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A DISCRETE ANISOTROPIC MODEL FOR SCHEIBE AGGREGATES

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A discrete anisotropic nonlinear model for the dynamics of Scheibe aggregates is investigated. The collapse of the colelctive excitations found by Möbius and Kuhn is described as a shrinking ring wave, which is eventually absorbed by an acceptor molecule. An optimal acceptor loss is found.

1. Introduction.

Recently, Huth al. proposed a nonlinear continuum model, based on ultrasonic Davydov solitons, for the energy transfer in Scheibe aggregates [5]. These are highly ordered molecular monolayers, which can be produced by Langmuir-Blodgett technique [1]. An oxacyanine dye, e.g., can be used as donor molecules and a thiacyanine dye as acceptor molecules. Even with a donor to acceptor ratio as high as 10^4, the aggregate exhibits highly efficient transfer of energy from impinging photons, via excited host molecules, to acceptor guest [7,8]. In Ref. [4] it is found that the coherent exciton picture provides an adequate description of the experimental results, which for a dotation

ratio of 10^4 indicates a life time of the coherent exciton, before it is absorbed by an acceptor molecule, of about 10^{-10} s [8]. In Ref. [3] the isotropic continuum model, proposed in [5], is used for a qualitative prediction of the lifetime. Here the dynamics of the ring wave solution to the cubic nonlinear Schrödinger equation in two spatial dimensions [6] is essential.

In Ref. [2] a discrete isotropic model of the Scheibe aggregate, based on the discrete selftrapping equation (DST) [4], was introduced. In this model, which reflects the molecular structure of the aggregate, blow-up of the excitation cannot occur. Initial results concerning the absorption at one acceptor molecule, placed at the center of the ring wave excitation, were reported. In the present work, the discrete model is generalized to the anisotropic case, corresponding to the actual geometry of the monolayer, as described in ref. [8]. Also the competition between the nonlinear contraction and the absorption at the acceptor molecule is investigated in more detail.

2. The discrete model.

The isotropic model proposed in [5] leads to the cubic nonlinear Schrödinger equation for the wave function of the molecular excitation $u(r,t)$

$$iu_t + u_{rr} + r^{-1}u_r + 2|u|^2u = 0 \tag{1}$$

in dimensionless variables [3] in the case two spatial dimensions with circular symmetry. Here r is the radial coordinate and t is the time. The first conserved quantity becomes

$$I_1 = \int_0^\infty |u|^2 r dr. \tag{2}$$

To arrive at the DST equation in the anisotropic case we replace $u_{rr} + r^{-1}u_r$ by $u_{xx} + u_{yy}$ and discretize Eq. (1) in accordance with Fig. 1. Thus the Laplacian becomes

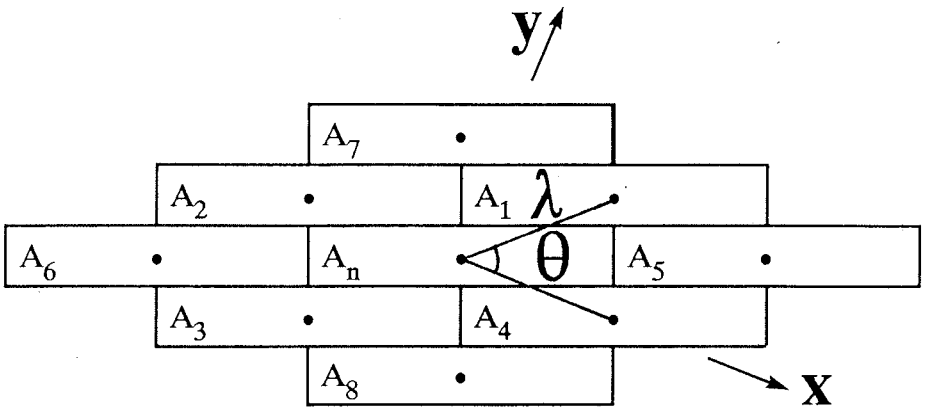

Fig. 1 - Möbius and Kuhn's brickstone work model of the Scheibe aggregate [8]. The intermolecular distance is denoted λ (8.72Å in physical units) and the anisotropy angle $\theta(= 54.6°)$. The excitation of the n'th molecule and 8 neighbours are denoted A_n, A_1, $A_2, \ldots, A_8$.

$$\Delta u \hookrightarrow \frac{1}{\lambda^2 \sin^2\theta}[A_1 + A_2 + A_3 + A_4 - 4A_n] + \frac{\cos\theta}{2\lambda^2 \sin^2\theta}[A_7 + A_8 - A_5 - A_6]. \tag{3}$$

For $\theta = \pi/2$ Δu in Eq. (3) reduces to the Laplacian used in the isotropic case [2]. In this manner we obtain the DST equation

$$i\,\dot{\mathbf{A}} + i\mathrm{diag}(\alpha)\mathbf{A} + \gamma\mathrm{diag}(|\mathbf{A}|^2)\mathbf{A} + \epsilon\mathcal{M}\mathbf{A} = 0 \tag{4}$$

where loss has been included. Here $u(n_x\lambda\cos\theta, n_y\lambda\sin\theta, t) \hookrightarrow A_n(t)$, A_n denoting the excitaton of molecule number n, placed at $(x, y) = (n_x\lambda\cos\theta, n_y\lambda\sin\theta)$, n_x and n_y being integers. **A** is the column vector $(A_1, A_2, \ldots, A_N)$, N being the total number of molecules in the model.

In the DST model each dipole molecule is described as a nonlinear dissipative oscillator, with a dispersive coupling to neighbouring oscillators. The coupling enters via the symmetric $N \times N$ dispersion matrix (zero elements not shown)

$$\vdash N_{hor} \dashv \quad \vdash N_{hor} \dashv \quad \vdash N_{hor} \dashv \ \ldots \ \vdash N_{hor} \dashv$$

$$(4.a) \qquad \epsilon \mathbf{M} = \epsilon \left[\begin{array}{ccccccccccccccccccccc}
 & \delta & & & & 1 & & & & & \delta & & & & & & & & & & \\
\delta & & \delta & & & 1 & 1 & & & & & \delta & & & & & & & & & \\
 & \delta & & \ddots & & & \ddots & \ddots & & & & & \ddots & & & & & & & & \\
 & & \ddots & & & & & 1 & 1 & & & & & \delta & & & & & & & \\
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 & & & & & & & & \delta & & & & & \ddots & 1 & & & & \delta & & \delta \\
 & & & & & & & & & \delta & & & & & 1 & 1 & & & & \delta &
\end{array} \right]$$

where $\epsilon = (\lambda \sin \theta)^{-2}$ is the dispersion parameter and $\delta = \cos \theta / 2$. N_{hor} is the number of molecules in each horizontal row in the model. Elements, -4, on the diagonal of the matrix (4a) have been removed by a gauge transformation.

The nonlinearity and the loss enters into Eq. (4) via the $N \times N$ diagonal matrices (zero elements not shown)

$$\gamma \mathrm{diag}(|\mathbf{A}|^2) = \gamma \begin{bmatrix} |A_1|^2 & & & \\ & |A_2|^2 & & \\ & & \ddots & \\ & & & |A_N|^2 \end{bmatrix}, \tag{4b}$$

$$\mathrm{diag}(\alpha) = \begin{bmatrix} \alpha_1 & & & \\ & \alpha_2 & & \\ & & \ddots & \\ & & & \alpha_N \end{bmatrix}. \tag{4c}$$

Here γ is the nonlinearity parameter ($\gamma = 2$ when Eq. (4) is a discretization of Eq. (1)). Our model include only a single acceptor molecule, placed centrally at site number $(N+1)/2$, N being odd. We shall consider absorption at this molecule and neglect radiative losses at the donor molecules. Thus the α components become $\alpha_i = \alpha_{acc}$ for $i = (N+1)/2$ and $\alpha_i = 0$ for $i \neq (N+1)/2$.

In the lossfree case ($\alpha_{acc} = 0$), the conserved quantity I_1 becomes

$$I_1 = \frac{\lambda^2}{2\pi} \sum_{n=1}^{N} |A_n(t)|^2. \tag{5}$$

To obtain initial values for the excitation **A** we sample a ring wave profile [6] with radius r_0 given by

$$r_0 = \lambda \sqrt{N_0/\pi}, \tag{6}$$

where the number of sampling points initially inside the ring wave, N_0, is chosen to be a typical number of molecules in the coherent exciton, 10^4. For the case considered in [3], we get in dimensionless units ($\lambda = 1$) $r_0 = 50.9$, $v_0 = 0$, $I_1 = 5.55$, $t_{collapse} = 809$. For convenience we use the scaling invariance of Eq. (1) and (2), $t \hookrightarrow \beta \cdot t$, $r \hookrightarrow \beta^{1/2} \cdot r$; $u \hookrightarrow \beta^{-1/2} \cdot u$, $I_1 \hookrightarrow I_1$, with $\beta = 1024$. For computational reasons we reduce N_0 by a factor 4, in order to limit the number of coupled DST equations, which have to be integrated over a few time units ($t_{collapse} \approx 1$). In Ref. [2] it was demonstrated that a moderate reduction of N_0 has no significant influence on the numerical results.

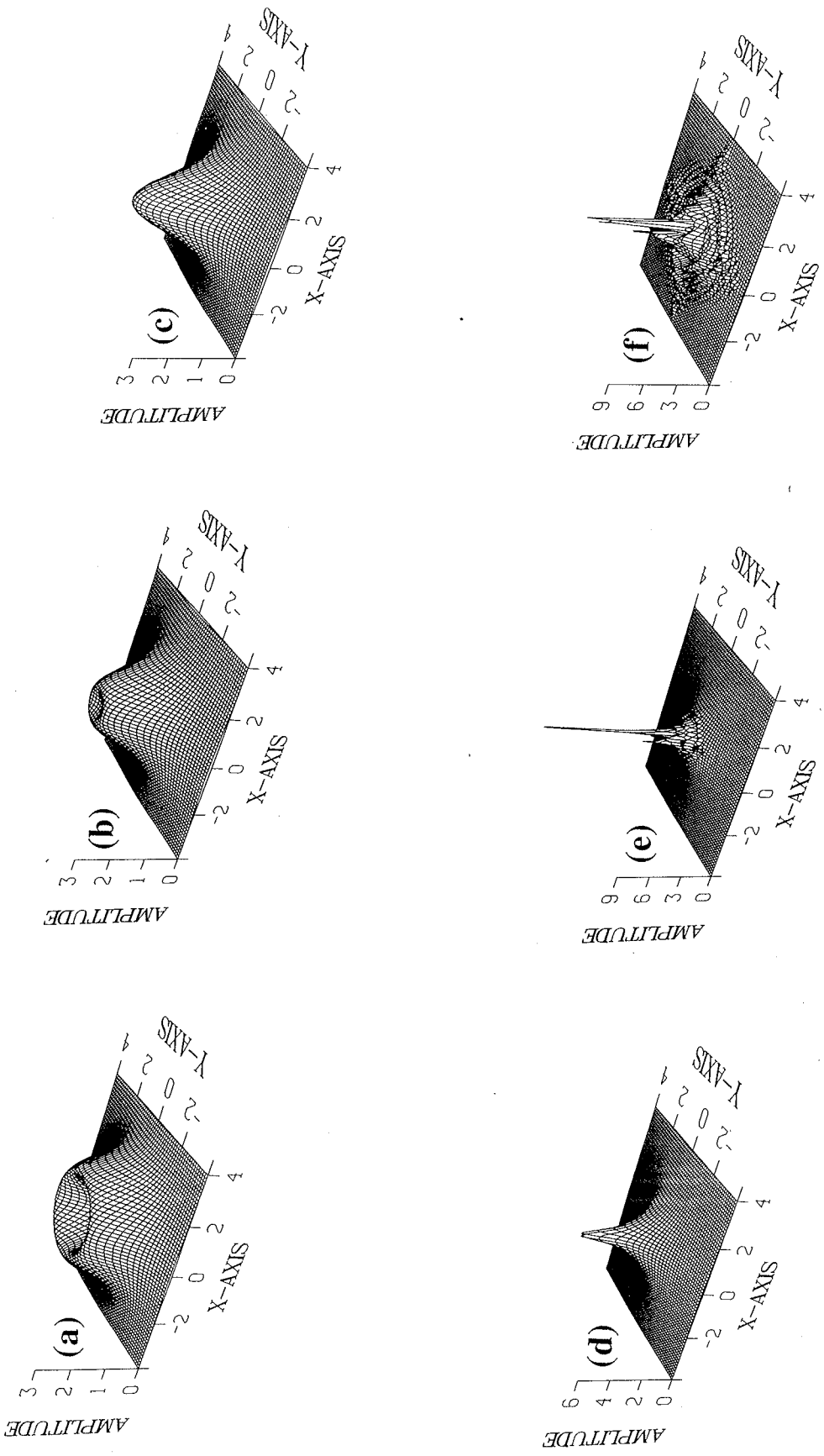

Fig. 2 - Evolution of ring wave in lossfree isotropic DST model. $\epsilon = 314.4$, $\delta = 0$, $\gamma = 2$, $r_0 = 1.59$, $I_1 = 5.55$, $N_0 = 10^4/4$, $\alpha_{acc} = 0$. $t = (a)0$, $(b)0.55$, $(c)0.6$, $(d)0.65$, $(e)0.7$, $(f)0.75$.

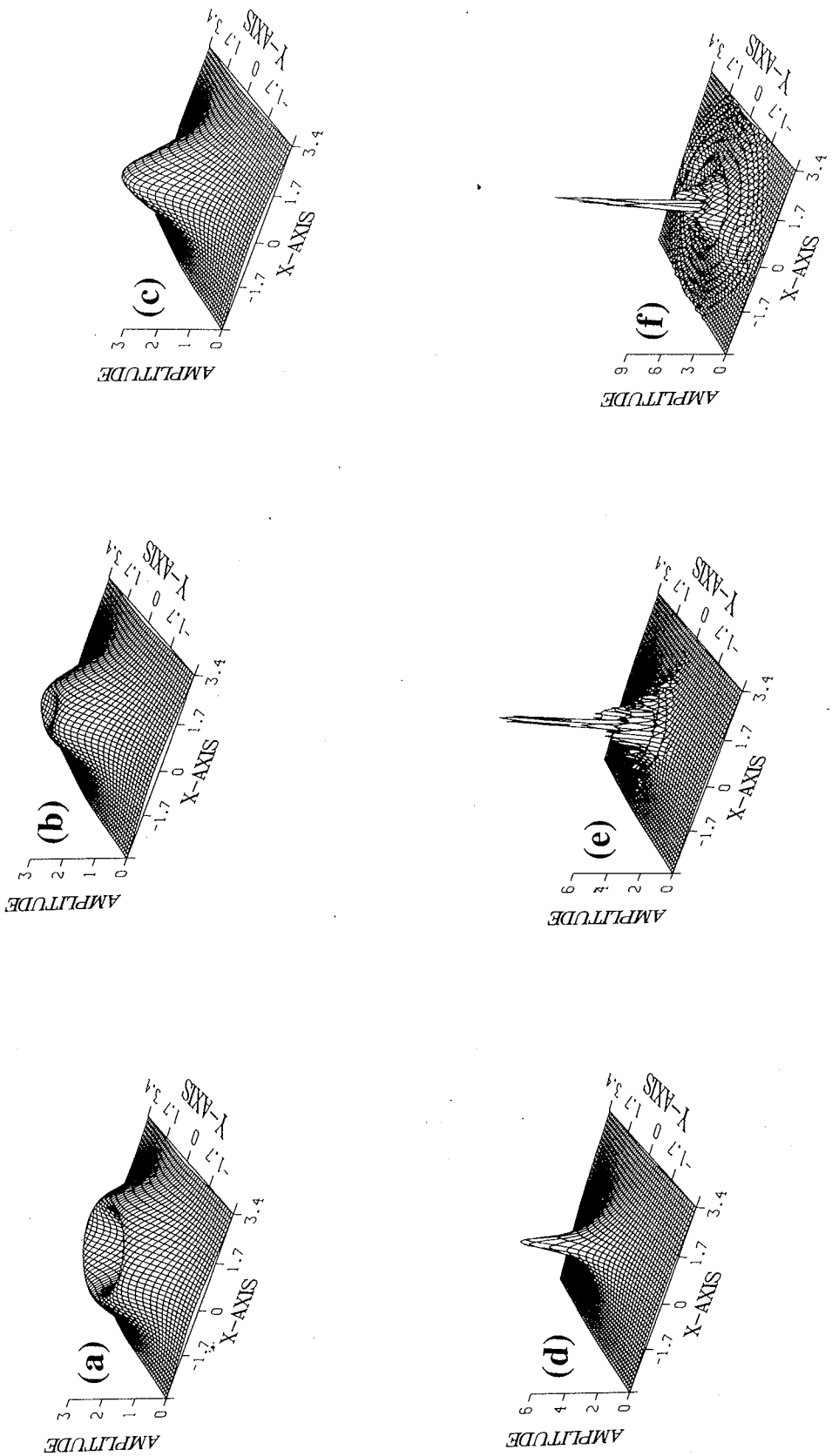

Fig. 3 - Evolution of ring wave in lossfree anisotropic DST model. $\epsilon = 385.2$, $\delta = 0.2896$, $\gamma = 2$, $r_0 = 1.59$, $I_1 = 5.55$, $N_0 = 10^4/4$, $\alpha_{acc} = 0$. $t = (a)0$, $(b)0.55$, $(c)0.6$, $(d)0.65$, $(e)0.7$, $(f)0.75$.

3. Numerical results.

Figure 2 shows the evolution of the ring wave in the isotropic DST model without loss. Initially the ring wave is seen to contract (Fig. 2a-c), as predicted by the continuum model [6]. At the final stage of this process a global maximum forms at the centre (Fig. 2c), corresponding to the beginning of the blow-up. However, no matter how fine the grid in the discrete model may be, the amplitude of the shinking ring wave in the centre area will eventually reach such a magnitude that the resolution of the grid becomes insufficient. As a consequence the *DST* model cannot reproduce the blow-up further and dispersive radiation among the coupled oscillators results (Fig. 2d-f). This is a realistic feature of the discrete model. However, in order to complete the energy transfer, absorption at the acceptor molecule can be introduced, as we shall see. The asymmetry with four preferred directions, which develops in Fig. 2e-f, is caused by the 4-nearest-neighbours approximation used in the discretization (Eq. (3)).

Figure 3 shows the corresponding time evolution of the ring wave in the anisotropic case where $\theta = 54.6°$, corresponding to Möbius and Kuhn's brickstone work model of the Sheibe aggregate. The effect of the anisotropy is seen to be important only in the dispersive phase of the evolution (Fig. 3e-f).

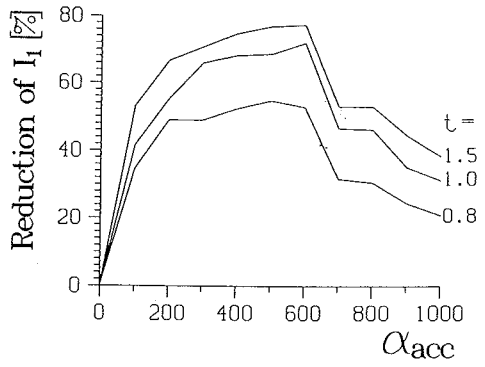

Fig. 4 - Reduction of I_1 as funtion of acceptor loss, α_{acc}, at times $t = 0.8$, 1.0 and 1.5 Anisotropy and initial data as in Fig. 3.

We now introduce losses at the acceptor molecule at site $(N+1)/2$

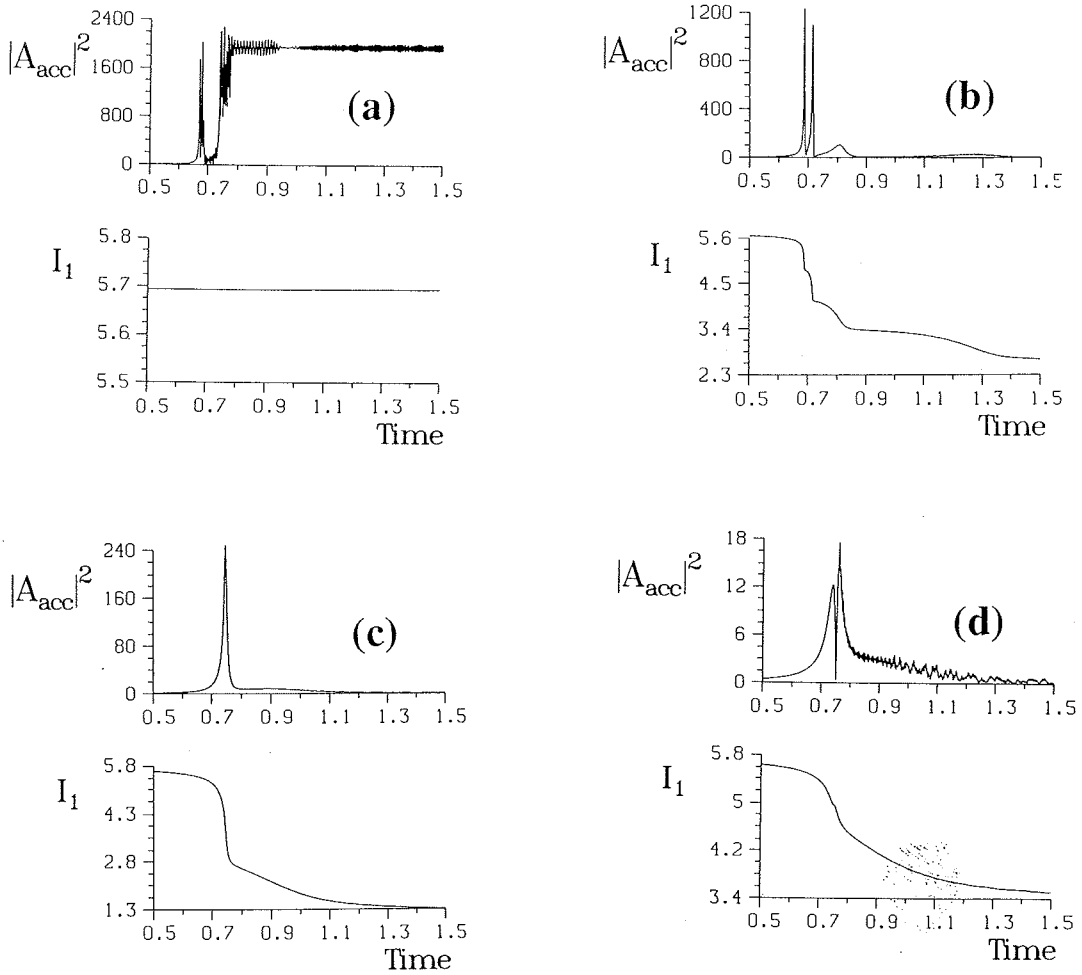

Fig. 5 - Time evolution of $|A_{acc}|^2$ and I_1 for anisotropy and initial data as in Fig. 3. The acceptor loss $\alpha_{acc} = (a)0$, $(b)100$, $(c)500$, $(d)800$.

and leave the anisotropy unchanged. In Figure 4 the reduction of the quantity I_1, given by Eq. (5), is shown at three different times after the ring wave radius has become zero, which is when the dissipation is significant. A maximal reduction is seen to occur for $\alpha_{acc} = 500-600$. In this range the loss matches the intrinsic impedance of the aggregate. The details in the time evolution of the intensity of the acceptor molecule excitation, $|A_{acc}|^2$, and I_1 are shown in Figure 5 for different values of α_{acc}. In the lossfree case (Fig. 5a) $|A_{acc}|^2$ raises, through oscillations, to an almost constant level (~ 2000), which persists at least until $t = 2.5$. A similar self-trapped state

was observed in the 1-dmensional DST model [9]. For the relatively small acceptor loss, $\alpha_{acc} = 100$, $|A_{acc}|^2$ vanishes only after a number of oscillations (Fig. 5b), each peak corresponding to a drop in I_1. This multifocal behaviour was also observed for the cubic 2-dimensional nonlinear Schrödinger equation with a nonlinearly localized loss term [10]. Near the optimal value, $\alpha_{acc} = 500$, only a single peak is observed (Fig. 5c) and a maximal reduction of I_1 is seen. For larger values of α_{acc} (Fig. 5d) the dissipation dominates over the nonlinear contraction and $|A_{acc}|^2$ remains small.

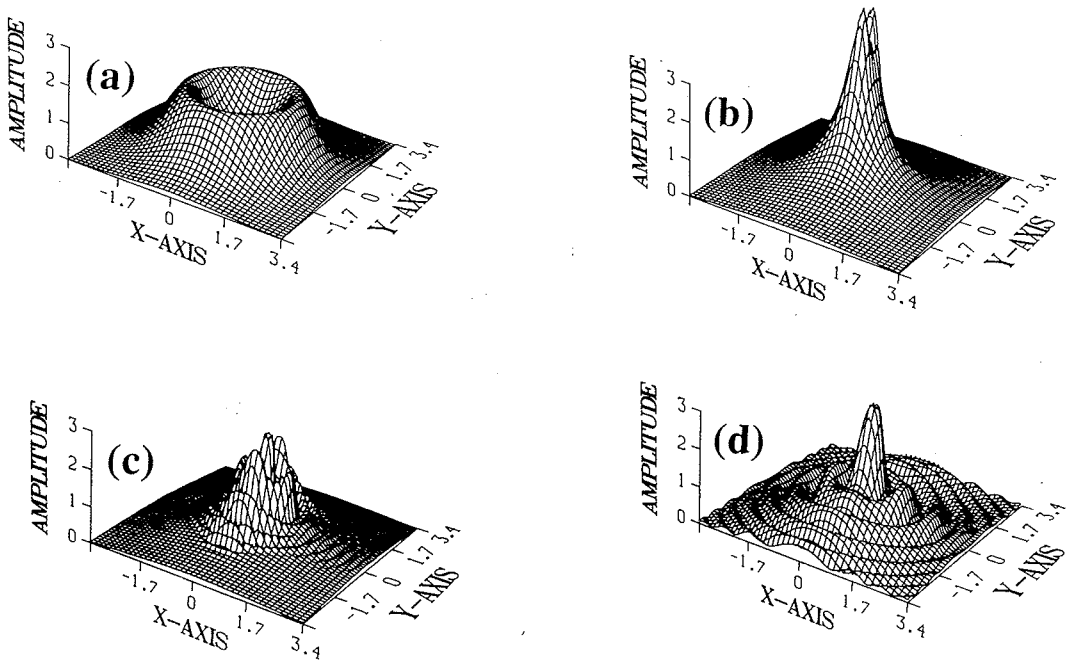

Fig. 6 - Evolution of ring wave in lossy anisotropic DST model. $\epsilon = 385.2$, $\delta = 0.2896$, $\gamma = 2$, $r_0 = 1.59$, $I_1 = 5.55$, $N_0 = 10^4/4$, $\alpha_{acc} = 500$; $t = (a)0$, $(b)0.7$, $(c)0.8$, $(d)0.9$.

Finally, Figure 6 shows the time evolution of the ring wave excitation in the optimal case ($\alpha_{acc} = 500$). As result of the dissipation the dispersion of the ring wave is delayed and reduced.

4. Conclusion.

We have shown that the anisotropy of the Möbius and Kuhn

brickstone work model of the Scheibe aggregate has a small influence on the collapse of the colective excitation, essentially manifesting itself in the dispersive phase. Thus the collapse time predicted by the isotropic model is essentially correct. We have also found that there is an optimal value of the acceptor loss ($\sim 500 - 600$), for which the reduction of the excitation intensity is maximal. To our knowledge the acceptor loss has not yet been estimated in the literature.

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