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Activation by Nonlinear Oscillations and Solitonic Excitations

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Local excitations in molecular systems are studied taking into account the influence of soft impurities. The dynamics of activation processes (high-energy events) due to nonlinear mechanisms is studied. The following examples of classical macroscopic systems with strong nonlinear interaction are investigated: 1D Toda chains, 1D Morse rings, and 3D systems of hard spheres including impurities. It is shown that solitonlike excitations may lead to the concentration of energy at definite sites (weak springs or soft spheres). The accumulation of energy is mainly due to soliton-fusion effects. In thermal equilibrium an optimum temperature exists, where the thermally averaged potential energy is preferably partitioned to the soft springs embedded into a hard-spring solvent. Further, we show that the effect of thermal energy localization and the temperature dependence also persists for solutions of soft spheres in hard-sphere solvents.

KEY WORDS: Nonlinear oscillations; solitonic excitations.

1. INTRODUCTION

This work is devoted to the study of activation processes in classical systems consisting of a finite number of molecules with strong nonlinear interactions. We will study the effect of strong anharmonic forces first for the simple case of Toda interactions

$$V(r) = \frac{a}{b}\,[\exp(-br) - 1] + ar \tag{1.1}$$

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These forces are constant for strong expansions beyond the rest positions and exponentially hard for strong compressions with respect to the equilibrium position. The results are extended to hard core forces which are zero for expansions and infinitely hard for compressions and finally to more realistic molecular forces approximated by Morse potentials:

$$V(r) = D[\exp(-ar) - 1]^2 \tag{1.2}$$

In mechanical equilibrium a classical system of interacting masses possesses only potential energy. By collisions we may accelerate one or a few masses and introduce in this way kinetic energy which will run in the form of an excitation through the system. In a thermal regime we may excite even a whole spectrum of excitations. In the case of a purely linear coupling we know all about these excitations: We will observe sinusoidal oscillations and waves, acoustical and optical phonons, etc. Eventually local excitations, i.e., wave packets, will be observed, which, however, show strong dispersion. In other words, local excitations are not stable in linear systems. On the other hand, one knows from the theory of infinite chains of molecules with very special interactions, such as, e.g., Toda interactions, about the possibility of solitons, i.e., absolutely stable local excitations.

The strong interest in local excitation is especially inspired by the theory of reaction rates.(1–3) An idea expressed by several authors is that catalytic activity in complex reaction systems is supported by nonlinear excitations capable or localizing energy at special reaction sites. The problem of the elementary excitations in biomolecules(4–8) and of their possible role with respect to functional relevant activation processes in enzyme molecules(9, 10) or strings of nuclei acids(11, 12) has been studied by several workers.

This work aims to give a contribution toward a general theory of nonlinear energy localization mechanisms suitable for the assistance of local activation processes. We will restrict ourselves to the investigation of simple classical models of molecular systems, such as one-dimensional chains and rings of masses which are connected to their adjacent neighbors by nonlinear springs, as well as three-dimensional systems of hard and soft balls.

In the following part of the paper we shall give a brief description of the basic dynamical effect—the soliton fusion—which might be responsable for an energy localization at a definite site. In the subsequent section we will examine the influence of this dynamical effect on special sites. In thermal equilibrium there is an optimum temperature where energy is mainly partitioned to soft sites, which may lead a considerable reaction rate enhancement. Finally, we will turn to a hypothetical example for nonlinear energy localization and recurrence under nonequilibrium conditions. A simple model of global enzyme structure will be used in order to demonstrate the maintenance and efficiency of the effect for an inhomogeneous chain of molecular masses interacting via Morse potentials with realistic parameters in the presence of frictional forces.

2. THE EFFECT OF NONUNIFORMITIES ON SOLITONIC EXCITATIONS

A wide class of intermolecular interactions is usually modeled by Morse potentials, Lennard-Jones potentials, or other empirical potentials consisting of a steep repulsive and a long-range attractive part. The so-called Toda potential(13) proves to be a standard model for this kind of interaction, which allows an analytical treatment of the equations of motion in the 1D case. Now we consider the dynamics of a nonuniform chain of masses at position y_n which are connected to their nearest neighbors by Toda springs with the nonlinear spring constant b_n. The Hamiltonian reads

$$H=\sum\left(\frac{p_n^2}{2m}+\frac{a}{b_n}\{\exp[-b_n(y_{n+1}-y_n)]-1\}+a(y_{n+1}-y_n)\right) \quad (2.1)$$

For an infinite uniform chain $[b_n=b\,\forall n\ (-\infty, +\infty)]$ Toda found the soliton(13)

$$\exp[-b(y_{n+1}-y_n)]-1=\sinh^2\chi\,\mathrm{sech}^2\left[\chi b-\left(\frac{ab}{m}\right)^{1/2}\sinh\chi t\right] \quad (2.2)$$

with the energy

$$E^s=\frac{2a}{b}(\sinh\chi\cosh\chi-\chi) \quad (2.3)$$

The soliton corresponds to a local compression of the lattice with spatial "width" χ^{-1}. The quantity

$$\tau=\left[\left(\frac{ab}{m}\right)^{1/2}\sinh\chi\right]^{-1} \quad (2.4)$$

defines the characteristic excitation time of a spring during soliton passage. The energy of a large-energy-containing and therefore extremely localized soliton satisfying the condition

$$\frac{\sinh^2\chi}{\chi}\gg 1 \quad (2.5)$$

reads according to (2.3) and (2.5)

$$E^s \sim \frac{2a}{b} \sinh^2 \chi \tag{2.6}$$

Now we consider a system consisting of two semi-infinite Toda chains of different spring parameters, $b_n = b \; \forall n < 0$ and $b_n = b_n \; \forall n \geqslant 0$ with $b_0 < b$. Although this nonuniform chain does not admit exact soliton solutions, the solution (2.2) can be conceived as a right-running soliton on the hard part with b far to the left of the interface, where it behaves as in a uniform chain. In the vicinity of the interface, however, it will be scattered and evolve into reflected and transmitted waves, including both solitons and radiation.(14, 15) In particular we observe sufficiently far to the right on the soft part the formation of a transmitted soliton(15)

$$\exp - [-b_0(y_{n+1} - y_n)] - 1 = \sinh^2 \chi_0 \operatorname{sech}^2 \left[\chi_0 n - \left(\frac{ab_0}{m} \right)^{1/2} \sinh \chi_0 t + \delta \right]$$

$$\sinh^2 \chi_0 = \frac{b_0}{b} \sinh^2 \chi \tag{2.7}$$

The last expression relates the transmitted soliton to the incident one; δ denotes a constant phase shift that occurs due to the scattering process. In the case of strong localization of both incident and transmitted solitons we find from (2.7) and (2.6) for the energy E_0 of the latter

$$E_0^s \sim \frac{2a}{b} \sinh^2 \chi \sim E^s$$

Hence the energy of the incident soliton is almost completely transferred to the transmitted one, i.e., scattering losses are less important for energetic solutions. From (2.2) and (2.7) we find according to (2.4) for the characteristic times τ and τ_0 of the incident and the transmitted soliton, respectively, the simple relationship

$$\frac{\tau_0}{\tau} = \frac{b}{b_0} \tag{2.8}$$

The existence of different time scales of soliton motion can be used to generate high-energy events by soliton fusion, which was demonstrated numerically.(15) The energy of two strongly localized solitons of equal magnitude impinging on the interface will be contained afterward mainly in one soliton transmitted to the soft part by a time less than τ_0 on the hard chain.

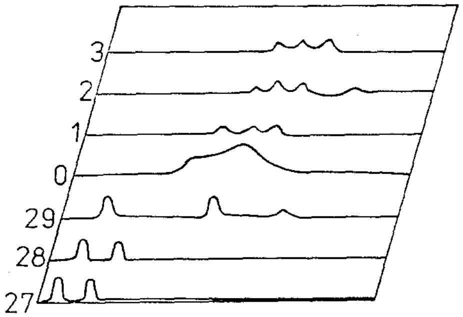

Fig. 1. Superposition of two solitons in a single soft spring ($n = 0$) embedded in a hard Toda lattice ($n = 1, \ldots, 29$) with parameters $m = 2$, $a = 10^{-2}$, $b = 10^2$, $b/b_0 = 10$. The solitons (each of energy $E = 1$) are separated from each other by a time 8.4τ on the hard lattice initially. The potential energy of springs is plotted versus time t and spring number n.

Now we consider a single soft spring embedded in a surrounding of an otherwise uniform hard chain [(2.1) with $b_n = n \; \forall n \neq 0$ and $b_0 < b$] instead of the interface between two extended chains of different stiffness. It turns out that this sole soft spring is able to trap and superpose narrow solitons impinging from both directions within a characteristic excitation time τ_0, as demonstrated in Fig. 1. We only note that this kind of soliton fusion leads to considerable concentrations of potential energy at the soft spring.(15) Interpreting a compression of this spring up to a certain critical value as an activation process, we have a novel mechanism to accumulate the energy of nonequilibrium excitations at a selected degree of freedom to be activated.

3. SOLITON-ASSISTED ACTIVATION PROCESSES

In the last section the fusion of solitons was introduced as a special nonequilibrium effect which is suited to supported local activation processes. Now we will show that this mechanism may lead to an activation enhancement which occurs even in thermal equilibrium due to the fusion of thermally generated solitons.

We consider a nonuniform Toda chain (2.1) of N particles which is fixed at the left-hand side ($y_0 = 0$) and introduce a pressure p acting on the right end particle. Among the N springs may be N_0 soft springs with spring constant b_0. After changing to spring coordinates $t_n = y_n - y_{n-1}$, the exact classical partition function can be calculated as for the uniform Toda chain.(13) Using the notations $\beta = 1/k_B T$, $\gamma = p/k_B T$, we obtain

$$
\begin{aligned}
Z(\beta, \gamma) &= \sum_{n=1}^{N} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dp_n\, dr_n \\
&\quad \times \exp\left\{ -\frac{\beta p_n^2}{2m} - \frac{\beta a}{b_n} [\exp(-b_n r_n - 1)] - (\beta\alpha + \gamma) r_n \right\} \\
&= \left(\frac{2\pi m}{\beta}\right)^{N/2} \left[\frac{1}{b} \exp\left(\frac{\beta a}{b}\right)\left(\frac{a}{b}\right)^{(a+\gamma)/b} \Gamma\left(\frac{a+\gamma}{b}\right)\right]^{N-N_0} \\
&\quad \times \left[\frac{1}{b_0} \exp\left(\frac{\beta a}{b_0}\right)\left(\frac{\beta a}{b_0}\right)^{-(\beta a+\gamma)/b_0} \Gamma\, 2\frac{\beta a+\gamma}{b_0}\Bigg)\right]^{N_0}
\end{aligned} \tag{3.1}
$$

The partition function splits into separate factors corresponding to hard and soft springs. The internal energy of the chain reads

$$
E = -\frac{\partial}{\partial \beta} \ln Z(\beta, \gamma) = \frac{N}{2\beta} + (N - N_0)\langle u \rangle + N_0 \langle u_0 \rangle
$$

with

$$
\begin{aligned}
\langle u \rangle &= \frac{a}{b}\left[\ln\left(\beta \frac{a}{b}\right) - \Psi\left(\beta \frac{a+p}{b}\right)\right] + \frac{p}{b} \\
\langle u_0 \rangle &= \frac{a}{b_0}\left[\ln\left(\beta \frac{a}{b_0}\right) - \Psi\left(\beta \frac{a+p}{b_0}\right)\right] + \frac{p}{b_0}
\end{aligned} \tag{3.2}
$$

expressing the average potential energies of a hard and a soft spring, respectively.

Now we elucidate soliton-induced effects in the thermal behavior of a nonuniform Toda chain. Because solitons are destroyed at open ends, we are led to fix the total length of the chain, which can be calculated from the partition function (3.1). Assuming further a vanishing number of soft springs embedded in a chain of hard springs, i.e., a strongly "diluted solution" $\eta = N/N_0 = 0$, whereas $N \to \infty$ and $N_0 \to \infty$, one obtains for the dimensionless pressure[16]

$$
\gamma = b\Psi^{-1}\left[\ln\left(\beta \frac{a}{b}\right)\right] - a \tag{3.3}
$$

By the help of (3.2) and (3.3) we can now calculate the average potential energies of the springs. Especially in the high-temperature limit the ratio of the average potential energies of a soft and hard spring yields

$$
\frac{\langle u_0 \rangle}{\langle u \rangle} \underset{\beta \to 0}{\simeq} \frac{b}{b_0} \tag{3.4}
$$

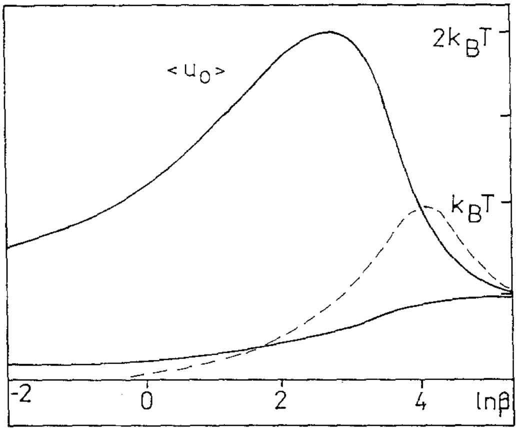

Fig. 2. Average potential energies of soft springs (upper curve) and hard springs (low curve) in a Toda lattice with fixed average length as a function of the logarithm of the reciprocal temperature ($b/b_0 = 10$). The spring energies are given in units of $k_B T$ for a vanishing fraction of soft springs ($\eta = 0$). In an intermediate temperature range a localization of thermal energy takes place at the soft springs. The dashed curve shows the potential energy of a soft Toda molecule. ($b_0 = 1000$) imbedded into a hard-sphere solvent ($\gamma = 1$).

The potential energies in units of thermal energy are presented in Fig. 2 as a function of temperature. In the high-temperature limit thermal energy is partitioned mainly to the kinetic degrees of freedom. Whereas the ratio of potential energies of soft and hard springs tends up to the maximum value defined by (3.4), the ratio of potential and kinetic energy tends to zero. with temperature approaching infinity. Hence only a vanishing part of thermal energy is located at soft springs. At low temperatures the equipartition theorem is valid and thermal energy is shared equally among all microscopic degrees of freedom. Between these limits there is an optimum temperature where the potential energy of soft springs may reach several $k_B T/2$.

The pecularities in thermal behavior of a nonuniform Toda chain can be attributed to the properties of solitons, which were outlined previously.(16) At high temperatures the dynamics is completely determined by extremely narrow and hence noninteracting solitons. In the intermediate temperature range that is characterized by a localization of thermal energy at the soft spring, thermal solitons become broader and their average distance in time is no longer greater than the characteristic time τ_0 of the soft spring. Thus a substantial superposition of incident solitons as presented in Fig. 1 takes place in the soft spring, giving rise to the elevation of average potential energy for intermediate temperatures. At low temperatures, however, strong interaction is no longer confined to the soft spring and individual solitons are destroyed.

So far we have considered only 1D chains. Now we will give a brief discussion of 3D systems of hard and soft spheres, proving that corresponding activation enhancement may occur also in higher dimensions. We consider first again the nonuniform Toda chain under a pressure p acting on the right end particle, but using now another notation. Introducing $\gamma = p/k_B T$, we can represent the average energy at soft sites in the form

$$\langle u_0 \rangle = \frac{\int dr_0\, u(r_0) \exp[-\beta u(r_0) - \gamma v_0]}{\int dr_0 \exp[-\beta u(r_0) - \gamma v_0]} \tag{3.5}$$

where $v_0 = r_0$ is the "volume" of the soft sites and γ is given by Eq. (3.3). Our new representation (3.5) may be interpreted as an average carried out over an isobaric Gibbs ensemble. This analogy enables us to transfer the results obtained for Toda chains to other diluted one-dimensional systems with known pressure as well as to diluted higher-dimensional systems. Let us consider now as one example a diluted solution of soft spheres with the volume $v_0 = 4\pi R^3/3$ imbedded into a hard sphere system. The pressure is then given in Percus–Yevick approximation by$^{(2)}$

$$\gamma = \rho(1 + \eta + \eta^2)/(1 - \eta)^3 \tag{3.6}$$

where ρ is the density of the hard spheres and $\eta = \rho v_0$ the relative packing. Introducing (3.6) into (3.5), a numerical evaluation shows that the average energy $\langle u_0 \rangle$ again shows a maximum in dependence on the temperature if the pressure γ is not too high (Fig. 2). In other words, the basic effect that soft sites (molecules) imbedded into a stiff solvent are able to collimate the energy of local excitations seems to persist in three dimensions. We hope to be able to confirm this effect by 2D and 3D simulations.

4. A MODEL OF ACTIVATION PROCESSES IN ENZYME MOLECULES

In this section we will give a short discussion of a model of global enzyme structure which was developed together with Romanovskii.$^{(10)}$ We will follow the hypothesis that solitary-wave dynamics could be involved in the primary processes of enzyme catalysis. It is well known that the active site of an enzyme occupies only a few percent of the whole volume of the macromolecule. On the other hand, the intramolecular motion of the whole structure is likely to influence the processes at the active site during catalysis. In the following we will treat the enzyme macromolecule in a simplified way as a mechanical system which possesses one selected degree of freedom strongly coupled to catalytic activity. As a crude model for the enzyme α-chymotrypsin we chose(10) a ring of 12 slightly different masses connected by Morse springs:

$$V(r_n)=D_n[\exp(-a_n r_n)-1]^2 \tag{4.1}$$

The first term of a Taylor expansion yields the harmonic approximation:

$$V(r_n)\sim D_n a_n^2 r_n^2=\frac{k_n}{2}r_n^2 \tag{4.2}$$

The equations of motion in the presence of external forces $F_n(t)$ and friction γ_n read as follows:

$$\begin{aligned}\dot{r}_n&=v_n-v_{n-1}\\ \dot{v}_n&=-\gamma_n v_n+m_n^{-1}[V'(r_n)]+F_n(t)\\ n&=0,1,\ldots,11\end{aligned} \tag{4.3}$$

Here the dots and primes stand for the derivatives with respect to time t and coordinates respectively; and r_n and v_n denote the deviation of the nth spring from its rest position and the velocity of the nth mass m_n, respectively. The masses $m_n=2083$ a.u. $\pm 10\%$ model the single domains of α-chymotrypsin(17) which are connected by hydrogen bonds, $D_n=17$ kJ/mole, $a_n=50\ \mathrm{nm}^{-1}$ $(n=1,\ldots,11)$, and enclosed by a hydrophobic core, $\gamma_n=0$ $(n=1,\ldots,10)$. The spring $n=0$ with $k_0=k/10$ and $a_0=a/50$ stands for a weak elastic interaction between two of the domains between which the active site is located. The motion of the soft spring may be exposed to the solvent, $\gamma_{11}=\gamma_0=2.86\times 10^{11}\ \mathrm{sec}^{-1}$. A compression of this soft or active spring enhances the probability for catalytic reactions significantly.(18, 10)

Now we will show the results of numerical integration of (4.1)–(4.3). First we considered the action of an initial impact $F_n(t)$ on the active spring modeling the release of vibrational energy due to the absorption of substrate molecules.(10) For this we applied a rectangular pulse $F_{11}(t)=-F_0(t)$ to the soft spring which was adjusted to provide an initial energy of 65 kJ/mole to the system. As can be seen from Fig. 3, this adsorption pulse leads to an initial compression of the active spring with a maximum potential energy of more than half of the total initial energy of the macromolecule. This first compression relaxes, thereby inducing the formation of two strongly localized pulses traveling in opposite directions away from the active spring. These pulses are not actual solitons in a strict sense because they possess a finite lifetime, which is, however, very large

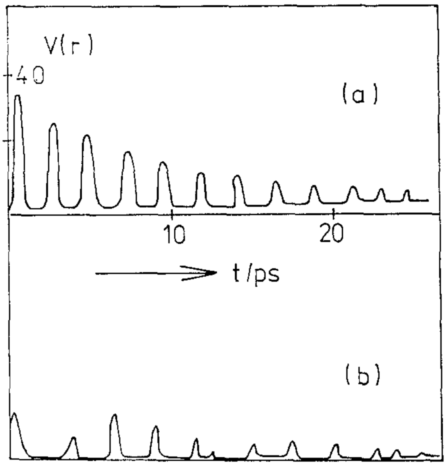

Fig. 3. Relaxation of compressional energy $V(r_0)$ of the active spring versus time t for (a) the nonlinear and (b) the linear model after an initial compression of the active spring due to an adsorption event.

compared to one period around the (undamped) Morse ring. They exhibit to our observation the same qualitative interaction behavior both in uniform and perturbed chains as the Toda solitons considered above. After a time approximately identical to the natural period of the active spring we observe a first recurrence of the energy due to a fusion of both quasisolitons after one rotation on the ring. This scenario is repeated until the pulses are damped out due to the solvent friction. It is worth noting that the dissipation of energy proceeds much more slowly than for an "isolated" active spring which is not coupled to the rest of the chain. Hence the nonreactive part of the macromolecule retards the relaxation of vibrational energy at the active site. For comparison we integrated (4.3) in the harmonic approximation (4.2) using the same parameters as before, so neglecting the nonlinearity of interaction for demonstration purposes. As can be seen from Fig. 3b, the initial compression localizes less than a quarter of the total energy at the soft spring. The wave packets made up of the few normal-mode frequencies of the system can be considered moving in opposite directions along the ring as in the nonlinear case. In contradiction to the latter case, these wave packets are not stable and we observe an incomplete superposition of the normal waves after a period. The motion of the soft spring is essentially determined by the lowest mode slightly "modulated" by the overtones. Due to the dispersion especially the high-frequency modes do not contribute effectively to a localization of vibrational energy at the active spring in the linear model.

We considered also the effect of an initial rectangular pulse put to a fourth spring, i.e., to a hard positioned asymmetrically with respect to the active one. This pulse was chosen to provide an initial total energy of 65 kJ/mole again. In the linear case the active spring was never excited significantly, whereas in the nonlinear model the energy was always transferred to the active spring, where it repeatedly returned also after a certain time when the motion proves to be almost harmonic. This effect of nonlinear energy transfer may be of relevance for the catalytic utilization of external energy sources, collisions with clusters of water molecules, etc.

In this section we developed some ideas of how soliton like dynamics could support reaction processes under nonequilibrium conditions. In particular we outlined that the nonlinearities occurring in biological macromolecules are sufficient to provide a localization and repeated recurrence of vibrational energy at a functionally relevant part.

5. CONCLUSIONS

The present work is closely related to the classical computer experiment by Fermi, Pasta, and Ulam which observed already that when an anharmonic lattice was disturbed from equilibrium, the system exhibited no tendency to redistribute its energy among the normal modes. Later this effect was understood on the basis of relatively stable solitonlike excitations. We have shown here that the dynamical effect of soliton fusion provides an efficient mechanism for localization of both thermal and nonthermal energy at activation sites that are part of a nonlinear molecular chain. This holds true even for mixtures of hard and soft spheres and for inhomogeneous Morse rings with interaction parameters applying to biological macromolecules. In thermal equilibrium we proved the existence of an optimum temperature where energy is preferably partioned to a few soft springs embedded into a nonuniform Toda chain consisting mainly of hard springs. Here we restricted ourselves to the investigation of the energetic activation of the soft springs. For a more accurate treatment of transition processes, e.g., chemical reactions, the simple TST model may be applied.(2) The effect of thermal energy localization persists also for solutions of soft spheres in hard-sphere solvents.(2) The corresponding theory was based on thermodynamic grounds only, since a statistical description of the underlying dynamics of the three-dimensional many-body system by nonlinear elementary excitations seems to be impossible. A further investigation of thermal energy localization for three-dimensional systems could be interest to the reaction theory of solutions.

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