

# Soliton-like excitations in the long molecular chains

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## Motivations for this work:

### Modeling loss-free energy transportation in biomolecular aggregates

- Time scale:  $10^{-13} - 10^{-11}$  s.
- Energy scale: 0.1-0.3 eV.
- Transfer distance: 10-100 Å

## Reasons for soliton propagation mechanism along tightly binding molecular subunits

- Chemical processes in biological systems are well understood on structural and thermodynamics levels.
- The reactive centers are linked by molecular chains of length of about  $100 \text{ \AA}$ . The energy quantum of order of  $0.1\text{-}0.2 \text{ eV}$  is produced within one reactive center and is transported without loss to next reactive site along the chain with many (of order  $10^2 - 10^3$ ) vibrational degrees of freedom.
- In order the energy transport does not accompanied by energy dispersion over all internal vibrations, the soliton mechanism has been suggested.

# Molecular chains consisting of hydrogen bonded subunits

- In harmonic limit the initial energy is rapidly distributed over all vibrations and cannot be transported. Non-linear coupling is introduced as a result of the strong anharmonicity of hydrogen bonds.
- If the coupling strength exceeds a certain threshold, solitons can be formed, suppressing energy distribution.
- A.S.Davydov. *Biology and Quantum Mechanics*. Pergamon. N.Y.1982.
- D.Hochstrasser, F.G.Mertens, H.Buttner. *Phys.Rev. A*. 40(1989)2602.
- D.Hennig. *Phys.Rev. E* 61(2000)4550.

# Energy transfer through 1D chain of CH<sub>2</sub>- fragments

Ballistic regime has been discovered for heat pulse propagation induced by instant vibrational excitation of the end fragment of long linear molecule. Propagation time is proportional to the chain length, about  $10^{-13}$  s per one CH<sub>2</sub> –fragment.

Forward and backward propagation, involving reflection from the chain ends results in phonon echo formation (partial recovery of the initial state population)

The echo is broadened when the coupling between the chain and its environment increases.

D.Dlott, et al. Proc. Nat. Acad.Sci USA 104(2007)14190,  
Science. 317(2007)787.

No hydrogen bonds, no highly anharmonic vibrations!

# Normal mode progressions in vibrational spectra of large molecules and nanosystems

Object	Molecule	Spectral range (cm <sup>-1</sup> )	Vibration type	Mean spacing (cm <sup>-1</sup> )	Progression shifts (cm <sup>-1</sup> )
Membranes	Phospho-lipides*	1150-1400	Wagging	16-18	3-8
Mono-layers	CH <sub>2</sub> -chains	710-1010	Rocking	20-22	-
		1180-1310	Wagging	20-26	-
Single-well nano-tubes	Zigzag and armchair configurations	140-230	Radial breathing	15 15	5
Photosystem I	Fe-Porphirin	690-1650	Of-plane distortions, E <sub>u</sub>	69	-
-	Fullerenes C <sub>60</sub> -C <sub>70</sub>	1180-1580	Skeleton distortions	18	-

# Model Hamiltonian

- The chain consisting of  $(2N+1)$  two-level sites with the same nearest neighbor interaction.

The site in the middle,  $n=0$ , is occupied by impurity.

$$H = E_0 Q_0^+ Q_0 + \Omega_0 \sum_n Q_n^+ Q_n + c(Q_0^+ Q_1 + Q_0 Q_1^+) + J \sum_{n \neq 0} (Q_n^+ Q_{n+1} + Q_n Q_{n+1}^+)$$

- The Hamiltonian (1) has the Caldeira-Leggett form and describes an interaction between the initial state (impurity center excitation) and reservoir with the dense discrete spectrum (half-chains)

# Secular equation

- Within site representation, the matrix of Hamiltonian is reduced to symmetric tridiagonal Jacobi matrix

$$F(\varepsilon) = \begin{vmatrix} \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \varepsilon & 1 & 0 & 0 & 0 & \dots \\ \dots & 1 & \varepsilon & C & 0 & 0 & \dots \\ \dots & 0 & C & E+\varepsilon & C & 0 & \dots \\ \dots & 0 & 0 & C & \varepsilon & 1 & \dots \\ \dots & 0 & 0 & 0 & 1 & \varepsilon & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \end{vmatrix} = (\varepsilon + E)D_N^2(\varepsilon) - 2C^2 D_N(\varepsilon)D_{N-1}(\varepsilon) = 0$$

$$D_N(\kappa) = \frac{\sin(N+1)\kappa}{\sin \kappa}, \quad \varepsilon = 2 \cos \kappa$$

$$F(\kappa) = \left( E + 2(1 - C^2) \cos \kappa \right) \sin(N+1)\kappa + 2C^2 \sin \kappa \cos(N+1)\kappa = 0$$



# Reservoir eigenstate representation

- Secular determinant has one none-zero line and one none-zero column describing energy dependent impurity-reservoir coupling

$$F(\varepsilon) = \begin{vmatrix} \varepsilon - \varepsilon_k^0 & \dots & 0 & C_k & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \varepsilon - \varepsilon_1^0 & C_1 & 0 & \dots & 0 \\ 0 & \dots & C_1 & \varepsilon - E & C_1 & \dots & 0 \\ 0 & \dots & 0 & C_{-1} & \varepsilon - \varepsilon_{-1}^0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & 0 & C_{-k} & 0 & \dots & \varepsilon - \varepsilon_{-k}^0 \end{vmatrix} = 0$$

$$\varepsilon_k^0 = 2 \sin \frac{k\pi}{N+1}, \quad C_k = C b_{1k} = C \cos \frac{k\pi}{N+1}$$

# Comparison with Zwanzig's model

- The simplest form of initial state-reservoir Hamiltonian corresponds to Zwanzig's model: equidistant spectrum and the same coupling for all reservoir states.
- In contrast to Zwanzig's model in the chain case: density of non-perturbed reservoir states increases and coupling strength decreases from the center to zone boundaries.
- Nevertheless, the main feature of Zwanzig's model is preserved: One eigenvalue of coupled system lies in each interval between levels of non-perturbed reservoir.

# Secular equation for generalized Zwanzig's model

- The correction functions taking into account energy dependent spacings and couplings can be introduced in secular equation to generalize Zwanzig's model

$$F(\lambda) = f_2(\alpha\lambda)(\lambda - \Gamma f_1(\alpha\lambda)\cot(\pi\lambda)) = 0 \quad , \quad \kappa = \frac{\pi\lambda}{N+1} \quad , \quad \alpha = \frac{\pi}{N+1}$$

- Coupling constant  $\Gamma \gg 1$  is define the energy range where reservoir states mainly contributed impurity-reservoir interaction are located

$$\Gamma = (N + 1) \frac{C^2}{\pi(1 - C^2)}$$

- Correction functions are close to 1 near the zone center

$$f_1(u) = u \cot u \quad , \quad f_2(u) = \frac{\sin u}{u}$$

- Eigenvalues

$$\varepsilon_n = 2\alpha\lambda_n f_2(\alpha\lambda_n)$$

# Equations of motion

- Wave function is expanded over eigen-functions of impurity and reservoir nonperturbed states with time dependent amplitudes
- Impurity amplitude is given by trigonometric series over eigenvalues which Fourier coefficients are equal to residues in the poles being the roots of secular equation

$$a_0(t) = \sum_{k=0}^{[N/2]} \frac{\cos(\varepsilon_k t)}{dF/d\varepsilon|_{\varepsilon=\varepsilon_k}}$$

# Recurrence cycles for Zwanzig's model

- Recurrence cycles result from discreteness of reservoir spectrum. Their period is defined by the mean inter-level spacing.
- Partial recovery of initial state (echo) appears in each recurrent cycle.
- The number of components and the total width of echo increase with increasing cycle number.
- There exists the critical cycle number for mixing of adjacent cycle components.
- As result of mixing regular-chaotic transition occurs in long-time evolution.
- V.A.Benderskii, L.A.Falkovskii, E.I.Kats.
- JETPL 88(2008)338;JETP108(2009)160; 109(2009)505.

# Time-dependent impurity amplitudes

$$\Phi(t) = a_0(t)\varphi_s + \sum_k a_k(t)\varphi_k$$

State vector  $[a_0, a_{\pm 1}, \dots, a_{\pm [N/2]}]$  obeys Heisenberg equations ( $\hbar = 1$ )

$$i\dot{a}_0 = Ea_0 + \sum_{k=-[N/2]}^{[N/2]} C_k a_k \quad , \quad ia_k = C_k a_0 + \varepsilon_k^0 a_k \quad , \quad a_0(0) = 0 \quad , \quad a_k(0) = 0$$

$$a_0(t) = \sum_{k=0}^{[N/2]} \frac{\cos(\varepsilon_k t)}{dF/d\varepsilon|_{\varepsilon=\varepsilon_k}}$$

Impurity amplitude is ( $E = 0$ )

$$a_0(t) = \frac{2}{1-C^2} \sum_{k=0}^{[N/2]} \frac{f_1^2(\lambda_k)}{(1+\pi\Gamma)f_1^2(\lambda_k) + (\alpha^2 + \pi/\Gamma)\lambda_k^2} \cos(2t \sin(\alpha\lambda_k))$$

Coupling determines reservoir states which contribution dominates in impurity-reservoir interaction. If  $C^2 < 1/2$ , correction functions are close to 1 for these states and the impurity evolution is close to those for Zwanzig's model. The contribution of states situated close the zone boundaries become significant when  $C^2 > 1/2$ .

# Recurrence cycles for 1D chain problem

- Generating function representation for first-order Bessel function

$$\cos(2t \sin \kappa) = J_0(2t) + \sum_{m=1}^{\infty} J_{2m}(2t) \cos(2m\kappa)$$

- The coefficients are only non-zero in the periodically repeated intervals

$$a_0(t) = \frac{1}{1 - C^2} \sum_{m=0}^{\infty} J_{2m}(2t) S_m$$

$$S_m = \frac{\Gamma}{\pi(1 + \alpha^2 \Gamma / \pi)} \sum_{k=0}^{[N/2]} \frac{\cos(2m\alpha\lambda_k)}{B^2 + \lambda_k^2 / f_1^2(\lambda_k)}, \quad B^2 = \frac{\Gamma}{\pi} \frac{1 + \pi\Gamma}{1 + \alpha^2 \Gamma / \pi}$$

- As a result, the impurity amplitude is partially recovered in each recurrence cycle. Period of recurrence cycles is almost independent of coupling and is defined by the chain length

$$T_m = N + 1$$

- Each recurrence cycle corresponds to propagation of excitation wave forward and backward of half-chains.

# Partial amplitudes of recurrence cycles

- Since coefficients are non-zero in the narrow periodically repeated intervals

$$[0, m_0], [N+1, N+1+m_0], \dots; [s(N+1), s(N+1)+m_0], \dots \quad m_0 \ll N+1$$

- an impurity amplitude is expanded into series over partial amplitudes of recurrence cycles

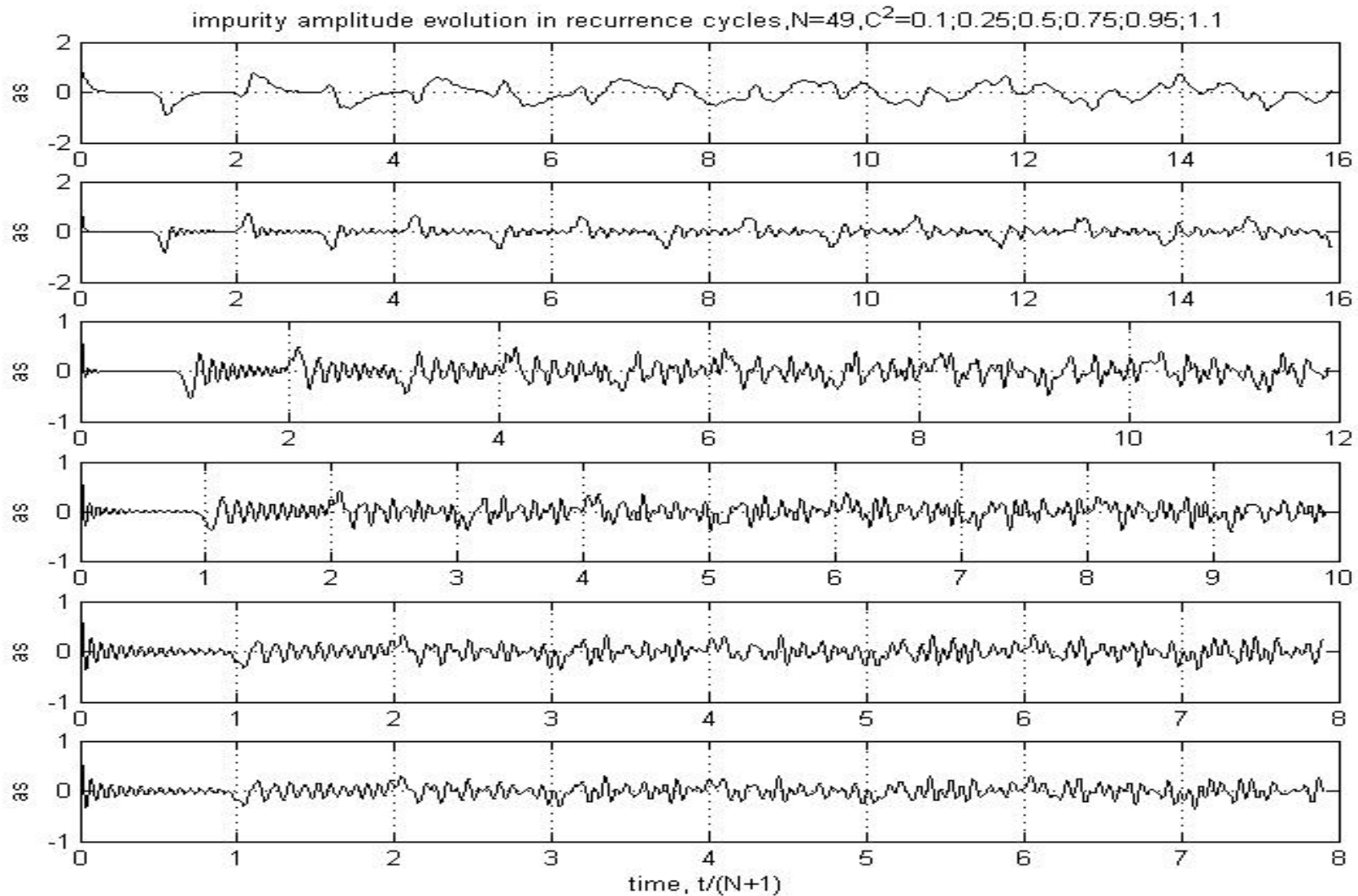
$$a_0(t) = \sum_s a_0^{(s)}(t - sT)$$

$$a_0^{(0)} = J_0(2t) + 2 \sum_{m=1}^{m_0} J_{2m}(2t) = 1 - \int_0^{2t} J_{2m_0-1}(x) dx$$

$$a_0^{(s)} = 2 \sum_{m=1}^{m_0} J_{2s(N+1)+2m}(2t) = \int_0^{2t} J_{2N+1}(x) dx - \int_0^{2t} J_{2N+2m_0+1}(x) dx$$



# Impurity amplitude evolution, $C^2=0.1;0.25;0.5;0.75;0.95;1.1$



## Impurity amplitude evolution.

$$C^2=0 -0.25.$$

- Alike Zwanzig's model, the number of echo components and their total width increase with recurrence cycle number. Evolution becomes more and more complicated with increasing cycle number. The intervals of non-zero coefficients  $S_m$  decreases with increasing coupling. The number of recurrence cycles with regular dynamics grows with coupling increase.

The mean population of impurity in recurrence cycle is equal to  $1/\Gamma$  independently of cycle number.

# Impurity amplitude evolution, $C^2=[0.4,0.8]$ .

- About only three non-zero coefficients  $S_m$  exist in each recurrence cycle

$$S_m \approx \begin{cases} 1, & m=s(N+2) \\ 1/2, & m=s(N+2)\pm 1 \\ 0, & m=s(N+2)\pm k, k\geq 2 \end{cases}$$

$$a_0(t) \approx \sum_{s=1} (-1)^s 2 \left( (1-C^2) \left( J_{2s(N+1)-2}(2t) + J_{2s(N+1)+2}(2t) \right) + J_{2s(N+1)}(2t) \right)$$

- Evolution remains regular in recurrence cycle which number exceeds that for Zwanzig's model.

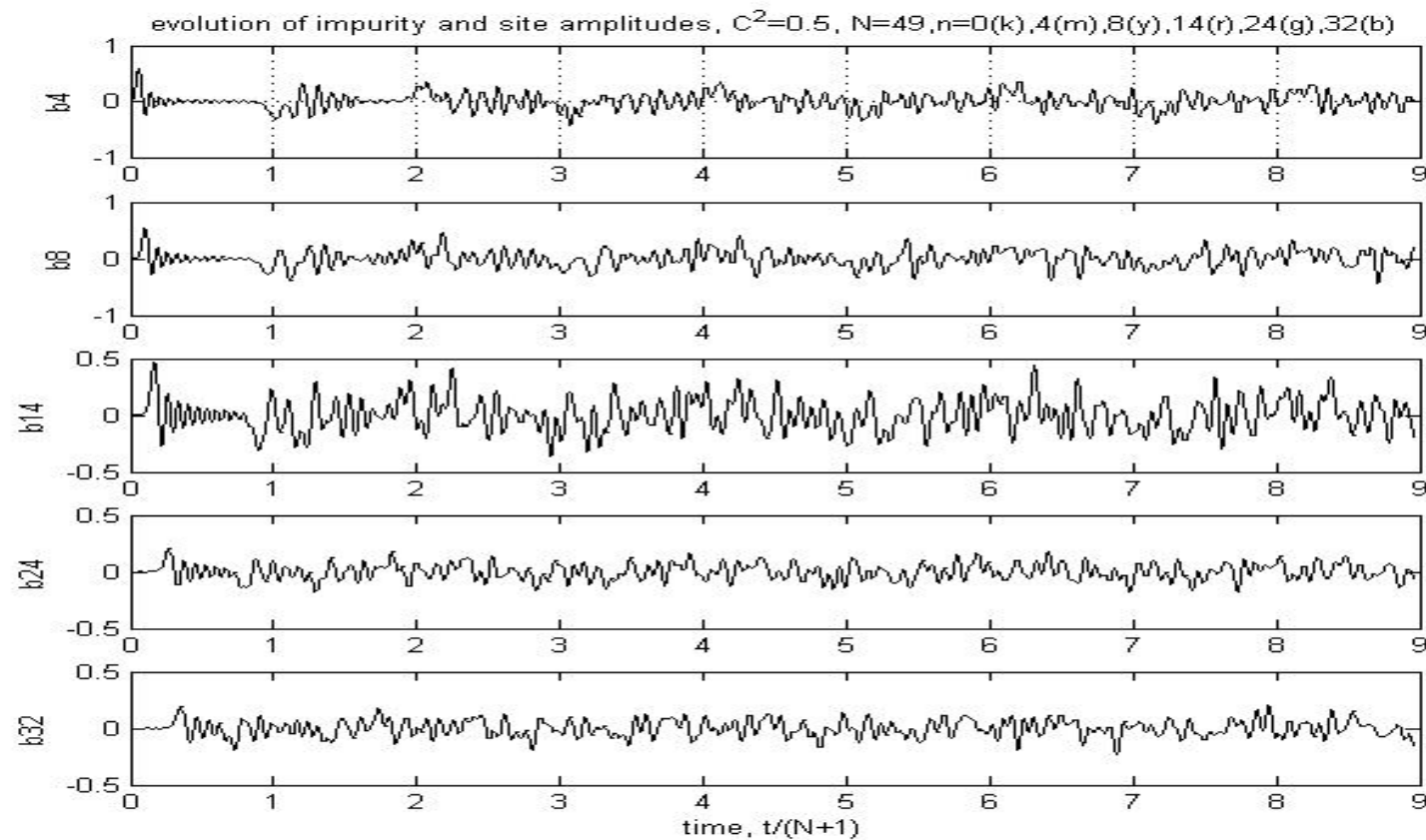
# Regular-stochastic-like transition

- Alike Zwanzig's model, there exists a critical number ( $s_c$ ) of recurrence cycle for overlap of the leading echo components of adjacent cycles. When  $s \gg s_c$ , evolution becomes stochastic-like due to even small fluctuations, inherent for any real system.
- Critical cycle number has a maximum at intermediate coupling

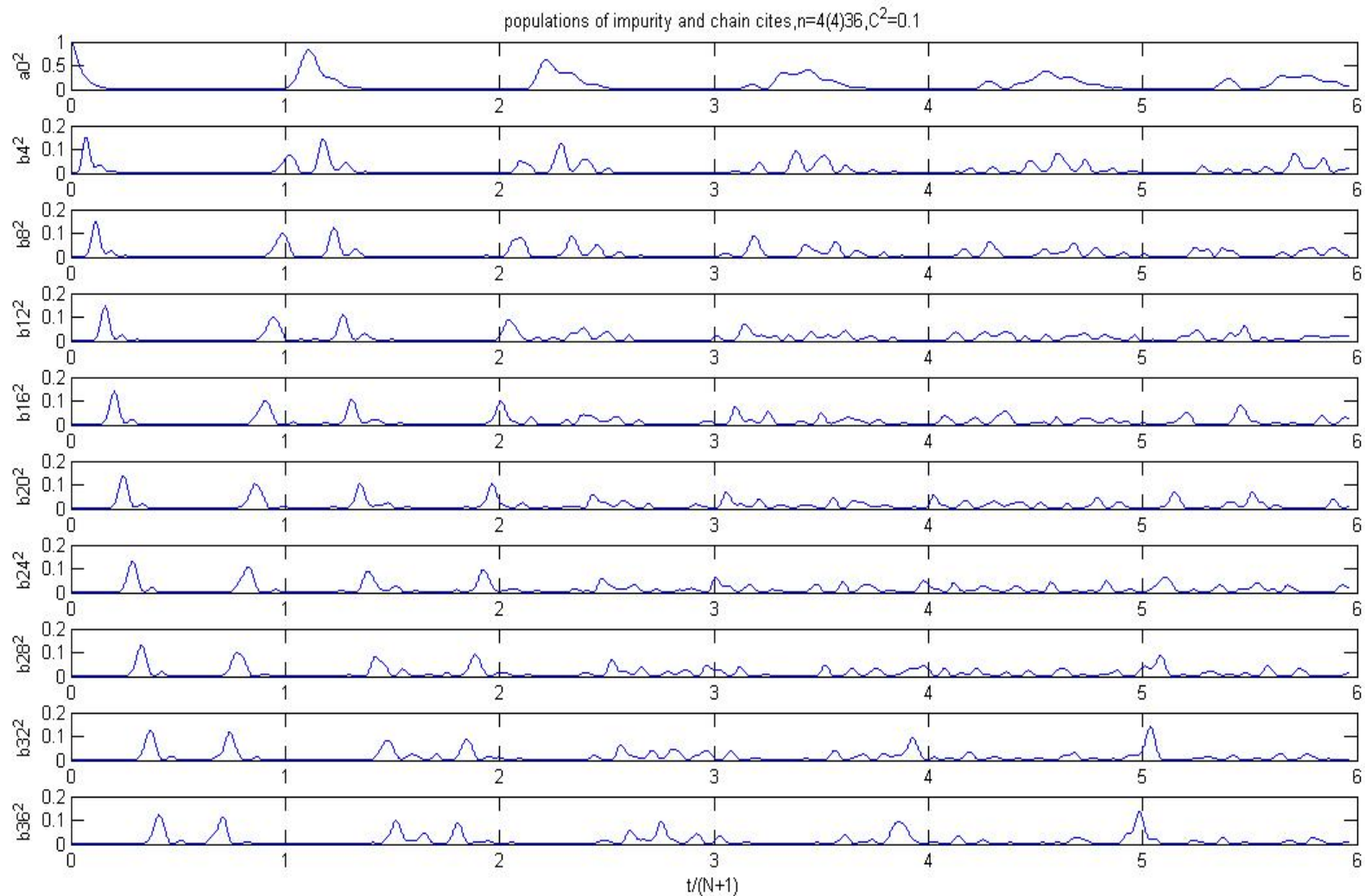
$$s_c \approx \begin{cases} (N+1)C^2/(1-C^2) & , \quad C^2 < 1/2 \\ (N+1)(1-C^2)/C^2 & , \quad 1/2 < C^2 < 1 \end{cases}$$

# Long-time evolution of site amplitudes

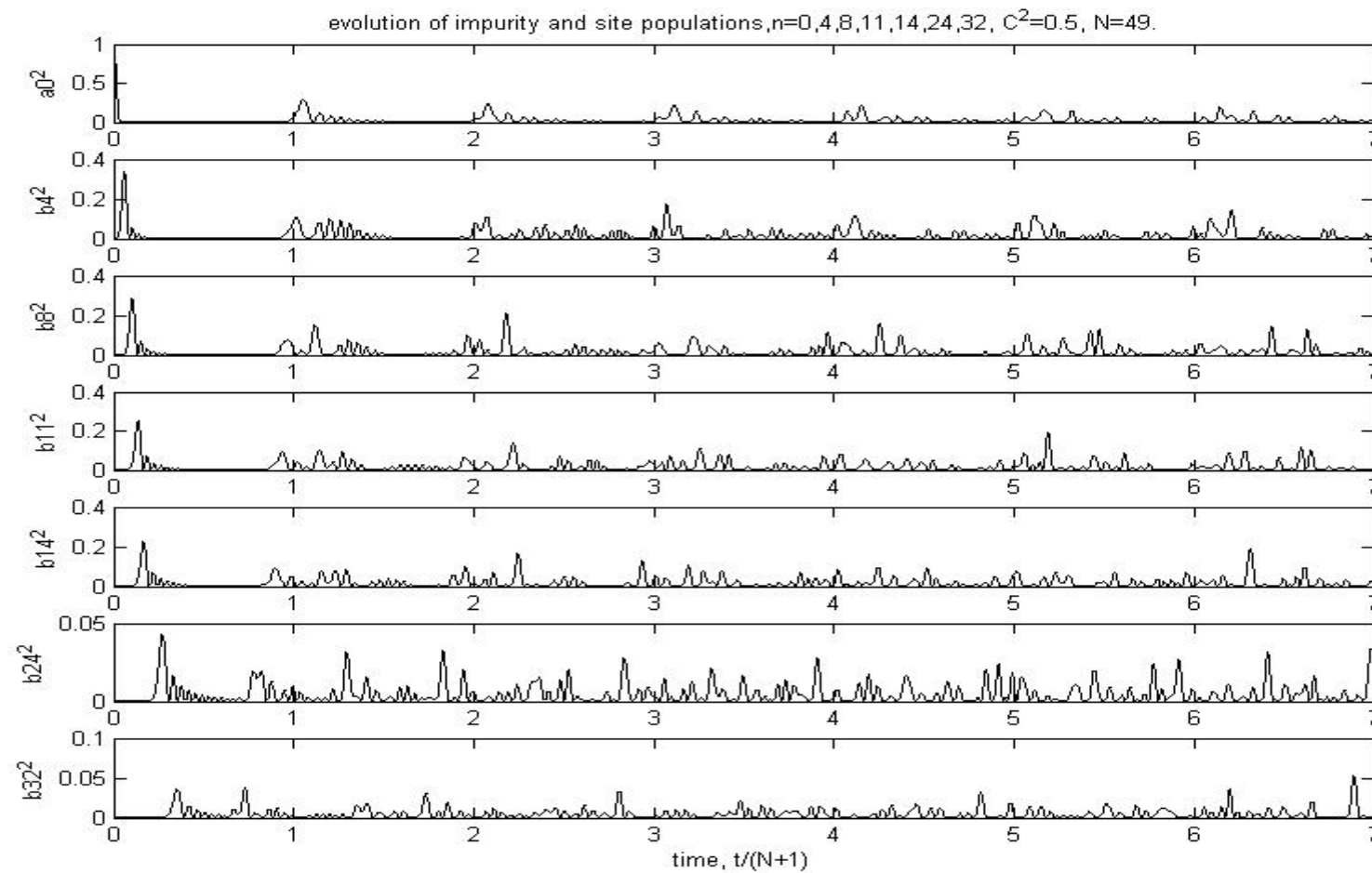
- Although site amplitudes demonstrate quite irregular evolution beginning even from the first recurrence cycle, the impurity amplitude evolution remains regular.



# Excitation wave propagation, $C^2=0.1$



# Excitation wave propagation, $C^2=0.5$



# Conclusion

- The model demonstrates the multiple loss-free forward and backward propagation of excitation along 1D chains with nearest neighbor interaction.
- Strong dependence of evolution on coupling constant enable us to reproduce experimentally observed ballistic regimes of thermal pulse propagation through long linear molecules.
- Regular-stochastic-like transition is predicted at the critical cycle number, which depends on coupling constant.