Department of Systems Analysis
Belarusian State University

MONTE CARLO SIMULATION OF ENERGY TRANSFER PROCESSES

Marina V. Repich, Petr V. Nazarov, Mikalai M. Yatskou

Department of Systems Analysis,
Faculty of Radiophysics and Electronics,
Belarusian State University
Nezalezhnasti Ave 4, 220050,
Minsk, Belarus.
fax: +375 17 2789345
repich@bsu.by

Relevance, Goal and Objectives

The **energy transfer** (ET) is a very important phenomenon in many physical and biological processes and molecular systems. The ET provides the ability of photosynthesis in chloroplasts. The knowledge about it is necessary during development of artificial photo harvesting antenna complexes, quantum data processing systems, etc. Very important application of ET is the **fluorescence spectroscopy**, especially Förster Resonance Energy Transfer (**FRET**) spectroscopy, providing detailed information about the structure and mobility of molecular complexes.

The existing theoretical models for ET processes describe a rather limited set of molecular systems and their fluorescent properties. A powerful alternative approach to analyze photophysical processes in the experimental systems is **Monte Carlo simulation modeling**. However, the standard simulation models of electronic excitation energy transfer mainly deal with a single ET mechanism. Whereas several ET mechanisms can compete simultaneously in experimental systems. Therefore the development of a **universal simulation model**, which can describe several different energy transfer mechanisms simultaneously, is of high importance.

This work is aimed on the development of the generalized simulation model for electron excitation energy transfer implementing the dipole-dipole (Förster) and exchange (Dexter) ET mechanisms.

The following **objectives** were set to be performed:

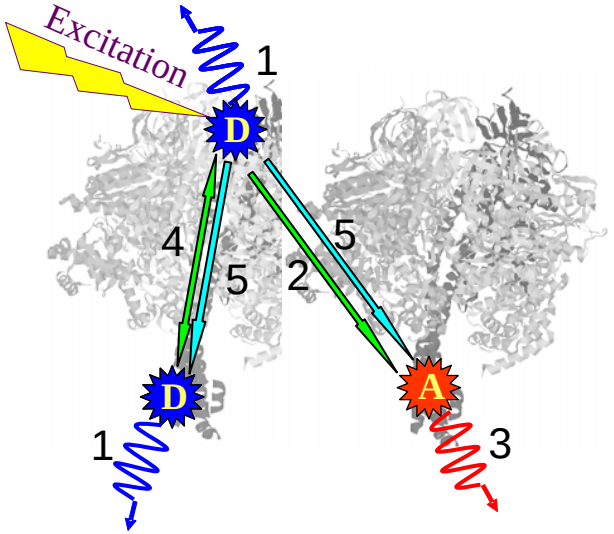
- Development of the generalized model of Förster and Dexter ET.
- Testing the model on the following spatial distributions of fluorescent molecules:
  - donor-acceptor pair
  - linear chain of molecules
  - uniform random distribution of molecules on the plane
- Studying the migration effect on the fluorescence.

The Considered Processes of Energy Transfer

Förster energy transfer process – columbic dipol-dipol interaction. The initially excited electron on the donor D returns to the ground state orbital on D, while simultaneously the acceptor A is transferred to excited state. Förster rate constant k_{et}^{F} is given by following Eq. 1

$$k_{et}^{F} = k_D \left(\frac{R_0}{r} \right)^6 \quad (1) \qquad R_0 = 0.211 \left(n^{-4} Q_D \kappa^2 J \right)^{1/6} \quad (2)$$

where k_D is the emission rate constant of the donor, r is the distance between the donor and the acceptor, and R_0 is the Förster radius. R_0 can be determined from spectroscopic data as shown in Eq.2, where κ^2 is the orientation factor, Q_D is the fluorescence quantum yield of the donor in the absence of acceptor, n is the average refractive index of the medium, and J – overlapping integral of donor emission and acceptor absorption spectra.



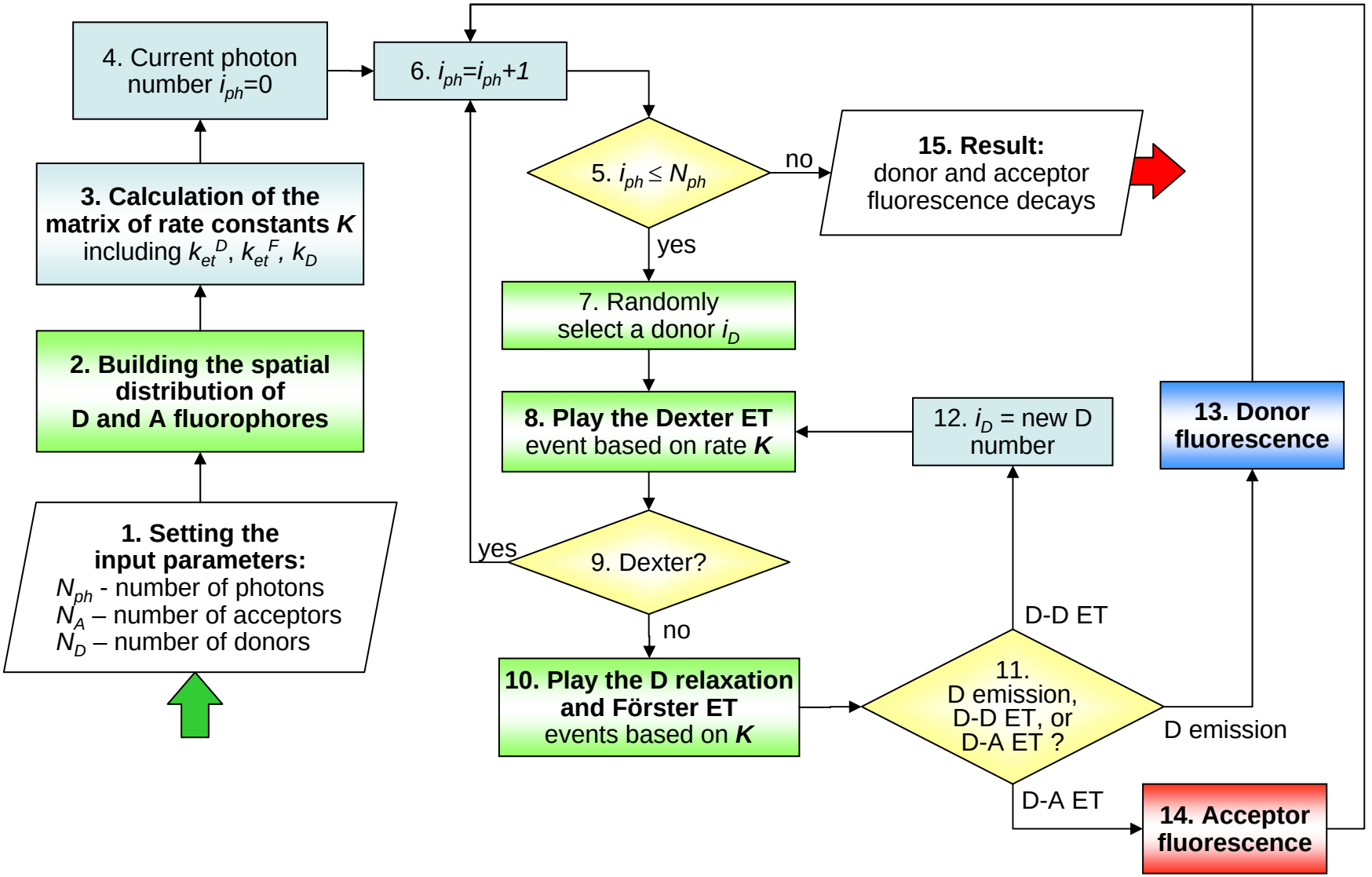
1 - Donor fluorescence, k_D
2 - Förster energy transfer, k_{et}^{F} (D-A)
3 - Acceptor fluorescence, k_A
4 - Energy migration, k_{et}^{F} (D-D)
5 - Dexter energy transfer, k_{et}^{D}

Dexter energy transfer process corresponds to an exchange of two electrons between D and A. The ET rate constant in this case k_{et}^{D} is given by Eq.3:

$$k_{et}^{D} = \frac{2\pi}{\hbar} e^{-2r/L} \int F_D(\lambda) \cdot \varepsilon_A(\lambda) \cdot d\lambda \quad (3)$$

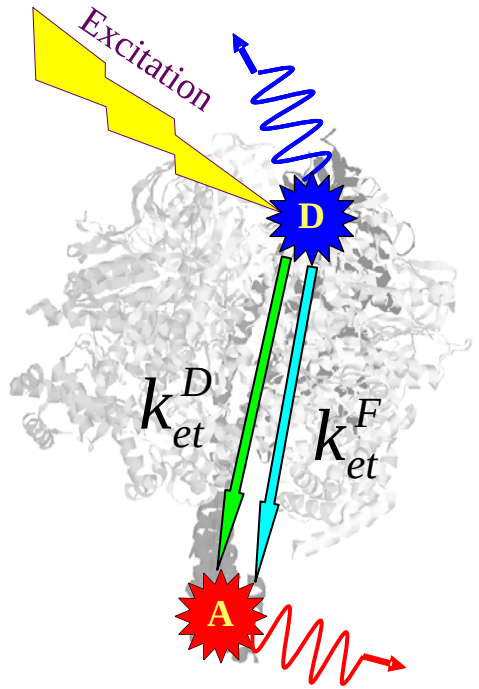
Where r is the distance between fluorophores, L – the average Bohr radius, F_D – donor emission spectrum, ε_A – acceptor extinction coefficient. In the current work we consider situation when Dexter mechanism of ET leads to quenching of fluorescence, therefore the excitation transferred via exchange mechanism is lost (emitted during phosphorescence, for instance).

Developed Simulation Model



Model Validation

Donor-acceptor pair



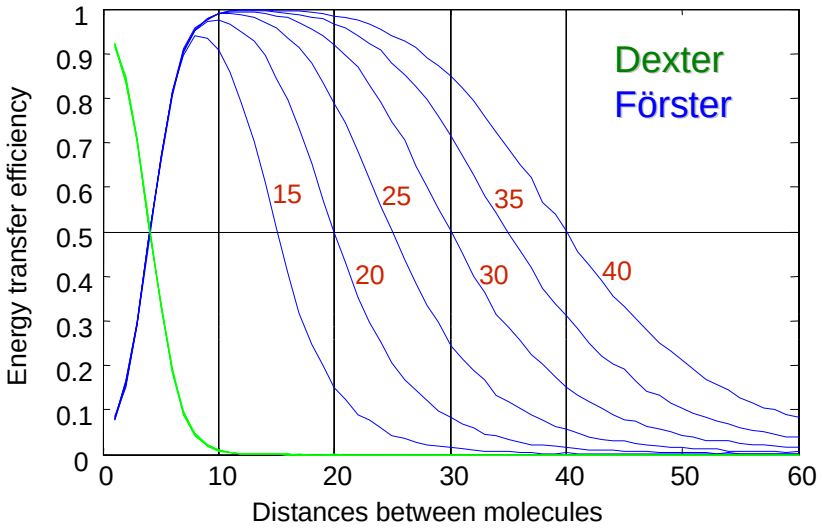
The developed simulation model of the Förster and Dexter energy transfer processes was tested for the case of a single donor-acceptor pair. The donor and acceptor fluorescences can be calculated in this case by:

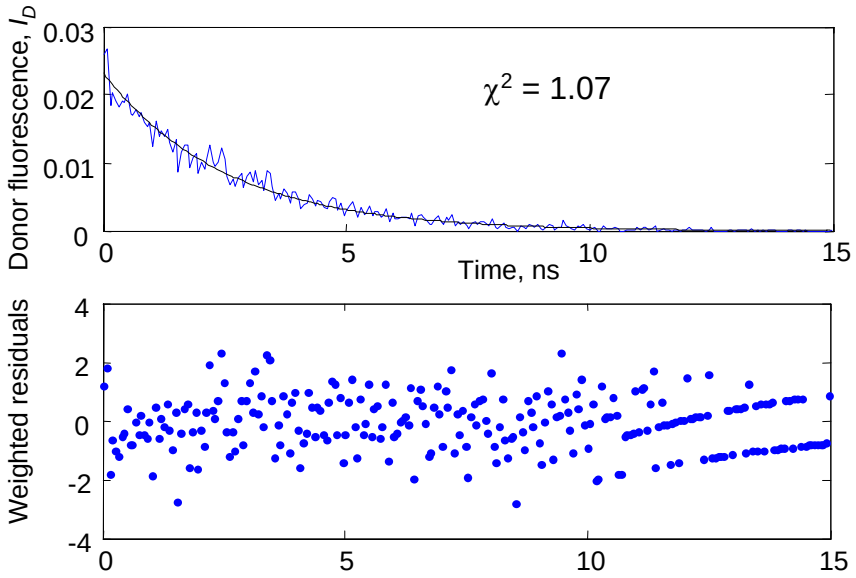
$$I_D(t) = N_0 k_D e^{-\left(k_D + k_{et}^F + k_{et}^D\right)\cdot t} \quad (8)$$

$$I_A(t) = \frac{k_{et}^F N_0 / k_D}{1/k_A - 1/k_D - k_{et}^F / k_A k_D}\left(e^{-k_D t - k_{et}^F t} - e^{-k_A t}\right) \quad (9)$$

The verification was performed using weighted residuals, their histogram, autocorrelation function and χ^2 criterion.

Efficiencies of F. and D. energy transfers





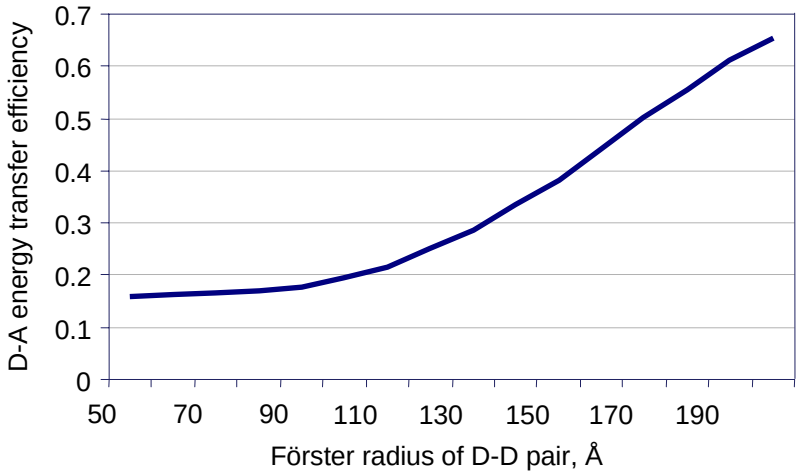
Simulation Results

Linear Chain of Molecules

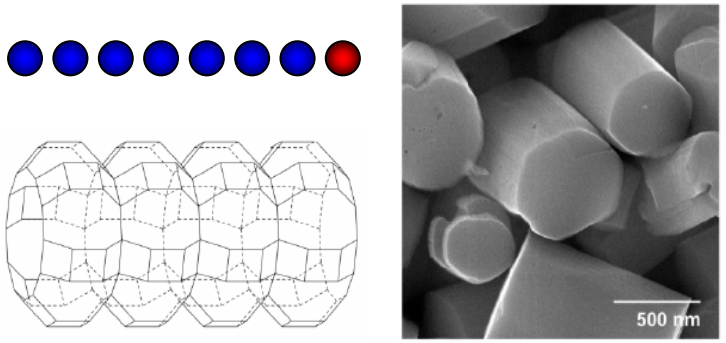
Linear chain of donors with a terminating acceptor is an idealization of zeolite crystals with fluorescent molecules embedded. Using the developed model the effect of homo energy transfer (energy migration) on donor-acceptor energy transfer was studied. The dependency between D-A energy transfer and D-D Forster (migration efficiency) distance is showed in the figure below.

To validate the model of energy migration the system containing only donors was considered. The figures on the right shows perfect agreement of simulated donor fluorescence with theoretically predicted – the migration in the homogeneous donor system (without acceptors) equals to the fluorescence of a single donor.

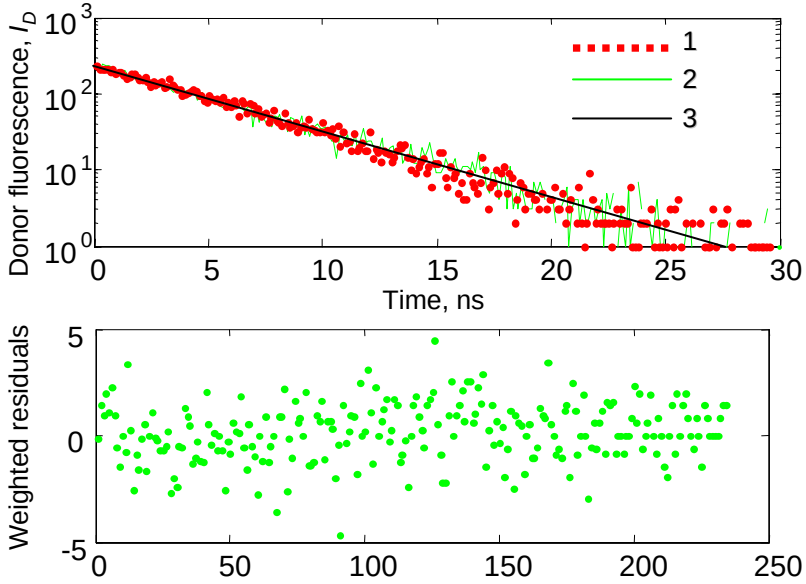
Dependency of D-A energy transfer on D-D Förster distance



Considered systems



Validation of migration model

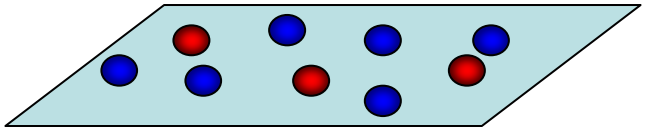


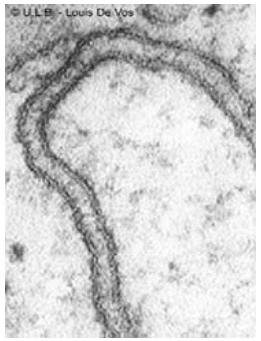
1 – chain of donors with the migration
2 – chain of donors without the migration
3 – fluorescence of a single donor

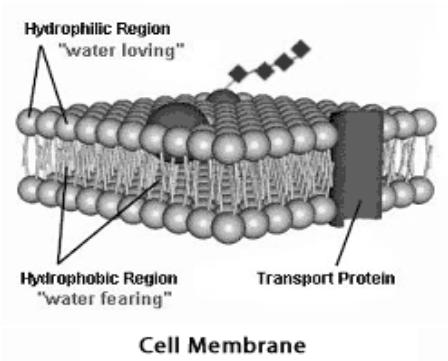
Simulation Results

Uniform Random Distribution of Molecules in the Plane

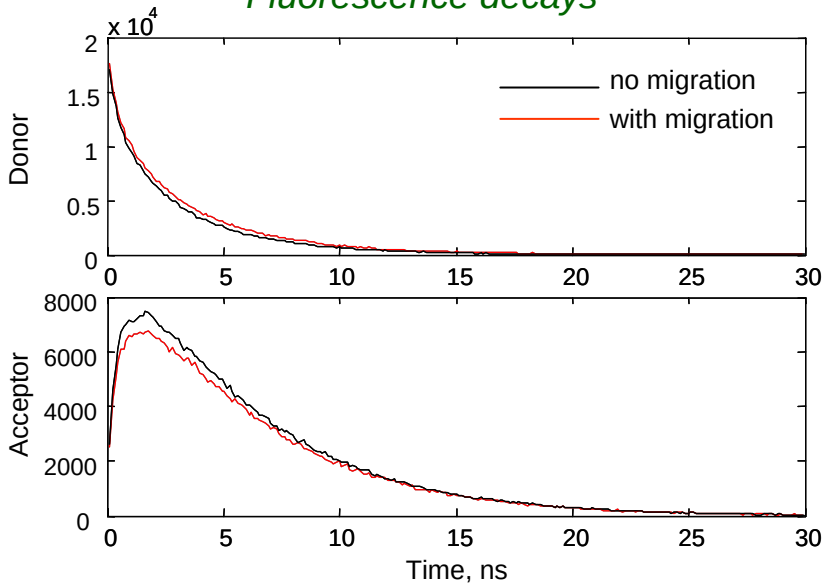
Uniform random distribution of molecules in the plane is an idealized model of biological membranes and thin films. Using the developed model the effects of energy migration and different mechanisms of energy transfers on donor and acceptor fluorescence were studied. The presence of the migration in the system increase the efficiency of donor-acceptor energy transfer. The effect of Dexter mechanism of energy transfer was found in the quenching of acceptor fluorescence.



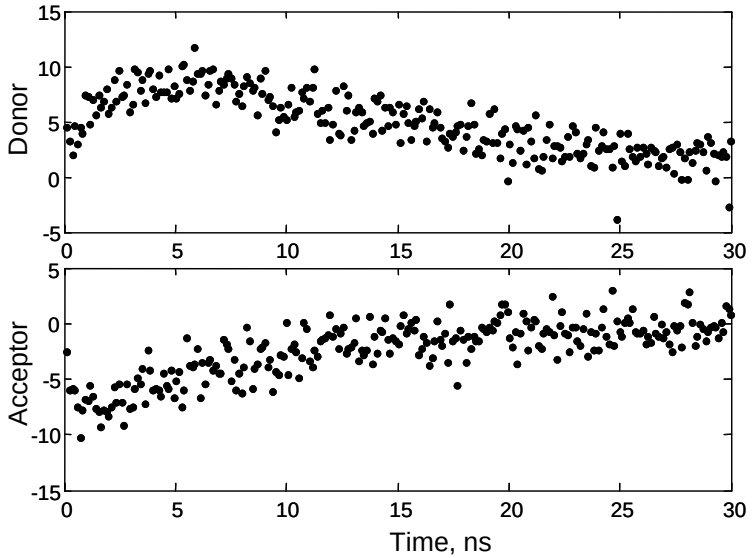




Fluorescence decays



Weighted residuals



Conclusions

- **The generalized model of energy transfer by Förster and Dexter mechanism was developed and validated for the simplest systems**
- **As it was found in numerical experiments, the homo energy migration in the system increases the hetero energy transfer**
- **The effect of Dexter energy transfer was observed only in acceptor fluorescence**

Future plans

- **Improve the biophysical model**
  - include others mechanisms of energy transfer (excitonic, radiation)
  - develop algorithm for the frequency domain fluorescence
- **Apply artificial neural networks as a “black box” model of energy transfer processes (to decrease the simulation time)**
- **Apply developed methods to real systems (proteins, biomembranes)**