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TITLE: DAVYDOV SOLITONS AT 300 KELVIN: THE FINAL SEARCH

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DAVYDOV SOLITONS AT 300 KELVIN: THE FINAL SEARCH

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The original proposal by Professor A. S. Davydov of a soliton mechanism for localization and transport of energy along linear chain molecules provided the impetus for several research efforts which have explored the properties of these nonlinear entities in differing degrees of realism. The general conclusion from all of this work is that the nonlinear equations of motion which have been used to describe these systems have soliton-like solutions when they are solved in the deterministic limit. This limit corresponds to the absolute zero of temperature, because it ignores the influence of random thermal perturbations on the system. However, the questions of existence and importance of the Davydov soliton remain controversial when non-zero temperature effects are taken into account, because numerical simulations and theoretical calculations done by independent research groups have reached diametrically opposed conclusions.

Our 1985 paper[1] was the first to simulate thermal perturbations at biologically relevant temperature (300 K). Since publishing that paper, we have done simulations for collisions of phonon wave packets with Davydov solitons and have also taken into account the presence of multiple quanta of the high frequency oscillator field in the Davydov equations of motion. We present these results here. However, for the major question about the temperature effects on the Davydov soliton, our conclusions remain unchanged from Ref. 1. We feel that we can not improve upon what we said there, so we refer the reader to that paper for a detailed discussion.

As explained in our other contribution in this volume, the multi-quantum Davydov *Ansatz* is

$$|\psi(t)\rangle = \left[\sum_n a_n(t) B_n^\dagger\right]^Q \exp\left\{-\frac{i}{\hbar}\sum_j \left[\beta_j(t)p_j - \pi_j(t)u_j\right]\right\}|0\rangle, \tag{1}$$

We insert this into the time-dependent Schroedinger equation using the Froehlich Hamiltonian and obtain the following equations of motion for the functions appearing in

(1).

$$m\ddot{\beta}_n = w(\beta_{n+1} - 2\beta_n + \beta_{n-1}) + \chi Q(|a_{n+1}|^2 - |a_{n-1}|^2), \tag{2a}$$

$$i\hbar\dot{a}_n = -J(a_{n+1} + a_{n-1}) + \chi(\beta_{n+1} - \beta_{n-1})a_n. \tag{2b}$$

To describe the interaction of the system with a thermal reservoir at temperature T, we have added a damping force and a noise force,

$$F_n = -m\Gamma\dot{\beta}_n + \eta_n(t), \tag{3}$$

to (2a) for the molecular displacements. We have taken the correlation function for the random force to be

$$<\eta_n(t)\eta_{n'}(t')> = 2m\Gamma k_B T\delta_{nn'}\delta(t-t') \tag{4}$$

(k_B is Boltzmann's constant). This extension converts (2a) to Langevin equations. The effect of the two terms in (3) is to bring the system to thermal equilibrium; we have verified numerically that over sufficiently long time intervals the mean kinetic energy satisfies

$$<\sum_n \frac{1}{2}m\dot{\beta}_n^2(t)> = \frac{1}{2}Nk_B T \tag{5}$$

(< · · · > denotes time average). Eqs. (2) with (3) included still imply the conservation of the norm $<\psi(t)|\psi(t)>$. The number of high frequency quanta present is

$$<\psi(t)|\sum_n B_n^{\dagger}B_n|\psi(t)> = Q \tag{6}$$

Our equations involve the combination of (4) and (5), which are the classical fluctuation-dissipation relation, with (2), which are obtained quantum mechanically. The justification for doing this is that for parameter values near those appropriate for the α helix a quantum of the highest-frequency acoustic mode $\hbar\omega_{max}$ is around 100 K. If we solve the equations at 300 K, then the occupation numbers of *all* phonon modes are accurately given by the classical distribution, and in that situation (5) is valid. The use of (5) for temperatures below, say, 200 K would not be valid because of quantum corrections to the phonon occupation numbers, but such temperatures are not biologically relevant. This point was emphasized in our original paper.

We have solved the set of stochastic differential equations in (2), (3), and (4) using techniques developed by Greenside and Helfand.[3] The solutions were done for a chain of 100 sites with periodic boundary conditions. The parameters used are given in Table I; in addition the mass was always taken to be 114 proton masses ($m = 1.904\times10^{-25}$ kg). The rate of spatial variation of the variables is determined by the ratio χ^2/wJ, which is given in the table. The quantity t_0 is $\sqrt{(m/w)}$ and is the time unit used for the calculations. The only parameter not determined from other considerations is the damping rate Γ in (4). We have used the (dimensionless) value $\Gamma = 0.005$, which is chosen so that the lowest (non-zero) phonon on our 100 site chain is substantially underdamped. This criterion is admittedly size dependent. However, since the self-trapping feature we want to study involves predominantly short wavelength phonons, we want to be sure that the damping force is not the major determinant of the evolution of those phonons. Furthermore, we have varied Γ from 0.0025 to 0.05 and have found no qualitative change in the results described nere.

Table I. Parameter values.			
	Discrete	Continuum	α-helix
w (N/m)	5.0	13.0	13.0
J (cm $^{-1}$)	20.0	31.2	7.8
χ (10^{-10} N)	0.75	0.48	0.62
χ^2/wJ	2.83	0.29	1.91
t_0 (10^{-13} s)	1.95	1.21	1.21

We present our results with certain diagnostics. One is "waveform" graphs: plots of $|a_n|^2$ and the discrete gradient $\beta_{n+1} - \beta_{n-1}$ as functions of n at a given t. A soliton is recognized as a maximum in $|a_n|^2$ and a minimum in $\beta_{n+1} - \beta_{n-1}$ occuring together. A second diagnostic is a "soliton detector": on the (t,n) plane, we mark those times and positions where both $|a_n|^2$ exceeds a certain level (chosen to be 0.02) and $\beta_{n+1} - \beta_{n-1}$ is negative. The temporal extent of the marked regions shows how long solitonlike entities can exist.

First we show an example which verifies that the equations (2) without thermal fluctuations do possess coherent, localized, propagating soliton solutions. Figure 1a shows the soliton-detector results at a very low temperature, $T = 0.02$ K, with the parameters labeled "α-helix" in Table I and with random initial conditions. We see that several solitons are nucleated and move along the chain. The waveform graph in Fig. 1b shows the correlation of the maximum in $|a_n|^2$ and the minimum in $\beta_{n+1} - \beta_{n-1}$ which characterizes the soliton. This is clear evidence that solitons can form in this system at zero temperature.

Figure 2 shows the effect of raising the temperature to 300 K with the other parameters remaining the same as for Fig. (1) and with random initial conditions. The nucleation and propagation processes that take place at low temperature are now seen not to occur. The random forces prevent the necessary correlations between the two fields from taking place.

The previous figure shows that continual random displacements characteristic of thermal equilibrium prevent the soliton from forming when these displacemnts have a large enough magnitude. The following set of figures show a deterministic simulation (no random forces) in which a pre-existing soliton is destroyed by repeated collisions with a phonon wave-packet when the wave-packet has a large enough amplitude. The sustained "tugging" on the soliton by the lattice displacements pulls the soliton apart. Two different simulations are shown. In the first the energy of the phonon wave-packet is 16 cm^{-1} which is approximately equal to the binding energy of the soliton. In the second the *total* energy in the phonon wave-packet is 212 cm^{-1}; this is approximately equal to the average kinetic energy *per particle* at T=300 K. For the low energy case (Fig. 3), in fact the phonon wave-packet is destroyed after about three collisions with the soliton. In the higher energy case (Fig. 4) the correlations characteristic of the soliton are destroyed after about ten collisions with the wave-packet. Since the situation of thermal equilibrium at T = 300 K corresponds to repeated collisions with wave packets with much higher energy than this value, it is not surprising that the solitons are not stable under these thermal disturbances.

In our other contribution in this volume[2], we described a derivation of the Davydov equations which include multiple quanta of the high frequency oscillator system. We present here results for two quanta ($Q = 2$) for two temperatures $T = 0$ and 300 K. Fig. 5 shows a simulation at $T = 0$ K with random initial conditions. One sees that nucleation and propagation of solitons occurs here. (The fact that two solitons are nucleated in this run is coincidental and not related to the fact that the number of quanta used is $Q = 2$.) Fig. 6 shows that raising the temperature to $T = 300$ K again prevents the soliton from forming. Although one might try larger number of quanta in hopes that some positive result might occur, we do not consider that to be very likely.

The purpose of this conference is to assess the current status of Davydov's 1973 proposal of the soliton mechanism for storage and transport of biological energy. We believe that recent developments, motivated by our 1985 paper, conclusively show that the proposal can not function as originally envisioned at the physiological temperatures which are of interest in biology. Our simulations are of course constrained by being based on the Davydov *Ansatz* and by introducing temperature in a way which is valid only in the classical limit (which seems well satisfied for α-helix parameter values). However, the recent quantum-dynamical calculation of the soliton lifetime[4] and the quantum Monte Carlo thermal equilibrium simulation of the *Hamiltonian*[5] have achieved an unusual synergism. (These works are also discussed in this volume; see the contributions by Schweitzer *et al.* and by Wang *et al.*) The QMC calculation shows that solitons can not exist in an equilibrium system above 10 K, and the quantum-dynamic calculation shows that if they do form by some non-equilibrium mechanism, they last at most two picoseconds. Taken together these two papers reach consistent conclusions covering both time and temperature variables and provide very strong evidence that the original soliton proposal does not work at biological temperature. The "crisis of bioenergetics" is still with us!

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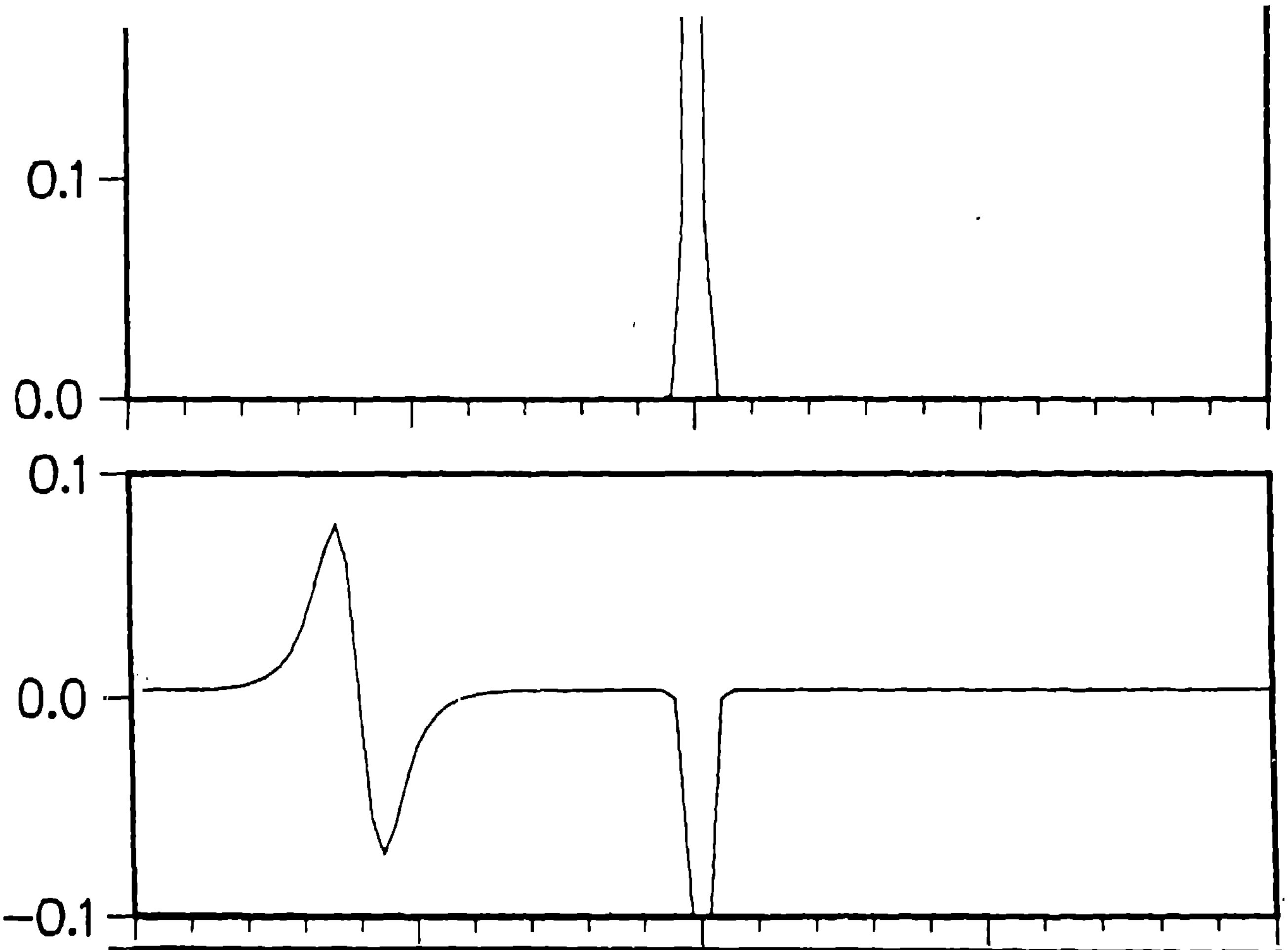
figures for DKNUM: 1. nucleation at T = 0 2. lack of nucleation at T = 300 K 3. Krumhansl wave packet - low energy 4. Krumhansl wave packet - high energy 5. Multi-quanta (N = 2) T = 0 6. Multi-quanta (N = 2) T = 300 K



Wave packet width 0.5
Wave packet height 0.16
Energy = wavepacket 16.31 cm^{-1}

Fig 1

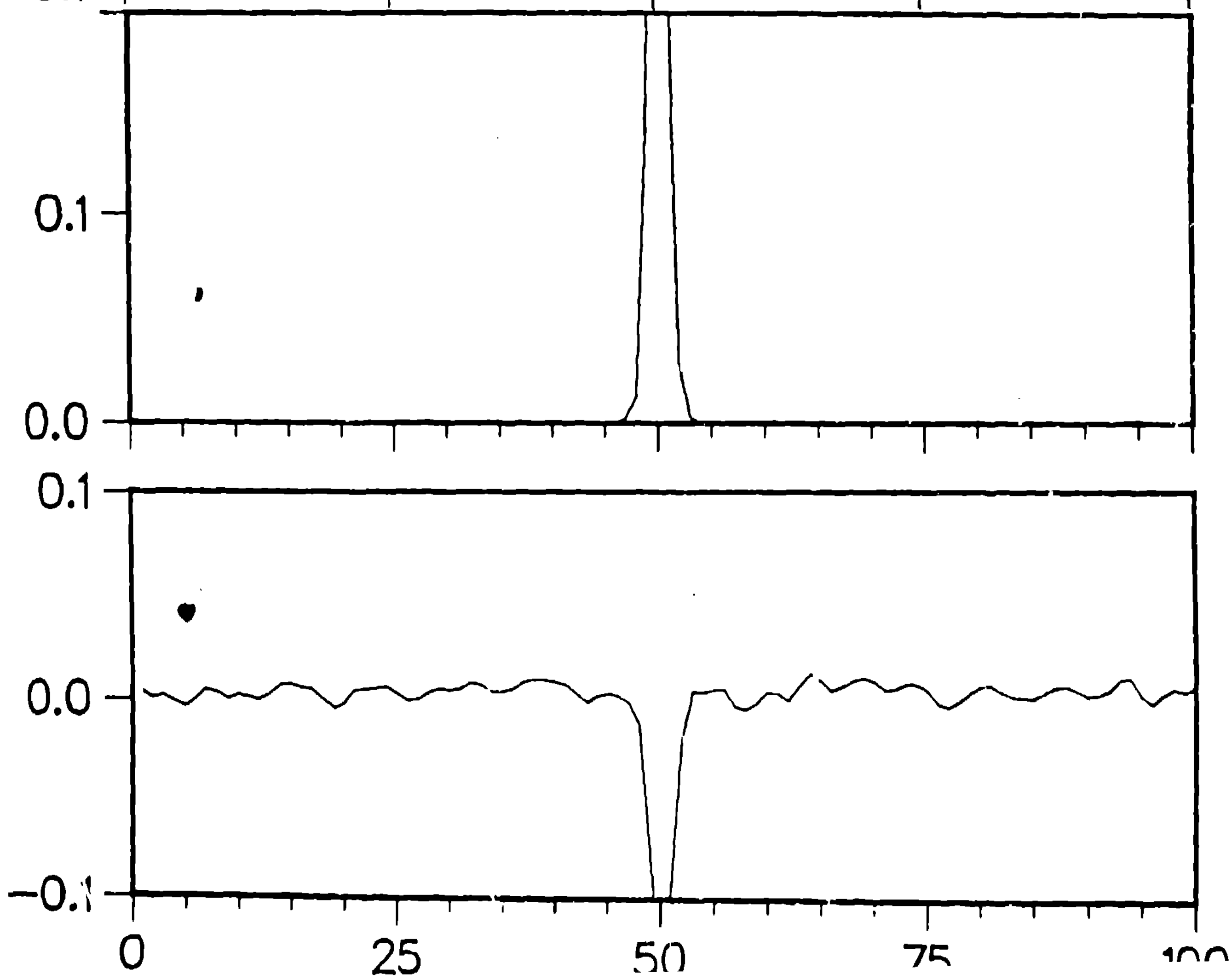
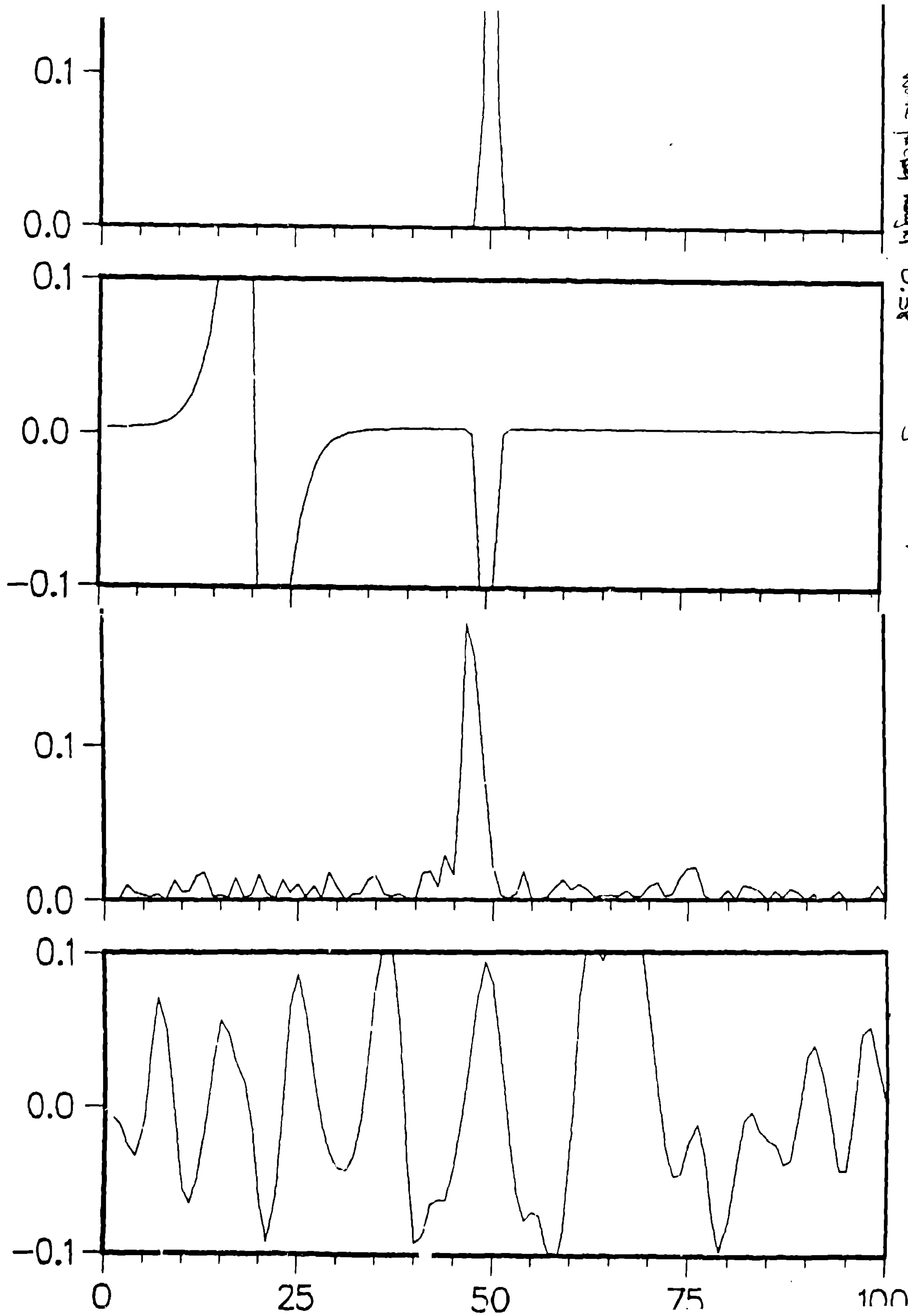


Fig 2



Wavepacket aimed at Davydov soliton
Wave packet width 0.5
Wave packet height 0.58
Energy in wavepacket 212.8

Fig 3

QUANT = 2

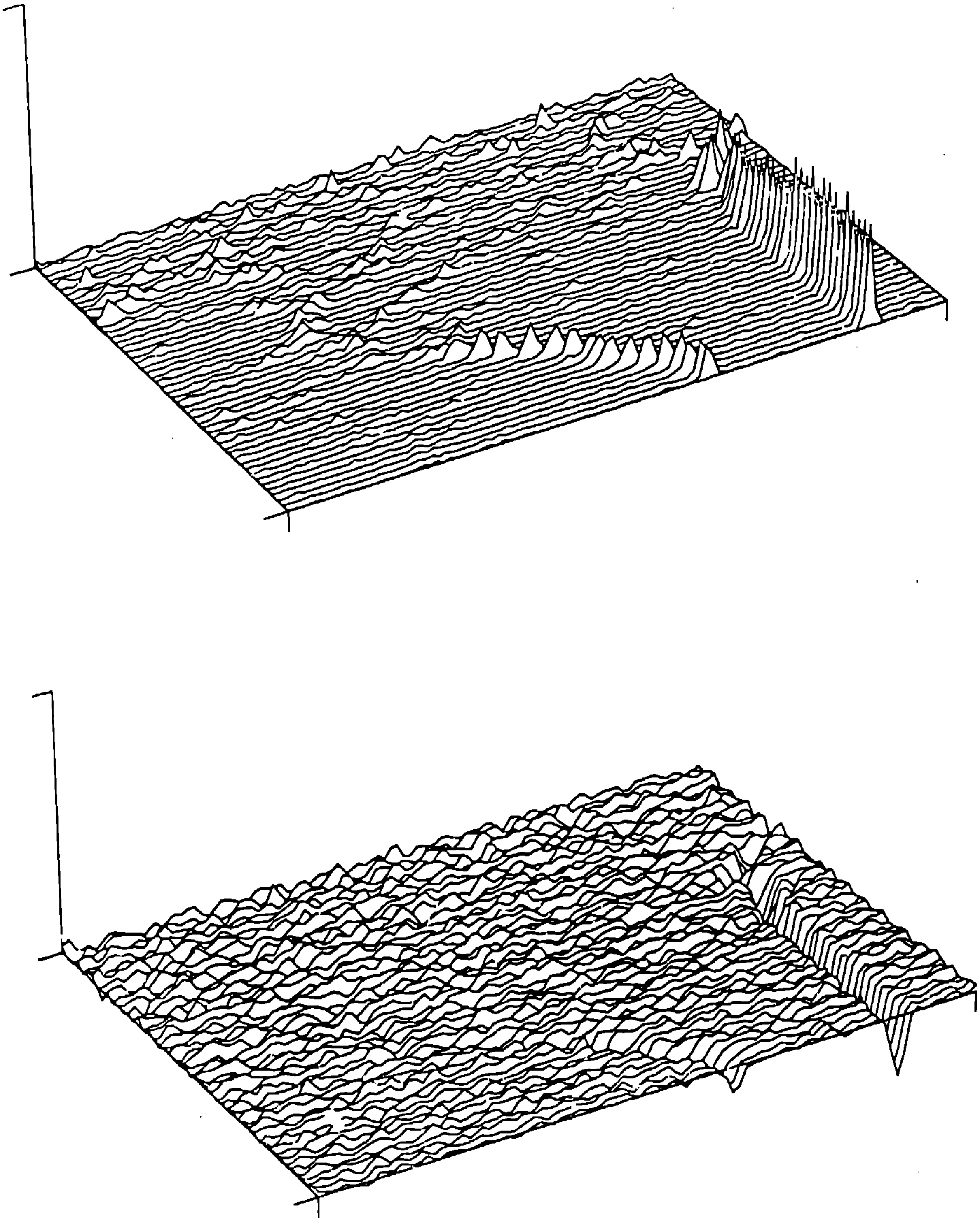
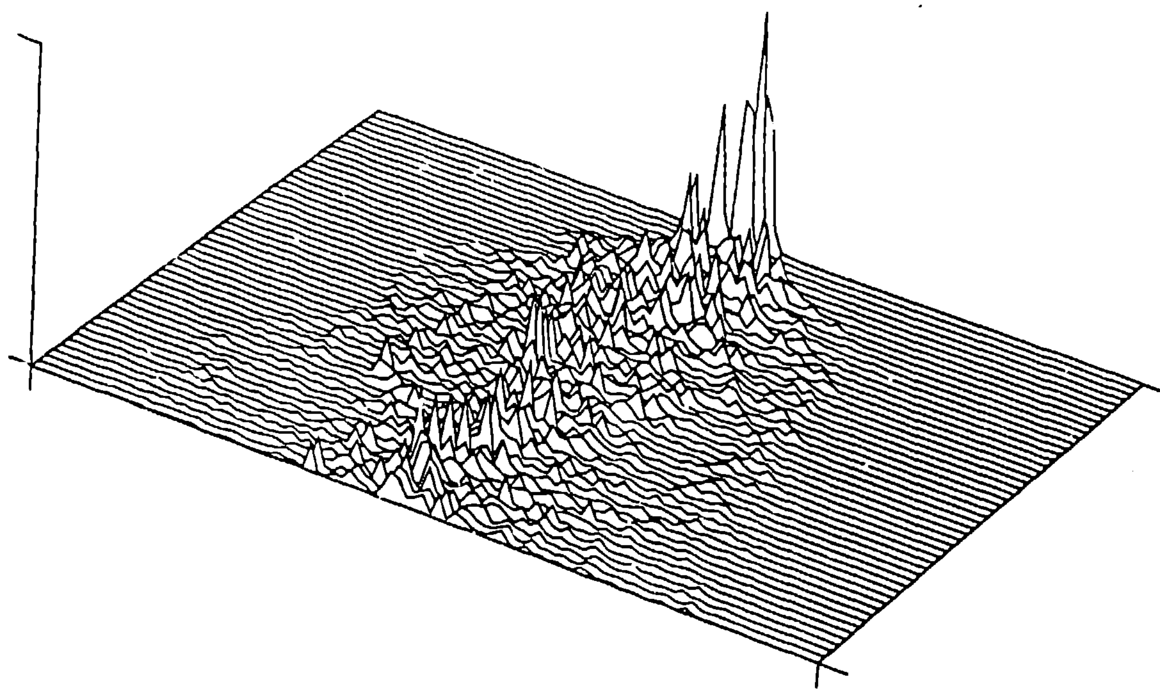


Fig 4

= 300 K
$\lambda = 1$
his is the same run as the
liton defector plot shown in the PCL



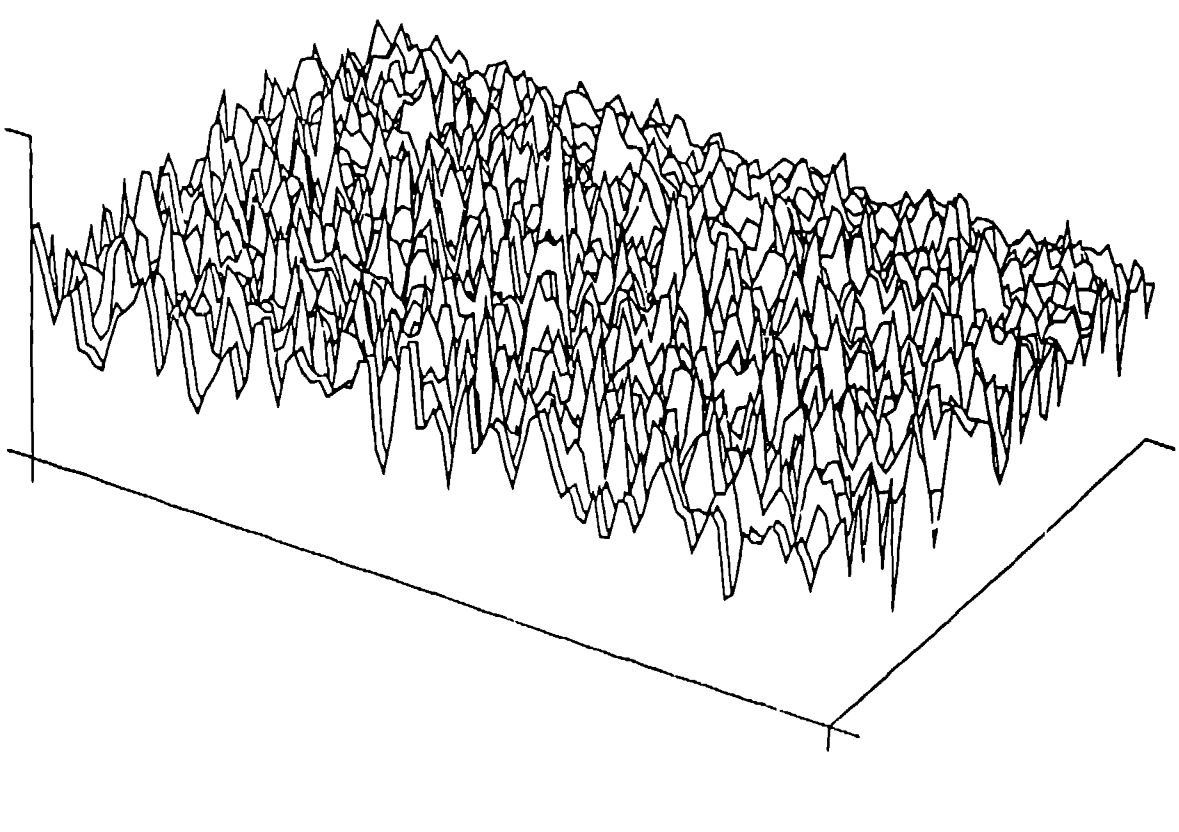
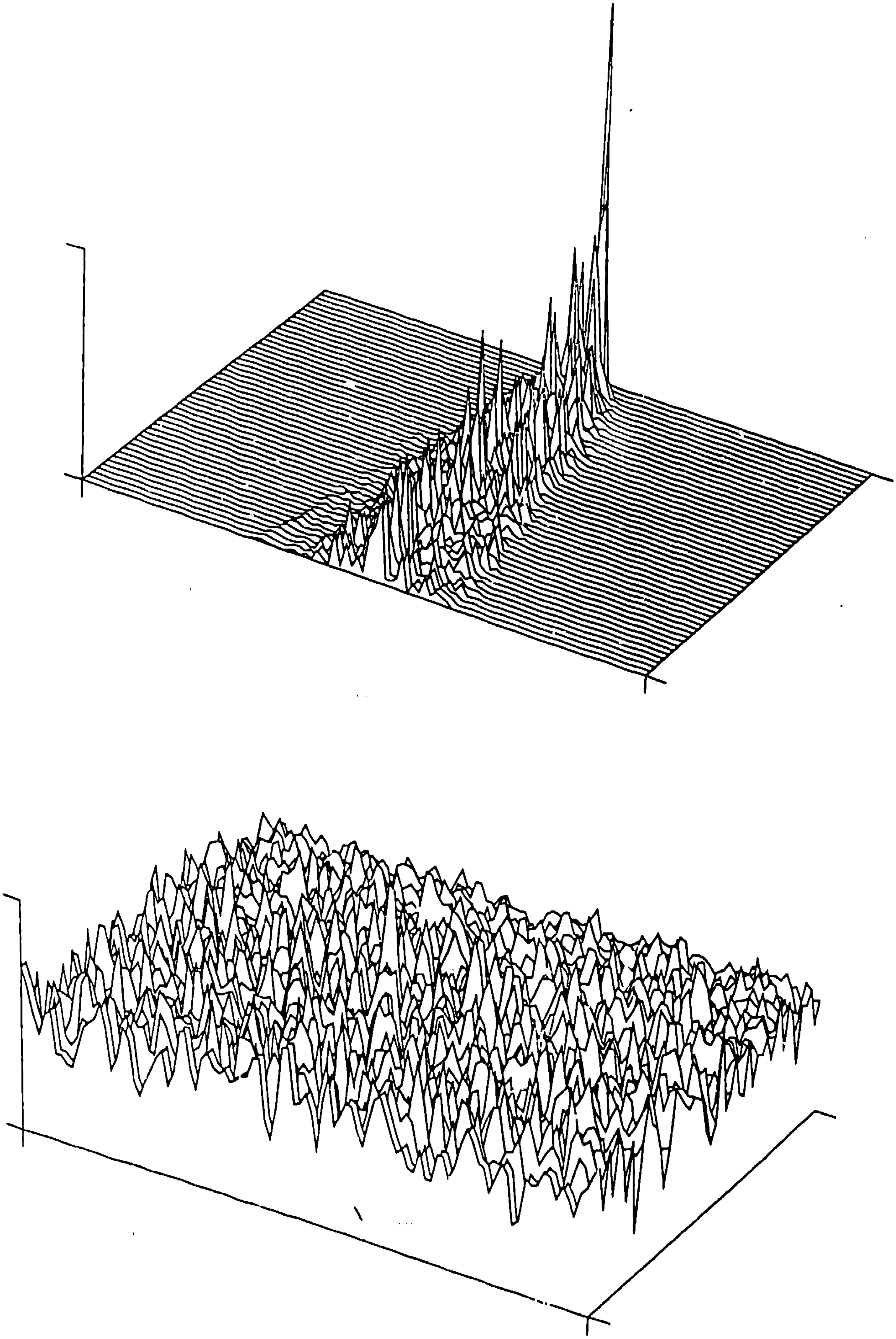


Fig C

= 2



Fi. 6