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NONLINEAR ENERGY LOCALIZATION AND MELTING*

M. PEYRARD

Laboratoire de Physique
Ecole Normale Supérieure de Lyon, CNRS URA 1325
46 allée d'Italie, 69007 Lyon, France

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We discuss nonlinear effects which could be the basis for a theory of melting involving processes by which energy, initially evenly distributed in a lattice, can localize itself into large amplitude excitations. In a first part, we show how nonlinearity can affect the equipartition of energy in a lattice, and introduce some properties of nonlinear excitations and solitons. A second part investigates more precisely the question of self-localization of the energy and the third part present a simple theory of DNA thermal denaturation. We show in particular how the addition of a specific type of nonlinear coupling can cause a sharp "melting" transition in this one-dimensional system.

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1. Introduction

The problem of understanding how solids melt has long challenged physicists. Although much progress has been done since the early work of Boltzmann, there are still many unresolved points. One of them is the explanation of the "Lindemann criterion" which says that a crystal melts when the amplitude of vibration of the atoms is about 10% of the interparticle spacing, and provides a relationship to predict the melting point.

The hope that lower dimensional systems would be simpler to understand stimulated studies of two-dimensional surface melting. There are even *one-dimensional systems* which exhibit a transition similar to melting: this is the case of DNA denaturation and it is this problem that led me to consider melting in the framework of nonlinear theories.

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Even in two dimensions the understanding of melting turned out to be very difficult [1]. Kosterlitz and Thouless reformulated the old dislocation theory into a more modern framework. In this approach, melting is seen as a defect unbinding theory. Dislocation pairs, present at low temperature, dissociate near the melting temperature, leaving free dislocations in the system. As a result the shear coefficient drops to zero, which indicates that the material is no longer in the solid phase. However, at that stage, although translational order is destroyed, there is still some rotational order which disappears at a higher temperature by a breaking of the dislocation themselves, leading to the liquid state. This theory predicts a smooth transition and a bump, without divergence, in the specific heat due do the gradual dissociation of the dislocation pairs. This is in contradiction with the microscopic Landau theory. In two dimensions however, the real nature of the transition is not known. Some experiments using rare gas absorbed on graphite suggest the existence of a continuous melting transition while others, as well a computer simulations, find a sharp melting [2].

Essentially all theoretical work has been based on the assumption of the validity of the standard precepts of statistical mechanics and it is assumed that the thermal energy is homogeneously distributed over the sample. In the case of DNA denaturation, *there are clear experimental evidences that this assumption is not true*. Similarly, theoretical and experimental results on solids show that, at high thermal energy, *i.e.* when the anharmonicity (or nonlinearity) of the lattice dynamics is sufficiently excited, equipartition does not exist. This suggests another vue of melting based on nonlinear local modes [2]. This approach, using the idea of energy self-focusing may not be in complete contradiction with the Kosterlitz–Thouless theory, because local modes could be precursors to the formation of dislocation pairs.

In this set of lectures, I want to develop this idea that nonlinear energy localization could explain the melting transition, as it seems to happen in DNA thermal denaturation. In Section 2, I will discuss the problem of equipartition of energy and show how nonlinear excitations of soliton type can be formed naturally in lattice dynamics. In Section 3, I will consider particularly the self-focusing of thermal energy, and Section 4 will be devoted to the specific problem of DNA thermal denaturation. For this particular problem, I will show how the introduction of a specific type of coupling nonlinearity, besides other nonlinearities considered previously, can change a smooth transition into a very sharp melting. This could perhaps suggest a connection between the smooth transition given by the Kosterlitz–Thouless and the first order melting transition that one expects from standard Landau theory.

2. Lattice dynamics, equipartition of energy and solitons

The theories of melting discussed in the introduction are based on the validity of the standard assumption of statistical mechanics and, in particular, it is assumed that the thermal energy is uniformly distributed among the different degrees of freedom, and is therefore homogeneous over the sample. The origin of this equipartition of energy is assumed to be the existence of anharmonic terms in the lattice equations of motion, which give rise to interactions between the linear normal modes of the crystal. The first attempt to check this assumption by numerical simulations was made in 1955 by Fermi, Pasta and Ulam. It gave a very surprising result, leading to what became known as the FPU problem which was solved (only partially) in 1965 by Zabusky and Kruskal.

2.1. The FPU problem and equipartition of energy

Arnold once stated that "the only computer experiments worth doing are those that yield a surprise". Clearly the Fermi Pasta Ulam numerical study belongs to this class [3]. In their work, FPU decided to investigate the behavior of a one-dimensional chain of 64 particles of mass m, with forces between neighbors containing nonlinear terms, for times long compared to the characteristic periods of the corresponding linear problem. Their aim was to study "experimentally" the rate of approach to the equipartition of energy among the various degrees of freedom of the system.

The hamiltonian of the system is

$$H = \sum_{i=0}^{N-1} \tfrac{1}{2}p_i^2 + \sum_{i=0}^{N-1} \tfrac{1}{2}K(u_{i+1} - u_i)^2 + K\tfrac{\alpha}{3} \sum_{i=0}^{N-1} (u_{i+1} - u_i)^3 , \qquad (1)$$

where u_i and $p_i = m\dot{u}_i$ are the coordinate and momentum of the *i-th* particle. They chose fixed boundary conditions $u_0 = u_N = 0$. The harmonic coupling constant is K, and α is a small parameter measuring the magnitude of the nonlinear term in the interatomic potential.

This hamiltonian can be expressed in terms of the normal coordinates A_k of the linearized Hamiltonian as

$$A_k = \sqrt{\frac{2}{N}} \sum_{i=0}^{N-1} u_i \sin\left(\frac{ik\pi}{N}\right) \qquad (2)$$

as

$$H = \tfrac{1}{2}\left(\sum \dot{A}_k^2 + m\omega_k^2 A_k^2\right) + \alpha \sum C_{klm} A_k A_l A_m , \qquad (3)$$

where $\omega_k = 2\sqrt{K/m}\sin(k\pi/2N)$ is the frequency of the $k-th$ normal mode, and C_{klm} are constants. In the harmonic case ($\alpha = 0$), the energy stored initially in a given mode stays in that mode and the system does not approach thermal equilibrium. When they started the simulation by exciting the lowest mode ($k = 1$), FPU thought that, for $\alpha \neq 0$, the mode coupling term in the hamiltonian would cause energy to flow to the other modes, leading in the long term to a complete equipartition of energy among the modes. At the beginning of the simulation, this is indeed what they observed: modes 2, 3, 4 became gradually excited. But, at their surprise, after about 157 periods of the fundamental mode, almost all the energy (with only a 3% difference) was back to the lowest mode. After this recurrence time, the initial state was almost restored. Much longer calculations performed later showed that this periodic recurrence of the initial state could be repeated many times and a "super-recurrence" which restores the initial state almost exactly was found, with a longer period.

2.2. Interpretation: the KdV equation and solitons

This remarkable result, known as the FPU paradox, shows that introducing nonlinearity in a system does not guarantee an equipartition of the energy. In order to understand the properties of the FPU system (and of most of the nonlinear systems), *it is essential to abandon the expansion on the linear modes* and to consider the full nonlinear excitations of the system. This was recognized by Zabusky and Kruskal [4] in 1965 who gave, ten years after the FPU discovery, an explanation of the FPU paradox in terms of "solitons", solution of the Korteweg de Vries equation. It is useful to examine the derivation of this equation for the FPU atomic chain since it illustrates the methods which are often used in the theory of nonlinear systems, and particularly an analysis of the scale of the different terms. A detailed derivation is given in Appendix A.

Let us introduce a dimensionless displacement v by $u/h = av$, where h is the lattice spacing. The parameter $a \ll 1$ sets the scale of the motions. Its small value should be related to the Lindemann criterion mentioned in the introduction. The equation of motion which derives from Hamiltonian (1) is

$$\begin{aligned}\ddot{v}_i =& \frac{c^2}{h^2}(v_{i+1} + v_{i-1} - 2v_i) \\ &+ c^2\frac{\alpha a}{h}\left[(v_{i+1} - v_i)^2 - (v_i - v_{i-1})^2\right] ,\end{aligned} \tag{4}$$

where $c = h\sqrt{K/m}$ is the speed of sound in the lattice. The discrete set of nonlinear differential equations (4) is not solvable. However, since

FPU started from an initial condition which included only the lowest mode and found a recurrence of the initial state before short wavelength modes could be significantly excited, their results can be analyzed in terms of signals with a slow spatial variation. This is equivalent to replacing the set of equations (4) by a partial differential equation for a function $v(x,t)$, depending continuously on space and time. Changing to a frame moving to the speed of sound c and using properly scaled space (ξ) and time (τ) variables in this frame (see Appendix A for details), one gets the Korteweg de Vries (KdV) equation

$$w_\tau + \tfrac{1}{2}pa\, ww_\xi + \tfrac{1}{24}w_{\xi\xi\xi} = 0\,, \qquad (5)$$

for the spatial derivative $w = v_\xi$ of the dimensionless displacement v, where p is a parameter related to the nonlinear term of the interatomic potential.

Using numerical simulations of the KdV equation, Zabusky and Kruskal exhibited some remarkable properties of its solution which marked the beginning of a new field in mathematical physics, the theory of *solitons,* and simultaneously provided a beautiful explanation of the FPU paradox. It is interesting to notice that the first observation of the "soliton" had been made in 1836 by J. Scott Russel on a Scottish canal. He had been so fascinated by the "great solitary wave" that he spent more than 10 years of his life to investigate it. Then the idea was forgotten. In 1895, Korteweg and De Vries found an analytical explanation of Scott Russel's observations, but it is only after the work of Zabusky and Kruskal that soliton studies started to flourish.

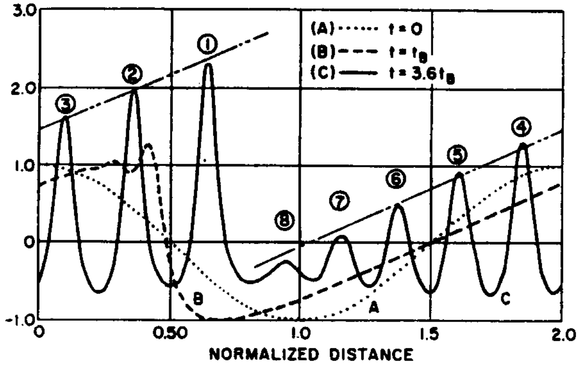

Fig. 1. Temporal evolution of the initial cosine condition introduced by Zabusky and Kruskal in the KdV equation (from Ref. [4]).

Zabusky and Kruskal simulated the KdV equation with the initial condition $w(\xi, 0) = \cos \pi\xi$, which corresponds to the lowest mode introduced by FPU. As shown in Fig. 1, they observed a very peculiar behavior which they described in the following way

> Initially the first two terms of Eq. (5) dominate and the classical overtaking phenomenon occur; that is w steepens in regions where it has a negative slope. Second, after w has steepened sufficiently, the third term becomes important and serves to prevent the formation of a discontinuity. Instead oscillations of small wavelength develop on the left of the front. The amplitudes of the oscillations grow and finally *each* oscillation achieves an almost steady amplitude and has a shape almost identical to that of an individual solitary-wave solution of (5). Finally, each such "solitary-wave pulse" or "soliton" begins to move uniformly at a rate (relative to the background value of w from which the pulse rises) which is linearly proportional to its amplitude.

This description does not only give the time evolution of the signal, but it explains also clearly the origin of the phenomena. It is interesting to notice that the original papers on solitons from Scott Russel or Zabusky and Kruskal contain rather pictorial descriptions of the formation and dynamics of soliton. This is perhaps associated to the unusual properties of the soliton for people who have been trained to think in terms of linear dispersive waves, so that they feel they need to explain what they have seen to the sceptical reader. The formation of the solitons is the clue to the FPU recurrence because the numerical study showed that the solitons are perfectly stable nonlinear excitations of the system. They are bell-shape localized excitations moving at constant velocity s given by

$$w(\xi,\tau) = \left(\frac{6s}{pa}\right) \operatorname{sech}^2 \sqrt{6s}(\xi - s\tau)\,. \tag{6}$$

Notice that, in the frame (ξ,τ), moving at the speed of sound with respect to the lattice, the KdV solitons must have a positive velocity, *i.e.* KdV solitons are supersonic excitations. Their amplitude is proportional to their velocity as observed by Zakusky and Kruskal. When they collide, they pass through each other and preserve their amplitude and velocity. Their nonlinear interaction appears only through a phase shift. The original work of Zabusky and Kruskal has now been completed by many theoretical studies and we know that the solitons can really be considered as the "nonlinear normal modes" of the system [5]. Their exceptional stability explains the FPU paradox: the solitons which emerged from the initial condition arrive after the recurrence period almost in the same phase as in the initial state and consequently they almost reconstruct the original waveform. As they are exactly preserved in the collisions, the sam process can repeat over and over again.

It is important to notice that Zabusky and Kruskal observed clearly the solitons, and therefore solved the FPU paradox, because they plotted the displacements *in real space* instead of looking at the Fourier modes. As shown in Fig. 1, the formation of the solitons is associated to a *localization in space* of the energy of the initial signal, each soliton being rather narrow. This is why they show up clearly when the displacement is plotted as a function of space.

If the solitons appear so naturally in the simulations, it is because they are stable excitations of the nonlinear lattice, contrary to the Fourier modes which are only useful in a purely linear lattice. As explained in the description given by Zabusky and Kruskal, the soliton results from an equilibrium between dispersion (third term in the KdV equation (5)) and nonlinearity (second term in the KdV equation (5)) which tends on the contrary to favor high amplitudes and gradients and to steepen the pulse. The important point is that this equilibrium is stable: if a pulse is too broad initially the dispersion is weak and nonlinearity dominate to make it steeper until the dispersion balances the nonlinearity. In a similar manner, a very sharp initial condition will broaden due to dominating dispersion until the equilibrium is reached. This is why solitons are so easy to generate in a nonlinear system. As shown by the numerical simulations of Zabusky and Kruskal, an arbitrary initial condition evolves spontaneously into the "nonlinear modes of the system". The inverse scattering transform, developed after the pionneering work of Zabusky and Kruskal is the equivalent of the Fourier transform for a nonlinear system [6, 7]. It can be used to determine the "soliton content" of a given initial condition and predict its evolution.

A possible objection to this enthusiastic view that seems to claim that solitons are everywhere in a nonlinear system is that Zabusky and Kruskal have been dealing with the KdV equation which is a very special equation. It describes an exactly integrable system in which solitons have their exact mathematical sense of excitations which are perfectly preserved into collisions, and can be analyzed by the inverse scattering transform. However it was obtained from the original physical system after a series of approximations (continuum limit approximation, dropping high order terms). Therefore one may wonder whether the same tendency to form solitons would be found in the original system. The answer is *yes* although the solitons are no longer exact solitons in the mathematical sense, but quasi-solitons [8]. Practically it means that narrow localized pulses are also formed from an arbitrary initial condition of sufficiently high amplitude to excite the nonlinearities. These pulses propagate at constant speed and pass through each other almost without losing energy. Even when their width is of the order of the lattice spacing, so that the continuum approximation breaks down, they lose less than 2 or 3% of their energies in collisions, so that they are still long lived excitations of the system.

The KdV-type solitons which appear in the FPU problem are only one class of solitons which can be relevant for lattice dynamics. Another class, the so-called "topological solitons" have been used to describe dislocations, or domain walls in ferroelectric or ferromagnetic materials [9]. Although this type of solitons may be relevant for melting, they are not discussed in these lectures due to lack of time.

In this section, we have seen on the example of the FPU problem, that the dogma of equipartition of energy should be taken with caution in nonlinear phenomena. Probably most of you knew already about the FPU paradox and solitons and believed that this is not relevant for a real system because the FPU model is so special (and in particular one-dimensional). I hope that the next section will convince you that nonlinear energy localization could be more common than it is usually thought, especially in the context of melting, *i.e.* close to a lattice instability where nonlinearities are highly excited.

3. Nonlinear energy localization

The introduction of solitons as possible excitations in the lattice dynamics of solids is an exciting idea due to the exceptional properties of the solitons. However there are also some objections that come immediately to mind after the discussion of the previous section:

- solitons are found in the *numerical* experiment of Fermi Pasta Ulam, but can they be observed in a *real* material?
- the FPU problem is a one-dimensional problem. We can expect a strong sensitivity to dimension, so, can the results be extended to a three dimensional system?

The first objection can be answered by presenting experimental evidences and I will do that below. The second objection is more fundamental because there is a theorem, due to Derrick [10] which shows that there are *no* permanent-profile soliton-like solutions in more than one dimension, which has been often cited as an argument that there are no solitons in multidimensional real systems. But the crucial term is *permanent-profile.* The Derrick's theorem does not forbid *time-dependent* solutions. These solutions are tightly connected to the experimental evidences that I want to discuss. Therefore, I will present them first. Moreover they will give me the opportunity to introduce the very important idea of *self focusing* or *spontaneous energy localization*, which the key to an alternate theory of melting.

3.1. The fundamental equation for self trapping of heat pulses in solids

The analysis of the FPU results has suggested that nonlinear effects can contribute to localize energy in a crystal lattice. This phenomenon has been experimentally observed in NaF crystals at low temperature by Narayanamurti and Varma [11]. In order to analyze their results, one must go beyond the simple FPU model. In the course of this analysis, we shall derive another soliton equation which is perhaps even more important than the KdV equation because it is more ubiquitous and its properties in dimensions higher than 1 are very interesting.

To study the propagation of heat pulses in a real solid, we must start from the full lattice dynamics equations [12]

$$m\ddot{u}_i^\alpha = \sum_{j,\beta} K_{ij}^{\alpha\beta} u_j^\beta + \sum_{jl,\beta\nu} K_{ijl}^{\alpha\beta\nu} u_j^\beta u_l^\nu + \sum_{jlm,\beta\nu\delta} K_{ijlm}^{\alpha\beta\nu\delta} u_j^\beta u_l^\nu u_m^\delta\,, \qquad (7)$$

where u_i^α is the displacement of the *i-th* atom in the α direction, and the K's are the derivatives of the interatomic potential. However, along a symmetry direction, the propagation of different polarizations decouple in the harmonic approximation, and the coupling of the lowest transverse phonon branch (*lt*) to other branches due to nonlinear terms is very weak, because it can only occur through a combination with one of the upper branches. Therefore, for the *lt* branch, only the self interaction due to nonlinear terms is important. Consequently, for this particular *lt* mode along a symmetry direction, the dynamics becomes very similar to that of the FPU problem, except that higher order terms in the potential have to be considered. We can again consider a scalar variable u and treat a one-dimensional problem. Let us label K_2, K_3, K_4, the potential parameters for nearest neighbor interactions at the different orders of nonlinearity. The only significant difference with the FPU case, is that we shall include the quartic term in the potential. As for the FPU problem, the cubic term is assumed to be small, *i.e.* $K_3 h/K_2 = \epsilon p/2$ with $\epsilon \ll 1$ and p of order 1, but we consider a quartic term of order 1 by defining $K_4 h^2/K_2 = q/3$, where q is of order 1 and h is the lattice spacing as before.

At a first glance, it may seem strange to consider a quartic term of the same order as the harmonic (quadratic) term because we are so used to assuming that nonlinearity is small. However, one should notice that we are speaking of the potential *coefficients* and not of the potential *energy*: if we assume, as in the FPU case, a small amplitude for the displacement u with the condition $u/h = a\,v$ with $a \ll 1$ and v of order 1, the quartic contribution in the potential energy will be of order a^2 with respect to the harmonic part. Moreover, I will show below with a simple example that, for surface melting, the quartic coefficient in the potential can even be *dominant* with respect to the harmonic one. Finally, the agreement with experiments provides another good argument for the chosen scaling!

With this scaling of the terms, the same calculation as in the FPU case (see Appendix A) gives for v the equation

$$v_{\theta\theta} = \epsilon^2 v_{XX} \left[1 + \epsilon^2 apv_X + \epsilon^2 qa^2 v_X^2\right] + \frac{\epsilon^4}{12} v_{XXXX} , \tag{8}$$

where θ and X are the dimensionless space and time variable respectively. Changing again to a frame moving at the speed of sound with $\xi = X - \epsilon\theta$ and introducing the slow time $\tau = \epsilon^3 \theta$, we obtain a modified KdV equation which generalizes the KdV equation obtained in the FPU case

$$w_\tau + \tfrac{1}{2} apww_\xi + \tfrac{1}{2} qa^2 w^2 w_\xi + \tfrac{1}{24} w_{\xi\xi\xi} = 0 . \tag{9}$$

Setting $q = 0$, we recover the KdV equation of the FPU problem. The major difference with the KdV case will be in the type of solutions that we seek for equation (9).

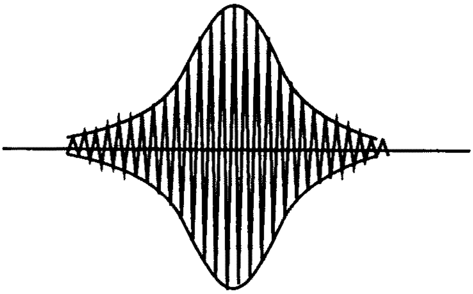

Fig. 2. Schematic drawing of a phonon wavepacket corresponding to a heat pulse in a crystal.

We are interested in explaining experimental results for heat pulses in a crystal. In a first approximation, such a pulse can be considered as a wavepacket of phonons. Therefore, as shown schematically in Fig. 2, the solution will contain *several scales* in space and time. There is a fast space-time scale associated to the vibrations inside the wavepacket, and a slower scale associated to the envelope of the wavepacket. A method which is appropriate to treat this problem is a *multiple scale expansion.* This approach is often used in the analysis of nonlinear phenomena, but it is more general and can be applied in various problems, for instance in kinetic theory as shown recently by J. Piasecki [13]. To apply this method, we must first identify a small parameter in the expansion. In Eq. (9), the parameter $a \ll 1$ which sets the scale of the atomic displacements is the natural small parameter. Then we expand the solution in a series of terms ordered with the powers of a,

$$w = w_0 + a\, w_1 + a^2\, w_2 + \cdots . \tag{10}$$

The physical variables ξ and τ are also replaced by a set of independent variables at the different scales

$$w(\xi,\tau) = w(\xi_0, \tau_0, \xi_1, \tau_1, \xi_2, \tau_2 \cdots), \tag{11}$$

with

$$\xi_0 = \xi \qquad \tau_0 = \tau, \tag{12a}$$
$$\xi_1 = a\xi \qquad \tau_1 = a\tau, \tag{12b}$$
$$\xi_2 = a^2\xi \qquad \tau_2 = a^2\tau. \tag{12c}$$

The derivatives are modified accordingly, *i.e.*

$$\frac{\partial}{\partial\tau} = \frac{\partial}{\partial\tau_0} + a\frac{\partial}{\partial\tau_1} + a^2\frac{\partial}{\partial\tau_2} + \cdots \tag{13a}$$
$$\frac{\partial}{\partial\xi} = \frac{\partial}{\partial\xi_0} + a\frac{\partial}{\partial\xi_1} + a^2\frac{\partial}{\partial\xi_2} + \cdots. \tag{13b}$$

These expressions are then introduced in the equation of motion (9) and the successive powers of a are identified as in a usual perturbation expansion and the resulting equations are solved order after order. Additional equations are imposed by requiring the validity of the perturbative expansion, *i.e.* by setting to zero any resonating term that would cause an infinite growth of one of the w_i's (secular terms). The details of the calculation are given in Appendix B. The result is that the solution is of the form

$$w(\xi,\tau) = \psi_1 e^{i(k_0\xi-\omega_0\tau)} + \text{C.C.} + a\left[\psi_0 + \psi_2 e^{2i(k_0\xi-\omega_0\tau)} + \text{C.C.}\right] + \cdots, \tag{14}$$

where ψ_1 is a function of the "slow" variables $\psi_1(\xi_1' = \xi_1 + \frac{3}{2}k_0^2\tau_1, \tau_2)$ and obeys a *Nonlinear Schrödinger Equation (NLS)*

$$i\frac{\partial\psi_1}{\partial\tau_2} + \frac{3}{24}k_0\frac{\partial^2\psi_1}{\partial\xi_1'^2} + \tfrac{1}{2}k_0\left[q - \frac{2p^2}{k_0^2}\right]|\psi_1|^2\psi_1 = 0. \tag{15}$$

Before studying the properties of the NLS equation, some comments are in order here:

- as expected, the solution has the form of a modulated wavepacket which is appropriate for the description of a heat pulse. However, one should not conclude that the standard treatment in terms of linear modes (phonons) would be as good, without the burden of the multiple scale expansion. As we shall see below, the NLS equation has unique features which would have been completely missed in a phonon expansion. In particular, it has solutions localized in space (*i.e.* decaying exponentially away from the center; they correspond to another class of soliton than the KdV solitons). These solutions *cannot* be represented by a phonon expansion unless one uses an infinite series because the phonons are extended excitations. The nonlinear approach has captured a feature that the linear expansion simply cannot show.

- Equation (15) is formally identical to the Schrödinger equation, although it appears in a purely classical context, but the "potential" $-|\psi_1|^2$ is expressed as a function of the solution itself. When the potential is a "well" that corresponds to localized solution, we are in a situation of *self-trapping.* It is precisely that situation which was observed for the propagation of heat pulses in NaF, and it is also this case which is important for melting.
- If one looks for permanent profile solutions of the modified KdV equation (9), one can find pulse-like solutions very similar to the solitons of the KdV equation. It may seem surprising that we can derive also a completely different solution in the form of a wavepacket. This is the richness of nonlinear equations which appears here. Instead of the unique solution of the linear equations (when the boundary conditions are given), one gets often a large variety of possible solutions which can be qualitatively different. Moreover, apart from the fully integrable systems for which all the solutions can be classified in a systematic manner, one is seldom sure that there are no other, yet unknown solutions, which could bring insight into new phenomena. This feature is not merely a mathematical property of the *equations* associated with different levels of approximations in the solution. It is rather easy to built *physical systems* (for instance nonlinear electrical lines) which can exhibit these different solutions, depending how they are excited [14].

3.2. Some properties of the NLS equation

The nonlinear Schrödinger equation

$$i\frac{\partial\psi}{\partial t}+P\frac{\partial^2\psi}{\partial x^2}+Q|\psi|^2\psi=0\,, \tag{16}$$

appears in many areas of physics because it provides a good description of intrinsically nonlinear systems which admit, in the limit of small amplitude, harmonic wave train solutions of the form [15, 16]

$$\psi=A\mathrm{e}^{i(kx-\omega(k)t)}\,. \tag{17}$$

When the nonlinearities are taken into account, they govern the evolution of the amplitude A (or envelope) of the wave. The NLS equation has been introduced to model Langmuir waves in a plasma, gravity wavepackets on water, propagation of vibrational energy along helical proteins [16], but its most successful application is perhaps nonlinear optics [17]. Since the original work of Hasegawa, Tappert and Kodama [18] showing that an optical pulse can propagate as a soliton into an optical fiber, the theoretical prediction has turned into a successful technical product which can transmit information on thousands of kilometers at the highest rate ever achieved. After years of mathematical physics, the soliton may well turn into a huge commercial success. Nonlinear optics is specially accessible to theoretical analysis because, at the current available intensities, the nonlinear coefficients are small and the power spectrum of the electromagnetic field is concentrated in the neighborhoods of discrete frequencies [17]. These properties allow one to remove all fast space and time scales from the Maxwell equations using a multiple scale expansion as we did for the lattice dynamics case.

Like the KdV equation, the NLS equation is a completely integrable equation, having exact soliton solutions, which can be studied with the inverse scattering method. Is it a fortunate accident that these equations derived from physical equations by standard perturbation methods have such remarkable mathematical properties? We do not know, but one may notice that the reduction process introduces new symmetries and new constraints (conservation laws) without destroying the existing ones. This increases the chance of getting a very special equation. What is even more remarkable is that, when physical perturbations, additional terms, discreteness effects, *etc*, are taken into account, the exceptional properties of the soliton solutions are almost preserved. In some cases, the additional terms coming from the physics make the system even more interesting by breaking its exact integrability in a manner which can be exploited for a particular purpose. For instance, using Raman effects, it has been possible to "feed up" a soliton with the energy of a small amplitude linear wave [17] to compensate for the inevitable losses, or to take advantage of discreteness effects to built large amplitude local modes from smaller ones [19].

The soliton solution of the NLS equation (16) can be easily found by looking for a solution under the form

$$\psi(x,t) = A(x - vt)\mathrm{e}^{i(\Omega t + \kappa x)}\,, \tag{18}$$

i.e. a wavepacket with permanent profile moving at speed v. Introducing this expression into Eq. (16), one gets an equation for $A(z) = A(x - vt)$. The cancellation of the imaginary part gives $\kappa = v/2P$, and the real part gives

$$P\frac{\partial^2 A}{\partial z^2} - (\Omega + P\kappa^2)A + QA^3 = 0\,, \tag{19}$$

which has a localized solution of amplitude a, $A = a\ \mathrm{sech}\gamma z$, provided that the condition

$$2P\gamma^2 = Qa^2 \tag{20}$$

is satisfied. This condition *requires that P and Q have the same sign*$(PQ > 0)$ for the existence of a soliton solution.

The soliton is given by

$$\psi(x,t) = a\ \mathrm{sech}\left[\sqrt{\frac{Q}{2P}}a(x - vt)\right]\mathrm{e}^{i(\Omega t + \kappa x)}\,, \tag{21}$$

with $\Omega = Qa^2/2 - v^2/4P$, $\kappa = v/2P$. Notice that, due to the exponential term, the NLS soliton does not move with a constant profile as the KdV soliton. Only the envelope keeps its profile. When the wavevector κ is very small ($\kappa \approx 0$), the solution appears as a bell-shaped envelope which oscillates in time at frequency Ω while it propagates. Such solutions are called "breather modes".

For the application to melting, the important result is not the exact form of the soliton solution, but the condition $PQ > 0$ which is also the *condition for a spontaneous energy localization in the system.* This localization occurs due to the *modulational instability* of a wave obeying the NLS equation. This can be easily seen by noticing that the NLS equation has a solution of the form of a plane wave

$$\psi(x,t) = A_0\mathrm{e}^{i(\kappa x - \Omega t)}\,, \tag{22}$$

where A_0 is a positive constant, provided that the condition $\Omega = P\kappa^2 - QA_0^2$ is satisfied. This condition is a nonlinear dispersion relation which shows that the frequency of the wave decreases when its amplitude increases. This solution is valid whatever the sign of PQ, but its stability depends on that sign. This can be checked by looking at the linear stability of the wave. Let us look for a solution

$$\psi(x,t) = [A_0 + b(x,t)]\exp\left(i[\Omega t + \kappa x + \theta(x,t)]\right)\,. \tag{23}$$

Introducing this solution into Eq. (16), and keeping only the linear terms in b and θ, one gets a system of linear differential equations governing the evolution of b and θ (see Appendix C for the details of the calculation). The solutions are of the form

$$b = b_0\mathrm{e}^{i(\delta x - \nu t)} + \mathrm{C.C.} \qquad \theta = \theta_0\mathrm{e}^{i(\delta x - \nu t)} + \mathrm{C.C.} \tag{24}$$

and correspond to a small modulation of the amplitude and phase of the plane wave. The parameters of this modulation verify

$$(2\kappa P\delta - \nu)^2 = P\delta^2(P\delta^2 - 2A_0^2Q)\,. \tag{25}$$

If P and Q have opposite signs ($PQ < 0$), the term $(2\kappa P\delta - \nu)^2$ is positive for any value of the modulation wavevector δ, so that ν is real. In this case, the plane wave is stable. On the contrary, for $PQ > 0$, ν has an imaginary part for $\delta^2 < 2A_0Q/P$. According to equation (24), this is associated to an exponential growth of the modulation. This generates a *self-modulation* of the wave. Figure 3 shows the evolution of a plane wave sent into a medium which exhibits modulational instability (in this case, a nonlinear electrical line). The wavefront provides the perturbation from which the modulational instability grows. Figure 3 shows that the spontaneous modulation of the wave evolves into a train of localized excitations which are envelope solitons. This example shows once more how the solitons can emerge from an arbitrary initial condition. Simultaneously, the energy density which was uniformly distributed in the initial plane wave shows large peaks around the solitons. Modulational instability provides an efficient mechanism for energy localization in a physical system, and this was already noticed in 1967 for water waves by Benjamin and Feir [20].

The experiments of Narayanamurti and Varma [11] demonstrate that this mechanism can indeed operate in a real solid and cause the self-focusing of heat pulses. A strong heat pulse is sent on one side of a NaF crystal at low temperature (1.4 to 4.2 K) with an alloyed metal film deposited on the surface to serve as a heater. The signal which is transmitted across the sample is detected with a superconducting film serving as a bolometer on the other side of the sample. The experiments can be performed along different crystallographic directions. When a symmetry axis is chosen, they show an important narrowing of the input pulse which is clearly a nonlinear effect: an increase of the input power by a factor 20 results in a multiplication of the output amplitude by a factor of 100 because, simultaneously the output pulse has become narrower. The results agree remarkably well with the theoretical predictions, discussed in the previous section, that the transverse pulse, being weakly coupled to other modes should obey the NLS equation and can show modulational instability if $PQ > 0$. In the case of the dynamics of a crystal lattice, the NLS equation (15) shows that the condition for instability can be fulfilled due to the presence of the quartic term (q term) in the hamiltonian. In the FPU case where $q = 0$, the coefficients of the NLS equation are such that $P > 0$ and $Q < 0$, so that they correspond to the modutionally stable case. On the contrary, if the quartic term is large enough (which is the case for NaF, as shown by the experiments of Narayanamurti and Varma), an instability can develop. Its time evolution can be predicted, at least initially, by calculating the maximum growth rate of the perturbation, given by the imaginary part of ν, as a function of the amplitude A_0 of the initial wave and compared with the experimental results at different input power.

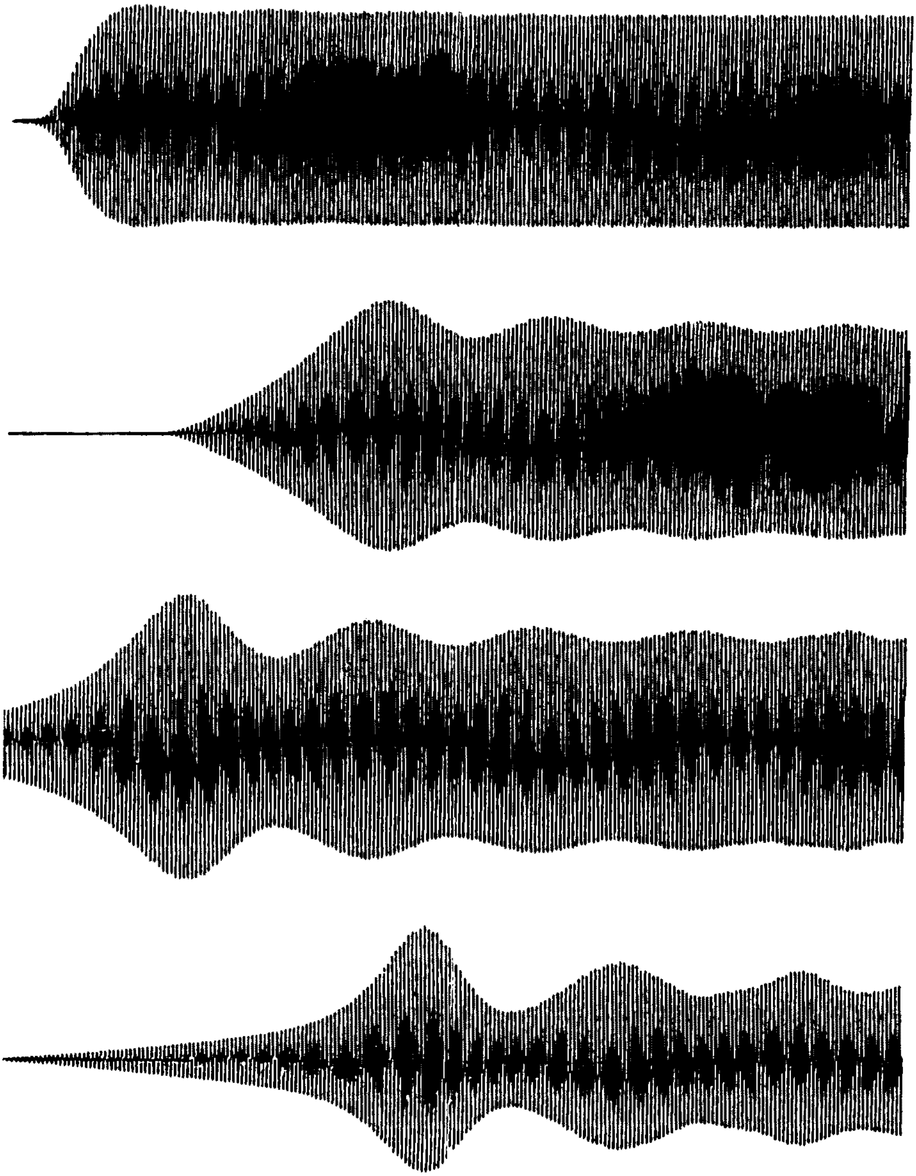

Fig. 3. Evolution of a sinusoidal signal sent at the input of a nonlinear electrical lines. The pictures show the signal at different times. It propagates along the line, but simultaneously, the perturbation due to the front of the signal generates a self modulation of the signal.

3.3. The NLS equation and surface melting

The experimental results obtained on NaF show unambiguously that, when the excitation of the crystal is sufficiently large, nonlinearity can cause a strong energy localization. Around melting temperature the thermal excitation is large so that we can expect strong nonlinear effects. Moreover we have seen the crucial role of the quartic term in the interatomic potential to determine the instability condition. A very simple model shows that surface melting is precisely a case where this quartic term can be very large, or even dominant, with respect to the harmonic (quadratic) term, so that we can expect a strong modulational instability at a crystal surface.

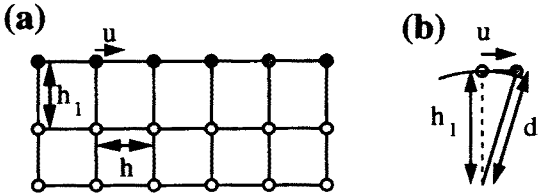

Fig. 4. Simple model for surface melting. (a) section of the model crystal in a plane orthogonal to the surface, (b) schematic drawing of the stretching of an interatomic bond for an in-plane motion.

The model is shown in Fig. 4. We consider the surface of a cubic crystal lattice, with lattice spacing h. Among the various motions of the atoms at the surface, the in-plane motion are particularly interesting because they are highly nonlinear. The qualitative reason is that, in order to stretch significantly the bond that connects an atom of the surface to its nearest neighbor of the first atomic layer below the surface, on needs a very large displacement (Fig. 4(b)). To describe completely the in-plane motions, one needs a two-component vector field. However, in order to simplify the presentation we shall consider only the motion along one crystallographic axis and use a scalar field u. In this case the problem reduces to the dynamics of a one-dimensional chain of the surface atoms, lying along the selected axis. Although the lattice spacing in the bulk is h, near the surface it is slightly different because the surface atoms are bound only on one side of the surface. We denote by h_1 the distance between the surface layer and the first atomic layer under the surface ($h_1 > h$). The simplest interatomic potential that we can introduce is a harmonic potential $V = {}^1\!/_2\, k(d-h)^2$ having the bulk interatomic distance as its equilibrium distance. In this expression, d is the interatomic distance when an atom is displaced from its equilibrium position. Assuming moreover that the atoms below the surface are fixed, d is given by

$$d^2 = h_1^2 + u^2 = h_1^2(1 + u^2/h_1^2)\,, \tag{26}$$

which can be expanded in series if $u^2 < h^2$ (remember the Lindemann criterion which says that, at the melting temperature $u \leq 0.1h$)

$$d \approx h_1 \left[1 + \tfrac{1}{2}\frac{u^2}{h_1^2} - \tfrac{1}{4}\frac{u^4}{h_1^4} + O\left(\frac{u^6}{h_1^6}\right)\right] . \qquad (27)$$

Introducing this expansion in the potential V and dropping the constant term, we obtain

$$V(u) = \tfrac{1}{2}kh_1 \left[(h_1 - h)\frac{u^2}{h_1^2} + \tfrac{1}{2}\left(h - \frac{h_1}{2}\right)\frac{u^4}{h_1^4}\right] + O\left(\frac{u^6}{h_1^6}\right) . \qquad (28)$$

Remembering that h_1, although bigger than h is very close to h, we notice that, in this case, the harmonic (quadratic) coefficient of the potential is *small* with respect to its nonlinear quartic part. Consequently, for the in-plane motions of surface atoms, *nonlinear effects can dominate* the dynamics, even though we have used an harmonic potential for the stretching of a bond.

Adding the in-plane interactions among the atoms, the Lagrangian of the atomic chain that we study is

$$L = \sum_i \tfrac{1}{2}m\dot{u}_i^2 - \tfrac{1}{2}k(u_{i+1} - u_i)^2 - \tfrac{1}{2}Au_i^2 - \tfrac{1}{4}Bu_i^4 , \qquad (29)$$

with $A = kh_1(h_1 - h)$ and $B = kh_1(h - h_1/2)$.

Taking as before the continuum limit we obtain

$$L = \int \left[\tfrac{1}{2}\lambda u_t - \tfrac{1}{2}\kappa(u_x)^2 - \tfrac{1}{2}\alpha u^2 - \tfrac{1}{4}\beta u^4\right] dx , \qquad (30)$$

with $\lambda = m/h$, $\alpha = A/h$, $\beta = B/h$, $\kappa = kh$.

The equation of motion for u is then

$$u_{tt} = \frac{\kappa}{\lambda}u_{xx} - \alpha u - \beta u^3 . \qquad (31)$$

Although the nonlinearity is now in an "on-site" potential rather than in the coupling term, this equation can be reduced to a NLS equation which shows modulational instability with the same type of multiple scale expansion as above. We will not present the calculation here because a similar (slightly more complicated) case will be discussed in the section on DNA denaturation.

3.4. Higher dimensions and discreteness

So far we have only considered one-dimensional cases and we have forgotten about the lattice discreteness through the continuum limit approximation. It turns out that, if one considers higher dimensions (for instance dimension two for surface melting) or include discreteness, the tendency to energy localization becomes even stronger.

Since the NLS equation has been applied to such physical problems as hydrodynamics, surface gravity waves, plasma physics, the question of its properties in dimension higher than one has been extensively studied. In multidimensional problems, the energy localization does not simply generate soliton solutions as discussed previously. It is much more dramatic and may lead to a *divergence* of $|\psi(\vec{r},t)|$ in a finite time known as *blow up*, or, in the context of plasma physics, *collapse*.

This phenomenon is easily observed in optics. The electric field of a beam propagating in the z direction in a nonlinear medium obeys a two-dimensional NLS equation [21]

$$2ik\frac{\partial E}{\partial z} + \left(\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2}\right) + \frac{3\varepsilon_2 k^2}{4\varepsilon_0}|E|^2 E = 0\,, \tag{32}$$

where k is the wavevector, ε_0 and ε_2 the linear and nonlinear coefficients of the dielectric constant. The blow-up appears in optics as a strong self-focusing of the beam which becomes extremely narrow while the energy density in its center increases so much that it can cause a breakdown of the medium (in this case an optical fiber breaks into pieces!). The same phenomenon is observed in plasmas. It leads to the formation of "hot spots" with a low density (called "caverns") which collapse in a finite time. The nature of the self focusing singularity, *i.e.* the exact law for the collapse has been analyzed in 1975 by Zakharov and Synakh [22] and studied later for wider classes of NLS equations with different dimensions and nonlinearities [23]. These studies show that it can occur in many physical models when the nonlinearities are sufficient.

However, when blow-up occurs in an evolution equation, it merely indicates that the assumptions made in the evolution equation break down. In a real physical system, the formation of the blow-up singularity is prevented by higher order nonlinearities, or dissipation. In the case of melting which concerns the dynamics of a lattice, the main physical feature which is absent from the NLS equation such as (16) or its counterparts in higher dimensions is the discreteness of the lattice which has been eliminated by the continuum limit approximation. Since it fixes a minimum length scale, discreteness will fix a lower limit to energy localization and therefore control the blow-up. Lattice discreteness can be restored in the equation describing the lattice dynamics at different levels. First, instead of starting from the partial differential equations (8) or (9), the multiple scale expansion can be performed directly of the lattice equations. This approach gives again a solution which has the form of a modulated wave, but the full discreteness is kept for the carrier wave which contains the fast space and time scales, while the continuum approximation is introduced only for the envelope which has a slow space variation [24]. This results again in the NLS equation for the envelope, but its coefficients P and Q are now functions of the wavevector of the carrier wave. The instability condition ($PQ > 0$) is only found for some range of the carrier wavevector, leading to a selection of the modes which tend to self-localize. A fully discrete NLS equation

$$i\frac{\partial \psi_n}{\partial t} + P(\psi_{n+1} + \psi_{n-1} - 2\psi_n) + Q|\psi_n|^2\psi_n = 0 \tag{33}$$

can also be derived in some limits for a nonlinear lattice [25] and used to determine conditions for instability which can then be checked with numerical simulations of the full lattice equations. In two-dimensional atomic lattices, little has been done yet to study the role of discreteness, but two-dimensional discrete NLS equations have been studied for electron transfer in molecular monolayers containing acceptor and donnor molecules [26]. Although the role of discreteness is not yet fully understood, the various studies confirm that a discrete lattice can indeed show spontaneous energy localization. Moreover, the chance for localization is generally found to be higher for a discrete lattice than for its continuum counterpart even though discreteness imposes a lower bound on the space scale over which energy concentrates.

Energy localization in a multi-dimensional system does not always lead to collapse. It has been shown recently that, in a nonlinear lattice of molecules that can rotate over a corrugated surface, modulational instability can generate two-dimensional breather modes which are very stable and have soliton-like properties in collisions [27]. This example shows that the Derick theorem forbidding permanent profile solitons in more than one dimension should not be invoked, as is done sometimes, to conclude that localized excitations cannot exit in most of the real systems because they are multidimensional.

The theoretical and experimental results that we have discussed in this section show that *spontaneous localization of energy in a nonlinear lattice is very likely to occur as soon as nonlinearities are sufficiently excited.* Depending on the conditions (dimension of the space, degree of nonlinearity), the phenomenon can lead to the formation of large amplitude soliton-like nonlinear excitations, or to a blow-up of the energy density which is only limited by discreteness or coupling to other degrees of freedom. Since the approach of the melting temperature is precisely a situation in which one can expect the lattice nonlinearity to play a large role, nonlinear energy localization deserves probably a better consideration in the theory of melting. The case of DNA denaturation, discussed in the next section, is interesting in this respect because it is an example in which the energy localization can be observed experimentally.

4. DNA thermal denaturation: a one-dimensional phase transition

DNA is central to all living beings, as it carries, for any species, all the information needed for birth, development, living and probably sets the average life-time of each species. Physically, DNA is a giant, double stranded linear macromolecule wound into the well known Watson-Crick double helix [28], with length ranging from millimeters (bacteria) to meters (humans) and even approaching kilometers (salamander). Yet DNA is always packed so as to fit a micrometer size space, either as a loose structure in procaryotes (bacteria), or in densely packed, dedicated unit, the nucleus, in eucaryotes (the more evoluted cells).

The genetic information (or coding sequence) of a gene is always deposited on one strand only of the double helix. Gene expression involves successively transcription — the gene is transcribed from the DNA by an enzyme, RNApolymerase (RNAP), onto a "messenger" RNA — and translation, the process by which the messenger is translated into the gene product (protein) by a special "factory", the ribosome. Gene expression is carefully controlled and regulated, to ensure supply of the gene product in amounts at the time and the place required by the actual circumstances (intra- or extracellular).

DNA transcription is a typical example in which the dynamics of the molecule is essential to a biological function since the double helix has to be locally opened in order to expose the coding bases to chemical reactions. This process is however very complex because it is activated by an enzyme and it is probably still beyond a detailed analysis. Thermal denaturation has some similarities with the transcription because it starts locally by the formation of a so-called "denaturation bubble" similar to the local opening occurring in the transcription. Therefore investigating thermal denaturation is a valid preliminary step toward the understanding of the transcription. At temperature well below the denaturation temperature, DNA shows also large amplitude motions known as "fluctuational openings" in which base pairs open for a very short time and then close again. There is a rather clear experimental evidence that these very large amplitude motions are highly localized [29] and involve only few base-pairs at a time. They correspond to the local modes created by energy localization discussed in the previous section. These motions are important because, when the base pairs reclose, they can trap some external molecules causing a defect in the sequence. This process has been proposed as a possible mechanism of chemical carcinogenesis [30]. The fluctuational openings can be considered as intrinsic precursors to the denaturation.

The denaturation or "melting" transition is the separation of the two complementary strands. It can be induced by heating or by changing the ionicity of the solvent. It has been extensively investigated experimentally and models have been proposed to explain the complicated denaturation curves found in the experiments [31]. However these models are essentially Ising-like where a base pair is considered as a two-state system which is either closed or open. Such an approach cannot reproduce the full dynamics of the denaturation and it relies on phenomenological parameters for the probability of opening or cooperative character of this opening, which are not easily derivable from first principle calculations.

On another hand, the nonlinear lattice dynamics of DNA has recently been the subject of many investigations based on the idea that vibrational energy might be trapped into solitary wave excitations. This idea, originally suggested by Englander *et al.* [32] to explain the open states of the DNA molecule, has given rise to many investigations using soliton-like solutions to describe open states, transition between the A and B forms, or energy transport along the molecule. Most of these investigations have focused on the *propagation* of solitons along the double helix. However the biological function of DNA does not necessarily involve transport along the molecule. Consequently, although it is clear that a realistic model will exhibit nonlinear effects owing to the very large amplitude motions known to exist, their ability to propagate along the helix is not a requirement of the model. Rather, for denaturation (and transcription) we are concerned by the *formation and growth* of these excitations. It is this question that I want to discuss in these lectures.

4.1. A simple model for DNA melting and its statistical mechanics

Let us consider an approach that goes further than the Ising models, but still keeps the model as simple as possible in an attempt to determine the fundamental mechanism of the melting. Therefore we consider a simplified geometry for the DNA chain in which we have neglected the asymmetry of the molecule and we represent each strand by a set of point masses that correspond to the nucleotides. The characteristics of the model are the following:

(i) The longitudinal displacements are not considered because their typical amplitudes are significantly smaller than the amplitudes of the smaller

transverse ones [33]. The stretching of a base-pair in the transverse direction is represented by a real variable y_n which can therefore describe all the states of the pair from closed ($y_n = 0$) to completely broken.

(ii) Two neighboring nucleotides of the same strands are connected by a harmonic potential to keep the model as simple as possible. On another hand, the bonds connecting the two bases belonging to different strands are extremely stretched when the double helix opens locally so that their nonlinearity must not be ignored. We use a Morse potential to represent the transverse interaction of the bases in a pair. It describes not only the hydrogen bonds but the repulsive interactions of the phosphate groups, partly screened by the surrounding solvent action as well. The hamiltonian of the model is then the following:

$$H = \sum_n \left[\frac{1}{2}m\dot{y}_n^2 + \frac{K}{2}(y_n - y_{n-1})^2 + D(\mathrm{e}^{-ay_n} - 1)^2\right]. \qquad (34)$$

Since we are interested in the thermal denaturation transition of the molecule, the natural approach is to investigate the statistical mechanics of the model. For a one-dimensional chain containing N units with nearest neighbor coupling, the classical partition function can be calculated by the transfer integral operator (TI) method [34, 36].

The calculation is similar to the one performed by Krumhansl and Schrieffer [37] for the statistical mechanics of the ϕ^4 field. For the potential part, it yields $\mathcal{Z}_y = \exp(-N\beta\epsilon_0)$, where ϵ_0 is the lowest eigenvalue of the transfer operator. We can then compute the free energy of the model as $\mathcal{F} = -k_\mathrm{B}T\ln\mathcal{Z} = -(Nk_\mathrm{B}T/2)\ln(2\pi mk_\mathrm{B}T) + N\epsilon_0$ and the specific heat $C_v = -T(\partial^2\mathcal{F}/\partial T^2)$. The quantity which gives a measure of the extent of the denaturation of the molecule is the mean stretching $\langle y_m\rangle$ of the hydrogen bonds, which can also be calculated with the transfer integral method [35].

In the continuum limit approximation, the TI eigenvalue problem can be solved exactly, but experiments on proton exchange in DNA [29] show some evidence of exchange limited to a single base pair which suggests that discreteness effects can be extremely large in DNA. Therefore we have solved numerically the eigenvalue equation of the transfer operator without approximations. The TI operator is symmetrized and the integral is replaced by sums of discrete increments, using summation formulas at different orders. The problem is then equivalent to finding the eigenvalues and eigenvectors of a symmetric matrix.

Figure 5 compares the thermal evolution of $\langle y_m\rangle$ obtained with the continuum approximation and the exact numerical calculation, for the model parameters discussed in the next section. Both methods show a divergence of the hydrogen bond stretching over a given temperature, but the melting

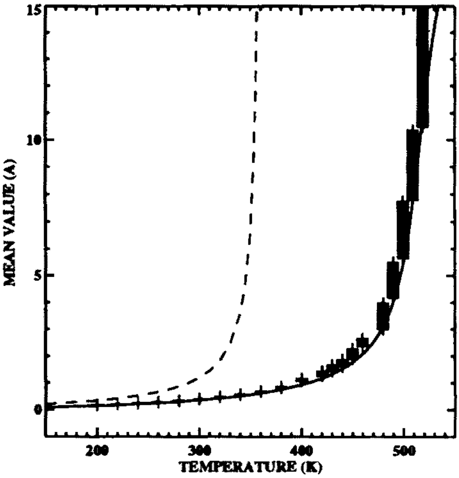

Fig. 5. Variation of $\langle y \rangle$ versus temperature: the dash line corresponds to the TI results in the continuum limit, the solid line gives the exact TI results obtained by numerical solution of the TI operator, and the plus signs correspond to molecular dynamics simulations.

temperature given by the numerical treatment is significantly higher, pointing out the large role of discreteness in DNA dynamics if one uses realistic parameters for the model. The TI calculation shows that the specific heat has a broad maximum around the denaturation temperature.

4.2. Energy localization in the DNA molecule

The thermodynamics of our DNA model shows that it exhibits a thermal evolution that is qualitatively similar to the denaturation of the molecule observed experimentally. But this statistical approach does not give informations on the *mechanism* of the denaturation, and in particular, does it start locally by the formation of denaturation bubbles in agreement with the experiments. In order to study this aspect, we have investigated the dynamics of the model in contact with a thermal bath by molecular dynamics simulation with the Nose method [38]. Most of the simulations have been performed with a chain of 256 base pairs with periodic boundary conditions, but in order to achieve better statistics, some simulations have been performed on a Connection Machine-200 with 16384 base pairs.

We have chosen a system of units adapted to the energy and time scales of the problem. Energies are expressed in eV, masses in atomic mass unit (a.m.u.) and length in Å. The resulting time unit is 1 t.u. = 1.0214 10^{-14}s. The choice of appropriate model parameters is a very controversial topic, as attested by the debate in the literature [39]. There are well established

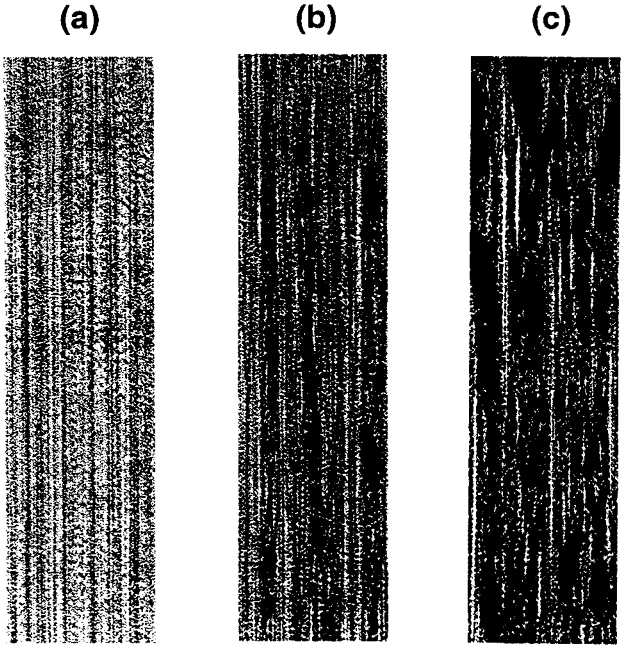

Fig. 6. Results of molecular dynamics simulations at three different temperatures (a) $T = 150$ K, (b) $T = 340$ K, (c) $T = 450$ K. The horizontal axis indicates the position along the 256 cells of the molecule and the vertical axis indicates time. The stretching y_n of the base pairs along the molecule is indicated by a grey scale, the lighter grey corresponding to $y \leq -0.1$ Å and black indicating $y \geq 1$ Å. Therefore black regions show broken base-pairs.

force fields for molecular dynamics of biological molecules, but they have been designed to provide a good description of the *small* amplitude motions of the molecule and are not reliable for the very *large* amplitude motions involved in the denaturation. In our model, the Morse potential is an effective potential which links the two strands. It results from a combination of an attractive part due to the hydrogen bonds between two bases in a pair and the repulsive interaction between the charged phosphate groups on the two strands. The potential for the hydrogen bonds can be rather well estimated but the repulsive part is harder to determine because the repulsion is partly screened by ions of the solvent. Consequently we had to rely on estimations. The parameters that we use have been chosen to give realistic properties for the model in terms of vibrational frequencies, size of the open regions, *etc*, but future work will be needed to confirm our choice. We do not expect however that a better choice would change *qualitatively* the results presented here. The parameters that we have chosen are: a dissociation energy $D = 0.04$ eV, a spatial scale factor of the Morse potential

$a = 4.45$ Å^{-1}, a coupling constant $K = 0.06$ eV/Å, a mass $m = 300$ a.m.u. The constant of the Nose thermostat has been set to $M = 1000$.

Figure 6 shows a time evolution of the dynamics of the model at three temperatures. The stretching of the base pairs is indicated by a grey scale, darker dots corresponding to larger stretching.

Looking at this figure, one notices immediately two major features. First, as one moves along an horizontal direction, *i.e.* along the molecule for a given time, the amplitude of the stretching varies very much from site to site. This is especially true at high temperature, but it is still noticeable at 150 K, well below the melting temperature. This shows that there is *no equipartition of energy in this nonlinear system on a time-scale which is very long with respect to typical periods of the molecular motions*, but on the contrary a tendency for the energy to localize at some points which is more and more pronounced as temperature increases. However, the "hot-spots" due to nonlinear energy localization are dynamical entities. They, move, appear and die, and on a *macroscopic time-scale* one can consider that the average energy of all the sites is the same. At high temperature, the figure shows large black regions which correspond to denaturated regions of the molecule. These black areas are the denaturation bubbles observed experimentally. At the highest temperature shown here (Fig. 6(c)) they extend over 20 to 50 base pairs and their boundaries are sharp. If the temperature is raised slightly above 540 K, the bubbles grow even more and finally extend over the whole chain: the molecule is completely denaturated.

The second remarkable feature on Fig. 6 can be observed by moving along a vertical line on the figure *i.e.* following the time evolution of a given base pair. If one choses one region of the molecule in which the energy is concentrated, one can see alternating black and light-grey dots. This is due to an *internal breathing* of the localized excitations that oscillate between a large amplitude (black dots in the figure) and a small amplitude state (light dots) in a regular manner. These motions are the fluctuational openings of DNA. They exist even well below the denaturation temperature and coexist with denaturated bubbles in the high temperature range. Fig. 6(b) shows that they play the role of precursor motions for the formation of the bubbles.

The calculation of the dynamical structure factor from the molecular dynamics results exhibits two types of excitations. In the high frequency range, one recognizes the phonon modes corresponding to linear motions of the chain. At low temperature their dispersion curve is well described by the linear dispersion curve resulting from the equations of motions of the model. Close to melting, on the contrary, most of the chain is on the plateau of the Morse potential and therefore experiences almost no restoring force that brings it back to $y = 0$. The dispersion curve is then the dispersion relation of a chain of harmonically coupled particles, without a substrate potential, *i.e.* a dispersion relation without gap. This is clearly observed in the molecular dynamics simulations and results in a phonon softening which should be observable experimentally in the vicinity of DNA melting transition. The second characteristic feature of the dynamical structure factor is a low frequency peak, associated to the fluctuational opening, which shifts to zero frequency as the denaturation bubbles form near the melting point.

The results of the molecular dynamics simulations illustrate the phenomenon of nonlinear energy localization discussed above and shows how it can drive a "melting transition". The localized "breathing modes" which are formed spontaneously in the system can be studied with standard methods of nonlinear dynamics. They are approximately described by soliton solutions of a nonlinear Schrödinger equation [40].

4.3. Is DNA melting a one-dimensional phase-transition?

The model discussed above has been able to describe some of the main features of DNA melting as it is observed experimentally. However there is a crucial point in which this model gives incorrect results, it is the *sharpness* of the phase transition. For an homopolymer, the experiments show that the melting occurs very abruptly over a temperature interval which is only a few K or even less. This poses a very fundamental question since DNA is basically a one dimensional system, which is not expected to have a phase transition. I want now to show that, *within a one-dimensional model with short range interactions*, a sharp transition is possible if one takes into account properly the nonlinearity of the base stacking interaction [41]. The possibility of a phase transition in one-dimensional DNA was already examined within the Ising-model approach by Poland and Scheraga [42] and Azbel [43] who concluded that it can be attributed to cooperativity effects and to the role of the winding entropy released when the two strands separate. Another view of this problem was proposed by Kosevich and Galkin [44] who showed that, for a double chain like DNA, one must not forget that the strands, when they are separated to form bubbles, explore a three-dimensional space. Therefore, although the model looks one-dimensional, when one counts the accessible states in the phase space this three-dimensional character appears. In our simple model, a corresponding feature comes from the Morse potential. When a portion of the chain is on the plateau of the Morse potential, it moves in fact in a two-dimensional space. Therefore the possibility of a phase transition cannot be ruled out. The interesting result is that it *does* exist provided the intra-strands interaction contain some nonlinearity. A simple extension of our DNA model (Eq. (34)) can describe the dynamics of these effects an gives a very sharp transition in agreement with the experiments. The stacking energy between two neighboring base pairs is described by the anharmonic potential:

$$W(y_n, y_{n-1}) = \frac{K}{2}\left(1 + \rho e^{-\alpha(y_n + y_{n-1})}\right)(y_n - y_{n-1})^2 . \tag{35}$$

This new intersite coupling, replacing the simple harmonic coupling of our previous approach, is responsible for qualitatively different properties. The choice of this potential has been motivated by the observation that the stacking energy is not a property of *individual* bases, but a character of the base *pairs* themselves [45]. When the hydrogen bonds connecting the bases break, the electronic distribution on bases are modified, causing the stacking interaction with adjacent bases to decrease. In Eq. (35), this effect is enforced by the prefactor of the usual quadratic term $(y_n - y_{n-1})^2$. This prefactor depends on the *sum* of the stretchings of the two interacting base pairs and decreases from $\frac{1}{2}K(1+\rho)$ to $\frac{1}{2}K$ when either one (or both) base pair is stretched. Although its form was chosen for analytical convenience, the qualitative features of potential (35) are in agreement with the properties of chemical bonds in DNA. They also provide the cooperativity effects that were introduced phenomenologically in the Ising models. A base pair that is in the vicinity of an open site has lower vibrational frequencies, which reduces its contribution to the free energy. Simultaneously a lower coupling along the strands gives the bases more freedom to move independently from each other, causing an entropy increase which drives a sharp transition.

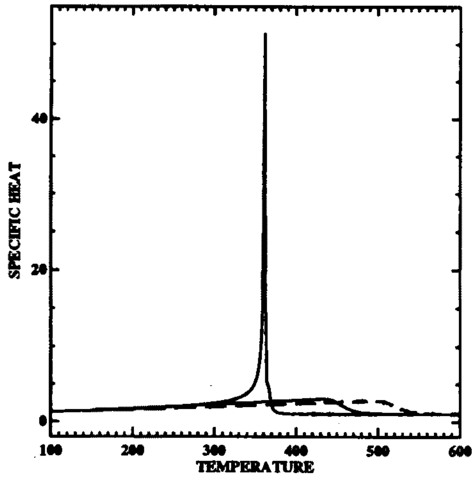

Fig. 7. Variation of the specific heat versus temperature for the DNA model. The very narrow peak corresponds to the anharmonic coupling case ($\alpha = 0.35, \rho = 0.5$), the dotted curve and the solid broad peak to harmonic coupling ($k' = 1.5k$ and $k'' = k$, respectively).

Our approach can be compared to recent views on structural phase transition in elastic media which stress that intrinsic nonlinear features characterize the physics of these transformations, and extend the standard soft mode picture [46]. It is important to notice that, although cooperativity in introduced through purely *nearest neighbor* coupling terms, it has a remarkable effect on the 1D transition. Figure 7 shows the drastic change introduced by the anharmonic coupling on the specific heat of the model calculated by the transfer integral method [41].

The full curve corresponding to the anharmonic stacking interaction shows a sharp peak very similar to that one would expect from a first-order phase transition, whereas the harmonic coupling investigated before gives only a smooth maximum. This result suggests that, although DNA structure is very complicated, a simple nonlinear model is able to reproduce with a good agreement the main experimental features of its dynamics for the fluctuational openings as well as the melting curves.

5. Conclusion

When it was discovered in 1965, the soliton generated a great enthusiasm. However, up to know, it has been essentially observed at a macroscopic level in hydrodynamics or optics. In these domains, it really brings new results and the theoretical studies have even suggested new experiments or new devices in which the solitons play a major role. This is the case for optical communications using solitons, or the generation of ultrashort optical pulses in femtosecond lasers which can be described in terms of the two-soliton solution of the NLS equation. At the microscopic level on the contrary the role of solitons in the statistical mechanics of solids is more limited, except in magnetic systems where there are clear signatures of solitons in nuclear magnetic resonance experiments or in neutron diffusion [47]. The direct observation of solitons in lattice dynamics is rather difficult and apart from the experience of Narayanamurti and Varma [11], the propagation of soliton-like excitations has not been clearly demonstrated although they are believed to play a large role in some properties of solids, like the central peak in ferroelectrics [50].

I believe that the interest for nonlinear excitations in solids will be strongly revived by the concept of *local modes* which is directly connected to the nonlinear energy localization discussed in these lectures. Since the original work of Kosevich and Kovalev [48] and the rediscovery of intrinsic localized modes by Takeno and Sievers [49] 13 years later, the topic has been expanding very fast, and the possibility to have stable localized modes have been found in many systems. These modes, which are breathing modes, *i.e.* modes with an internal oscillations are not restricted to one-dimensional systems. They can form by spontaneous localization of thermal energy when a sufficient level of excitation is reached and are therefore good candidates for a new approach to the theory of melting. When one thinks in terms of local modes, it is rather simple to understand the seemingly surprising Lindemann criterion saying that a crystal melts when the amplitude of the thermal fluctuations is of the order of 10% of the lattice spacing. If one assumes that the thermal energy is uniformly distributed among the various degrees of freedom, it is difficult to explain how such a "small" displacement can cause the destruction of the lattice. But, if the same amount of thermal energy self-focuses into spatially localized modes, in some places of the crystal the amplitude can become very high and cause melting.

The example of DNA denaturation provides an example where the analysis is sufficiently simple because a one-dimensional model can be used, and where experiments can probe the existence of local modes. The model has also shown the crucial role of the nonlinear interaction to change the nature of the transition. One may wonder whether a similar effect could not be introduced in the Kosterlitz Thouless theory of melting, which gives a smooth transition, to modify the nature of the transition and find an abrupt transition in better agreement with the experiments.

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Appendix A

Derivation of the KdV equation for a nonlinear lattice

We consider a one-dimensional lattice of particles of mass m, coupled by the potential

$$V(r) = \tfrac{1}{2}K_2 r^2 + \tfrac{1}{3}K_3 r^3 + \tfrac{1}{4}K_4 r^4 \,, \tag{A1}$$

where r is the interatomic distance. Denoting by $u_i(t)$ the displacement of atom i with respect to its equilibrium position, its equation of motion is

$$\begin{aligned} m\ddot{u}_i &= K_2(u_{i+1} + u_{i-1} - 2u_i) \\ &+K_3\left[(u_{i+1} - u_i)^2 - (u_i - u_{i-1})^2\right] + K_4\left[(u_{i+1} - u_i)^3 - (u_i - u_{i-1})^3\right] . \end{aligned} \tag{A2}$$

If we introduce the dimensionless displacement v by $u/h = av$ where h is the lattice spacing, and $a \ll 1$ gives the scale of the displacement, we get

$$\begin{aligned}\ddot{v}_i =&\frac{K_2}{m}\Big\{(v_{i+1}+v_{i-1}-2v_i)\\ &+\frac{aK_3h}{K_2}\left[(v_{i+1}-v_i)^2-(v_i-v_{i-1})^2\right]\\ &+\frac{a^2K_4h^2}{K_2}\left[(v_{i+1}-v_i)^3-(v_i-v_{i-1})^3\right]\Big\}\,. \end{aligned} \tag{A3}$$

We are interested in displacements which show only a small variation from one site to the next, which allows us to use a continuum limit approximation, *i.e.* replace the discrete set of functions $v_i(t)$ by a function $v(x,t)$ depending continuously on space as well as time. Let us introduce dimensionless space and time variables by

$$X=\frac{\epsilon x}{h}\,,\qquad \theta=\frac{ct}{h}\,, \tag{A4}$$

where c defined by $K_2/m = c^2/h^2$, which has the dimensions of a velocity, is the speed of sound (long wavelength linear excitations of the lattice) and $\epsilon \ll 1$ is introduced to express in a mathematical sense the slow spatial variation of the fuction v. In terms of these new variables, $\partial^2 v/\partial t^2$ becomes $(c^2/h^2)(\partial^2 v(X,\theta)/\partial\theta)$, and $v_{i\pm1}(\theta)$ is expressed with a Taylor expansion of $v(X,\theta)$ around $X_i = ih$

$$\begin{aligned}v_{i\pm1}(\theta) =&v[\epsilon(\frac{x_i\pm h}{h}),\theta]=v(X_i\pm\epsilon,\theta)\\ =&v(X_i,\theta)\pm\epsilon\frac{\partial v}{\partial X}(X_i)\frac{1}{2}\epsilon^2\frac{\partial^2 v}{\partial X^2}(X_i)\\ &\pm\frac{1}{6}\epsilon^3\frac{\partial^3 v}{\partial X^3}(X_i)+\frac{1}{24}\epsilon^4\frac{\partial^4 v}{\partial X^4}(X_i)+O(\epsilon^5)\,. \end{aligned} \tag{A5}$$

Consequently we have

$$v_{i+1}(\theta)+v_{i-1}(\theta)-2v_i(\theta)=\epsilon^2\frac{\partial^2 v}{\partial X^2}(X_i)+\frac{\epsilon^4}{12}\frac{\partial^4 v}{\partial X^4}(X_i)+O(\epsilon^6)\,, \tag{A6}$$

and, from

$$(v_{i+1}-v_i)=\epsilon^2\frac{\partial v}{\partial X}(X_i)+O(\epsilon^3)\,, \tag{A7a}$$

$$(v_i-v_{i-1})=\epsilon^2\frac{\partial v}{\partial X}(X_{i-1})+O(\epsilon^3) \tag{A7b}$$

with a second Taylor expansion for the derivatives, we get

$$(v_{i+1} - v_i)^2 - (v_i - v_{i-1})^2 = \epsilon^2 \left[\epsilon \frac{\partial}{\partial X}\left(\frac{\partial v}{\partial X}(X_i)\right)^2 + O(\epsilon^2)\right]$$
$$= \epsilon^3 \frac{\partial}{\partial X}\left[\frac{\partial v}{\partial X}(X_i)\right]^2 + O(\epsilon^4)\,. \tag{A8}$$

Similarly we get

$$(v_{i+1} - v_i)^3 - (v_i - v_{i-1})^3 = \epsilon^4 \frac{\partial}{\partial X}\left[\frac{\partial v}{\partial X}(X_i)\right]^3 + O(\epsilon^5)\,. \tag{A9}$$

As explained in the text, we assume that the third order nonlinearity is small and define $K_3 h/K_2 = \epsilon p/2$, while the quartic nonlinearity is taken of order 1 by setting $K_4 h^2/K_2 = q/3$. Introducing the different expressions calculated above into Eq. (A3), keeping only the terms up to order ϵ^4, and dividing by $c^2/h^2 = K_2/m$, we obtain

$$\frac{\partial^2 v}{\partial \theta^2} = \epsilon^2 \frac{\partial^2 v}{\partial X^2}\left[1 + \epsilon^2 a p \frac{\partial v}{\partial X} + \epsilon^2 a^2 q \left(\frac{\partial v}{\partial X}\right)^2\right] + \frac{\epsilon^4}{12}\frac{\partial^4 v}{\partial X^4} + O(\epsilon^5)\,. \tag{A10}$$

This equation is still difficult to solve, but it can be put into a simpler form by changing to the frame moving at the speed of sound c. In the absence of dispersion and nonlinearity, any deformation v propagates in the lattice at the speed of sound and therefore it appears as static in the frame which moves at velocity c. Here we consider a case with weak dispersion and weak nonlinearity. This can been seen from Eq. (A10) because the dispersive and nonlinear terms are of order ϵ^4. Therefore, we can expect that a deformation v will change very slowly in the frame moving at the speed of sound. This can be made quantitative by looking for a solution which is function of a "slow time" $\tau = \epsilon^3 \theta$. The change of frame means that the space variable is $\xi = (\epsilon/h)(x - ct) = X - \epsilon\theta$, and the space and time derivatives are modified accordingly

$$\frac{\partial}{\partial X} = \frac{\partial}{\partial \xi} \tag{A11}$$
$$\frac{\partial^2}{\partial \theta^2} = \epsilon^6 \frac{\partial^2}{\partial \tau^2} - 2\epsilon^4 \frac{\partial^2}{\partial \xi \partial \tau} + \epsilon^2 \frac{\partial^2}{\partial \xi^2}\,. \tag{A12}$$

If these expressions are introduced into Eq. (A10) for which only terms up to order 4 must be conserved since we have already dropped some terms of the order ϵ^5, we find that the term $v_{\xi\xi}$, which is of order ϵ^2 cancels on both sides and, if we define $w = v_\xi$ the remaining terms, which are all of order ϵ^4 give the equation

$$w_\tau + \tfrac{1}{2}apww_\xi + \tfrac{1}{2}qa^2w^2w_\xi + \tfrac{1}{24}w_{\xi\xi\xi} = 0\,, \tag{A13}$$

which is Eq. (9) of Section 3.1. If we consider an interatomic potential (A1) without the quartic term as for the FPU problem, *i.e.* we set $q = 0$, Eq. (A13) reduces to the KdV equation (5) of Section 2.2. The final equation is not invariant with respect to time reversal while the initial one was, but one must keep in mind that Eq. (A13) is written in a frame moving at the speed of sound c. In this frame, a solution with positive velocity is a supersonic signal in the original lattice, while a solution with a negative velocity is a subsonic signal in the lattice. The KdV solitons are *always supersonic* signals.

Appendix B

Multiple scale analysis of the modified KdV equation

We present here in details the calculation that was only sketched in Section 3.1. We start from equation (9) and expand the solution in a series of terms ordered with the powers of a,

$$w = w_0 + a\,w_1 + a^2\,w_2 + \cdots\,. \tag{B1}$$

The physical variables ξ and τ are also replaced by a set of independent variables at the different scales

$$w(\xi,\tau) = w(\xi_0,\tau_0,\xi_1,\tau_1,\xi_2,\tau_2\cdots)\,, \tag{B2}$$

with

$$\xi_0 = \xi\,, \qquad \tau_0 = \tau\,, \tag{B3a}$$
$$\xi_1 = a\xi\,, \qquad \tau_1 = a\tau\,, \tag{B3b}$$
$$\xi_2 = a^2\xi\,, \qquad \tau_2 = a^2\tau\,. \tag{B3c}$$

The derivatives are modified accordingly, *i.e.*

$$\begin{aligned}\frac{\partial}{\partial\tau} &= \frac{\partial}{\partial\tau_0} + a\frac{\partial}{\partial\tau_1} + a^2\frac{\partial}{\partial\tau_2} + \cdots \\ &= D_0 + aD_1 + a^2D_2 + \cdots\,,\end{aligned} \tag{B4a}$$

$$\begin{aligned}\frac{\partial}{\partial\xi} &= \frac{\partial}{\partial\xi_0} + a\frac{\partial}{\partial\xi_1} + a^2\frac{\partial}{\partial\xi_2} + \cdots \\ &= \Delta_0 + a\Delta_1 + a^2\Delta_2 + \cdots\,,\end{aligned} \tag{B4b}$$

where we have introduced the simpler notations D for a time derivative and Δ for a space derivative with an index to specify with respect to which variable the derivative is calculated. With this notation $\partial^3/\partial\xi^3$ becomes

$$\frac{\partial^3}{\partial\xi^3} = \Delta_0^3 + 3a\Delta_0^2\Delta_1 + 3a^2\Delta_0^2\Delta_2 + 3a^2\Delta_0\Delta_1^2 + O(a^3)\,. \tag{B5}$$

Introducing these expressions in the equation of motion (9) and identifying the successive powers of a, we get

Order a^0:

$$D_0 w_0 + \tfrac{1}{24}\Delta_0^3 w_0 = 0 \tag{B6}$$

which has the solution

$$w_0 = A(\tau_1, \tau_2, \cdots \xi_1 \xi_2 \cdots) \exp\big(i(k_0\xi_0 - \omega_0\tau_0)\big) + \text{C. C.}, \tag{B7}$$

provided that $\omega_0 = -k_0^3/24$.

Order a^1:

$$D_0 w_1 + \tfrac{1}{24}\Delta_0^3 w_1 = -D_1 w_0 - \tfrac{1}{2} p w_0 \Delta_0 w_0 - \tfrac{3}{24}\Delta_0^2\Delta_1 w_0\,. \tag{B8}$$

In this equation we can replace w_0 by its value (B7) and solve for w_1, but the r.h.s. of Eq. (B8) contains terms with a factor $\exp i(\omega_0\tau_0 - k_0\xi_0)$ which are resonant terms for the linear operator of the l.h.s. These terms *must* vanish because otherwise w_1 will diverge in time and the perturbation expansion breaks down. Canceling these secular terms gives a first equation for A

$$-\frac{\partial A}{\partial \tau_1} + \frac{3}{24}k_0^2\frac{\partial A}{\partial \xi_1} = 0\,, \tag{B9}$$

which means that, concerning the variables at order ϵ, the envelope A is a function of the variable $\xi_1' = \xi_1 - V_g\tau_1$, where $V_g = -3k_0^2 4/2$ is the group velocity of the carrier wave of frequency ω_0 and wavevector k_0. Once the secular terms have been canceled, the equation at order a simplifies into

$$D_0 w_1 + \frac{1}{24}\Delta_0^3 w_1 = i k_0 \frac{p}{2} A^2 \exp\big(2i(k_0\xi_0 - \omega_0\tau_0)\big) + \text{C.C.} \tag{B10}$$

which has the solution

$$w_1 = \frac{2}{k_0^2} p A^2 \exp\big(2i(k_0\xi_0 - \omega_0\tau_0)\big) + \text{C.C.}. \tag{B11}$$

Order a^2:

$$\begin{aligned} D_0 w_2 + \frac{1}{24}\Delta_0^3 w_2 = &- D_1 w_1 - D_2 w_0 - \frac{1}{2} p w_0 (\Delta_0 w_1 + \Delta_1 w_0) \\ &- \frac{1}{2} p w_1 \Delta_0 w_0 - \frac{1}{2} q w_0^2 \Delta_0 w_0 - \frac{3}{24}\Delta_0^2\Delta_1 w_1 \\ &- \frac{3}{24}\Delta_0^2\Delta_2 w_0 - \frac{3}{24}\Delta_0\Delta_1^2 w_0\,. \end{aligned} \tag{B12}$$

This linear differential equation for w_2 can be solved since we know the r.h.s., *i.e.* w_0 and w_1, but, as for the order a^1, the r.h.s. contains secular terms in $\exp i(k_0\xi_0 - \omega_0\tau_0)$, which must be canceled to prevent a divergence of w_2. Identifying these secular terms and setting them to 0 gives

$$-\frac{\partial A}{\partial \tau_2} - \frac{1}{2} i k_0 \frac{2p^2}{k_0^2} A^2 A^* + i k_0 \frac{q}{2} A^2 A^* + \frac{3}{24} k_0^2 \frac{\partial A}{\partial \xi_2} - \frac{3}{2} i k_0 \frac{\partial^2 A}{\partial \xi_1^2} = 0 \qquad \text{(B13)}$$

which can be written also as

$$i\left[\frac{\partial A}{\partial \tau_2} - \frac{3}{24} k_0^2 \frac{\partial A}{\partial \xi_2}\right] + \frac{1}{2} k_0 \left[q - \frac{2p^2}{k_0^2}\right] |A|^2 A + \frac{3}{24} k_0 \frac{\partial^2 A}{\partial \xi_1^2} = 0\,. \qquad \text{(B14)}$$

Since we have noticed that, according to Eq. (B9), A could be naturally expressed in a frame moving at speed V_g, we change to such a frame, *i.e.* we introduce new variables

$$\xi' = \xi + \frac{3}{24} k_0^2 \tau\,, \qquad \tau' = \tau\,, \qquad \text{(B15)}$$

In this frame, Eq. (B14) simplifies into

$$i\frac{\partial A}{\partial \tau_2'} + \frac{1}{2} k_0 \left[q - \frac{2p^2}{k_0^2}\right] |A|^2 A + \frac{3}{24} k_0 \frac{\partial^2 A}{\partial \xi_1'^2} = 0 \qquad \text{(B16)}$$

which is the Nonlinear Schrödinger equation (15) with $A = \psi_1$.

Appendix C

Modulational Instability in the NLS equation

Let us start from the NLS equation

$$i\frac{\partial \psi}{\partial t} + P\frac{\partial^2 \psi}{\partial x^2} + Q|\psi|^2\psi = 0\,. \qquad \text{(C1)}$$

The plane wave

$$\psi = A_0 \exp\big(i(\kappa x - \Omega t)\big)$$

is a solution of Eq. (C1) if $\Omega = P\kappa^2 - QA_0^2$. In order to study the stability of this solution we look for the time evolution of a small perturbation of its amplitude or phase. This is done by chosing

$$\begin{aligned}\psi(x,t) &= [A_0 + b(x,t)] \exp\big(i[\Omega t + \kappa x + \theta(x,t)]\big)\\ &= [A_0 + b(x,t)] \mathrm{e}^{i\Phi}\,, \end{aligned} \qquad \text{(C3)}$$

where $b(x,t)$ and $\theta(x,t)$ are supposed sufficiently small so that we can keep only the expressions which are firts order in b and θ. Therefore we have

$$\begin{aligned}
\frac{\partial\psi}{\partial t} &= \frac{\partial b}{\partial t}\mathrm{e}^{i\Phi} + i\Omega(A_0+b)\mathrm{e}^{i\Phi} + i\frac{\partial\theta}{\partial t}\mathrm{e}^{i\Phi} + O(b^2,\theta^2,b\theta)\\
\frac{\partial^2\psi}{\partial x^2} &= \frac{\partial^2 b}{\partial x^2}\mathrm{e}^{i\Phi} + i\kappa\frac{\partial b}{\partial x}\mathrm{e}^{i\Phi} - \kappa^2(A_0+b)\mathrm{e}^{i\Phi} - \kappa\frac{\partial\theta}{\partial x}A_0\mathrm{e}^{i\Phi}\\
&\quad + i\kappa\frac{\partial b}{\partial x}\mathrm{e}^{i\Phi} + i\frac{\partial^2\theta}{\partial x^2}A_0\mathrm{e}^{i\Phi} - \kappa\frac{\partial\theta}{\partial x}A_0\mathrm{e}^{i\Phi} + O(b^2,\theta^2,b\theta)\\
|\psi|^2\psi &= (A_0^3+3A_0^2b)\mathrm{e}^{i\Phi} + O(b^2,\theta^2,b\theta)
\end{aligned}$$

Introducing these expressions in Eq. (B16), the cancellation of the real part gives

$$\begin{aligned}
-\Omega(A_0+b) + P\frac{\partial^2 b}{\partial x^2} + QA_0^2(A_0+b) - A_0\frac{\partial\theta}{\partial t}&\\
-P\kappa^2(A_0+b) - 2P\kappa A_0\frac{\partial\theta}{\partial x} + 2QA_0^2b = 0\,, &\qquad (C4)
\end{aligned}$$

and the cancellation of the imaginary part gives

$$\frac{\partial b}{\partial t} + 2\kappa P\frac{\partial b}{\partial x} + PA_0\frac{\partial^2\theta}{\partial x^2} = 0\,. \qquad (C5)$$

But the three first terms of Eq. (C4) cancel because of the dispersion relation connecting Ω and κ (here for a wave of amplitude A_0+b). The remaining system of linear differential equations for $b(x,t)$ and $\theta(x,t)$ has solutions of the form

$$b = b_0\mathrm{e}^{i(\delta x-\nu t)} + \text{C.C.}\,,\qquad \theta = \theta_0 e^{i(\delta x-\nu t)} + \text{C.C.}\,, \qquad (C6)$$

where b_0 and θ_0 obey an homogeneous system of algebraic equation which has only a trivial zero solution unless its determinant vanishes, which gives the condition

$$(2\kappa P\delta-\nu)^2 = P\delta^2(P\delta^2-2A_0^2Q)\,. \qquad (C7)$$

connecting the parameters δ and ν of the modulation to the coefficients P and Q of the NLS equation. The plane wave is stable only if ν is real. If this is not true, among the two roots in ν, one has a positive imaginary part which causes an divergence of the perturbation. As discussed in Section 3.2., an inconditional stability (stability for all modulation wavevectors δ) can only be achieved if the condition $PQ>0$ is satisfied.

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