Propagating vibrational excitations in molecular chains

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Loss-free energy transportation in bio-molecular aggregates takes place within the following ranges

- Time scale: $10^{-13}-10^{-11}$ s.
- Energy scale: 0.15-0.25 eV.
- Transfer distance: 10-100 Ǻ

Evidence for loss-free propagation along molecular chains

- Chemical processes in biological systems are well understood on structural and thermodynamic levels.
- The reactive centers are linked by molecular chains of 10 - 100 Ǻ in length . The energy quanta 0.15-0.20 eV are produced upon chemical conversion in one reactive center and is transported without loss to another reactive site via the chain.
  $10^2 - 10^3$
- In order the energy transport does not accompanied by energy dispersion over large amount of internal vibrations, the special mechanisms of loss-free transport have 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.
- Presumably, this mechanism is realized in peptide and DNA chains.
- Quantum dynamic estimation of soliton parameters does not contradict this model.

- 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_2-fragments

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

Propagation is observed in the first time using pulse excitation of the end fragment of long linear molecule.
Propagation time is proportional to the chain length (N=15-20), velocity equals ~ 0.2 ps per one CH_2 –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.

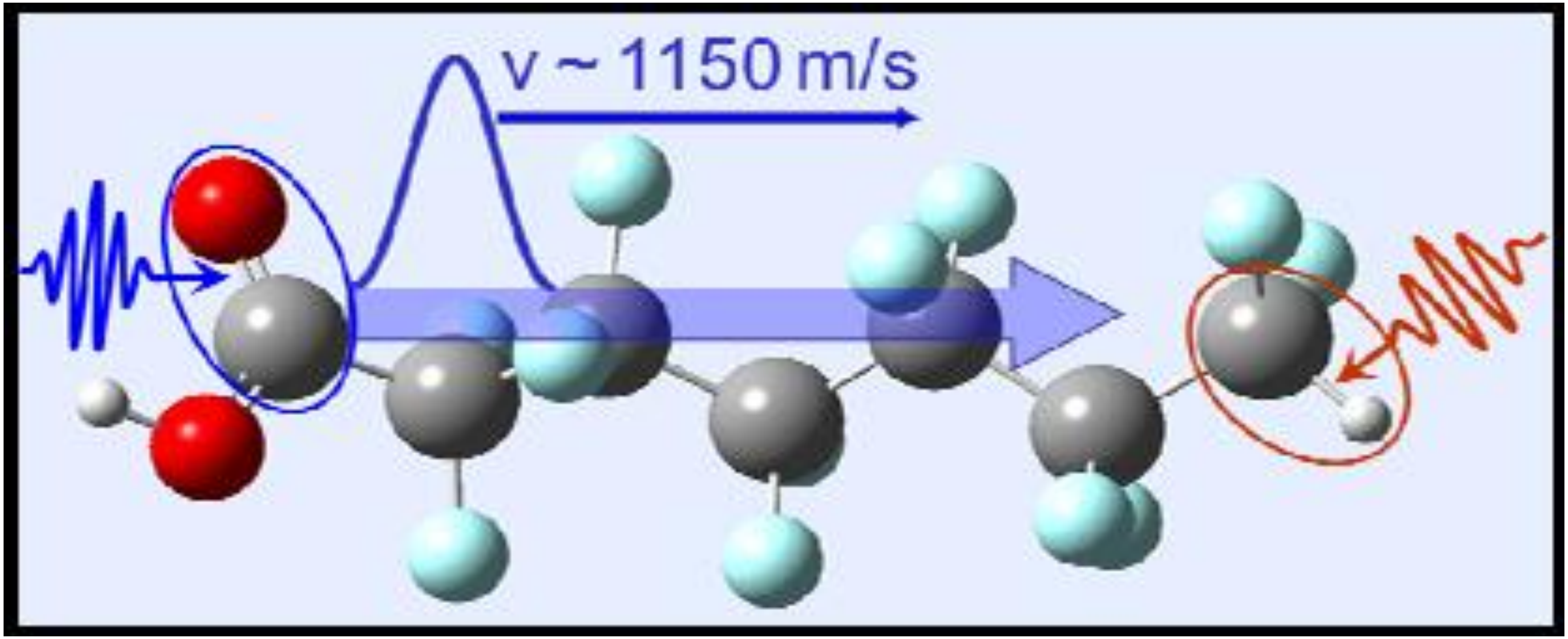
No hydrogen bonds, no highly anharmonic vibrations!

Non-linear Double IR-resonance

Rubtsov I.V. Acc.Chem.Res. 2009. (42)1385

Pumped and observed impurity sites are linked by molecular chain.

Short laser pulse produces excess population of pumped site and probing pulse controls time dependent population of observed site. Using molecular chains of different length propagation time and transport efficiency has been measured



Experimentally determined dependences on chain length N for molecular chains consisting of N fragments (CH2O) and CF2

Rubtsov I.V. et all . Phys.Chem.Chem.Phys. 2012 (14)10445, J.Chem.Phys. 2012(136)144503

- First passage time Tm linearly depends on N.
- Maximum of observed site population achieved at t=Tm decreases exponentially with increasing N with characteristic damping length of 5-8 fragments

Delocalized modes of molecular chains

Each polyatomic fragment has ~ (5-7) normal vibrations. They are mixed due to cross-anharmonic interactions between nearest neighbor cites. The vibrational band with complicated dispersion law is formed in the range 900-1400 cm(-1). Mean density of states is ~5 cm (about 100 levels) when number of fragments is N=20.

Theoretical model

- Normal random distribution of interaction matrix elements

The band of delocalized states includes several branches originated from different vibrations of each fragment. Interaction matrix elements are different for different branches and for different cite numbers.

In order to take into account both source of chain non-homogeneousness, we suggest (in spirit of random matrix description of dense spectra) the normal random distribution for interaction matrix elements.

- Calculation of eigenvalues and time dependent amplitudes for different events of random process

Since the pumped and observed sites are coupled with all branches, the propagation dynamics is characterized by ensemble of trajectories related to different branches.

- Average procedure over Gaussian ensemble.

Eigenvalue problem

- Secular determinant with random non-diagonal elements

$$F(\varepsilon)=\begin{vmatrix}
\varepsilon-E_s & C_s & \cdots & & & & & & & \\
C_s & \varepsilon & f_1 & & & & & & & \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & & \\
 & & \cdots & \varepsilon & f_n & 0 & 0 & \cdots & & \\
 & & \cdots & f_n & \varepsilon & f_{n+1} & 0 & \cdots & & \\
 & & \cdots & 0 & f_{n+1} & \varepsilon & f_{n+2} & \cdots & & \\
 & & \cdots & 0 & 0 & f_{n+2} & \varepsilon & \cdots & & \\
 & & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
 & & & & & & & f_{N-1} & \varepsilon & C_f \\
 & & & & & & & \cdots & C_f & \varepsilon-E_f
\end{vmatrix}=0$$

$$\left\langle f_k \right\rangle = 1 \quad , \quad \left\langle f_k^{\,2} \right\rangle = 1+\sigma^2$$

Equations of motion

- For each event of random process, t- dependent wave function

$$\Psi(t) = a_s(t)\varphi_s + \sum_{n=1}^{N} a_n(t)\varphi_n + a_f(t)\varphi_f$$

$$i\dot{a}_s = E_s a_s - C_s a_1$$

$$i\dot{a}_1 = -C_s a_s - a_2$$

$$i\dot{a}_n = -a_{n-1} - a_{n+1}$$

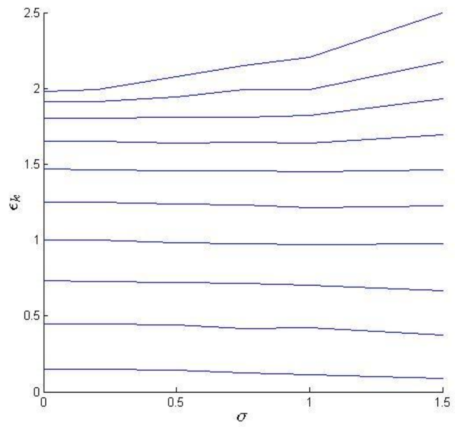
$$i\dot{a}_N = -a_{N-1} - C_f a_f$$

$$i\dot{a}_f = -C_f a_N + E_f a_f$$

$$a_k(t) = \sum_k \exp(i\varepsilon_k t) F_k(\varepsilon_k) \left(\left. \frac{dF}{d\varepsilon} \right|_{\varepsilon=\varepsilon_k} \right)^{-1}$$

Averaged eigenvalues

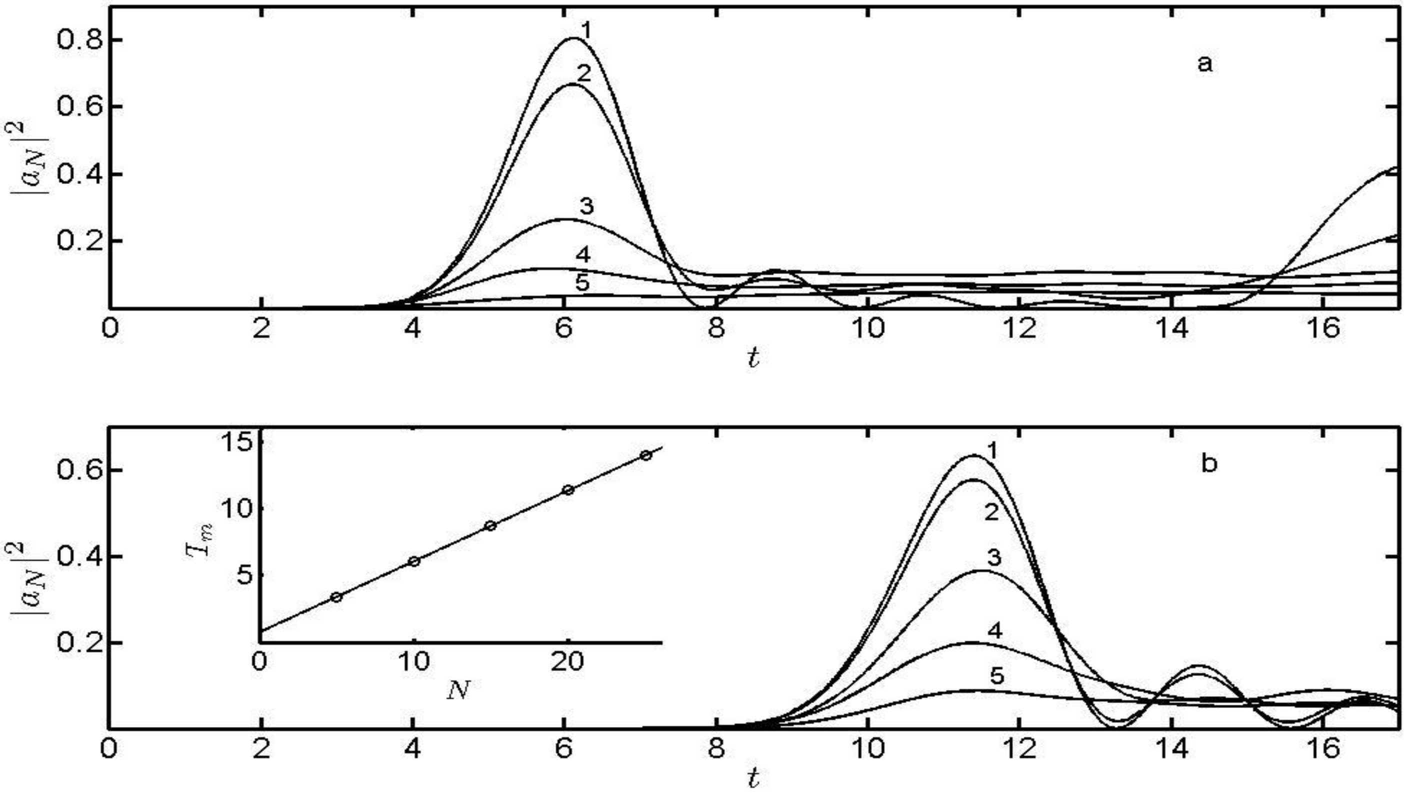
- Eigenvalues averaged over ensemble are monotonically shifted with increasing dispersion of non-diagonal matrix elements



If non-perturbative spectrum is regular, random non-diagonal interactions do not induce spectral chaos

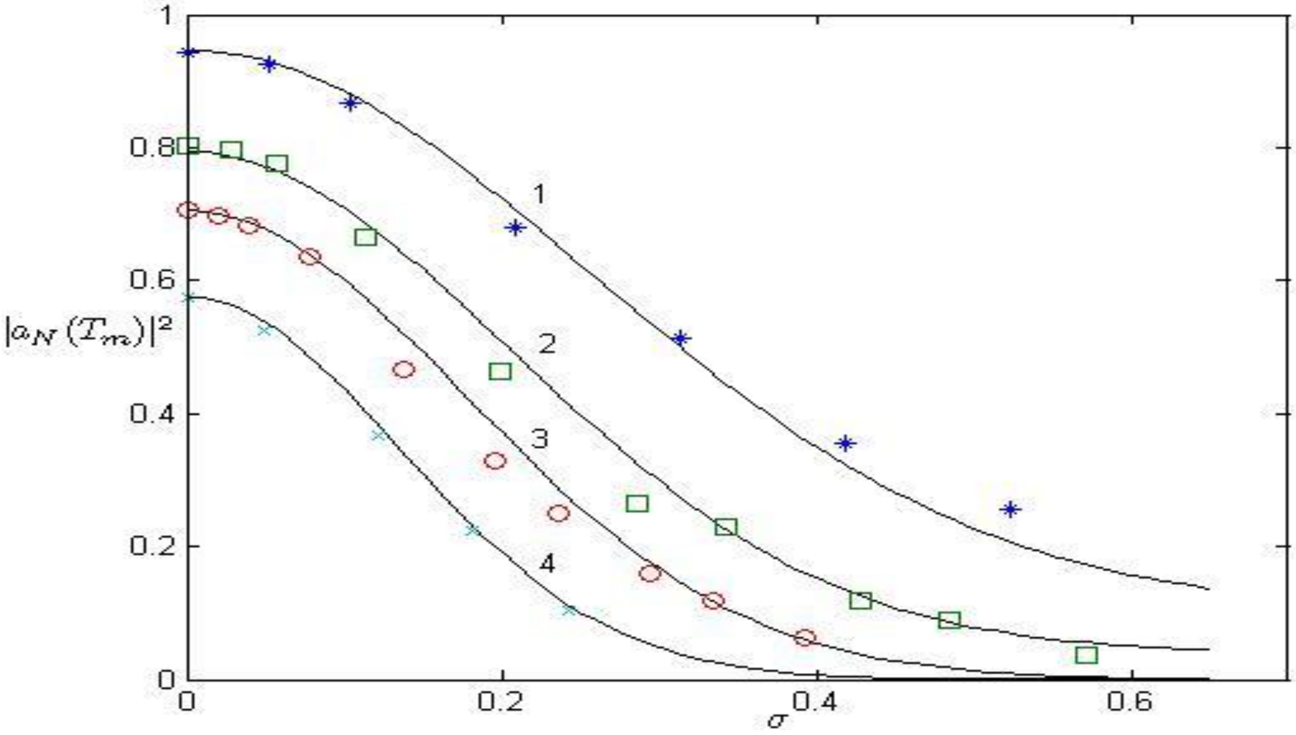
First passage time and maximum observed site population

- Dispersion values 0,0.2,0.5.0.75, 1.0 for curves 1-5



Exponential decrease of observed site population with increasing chain length and dispersion

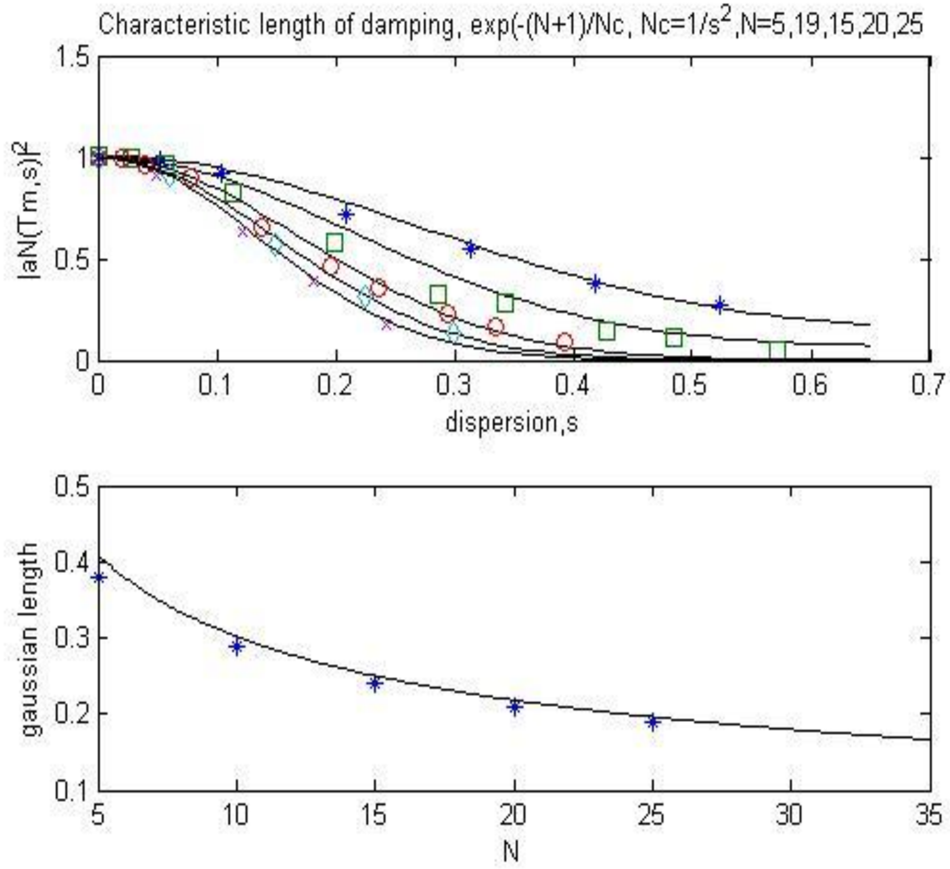
- Gaussian curves 1-4 : N=5,10,15,25



Transfer length

$$\left|a_N\left(T_m,\sigma\right)\right|^2 = \left|a_N\left(T_m,0\right)\right|^2 \exp\left(-\left(\sigma/\sigma_c(N)\right)^2\right)$$

$$\sigma_c(N) = \left(N+1\right)^{-1/2}$$

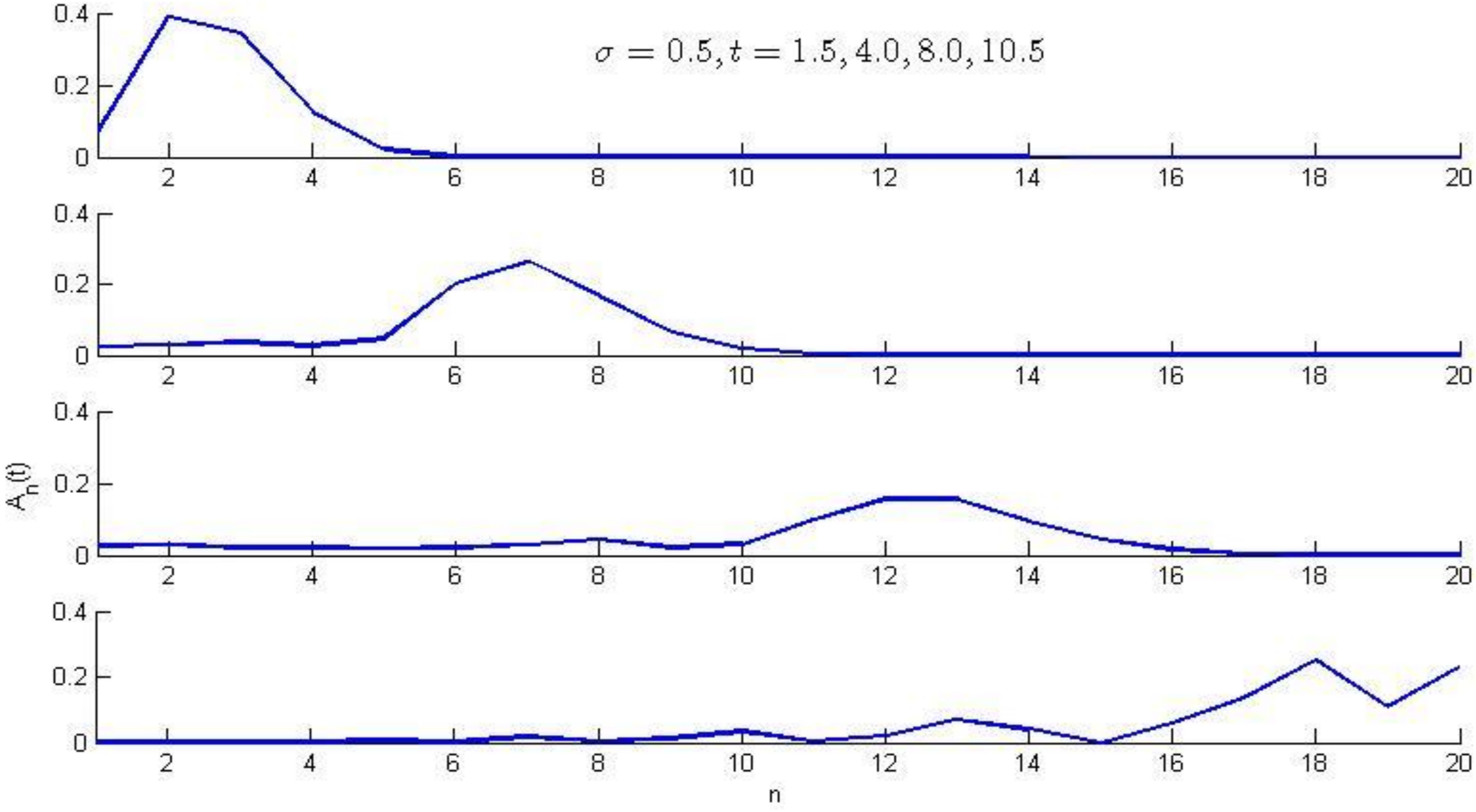


Comparison of experimental data with calculation results

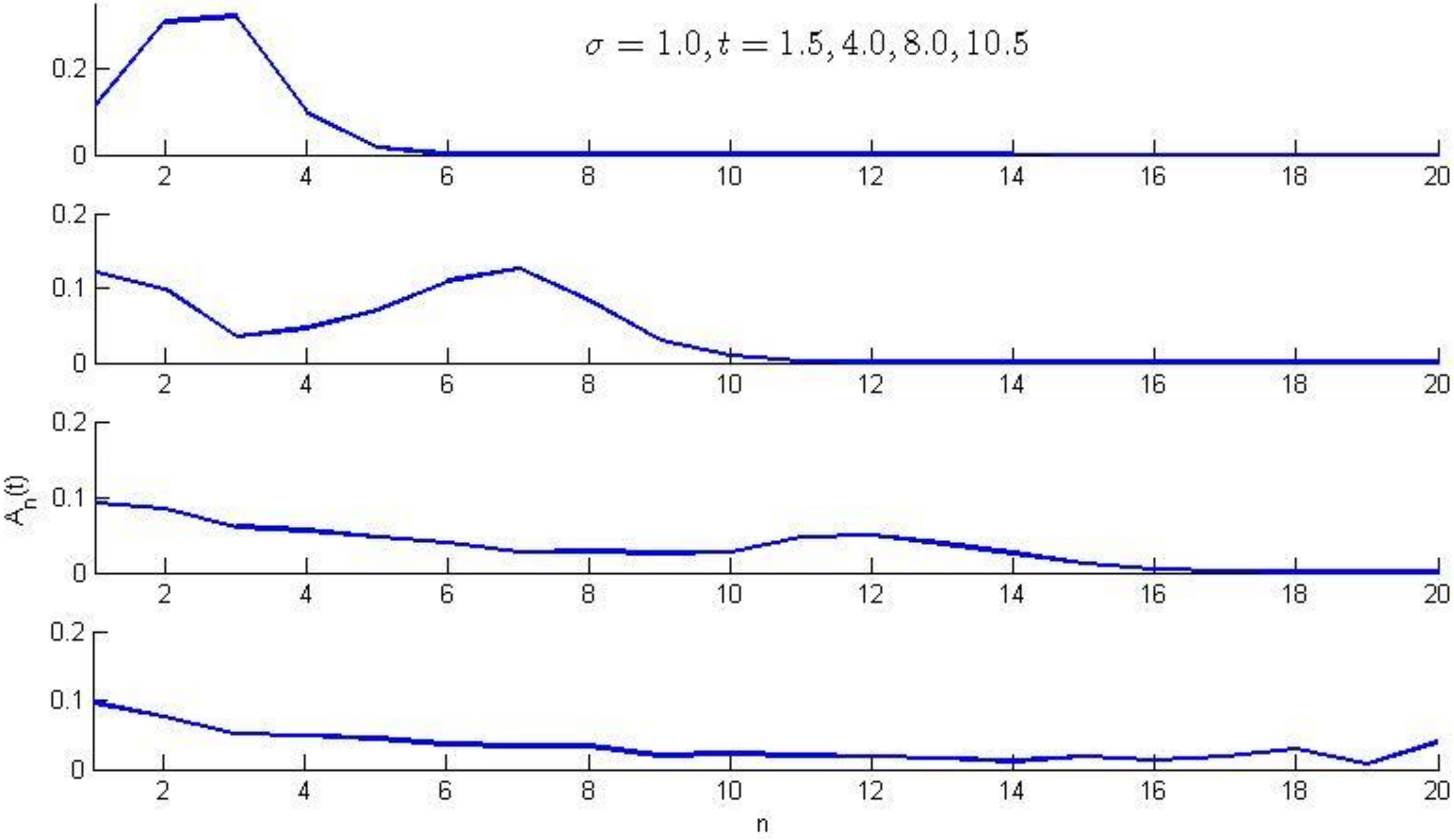
- Both experimental findings (linear dependences of first passage time and exponential decrease of amplitude with increasing chain length) are explained within theoretical model.
- Model predicts efficient energy transport existence when dispersion of interaction does not exceeds spacing between adjacent levels in vibrational band.

Ballistic-like propagation: dispersion is smaller than spacing between adjacent levels in the center of band.

- N=20



Diffusion-like propagation: dispersion becomes greater than spacing between adjacent levels



Conclusion

1. Vibrational excitations can propagate along the molecular chains. However the propagation is neither ballistic nor diffusion like. This behavior, arising from complexity of vibrational band in linear molecules, can be characterized by one phenomenological parameter, a dispersion of random interaction between adjacent cites.
2. The time Tm for the first passage of the excitation along the chain, scales linearly with number of chain fragments N in agreement with experimental data.
3. Vibrational energy, transported to the chain end at t = Tm is dramatically decreases when the dispersion exceeds interlevel spacing in vibrational band.
4. Since the dispersion increases in flexible chains, effective molecular wires providing fast loss-free transfer are to be rod-like in contrast to the typical polymer chains going up to the ball with increasing length.
5. One-parametric model presented in this report can be generalized using results of quantum chemical simulations.