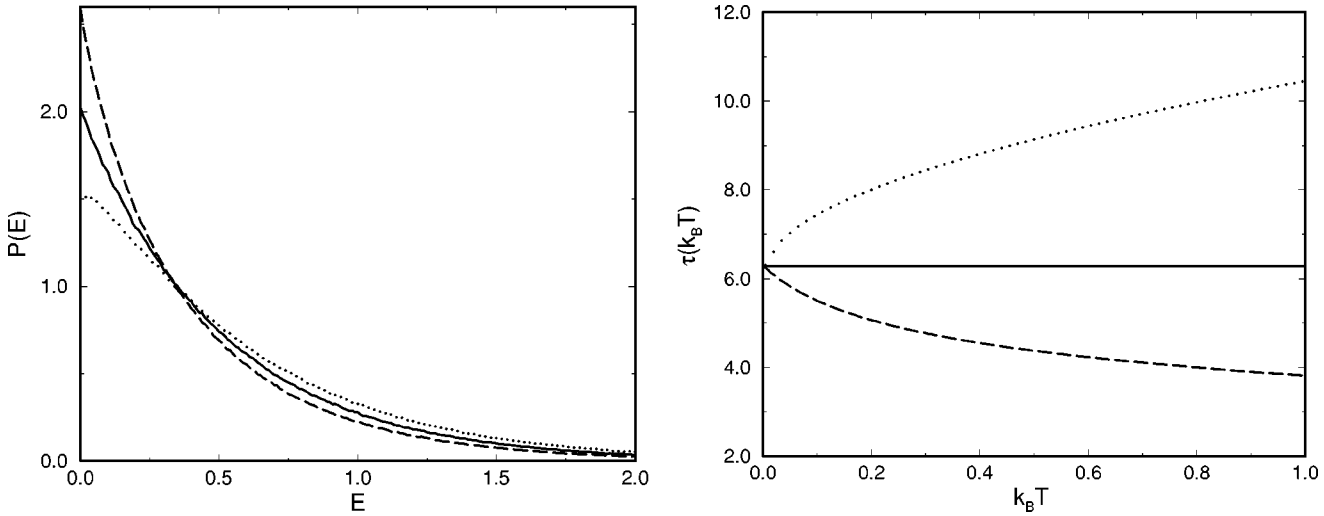

FIG. 4. Left panel: energy distribution in single thermalized oscillators for the three potentials at $k_BT=0.5$. Right panel: average oscillation period for the three oscillators as a function of temperature. Solid lines: harmonic potential, $V_0(x)$. Dotted lines: soft anharmonic potential, $V_s(x)$. Dashed lines: hard anharmonic potential, $V_h(x)$.

soft oscillators have the highest energies and the greatest energy fluctuations. This observation provides a basis to be used in answer to the first question posed in the introduction. In an ensemble of independent oscillators in thermal equilibrium there is of course a greater energy in some oscillators than in others simply because there are energy fluctuations in a system in thermal equilibrium. These fluctuations are greater in soft anharmonic oscillators than in harmonic or hard anharmonic oscillators.

The second noteworthy feature of the landscape illustrates the answer to the second question posed in the introduction, namely, how long it takes in an equilibrium ensemble for the fluctuations to relax and the energy landscape to change. The trend for our independent oscillators is clear: the soft oscillators retain a given energy for a longer time than do the harmonic, which in turn hold on to a given energy longer than do the hard oscillators. This is particularly evident for those oscillators that acquire a high energy through a fluctuation: in the soft oscillator landscape the dark streaks are clearly visible. The reason for this behavior becomes clear if we write the equation of motion for the energy of each oscillator $E=p^2/2+V(x)$. Setting $p=\dot{x}$ and using Eq. (2) one finds that for any type of oscillator

$$\dot{E}=-\gamma p^2+p\,\eta(t). \tag{8}$$

Thus, the energy exchange with the surroundings involves only the *momentum* variable (i.e., the kinetic energy). Consider an oscillator that has acquired a given high-energy fluctuation E, and consider how this energy is distributed between the oscillator displacement and momentum. In a harmonic oscillator the energy during one cycle of oscillation is equally partitioned between kinetic and potential. In a soft oscillator, however, the energy spends relatively more time in potential than in kinetic form (and the opposite is true for the hard oscillator). Thus, during the major portion of the cycle the momentum of a soft oscillator is relatively low (while its displacement is large); the energy in the soft oscillator can therefore not enter from and leave to the thermal

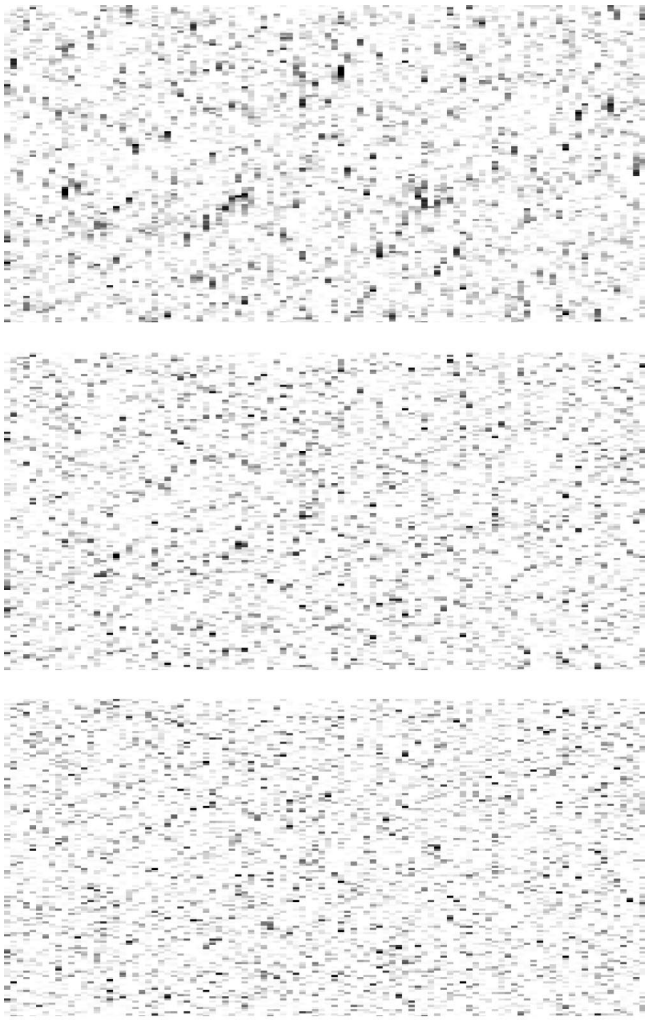

FIG. 5. Energy (in gray scales) for ensembles of 100 thermalized independent oscillators as a function of time. The oscillators are lined up (but not connected) along the x-axis and time advances along the y-axis. The temperature is $k_BT=0.5$ and the dissipation parameter is $\gamma=1$. Top panel: soft oscillators; middle panel: harmonic oscillators; lower panel: hard oscillators.

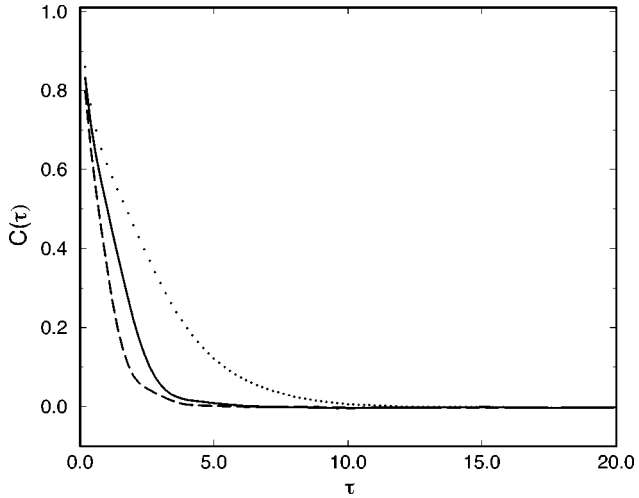

FIG. 6. Energy correlation function vs time for independent oscillators with $k_BT=0.5$ and $\gamma=1$. Note that the energy changes most slowly in the soft potential ensemble. Solid line: harmonic potential. Dotted line: soft anharmonic potential. Dashed line: hard anharmonic potential.

surroundings as easily as in the other oscillators. The energy relaxation process is therefore slower, and a soft anharmonic oscillator retains a high energy it might have gained via a fluctuation for a longer time.[12]

The energy relaxation process visible in Fig. 5 is shown more quantitatively in Fig. 6. Here we have plotted the normalized energy correlation function

$$C(\tau)=\left\langle \frac{\langle E(t)E(t+\tau)\rangle-\langle E(t)\rangle\langle E(t+\tau)\rangle}{\langle E^2(t)\rangle-\langle E(t)\rangle^2}\right\rangle. \tag{9}$$

The inner brackets indicate an average over time t (200 000 iterations) and the outer brackets an average over an ensemble of 1000 oscillators. The correlation function is normalized so that all energies, high and low, contribute ''equally.'' It is thus a measure of the full exchange of energy with the heat bath, both through the dissipative term and also via the fluctuations. We note that the trend in Fig. 6 (slower decay as the oscillators soften) is consistent with the corresponding slowing trend for each temperature in the right panel of Fig. 4. Also note that on average the energy of an oscillator changes on the time scale of half a period of oscillation, i.e., on the time scale it takes the oscillator to move from one side of the potential well to the other.

We have thus summarized and illustrated our earlier findings,[12] namely, that in an array of independent oscillators in thermal equilibrium at a given temperature there are larger energy fluctuations and longer retention of energy the softer the oscillators. This is an entropy-driven localization, arising from the fact that the density of states in soft oscillators increases with increasing energy. It minimizes the free energy because it is entropically favorable for oscillators to populate phase space regions where the density of states is higher, which in an ensemble of soft oscillators leads to a greater spatial variability than in harmonic or hard oscillators. The temporal persistence of this greater variability is a consequence of the fact that coupling to a heat bath occurs only via the kinetic energy. In the soft ensemble the energy is in potential form a greater fraction of time than in kinetic form, which is not the case for the other two ensembles.

We gave this scenario the name stochastic localization in our earlier work,[12] but will refer to it as *entropic localization*, a term that more accurately reflects its physical causes. It is important to stress that entropic localization in soft oscillators is robust in the sense that it becomes *more* pronounced as temperature increases provided the potential continues to soften, and that it is achieved regardless of the initial condition of the system.

The remaining parameters that can be varied at this point are the *dissipation parameter* and the *temperature*. A change in the dissipation parameter does not affect Fig. 4 since this is an equilibrium distribution. In Fig. 5 a higher dissipation parameter would cause a more rapid decay of energy fluctuations (and, correspondingly, a lower dissipation parameter allows an energy fluctuation to survive for a longer time). Thus, although high dissipation does not interfere with the appearance of greater energy fluctuations in the soft oscillators, it works against the temporal retention of excess energy by any one oscillator. The energy correlation function decays more slowly for the soft oscillator for any dissipation, and this decay is more rapid (for all the oscillators) as the dissipation increases. In any case, for a given dissipation parameter the softer potential retains energy for a longer time.

The temperature affects the quantitative outcome of Figs. 4 and 5. In Fig. 4 the distributions broaden with increasing temperature, but the differences between the different oscillators remain and, in particular, the fact that the distribution for the soft oscillator is the broadest continues to be true. In Fig. 5 higher temperatures produce relatively greater graininess in the soft oscillator figure than in the other two. This is clearly observed in the sequence of Fig. 7, which shows the evolution of ensembles of soft oscillators for different temperatures. A temperature increase leads to stronger entropic localization and this effect also appears in the energy correlation functions, as shown in Fig. 8. This behavior is contrasted with that of harmonic and hard anharmonic oscillators, whose energy landscapes and energy correlation functions show essentially no temperature dependence in this range. The energy fluctuations in these latter cases dissipate very quickly. Note that the temperature dependence of the correlation times implicit in Fig. 8 is consistent with the temperature dependence of an average period of oscillation of a soft oscillator as shown in the right panel in Fig. 4: with increasing temperature the correlation time continues to be approximately half a period.

With this background, we are now ready to consider the behavior of *chains* of oscillators, where everything that we have found so far has to be reconsidered in the face of the additional forces now present through the oscillator–oscillator coupling.

IV. COUPLED OSCILLATORS

In this section we explore the consequences of coupling the oscillators discussed in the previous section with harmonic springs. In this exploration we attempt to bring some order to seemingly contradictory reports that the coupled oscillators must be hard in order for such an array to localize

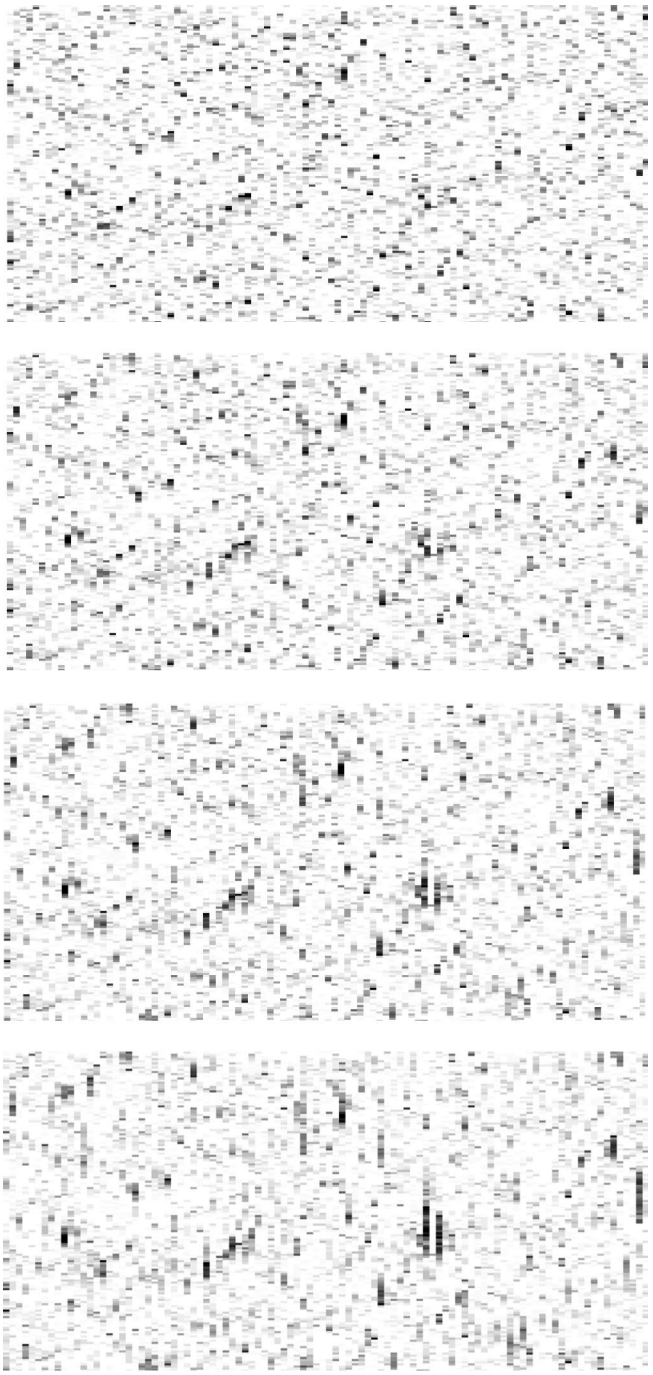

FIG. 7. Energy landscapes for thermalized independent soft oscillators as a function of time for different temperatures. The dissipation parameter is $\gamma=1$. Temperatures from top to bottom: $k_BT=0.1,\ 0.5,\ 1.0$, and 2.0.

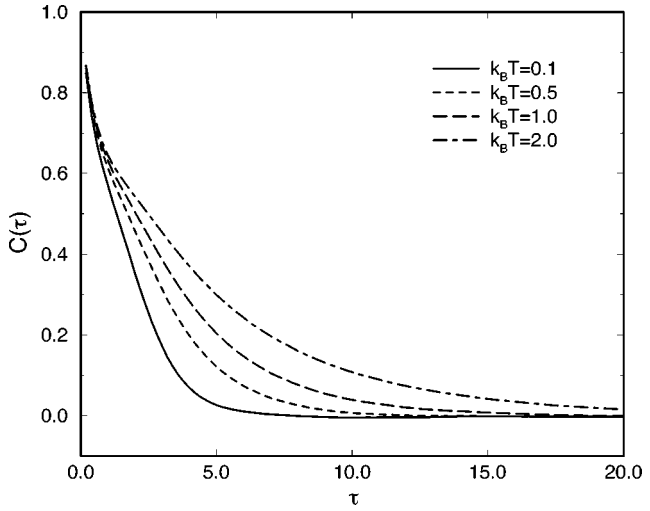

FIG. 8. Energy correlation function vs time for independent soft oscillators with $\gamma=1$ and different temperatures (the same as in Fig. 7).

energy effectively, or that the coupled oscillators must be soft in order to accomplish such localization. To anticipate our results, we will show that both claims are correct, but each in a different parameter regime and for different physical reasons. The variable parameters in this discussion are the temperature k_BT, the dissipation parameter γ, and the coupling strength k.

In order to determine the conditions that may lead to energy localization in a thermalized chain of oscillators it is useful to investigate the ways in which energy may escape from a given oscillator. It is apparent from the Langevin Eq. (2) that there are now two channels of escape. As in the last section, one is the friction term that dissipates the energy to the bath. The other is the coupling term that transfers energy to the nearest-neighbors. The difference between these two mechanisms is that the dissipation is determined entirely by the kinetic energy of the oscillator. Energy transfer along the chain, on the other hand, while still dependent on the kinetic energy, is primarily determined by the extension or contraction of the springs connecting neighboring oscillators, that is, by the potential energy through the relative oscillator displacements. To make these statements more quantitative, it is useful to generalize the concept of a local energy by defining a local function whose sum over sites is the total energy of the chain. To include the contribution from the nearest-neighbor restoring forces one writes

$$E_i \equiv \frac{p_i^2}{2} + V(x_i) + \frac{k}{4}[(x_i - x_{i+1})^2 + (x_i - x_{i-1})^2], \qquad (10)$$

and the total energy of the system is then $E=\Sigma_i E_i$. The rate of change of the local energy is easily found to be

$$\dot{E}_i = -\gamma p_i^2 + p_i \eta_i(t) - \frac{k}{2}(x_i - x_{i+1})(p_i + p_{i+1}) - \frac{k}{2}(x_i - x_{i-1})(p_i + p_{i-1}). \qquad (11)$$

Note that although this expression does not explicitly involve the potential, the rate of local energy loss of course does depend on the potential through the displacements and momenta.

The dynamics of the local energy will thus depend on the interplay of the thermal (fluctuations), dissipative, and intrachain forces. In order to highlight the main comparisons and contrasts, we frequently will juxtapose the behavior of chains for which one or the other of the energy exchange channels is clearly the dominant one, and in each case assess the effects of temperature changes.

The effect of interoscillator coupling on entropic localization is illustrated in Fig. 9. In this figure we show the system of soft oscillators that were uncoupled in Fig. 7 (specifically, the case with $k_BT=0.5$ and $\gamma=1$), but now provid-

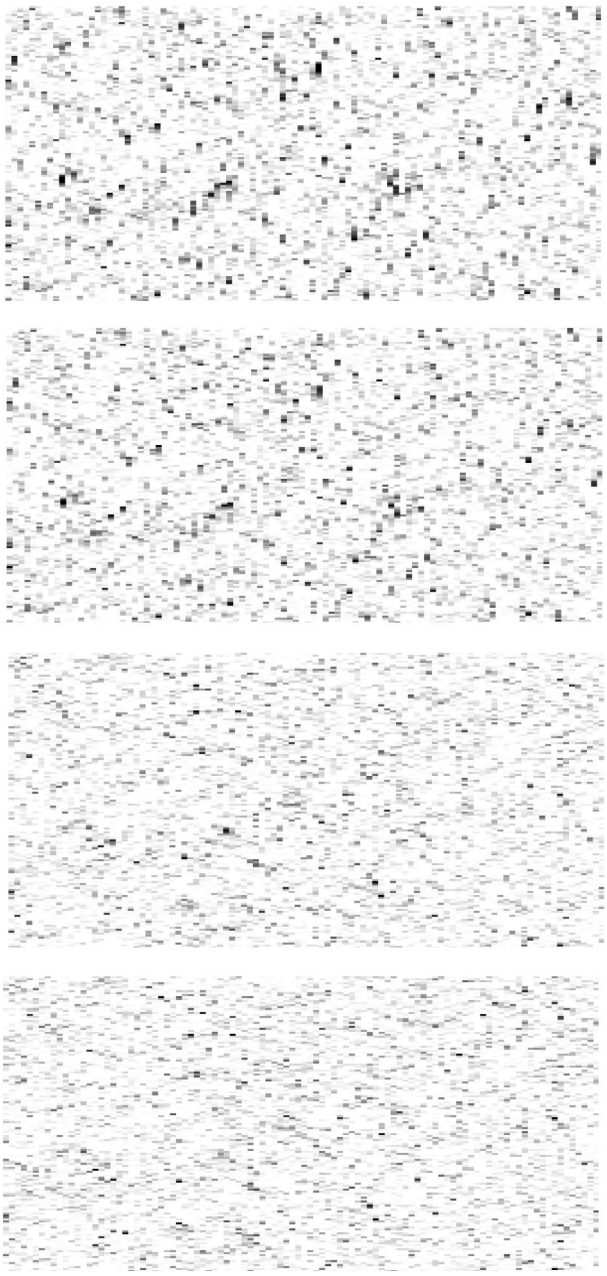

FIG. 9. Energy landscapes for thermalized soft oscillators as a function of time. The dissipation parameter is $\gamma=1$ and the temperature $k_BT=0.5$. From top to bottom the coupling constants are $k=0$, 0.05, 0.5, and 1.0.

ing successively larger values for the coupling constant k. Entropic localization is still apparent for small values of k, but as coupling increases there is clear degradation of entropic localization. This is to be expected since energy exchange is sensitive to large oscillator amplitude differences in soft oscillators.

The associated energy correlation functions

$$C(\tau)=\left\langle \frac{\langle E_i(t)E_i(t+\tau)\rangle-\langle E_i(t)\rangle\langle E_i(t+\tau)\rangle}{\langle E_i^2(t)\rangle-\langle E_i(t)\rangle^2}\right\rangle_i , \quad (12)$$

for the cases in Fig. 9 are shown in Fig. 10. These curves confirm the degradation of entropic localization with increasing k.

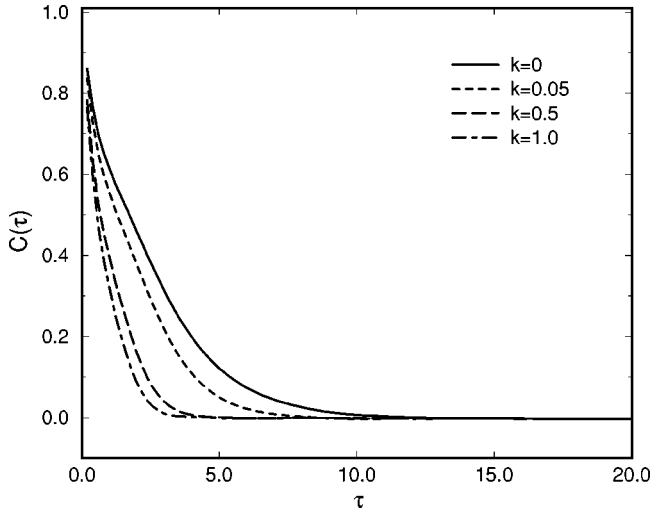

FIG. 10. Local energy correlation function vs time for chains of soft oscillators with $\gamma=1$, $k_BT=0.5$ and different values for the coupling constant (same as in Fig. 9).

We thus turn to chains of coupled oscillators with low dissipation ($\gamma=0.05$) and focus, in particular, on strongly coupled chains (if both k and γ are small we know pretty much what happens from the analysis in the previous section). In Fig. 11 we have drawn the energy landscape for the soft (top panel), harmonic (middle panel), and hard oscillators (lower panel) providing $k_BT=0.5$, $\gamma=0.05$, and $k=1.0$. From this figure it is clearly evident that now the localization of energy at a given site is greater in the hard case than in the harmonic case, and this in turn, is greater than in the soft case. The confirming local energy correlation functions for these cases are plotted in Fig. 12. Clearly, for a given temperature the hard array retains energy at a given location for a longer time than do the other two arrays.

In the low-γ, large-k regime the effective energy exchange channel is sensitive to the oscillator amplitude rather than to its kinetic energy, so we expect entropic localization in the soft array to be degraded since soft oscillators have large amplitudes. Furthermore, as the harmonic coupling increases it eventually overwhelms the local soft potential and the soft chain becomes an essentially harmonic chain at sufficiently large k. On the other hand, hard oscillators exchange little energy via the coupling channel since they do not reach large amplitudes. This, and the fact that dissipation to the bath via kinetic energy (the other energy exchange channel) has been minimized (low γ), leads to persistent energy localization in the hard array. This is an energetic localization mechanism. The frequency mismatch between an energetic hard oscillator and its less energetic neighbors, and the dearth of density of states at high energies, further contribute to this persistence.

The energetic localization mechanism in strongly coupled hard oscillators is robust against temperature increases. Indeed, according to our explanation, the localization should become more pronounced and persistent as temperature increases provided the dissipation is sufficiently weak. In Fig. 13 we have drawn the energy landscapes for a strongly coupled ($k=1.0$) array of hard oscillators, weakly coupled to the bath ($\gamma=0.05$) at different temperatures. The

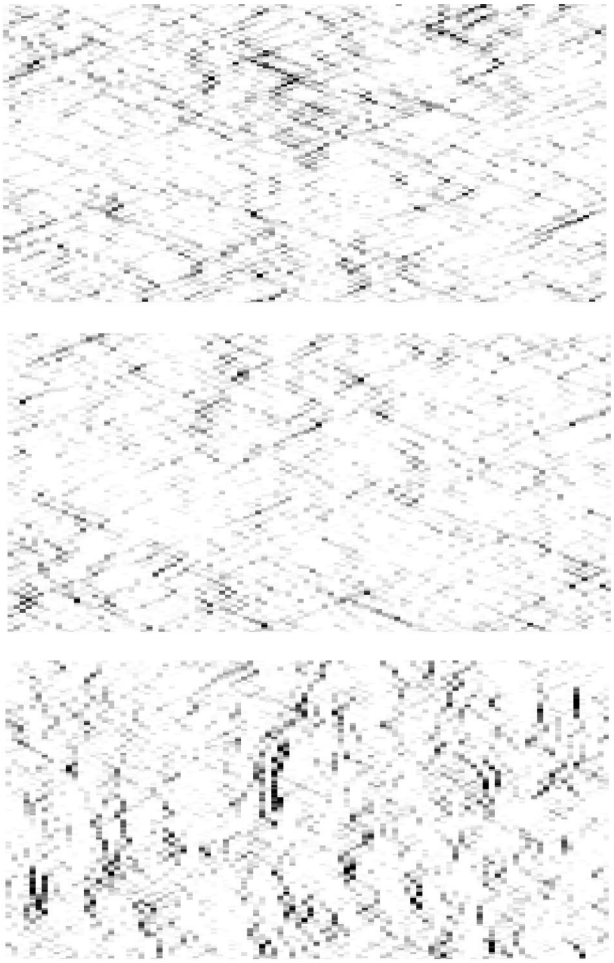

FIG. 11. Energy landscapes for thermalized strongly coupled oscillators as a function of time. The dissipation parameter is $\gamma=0.05$, the temperature $k_BT=0.5$, and the coupling constant $k=1.0$. Top panel: soft oscillators; middle panel: harmonic oscillators; lower panel: hard oscillators.

figure qualitatively confirms these expectations. The corresponding energy correlation functions are plotted in Fig. 14: $C(\tau)$ for the hard chain does decay more slowly with increasing temperature. Thus, localization in this strongly coupled system of hard oscillators becomes more effective with increasing temperature and is not entirely fragile against dissipative forces. On the other hand, the soft and harmonic correlation functions (not shown here) are essentially independent of temperature. Note that the trend in Figs. 12 and 14 is ''opposite'' to that of the uncoupled oscillators in the right hand panel of Fig. 4. In the strongly coupled chain harmonic and soft oscillators in fact lose their energy rather quickly on the time scale of one oscillation period of an isolated oscillator, but the hard oscillators retain energy correlations for longer than a period, indeed for many periods at the highest temperatures shown. With increasing temperature the hard oscillators retain energy more effectively even while the average oscillation period decreases. In fact, the decay of the correlation functions appears to involve two time scales, one of the order of an oscillation period and another much longer one that grows with temperature.

The temporal irregularities (oscillations) visible in Figs. 12 and 14 are reproducibly there at all temperatures; we do not know their source.

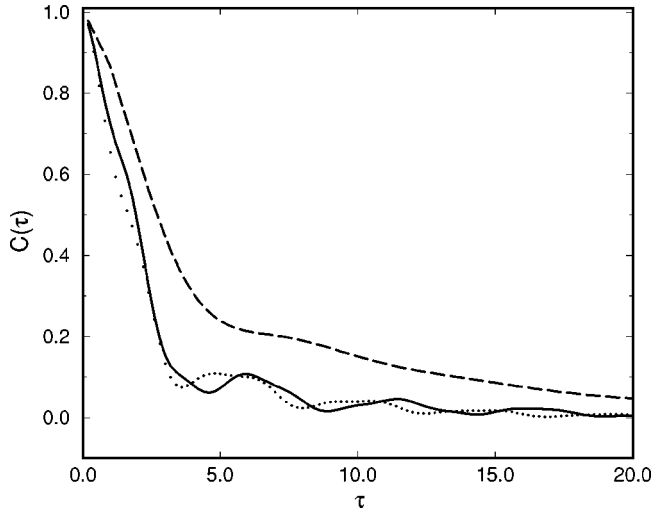

FIG. 12. Energy correlation function vs time for coupled oscillators with $\gamma=0.05$, $k_BT=0.5$, and $k=1.0$. Solid line: harmonic potential. Dotted line: soft anharmonic potential. Dashed line: hard anharmonic potential.

V. MOBILITY OF LOCALIZED ENERGY FLUCTUATIONS

The upper two energy landscapes in Fig. 11 show what might appear as fairly dispersionless energy transport. Narrow high-energy pulses move visibly along the chain before disappearing, while others appear (via thermal fluctuations) to repeat the process elsewhere along the chain. However, this cannot be claimed to represent nonlinear behavior since the middle panel in Fig. 11 in fact represents a completely harmonic system! This serves as a cautionary note about the overinterpretation of such results.

We noted earlier that with increasing k the soft chain eventually becomes essentially harmonic because the intermolecular harmonic interactions overwhelm the local soft potential (the only way to prevent this is by considering soft interoscillator interactions, which we defer to another paper).[20] The upper panel in Fig. 11 exhibits mostly this essentially harmonic behavior—it is quite similar to the middle panel—but not entirely so. The soft oscillator chain clearly shows higher-energy regions than the harmonic (darker patches, a not fully degraded remnant of entropic localization) that move more rapidly (steeper streaks) over longer distances (longer streaks) than in the harmonic chain. Therefore, the soft anharmonicity is clearly still playing some role, albeit a diminishing one with increasing coupling. To provide some quantification, we introduce the dynamical energy correlation function

$$C(j,\tau)=\left\langle \frac{\langle E_i(t)E_{i+j}(t+\tau)\rangle-\langle E_i(t)\rangle\langle E_{i+j}(t+\tau)\rangle}{\langle E_i^2(t)\rangle-\langle E_i(t)\rangle^2}\right\rangle_i . \tag{13}$$

This correlation function plotted as a function of j for various time differences τ is shown in Fig. 15 for a soft chain and in Fig. 16 for a harmonic chain. For a given coupling constant k and delay time τ, the correlation function peaks at the site

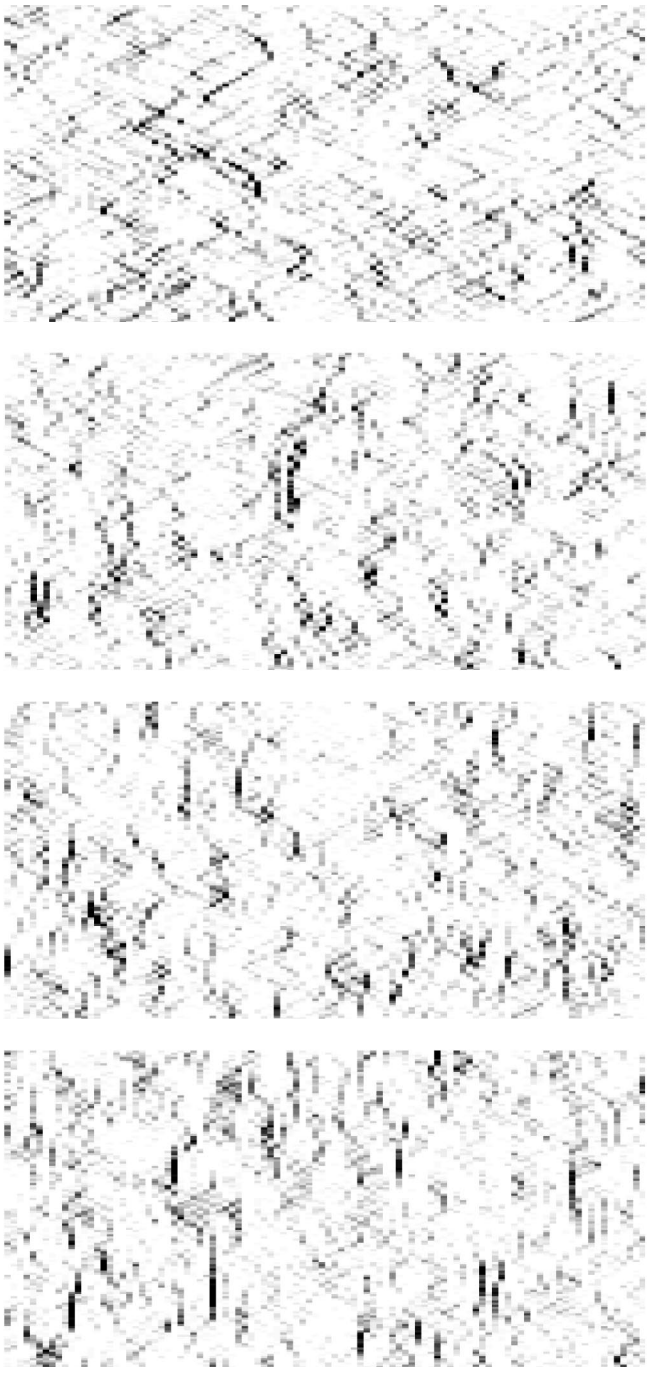

FIG. 13. Energy landscapes for thermalized coupled hard oscillators as a function of time. We take $\gamma=0.05$ and $k=1.0$. Temperatures from top to bottom: $k_BT=0.1,\ 0.5,\ 1.0$, and 2.0.

$i+j$ to which most of the energy originally at i has migrated. The change of the peak position with k indicates the velocity of the migration, and the height and width of the pulse reflect the dispersive dynamics.

The following results are evident:

(a) Increasing k in either soft or harmonic chains increases the velocity at which a fluctuation propagates.

(b) The velocity for a given set of parameters is greater in the soft chain.

(c) Dispersion is slower in the soft chain.

However, as noted before, the differences between soft and harmonic chains at large k are fairly marginal. More dramatic differences in mobility features occur with anharmonic intermolecular potentials, a situation that will be presented elsewhere.[20]

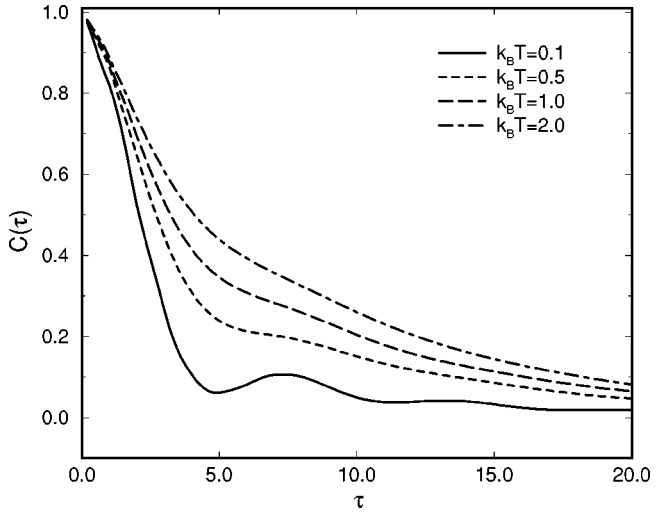

FIG. 14. Energy correlation function vs time for strongly coupled hard oscillators with $\gamma=0.05$, $k=1$ and different temperatures (same as in Fig. 13).

VI. CONCLUSIONS

We have presented a fairly complete characterization of the thermal equilibrium behavior of oscillator chains with ''diagonal anharmonicity,'' that is, chains with nonlinear onsite potentials and harmonic intersite potentials. Our particular interest lies in the characterization of possible spatial energy localization in such systems, and of the temporal persistence of such localization.

The instantaneous localization of energy of a system in thermal equilibrium is a manifestation of the thermal fluctuations: it is an equilibrium property unrelated to system dynamics. We argued that not only do soft anharmonic chains have a higher total energy at a given temperature than do

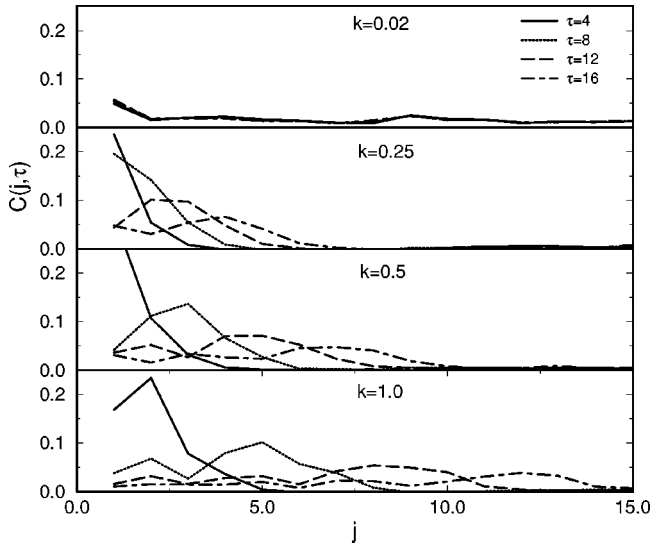

FIG. 15. Dynamical energy correlation function $C(j,\tau)$ for soft chains with $\gamma=0.05$ and $k_BT=1.0$.

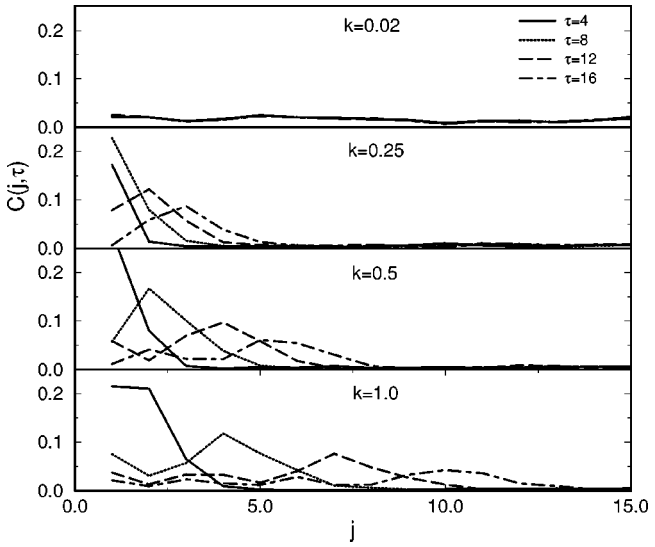

FIG. 16. Dynamical energy correlation function $C(j,\tau)$ for harmonic chains with $\gamma=0.05$ and $k_BT=1.0$.

harmonic or hard chains, but also that thermal fluctuations are more pronounced in the soft anharmonic chains. This is a consequence of the fact that free energy maximization favors the occupation of phase space regions with a high density of states. The density of states increases with energy in a softening potential, so it is entropically favorable for a few soft oscillators to have rather high energies. This in turn leads to greater spatial energy variability than in harmonic or hard chains, that is, soft chains have ''hotter spots.'' The effect becomes more pronounced with increasing temperature. This entropic energy localization mechanism in soft chains is degraded as the harmonic intersite potential increases because the harmonic contributions become dominant over the local soft anharmonicity effects.

In addition to the capacity for instantaneous localization of energy (which is greatest in soft chains), one is interested in the temporal degradation of a high energy fluctuation. That is, given a ''local hot spot'' (which is easier to find in soft chains, but nevertheless does occur in harmonic and hard chains due to thermal fluctuations), how does such a fluctuation evolve in time? Such a fluctuation never grows spontaneously, nor does it persist indefinitely. Rather, it eventually degrades, either through dissipation into the bath or through dispersion along the chain.

The rate of dissipation into the bath depends on the value of the dissipation parameter and also on the kinetic energy of the oscillators. If the dissipation parameter is small, this channel is of course slow for any chain. However, even if the dissipation parameter is large, dissipation can still be slow if the energy is not primarily in kinetic form. This is the case for soft chains provided the interatomic potential is weak (since otherwise the chain is essentially harmonic). In soft chains the energy is in potential form for a longer fraction of the time than in the other chains. As temperature is increased, this effect becomes more pronounced because ever softer portions of the potential become accessible, and the energy is stored as potential energy a greater fraction of the time. *Thus an increase in temperature in weakly coupled soft chains leads not only to greater energy fluctuations but also to a slower decay of these fluctuations.*

Energy dispersion along the chain depends on the magnitude of the coupling constant and also on the relative oscillator displacements. If the coupling constant is small, this channel is slow for any chain. If it is large, then this channel can still be slow if relative displacements of neighboring oscillators are small. This is the case for the hard chain, where displacements are relatively small and don't change much with increasing energy. Furthermore, because in a hard oscillator the frequency increases with increasing energy, there is a frequency mismatch between a ''hot'' oscillator and its ''colder'' neighbors that further impedes energy transfer. This leads to greater persistence of local high-energy fluctuations with increasing temperature. *Thus an increase in temperature in weakly dissipative hard chains leads not only to greater energy fluctuations but also to a slower decay of these fluctuations.*

The soft chain, on the other hand, increasingly loses its soft character as the interoscillator energy transfer channel strengthens, and therefore both the landscape and the dynamical effects of anharmonicity quickly disappear as this coupling constant is increased.

Finally, we showed that in harmonically coupled nonlinear chains (that is, in chains with diagonal anharmonicity) in thermal equilibrium, high-energy fluctuation mobility does not occur beyond that which is observed in a harmonic chain. The situation might be quite different if there is nondiagonal anharmonicity, that is, if the interoscillator interactions are anharmonic. Our results on these systems will be presented elsewhere.[20]

Further presentations will also deal with bistable ''impurities'' connected to chains of the types that we have considered here.[23]

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