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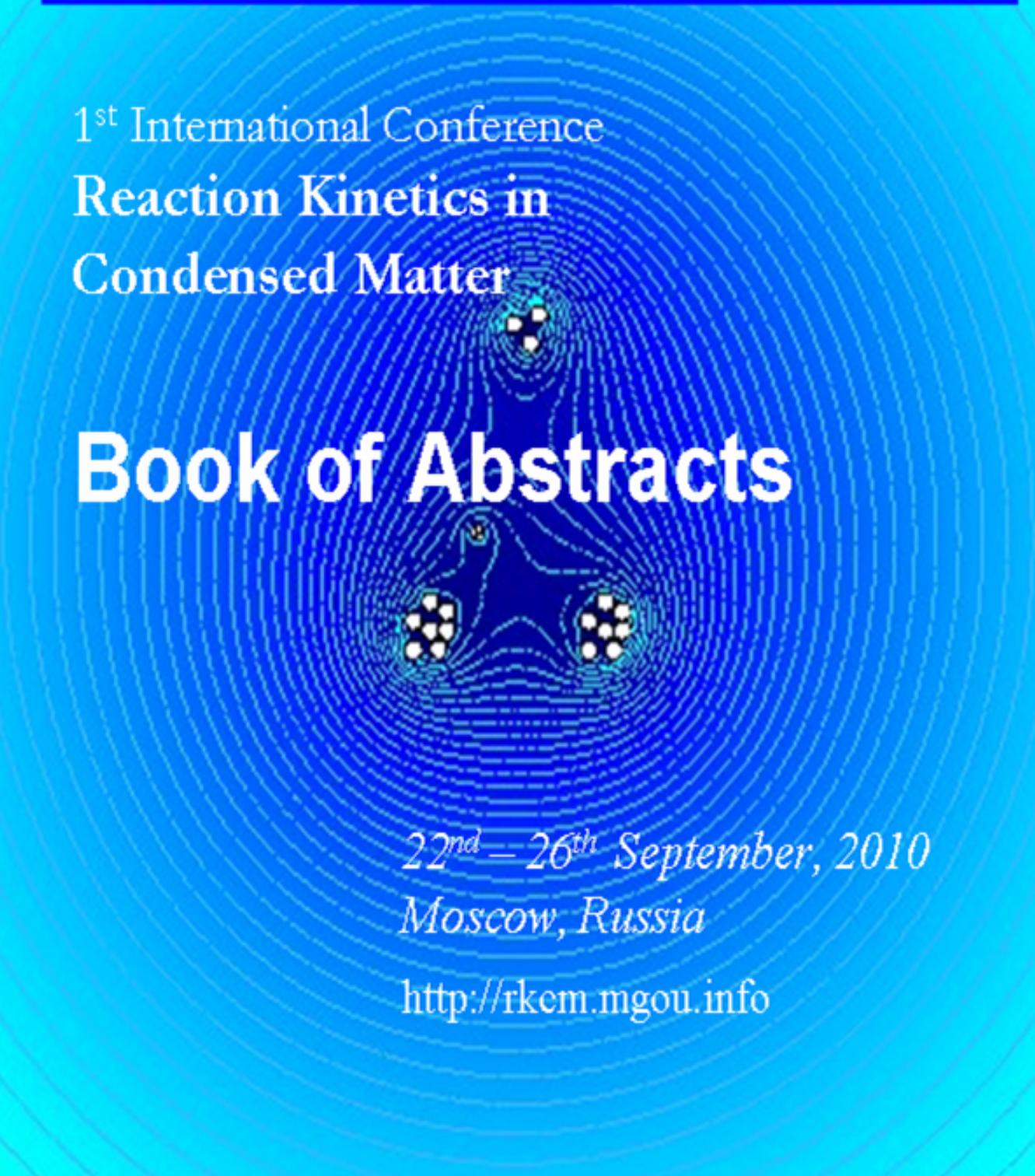
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1st International Conference
**Reaction Kinetics in
Condensed Matter**

Book of Abstracts



22nd – 26th September, 2010
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Moscow Region State University



1st international conference on
Reaction Kinetics in Condensed Matter
RKCM'10 - Moscow

September 22 (Wednesday) - September 26 (Sunday)

Moscow Region State University, Moscow, RUSSIA

Moscow 2010

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Acknowledgements

RKCM'10 is supported by scientific grants:

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Aim

Reaction Kinetics in Condensed Matter 2010 (RKCM'10) is the first of the new series of international conference in the field of kinetics of chemical reactions in condensed matter. **RKCM'10** will particularly fill the void left by the disappearance of Fast Reactions in Solution (FRIS, a discussion meeting of the Royal Society) in conferences on general chemical kinetics and to adapt and broaden the subjects related to kinetics of chemical reactions. The main concern of the conference will be investigating chemical reactions from the physical point of view, revealing new physical mechanisms of chemical processes and elucidating physics behind the chemical event.

Special attention will be given to bridge the enormous gap between the most advanced statistical mechanical theories and the latest experimental techniques in a wide variety of fields from reactions in amorphous solids (polymers for example, with an increasing potential for new technologies in energy conversion, light emitting devices, organic electronics etc.) chemical reactions in crowded biological media. It is interesting to note that most of these topics present indeed a common problematic, i.e. the current description of the rate of the chemical events when coupled to the reactants mobility or diffusion. Unfortunately, the lack of a common arena to gather theoreticians and experimentalists make the firsts unaware of the range of problems of the latter, and artificially hides to the latter the descriptive tools already developed by the firsts.

So **RKCM'10** will devote to all aspects of experiments and theory of chemical kinetics in condensed matter: past and future, untested predictions, experiments required, unexplained experimental results etc. In order to find common scientific interests and speak common language the participants are strongly encouraged not only to present their own results but also to give an introduction into their subfield of **RKCM'10**. The conference shall foster and encourage world wide cooperation and communication in those fields. Moreover, **RKCM'10** will also place emphasis on getting students and young researchers involved in investigations of the problems within the scope of this conference.

Topics

The topics to be covered in **RKCM'10** are as follows:

- a. Normal and anomalous diffusion: reactions in spatially restricted systems, polymers and amorphous media
- b. Fast reactions in different media: electron transfer, energy transfer, diffusion-influenced processes, fluorescence quenching
- c. Effects of external magnetic and electric fields on reaction kinetics
- d. Physical insights into fast reactions in biological media
- e. New experimental methods in chemical kinetics
- f. New spectroscopic techniques for kinetics in condensed matter
- g. Sterically specific reactions in bio and nano-systems

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* the author representing the Paper is underlined

Charge Recombination in Organic Solar Cells

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1. Introduction

In organic solar cells charge recombination is a key loss process. We have theoretically studied charge recombination in organic solar cells to suppress recombination loss. Charge recombination in organic solar cells is divided into two phases, geminate charge recombination phase and bulk charge recombination phase.

2. Results

Geminate charge recombination is usually analyzed by Onsager theory [1] or Braun model [2]. However, the former is based on an unrealistic assumption that an electron and a hole recombine only when their separation becomes zero, while the latter is based on an empirical assumption that the separation process follows exponential kinetics. We have rigorously extended Onsager theory to a realistic case in which an electron and a hole recombine at a nonzero separation with a finite intrinsic recombination rate [3]. We have shown that the correctly calculated charge separation yield is significantly different from that obtained from the empirical Braun model.

In order to increase the efficiency of organic solar cells bulk heterojunction systems are developed in which electron transport region and hole transport region are separated by an interface. We have studied geminate charge recombination in these systems and shown [4] that in these systems the charge separation yield is maximized when the mobilities of electron and hole are equal (see Fig. 1), unlike the assertion of Peumans and Forrest [5]. We have also shown that the charge separation yield is enhanced by one order of magnitude by adopting heterojunction systems instead of the homogeneous systems.

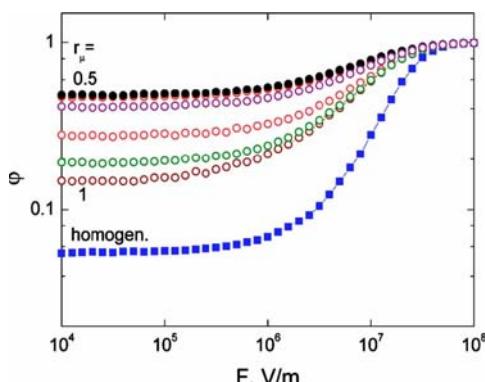


Fig. 1: Effect of the ratio of the electron mobility μ_e and the hole mobility μ_h on charge separation probability ϕ in heterojunction systems. The electron and hole mobilities are given by $\mu_e=r_\mu\mu$ and $\mu_h=(1-r_\mu)\mu$. The sum μ of the mobilities is fixed at 10^{-6} cm²/Vs. The circles represent the results for $r_\mu=0.5, 0.7, 0.9, 0.99, 0.999$ and 1 from top to bottom. The squares represent the results in homogeneous systems.

Bulk charge recombination is usually analyzed by Langevin theory [6]. However, it is also based on the same unrealistic assumption as used in Onsager theory of geminate recombination. We have extended Langevin theory to a realistic case of a finite intrinsic recombination rate at nonzero separation and explained recent experimental results on bulk charge recombination in organic solar cells [7] (see Fig. 2).

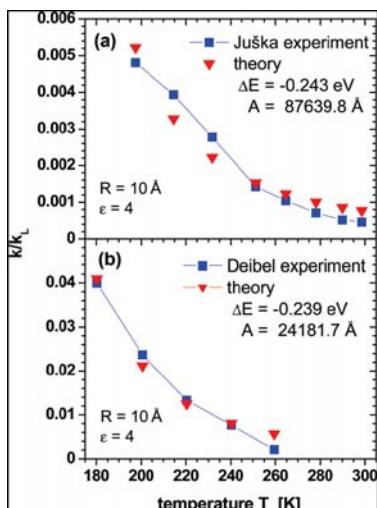


Fig. 2: Effect of the temperature on the bulk recombination rate constant k . k_L is the Langevin rate constant. ΔE is the difference between the activation energy of the diffusion coefficient and that of the intrinsic recombination rate constant.

We have also analyzed the effect of energetic disorder in the medium on bulk charge recombination kinetics [8] by using the multiple trapping model.

Finally we show theoretically how we can optimize various parameters involved in organic solar cells to suppress recombination loss.

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Weak Ergodicity Breaking: from Blinking Quantum Dots to mRNA Diffusing in the Cell

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1. Introduction

In nature the noisy signal representing a Physical observable is in many cases unpredictable, though the long time average of the signal converges in statistical sense to the ensemble average (ergodicity). Recently, observations of dynamics of single molecules, e.g. blinking quantum dots [1-4], and motion of single mRNA in the cell revealed non-ergodic processes [5, 6]. These signals are characterized by power law sojourn times, in micro states of the system (e.g. in state on and off for the dots) in such a way that the average time spent in a micro state diverges.

2. Results

Two basic questions addressed in my talk are:

- (i) what theory replaced ergodic Boltzmann-Gibbs statistical mechanics for such systems [7];
- (ii) what are the possible Physical and Chemical mechanisms responsible for the anomalous non Gaussian dynamics [1-4].

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Theory and Simulation of Diffusion-Influenced Bimolecular Reactions

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1. Introduction

Molecular recognition is central to chemistry and biology. Recognition involves the binding of a receptor and a ligand. We have been developing theories and simulation methods for calculating receptor-ligand binding rate constants. Various realistic aspects are accounted for in order to accurately model biochemical reactions. These include stereospecificity of the receptor-ligand complexes, interactions of receptor and ligand molecules, conformational changes of the reactant molecules, and intracellular crowding [1-5].

2. Results

In solutions, relative diffusion of reactant molecules bring them together to bind. In the Smoluchowski formalism, the kinetics of such diffusion-influenced bimolecular reactions is described by a time-dependent rate coefficient, $k(t)$. This rate coefficient is determined by the pair distribution function. For rigid, anisotropic molecules, the pair distribution function can be written as $p(\mathbf{r}, \omega_1, \omega_2, t)$, where \mathbf{r} is the relative separation of the reactant molecules and ω_1 and ω_2 represent their orientations. We write $(\mathbf{r}, \omega_1, \omega_2)$ collectively as \mathbf{x} . $p(\mathbf{x}, t)$ satisfies the Smoluchowski equation, i.e., the diffusion equation with the inter-molecular potential $U(\mathbf{x})$ accounted for. In a certain “reaction” region, denoted by Γ , the reactant pair can form the complex; this step is modeled by an intrinsic rate constant $\kappa(\mathbf{x})$. The Smoluchowski equation is solved subjected to the initial condition $p(\mathbf{x}, 0) = \exp[-\beta U(\mathbf{x})]/(8\pi^2)^2$ and the outer boundary value $p(\mathbf{x}, t) = 1/(8\pi^2)^2$ as $r \rightarrow \infty$ and a reflecting boundary condition on the inner contact surface. The rate coefficient is given by

$$k(t) = \int_{\mathbf{x} \in \Gamma} d\mathbf{x} \kappa(\mathbf{x}) p(\mathbf{x}, t)$$

The initial value of the rate coefficient is

$$k(0) = \int_{\mathbf{x} \in \Gamma} d\mathbf{x} \kappa(\mathbf{x}) \exp[-\beta U(\mathbf{x})]/(8\pi^2)^2$$

We developed an efficient algorithm for calculating $k(t)$ from simulating the translational and rotational diffusion of the reactant pair [1, 2]. The algorithm is based on the identity

$$p(\mathbf{x}, t) = S(t | \mathbf{x}) \exp[-\beta U(\mathbf{x})]/(8\pi^2)^2$$

where $S(t|\mathbf{x})$ is the survival probability of the reactant pair starting from configuration \mathbf{x} . The rate coefficient can then be written as

$$k(t) = k(0) \langle S(t | \mathbf{x}) \rangle_{\mathbf{x}}$$

where $\langle \dots \rangle_{\mathbf{x}}$ denotes averaging over an initial distribution proportional to $\kappa(\mathbf{x})\exp[-\beta U(\mathbf{x})]$.

Of particular interest is the steady-state rate constant, k_{ss} . We have derived a very useful approximation for k_{ss} . When the reaction region is small, meaning that the binding is highly stereospecific, and the interaction potential is long-ranged, as in the case of electrostatic interactions, we showed that [2,6]

$$k_{ss} \approx k_{ss}^0 \langle \exp(-\beta U(\mathbf{x})) \rangle_{\Gamma}$$

where k_{ss}^0 is the rate constant in the absence of the long-range interaction potential and $\langle \dots \rangle_{\Gamma}$ signifies averaging over the reaction region. k_{ss}^0 is the basal rate constant set by relative translational and rotational diffusion between the binding molecules.

The above approximate formula, referred to as the transient-complex theory, has been used to calculate, with high accuracy, binding rate constants for a number of protein-protein and protein-RNA complexes [3]. The theory was used to dissect a record-setting rate constant, at $> 10^{10} \text{ M}^{-1}\text{s}^{-1}$, of a ribotoxin binding to a biologically essential RNA loop on the ribosome [7]. The basal rate constant k_{ss}^0 is $10^4 \text{ M}^{-1}\text{s}^{-1}$. Electrostatic attraction between the binding molecules provides a 5×10^6 -fold rate enhancement. In comparison, the binding rate constant to the isolated RNA loop is electrostatically enhanced by 5×10^2 -fold, in line with the results found in other protein–protein and protein–RNA complexes. There are two contributions to the additional 10^4 -fold rate enhancement. First, the rest of the ribosome provides extra electrostatic attraction to the ribotoxin. Second, neighboring ribosomal proteins reshape the binding interface to position the transient complex into a region in configurational space where the electrostatic attraction between the ribotoxin and the RNA loop is particularly strong.

We have also accounted for conformational changes of the binding molecules [5] and effects of macromolecular crowding [3, 4].

3. Conclusion

These theories and simulations are allowing us to realistically model the kinetics of biochemical reactions.

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Effect of Interparticle Interaction on Kinetics of Geminate Recombination of Subdiffusing Particles

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1. Introduction

Diffusion assisted reactions (DARs) is the important stage of a large number of chemical and physical condensed phase processes. In many of these processes the DARs are known to be strongly affected by interaction between reacting particles. The effect of the interaction on the DAR kinetics is actively studied both experimentally and theoretically for a long time.

In the case of conventional diffusion the problem of the analysis of DAR kinetics reduces to solving the Smoluchowski equation for the pair distribution function (PDF) of reacting particles. This equation is fairly complicated and can, in general, be solved only numerically. As for analytical study, usually it is made with the use of steady state analytical solutions. The general time dependent analytical solutions can be found only for very few interaction potentials, for example, in the case Coulomb interaction. These solutions, however, are very cumbersome and complicated for applications.

Some years ago much more simple and rigorous method of analytical solution of the Smoluchowski equation was proposed, which is applicable in the practically interesting limit of deep well of attractive interaction (reactivity assumed to be localized in the well) [1-3]. The solution shows that the interaction strongly manifests itself in the reaction kinetics resulting in the long life time of particles within the well (i.e. caging). The time evolution of the PDF of pairs captured and reacting in the well appears to be non-exponential [1-3]. This specific feature of the PDF time evolution shows itself, for example, in non-exponential kinetics of geminate DARs with the long time tail of inverse power type [1-3].

2. The method of analysis and results

In this work we will consider the kinetics of geminate reaction of interacting particles undergoing subdiffusive motion. Recall that subdiffusion is a certain type of anomalous diffusion, which is characterized by the anomalously slow time dependence of the mean square of displacement $\langle r^2 \rangle \sim t^\alpha$ with $\alpha < 1$. Recently, the specific features of the kinetics of subdiffusion assisted reactions (SDARs) are a subject of active discussions. The anomaly of diffusion is shown to affect fairly strongly the reaction kinetics leading to the effective slowing down of the reaction at long times, to the strong fluctuations of concentrations of reacting particles at long times, etc.

In the absence of interparticle interaction (i.e. in the case of free subdiffusion) the time evolution of the PDF of subdiffusing particles is usually described by the analog of diffusion equation, which is called fractional diffusion equation and in which the effect of diffusion anomaly shows itself in anomalously long time memory. The predictions of the theory based on fractional diffusion equation are analyzed in a large number of papers.

As for the SDARs of interacting particles, these processes are not studied theoretically yet. The kinetics of them is also determined by the corresponding PDF, but the PDF evolution is described by the fractional Smoluchowski equation. Similarly to the case of conventional diffusion, the fractional equation is much more complicated for numerical and analytical analysis than that for free diffusion.

In our work we propose the analytical solution of the fractional Smoluchowski equation in the above-mentioned limit of deep well, assuming the reactivity to be localized within the well. With the use of the obtained solution the PDF evolution and the kinetics of geminate SDARs are analyzed in detail in this limit.

The analysis shows that, unlike the case of conventional DAR, the SDAR kinetics strongly depends on the mechanism of reaction. In particular, the kinetics appears to be essentially different for two models of reactivity: the subdiffusion assisted activated rate model [or, more generally, the kinetically (i.e. mobility) controlled reaction model] and the first order reaction model. This strong difference enables one to select the realistic reaction mechanism by comparison of theoretical predictions with the experimental data.

The obtained results are applied to the interpretation of the experimental kinetics of photoluminescence decay in amorphous semiconductors *a*-Si:H resulting from geminate recombination of photoexcited electrons (*e*) and holes (*h*) [4-6]. Electrons in these semiconductors are known to be highly mobile, undergoing subdiffusive (dispersive) migration, while holes are nearly immobile [4, 5].

Recently, fairly detailed experimental investigation of the kinetics of geminate *e-h* recombination at different temperatures has been carried out [6] and experimental results have been semiquantitatively described within the free subdiffusion model. It is worth noting, however, that the kinetics of the process under study is, clearly, significantly affected by the Coulomb *e-h* interaction which is quite strong in the investigated semiconductors: for the dielectric constant $\epsilon \approx 10$ characteristic for these semiconductors and temperatures $T < 300$ K the Onsager radius (distance, at which the Coulomb interaction is equal to the thermal energy) is estimated as $l_e > 50\text{\AA}$.

Analysis of theoretical kinetic dependences, obtained in this work, shows that the activated rate model describes the experimental results better than the first order reaction one. This analysis allowed us to obtain the characteristic model parameters of the system: the parameter α characterizing the diffusion anomaly, the rate of escaping from the *e-h* interaction well, etc., which result in the best fitting, and estimated their dependence on temperature. The proposed interpretation is compared with another one applied in Refs. [4, 5] to treat some earlier experimental results on the same process.

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Free Energy Gap Law and Nonequilibrium Phenomena in Charge Recombination of Excited Donor-Acceptor Complexes

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1. Introduction

One of unanswered question of charge recombination (CR) reaction concerns the free energy dependence of the CR rate constant, k_{CR} , in the excited donor-acceptor complexes (DAC). The experimental investigations of CR in DACs after their photoexcitation by a short laser pulse at the carrier frequency of the charge transfer band demonstrated unexpected dependence of k_{CR} on the reaction free energy in the weakly exergonic region. The logarithm of the CR rate constant decreases monotonously, nearly linearly, with increasing the reaction exothermicity, $-\Delta G_{\text{CR}}$, whereas the standard equilibrium nonadiabatic Marcus theory predicts a bell-shaped dependence.

In this report we present: (1) the hot electron transition mechanism which leads to straightening of the Marcus parabolic dependence, (2) the fit of the available experimental data on the free energy gap law to the generalized stochastic model, (3) the analysis of the extent of the vibrational nonequilibrium in the CR of excited DACs, (4) the estimation of the extent of deviation of CR dynamics from exponential decay.

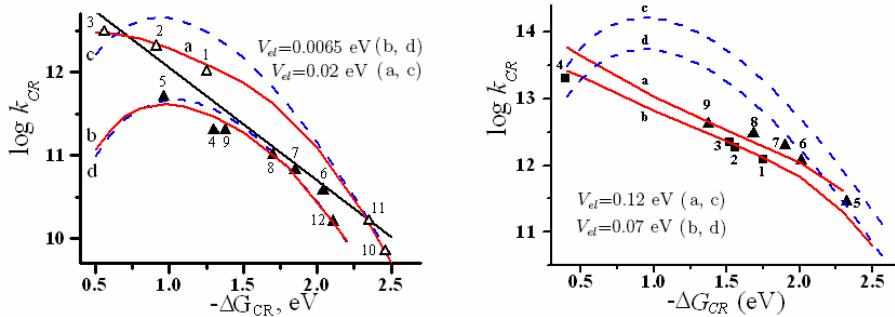
2. Multi-channel stochastic model

Ultrafast CR dynamics of excited DACs assisted by intramolecular high-frequency vibrational modes in polar solvents have been investigated within framework of generalized stochastic approach. The model is based on a two-level approach that includes an excited electronic state with charge transfer and the ground neutral state. One takes into account: (1) both the reorganization of the solvent, and the reorganization of the intramolecular quantum high-frequency modes; (2) the relaxation of vibrational excited states; (3) the formation of the electronic excited state with a strongly nonequilibrium nuclear configuration by a short laser pulse. The model allows to simulate the effect of nonequilibrium on CR dynamics in the excited DACs. In the framework of the generalized stochastic approach the CR dynamics are described by a set of Smoluchowski-like equations. In the numerical simulation of the Smoluchowski-like equations the Brownian simulation method in the form proposed before in Ref. [1] was used. The adequacy of this model was tested for a number of DACs and solvents [2, 3].

3. Results of CR dynamics simulation

The results of numerical simulation of the CR dynamics for a number of DACs are presented in Fig. 1. Considerable difference between effective, k_{CR} , and thermal, k_{th} , CR rates is demonstrated. The experimental data borrowed from Refs. [4-6] are pictured by

symbols. The behavior of CR rate constant k_{CR} strongly depends from values of electronic coupling, V_{el} . For smaller values of electronic coupling the Marcus dependence of the effective rate constant on the reaction exothermicity has typical for thermal reactions a bell-shaped form with a small deviation from the thermal rate in the vicinity of the maximum (panel 1, lines b and d, Fig. 1). However the curves with large V_{el} are characterized by rectification especially in the weakly exothermic. For good approximation be proposed separate the DACs into a few groups with different values of electronic coupling. The nonequilibrium nature of the CR leads to the deviation of the effective CR rate constant from its thermal value. In strongly exothermic region the effective CR rate is close to the thermal one (panels 1 and 2, Fig. 1). In the region of moderate exothermicity k_{CR} is less than k_{th} and in the weakly exothermic region the inverse relation, $k_{\text{CR}} > k_{\text{th}}$, is fulfilled. The effective and thermal rate constants at $-\Delta G_{\text{CR}} = 0.56$ eV the complex Per-TCNE in acetonitrile solution have practically the same value (symbol 3, panel 1, Fig. 1), mainly proceeds in nonthermal regime. The exponential decay of the excited complexes is not direct evidence of the equilibrium regime of CR. For example, the CR in the excited Per-TCNE in acetonitrile is known to proceed in exponential regime but CR reaction occurs mainly in nonthermal regime. In this area the thermal rate decreases because of the Marcus activation barrier and the effective rate constant can even rise since the wave packet is initially placed in the area of more powerful sinks so that the inequality $k_{\text{CR}} > k_{\text{th}}$ is held. The model provides correct description of the nonexponential CR dynamics in excited DACs.



Panel 1

Panel 2

Fig. 1: The free energy dependence of k_{CR} (in s^{-1}) for a number of the DACs (panel 1 [4], panel 2 [5, 6]). Solid straight line is linear approximation to the experimental data. For comparison the thermal rate constant shown as dashed curves (lines c, d).

Acknowledgements

This work was supported by the Ministry of education and science of the Russian Federation (contract P1145) and the Russian foundation for basic research (Grant No. 08-03-00534).

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Abnormal Diffusion, Super-Memory and Relaxation of Stimulated Electro-Photo-Conductivity in Compensated Hetero-Semiconductors

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1. Introduction

First, semiconductors with a high optical “super-sensitivity” and a “super-memory” were discovered in results of irradiation of *n*-Si with fast neutrons and deuterons [1]. Bombarding particles form compensating “clusters of defects” that play a role of “traps” for electrons of conductivity. In results, *n*-Si gets properties of insulator with a very low (dark) conductivity but a high optical sensitivity. After its exciting with (IR-) optical photons corresponding to the energetic levels of acceptor “traps”, such a trigger-like system returns properties of semiconductor, and after shutting down excitation, slowly relaxes to an equilibrium stage (of a quasi-insulator). The phenomenon of slow relaxation (called as a “memory”) is caused by the electrical double layer (EDL) barriers arising around compensating clusters and damping a diffusive relaxation. As far as we know it is a chronologically first case of “abnormal” diffusion (so popular nowadays, e.g., in biological research)! Initial experimental data concerning photo-voltaic characteristics on these systems were presented in our early paper [1]; first theoretical model and theory of “super-sensitivity” and “super-memory” were proposed in our work [2]. The discovery stimulated a new generation of effective IR-photo-sensors (patented).

2. Results

Here, we will overview a relaxation of stimulated photo-electro-conductivity in the “cluster-like” compensated hetero-semiconductors (CHS), i.e., kinetics of their conductivity after shutting down small thermal excitations or arbitrary (“admixture”) optical ones. An initial model presents a flat (large and thin) periodic stripe-kind hetero-semiconductor system with spatially separated groups of *n*-donor and *n*-acceptor levels. The “matrix” is the *n*-type semiconductor (with initially highly ionized donor levels of concentration N_d^+) of the width $2l_1$; while compensating acceptor stripes (of concentration N_a and the width $2l_2$) contain of electron “traps” (with low electron filling at the excited stage: $N_a \gg N_a^-$); a compensation level is considered as high. The external electric field is parallel to stripes oriented along the OX -axis. Mathematically, our physical model is presented with a system of standard equations; in part, the basic equations for a “matrix” (1) are

$$\begin{cases} \partial n / \partial t = (1/e) \operatorname{div} j_n - \gamma_d n N_d^+ + g_d (N_d - N_d^+) \\ \partial N_d^+ / \partial t = -\gamma_d n N_d^+ + g_d (N_d - N_d^+) \\ \partial^2 \Phi / \partial z^2 = (4\pi e^2 N_d / e k T) (N_d^+ / N_d - n / N_d) \end{cases}. \quad (1)$$

The equations for the each compensating stripe (2) are

$$\begin{cases} \partial n / \partial t = (1/e) \operatorname{div} j_n - \gamma_a n (N_a - N_a^-) + g_a N_a^- \\ \partial N_a^- / \partial t = \gamma_a n (N_a - N_a^-) - g_a N_a^- \\ \partial^2 \Phi / \partial z^2 = -(4\pi e^2 N_a / e k T) (N_a^- / N_a + n / N_a) \end{cases}. \quad (2)$$

Accounting a system symmetry periodicity, boundary conditions are written as

$$(\partial \Phi / \partial z) \Big|_{z=-l_2} = (\partial \Phi / \partial z) \Big|_{z=l_1} = (\partial n / \partial z) \Big|_{z=-l_2} = (\partial n / \partial z) \Big|_{z=l_1} = 0. \quad (3)$$

Additional equations follow from conditions of discontinuity of the potential Φ and the current j_n at borders of the matrix and the compensating stripes

$$\Phi^1 \Big|_{z=0} = \Phi^2 \Big|_{z=0}; \quad (\partial \Phi^1 / \partial z) \Big|_{z=0} = (\partial \Phi^2 / \partial z) \Big|_{z=0}, \quad (4)$$

$$j_n^1 \Big|_{z=0} = j_n^2 \Big|_{z=0}; \quad (\partial j_n^1 / \partial z) \Big|_{z=0} = (\partial j_n^2 / \partial z) \Big|_{z=0}. \quad (5)$$

The initial conditions ($t=0$) follow from the solution of the stationary problem [2]:

$$n^1 \Big|_{t=0} = n_0^1(z); \quad n^2 \Big|_{t=0} = n_0^2(z); \quad N_a^- \Big|_{t=0} = N_{a0}^-(z); \quad N_d^+ \Big|_{t=0} = N_{d0}^+(z). \quad (6)$$

Above we used known conventional significations. We suggest that conductivity is proportional to free electron concentration ($\sigma(t) \sim n(t)$), and a diffusion approximation is considered: when the electron flux into “traps” across the EDL barriers dominates over the reverse field flux ($|n \partial \Phi / \partial z| \ll |\partial n / \partial z|$). For this case, the full system of equations (1)-(6) is solved by employing methods of the Laplace-Carson integral transformation and the reverse transformation with complex integrating. After averaging, the kinetic dependence of mean photo-electro-conductivity on the time is received. In part, for a case of slow relaxation, one gets a kinetic dependence:

$$\bar{\sigma}(t) = \sigma_0 \exp(-t/\tau), \quad \tau = (l_1/l_2)^2 (D_2/D_1) (1/\gamma_a N_a). \quad (7)$$

A full time of relaxation is presented by a formula:

$$t_d \approx (\pi e^2 N_d l_1^2 / 2 \varepsilon k T)^{1/2} (\gamma_a N_a l_1^2 l_2^2 / D_1 D_2). \quad (8)$$

Here D_i are the electron diffusion coefficients for i -area. The expression (8) links t_d with parameters of CHS. High EDL barriers around compensating stripes provide a longtime conductivity relaxation, i.e., a “super-memory” of initial excitation of CHS (related with an “abnormal” diffusion of free electrons from a “matrix” into “cluster traps”). Numerical estimations show that t_d can be very large (up to weeks)! The results are well verified with real data, thereby confirming an adequacy of our model and theoretical approach.

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Hot Charge Recombination in Ruthenium(II)-Cobalt(III) Compounds

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1. Introduction

Photoinduced electron transfer (ET) in condensed media is often followed by return ET (RET) reducing the quantum yield of the ET-product formation. Apparently, the low product yield can be observed if the thermal rate of recombination, k_{RET} , is much larger than the rate of charge separation, k_{ET} . But similar result can also be observed in the opposite limit when the ET-products are long-lived. In this case the reduction of the ET-product yield may be due to nonequilibrium («hot») electronic transitions proceeding in parallel with solvent relaxation.

Particularly this situation is realized in ruthenium(II)-cobalt(III) charge transfer compounds investigated experimentally in a series of papers [1-3]. The photoinduced electron transfer reactions of $[(\text{tpy}) \text{Ru}^{\text{II}}(\text{tpy}-\text{tpy}) \text{Co}^{\text{III}}(\text{tpy})]^{5+}$ and $[(\text{tpy}) \text{Ru}^{\text{II}}(\text{tpy}-\text{ph}-\text{tpy}) \text{Co}^{\text{III}}(\text{tpy})]^{5+}$ in solvents of different viscosities were studied by means of subpicosecond transient absorption spectroscopy. The quantum yields of thermalized ET-products were found to be rather low (0.4 – 0.6) and to depend on the chemical system and solvent. This indicates a possible role of hot electronic transitions in these reactions.

The aim of the present study is to clarify the microscopic mechanisms of ultrafast intramolecular excited-state electron transfer (EET) as well as RET in these compounds. The questions to be answered are: (a) can the theory quantitatively reproduce the EET and the following EET-product decay dynamics? (b) Why complexes with similar parameters demonstrate essentially different behaviour? (c) Can the theory describe the influence of the solvent relaxation time on the product yield? (d) What are the reasons of two timescales in the EET-product decay?

2. The model and results

To answer these questions the 4-level stochastic model of the reaction is developed (see Fig. 1). The model accounts for the fast relaxation of intramolecular high-frequency

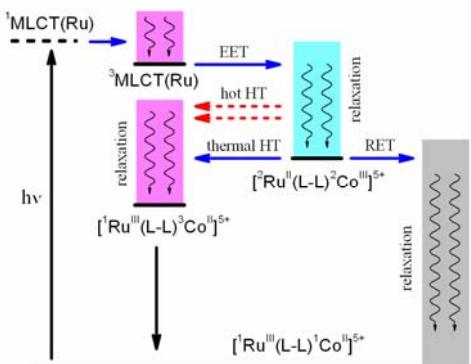


Fig. 1: Scheme of electronic states and transitions in $\text{Ru}^{\text{II}}\text{-}\text{Co}^{\text{III}}$ compounds. MLCT – metal-to-ligand charge transfer state.

vibrations and the explicit description of solvent relaxation as well as thermal and hot electronic transitions. The model was studied numerically.

Fitting the theory to the experimental data [1-3] allowed finding microscopic EET, HT and RET parameters and determining the reaction mechanisms. Simulations of the reaction kinetics in acetonitrile (ACN) and butyronitrile (BN) reproduced the experimentally observed quasi-exponential forward electron transfer with the rates, weakly dependent on dynamic properties of the solvent. This is a clear indication that EET proceeds in nonadiabatic regime and the nuclear subsystem remains quasi-equilibrium in the course of the reaction. On the other hand, population dynamics of the EET-product state, $P_{\text{ET}}(t)$, show significant changes upon moving from the fast solvent (ACN) to the slower one (BN). Both the experimental data and the simulation results indicate: 1) considerable decrease in quantum yield of EET products ($\sim 20\%$), 2) pronounced deviations of $P_{\text{ET}}(t)$ from a single-exponential decay in BN compared to ACN. These results however cannot be attributed to the dynamic solvent effect since the HT and RET electronic couplings are found to be weak, but can be explained in terms of hot electronic transitions.

Our analysis shows that dynamics of EET-product population includes three stages: 1) the rise of $P_{\text{ET}}(t)$ due to $^3\text{MLCT}$ state decay; 2) the hole transfer (HT) reaction in non-equilibrium regime, and 3) the return electron transfer in thermal regime. In ACN the timescales of EET and solvent relaxation are close to each other so the second (hot) stage is of minor importance. On the contrary, the diffusive relaxation in BN is much slower, hence the nonequilibrium stage becomes prominent. Moreover, in BN, in contrast to ACN, particles accumulate in the vicinity of the sharp bend of the reactive trajectory. This results in two important consequences. First, hot HT proceeds more effectively during EET and lead to the reduction of the EET-product yield. Second, high concentration of particles in vicinity of the active HT sinks accounts for considerably higher rate of $P_{\text{ET}}(t)$ decay at nonequilibrium stage in BN. This can be regarded as the main reason of the noticeable bi-exponential EET-product dynamics observed in $[(\text{tpy}) \text{Ru}^{\text{II}} (\text{tpy-tpy}) \text{Co}^{\text{III}} (\text{tpy})]^{5+}$ compound in BN.

3. Conclusion

The four-level stochastic point-transition model is capable to provide good quantitative description of photoinduced charge transfer reactions studied experimentally in Refs. [1-3]. The model is able to explain both the low quantum yields of thermalized EET-products and the features of forward and back electron transfer in solvents with essentially different dynamic properties. The nonequilibrium effects are shown to be of primary importance in these reactions.

Acknowledgements

This work was supported by the Ministry of education and science of Russia (contract P1145) and the Russian foundation for basic research (grant 08-03-00534).

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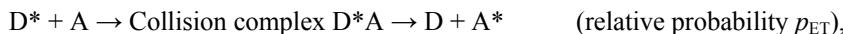
Energy Transfer at the Encounters of Chemi-Excited Ketones with Acceptors: Elucidation of the Probability per One Collision Using the Frenkel Cage-Effect Theory

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1. Introduction

Intermolecular energy transfer (ET) between an electronically excited donor (D) and acceptor (A) is of peculiar interest for photochemistry, photophysics and chemiluminescence [1]. For the liquid-phase ET, the following features are of import:



which is an elementary step depending on an overlap of partners' electronic clouds and a matrix element of the exchange interaction. In solutions, this process is hidden because the partners experience numerous repeated collisions in *the encounter complex* D^*A :



and it is noteworthy that k_{ET} may reach a limited, diffusion controlled, value $k_{\text{diff}} = aT/\eta$ (a is usually taken as $8R/2000$ or $8R/3000$) even at low p_{ET} . However, at moderate viscosities, k_{ET} is substantially lower. In this work, we demonstrate that the *gas-phase* probability p_{ET} may be acquired *in solutions* in the framework of the theory [2] put forward by outstanding (though controversial) Soviet physicist Jakov I. Frenkel (1894-1952).

2. Experimental

We studied the energy transfer from the chemically generated excited triplet donor (D), namely, benzophenone, which was a product of oxidation of diphenylmethane. The efficient luminophore, europium(III) tris(thenoyltrifluoroacetone)-1,10-phenanthroline served as energy acceptor (A). In this case, a sequence of the following steps takes place:
 (a) intermolecular triplet-triplet energy transfer from D^* to the ligands of A,
 (b) intramolecular energy transfer from the ligands to a central Eu^{3+} ion,
 (c) emission of a 613-nm photon by the excited Eu^{3+} ion.

The so generated *indirect* chemiluminescence was measured with a photodetector. The k_{ET} values were obtained from the dependence of the emission intensity upon [A] at various concentrations (from 10 to 85% in benzene) of rather viscous diphenylmethane.

3. The model

The model implies that a number of collisions, t/τ_c , occurs during the lifetime, t , of a solvent cage containing an encounter complex $\{D(T_1) A(S_0)\}$; τ_c is “the characteristic time of one collision”. Every collision may result in energy transfer with an expected average relative probability p_{ET} . Then, $(1-p_{ET})$ is the probability of saving the excitation energy after one collision, whereas $(1-p_{ET})^{t/\tau_c}$ is that after t/τ_c collisions, and $1-(1-p_{ET})^{t/\tau_c}$ is the overall probability of deexcitation, i.e. the probability of energy transfer after t/τ_c collisions.

To obtain the total relative probability of the energy transfer, *i.e.* k_{ET}/k_{diff} , one should take into account the distribution of the encounter complexes (*i.e.* cages) over their lifetimes, which according to Frenkel [2] is $\exp(-t/\tau)dt/\tau$, where τ is the mean lifetime of a cage. Hence, the k_{ET}/k_{diff} values obey Eqs. 1 and 2, in which $m = \tau/\tau_c$ is the mean number

$$k_{ET}/k_{diff} = \int_0^{\infty} [1-(1-p_{ET})^{t/\tau_c}] \exp(-t/\tau) dt/\tau = [1-(m \ln(1-p_{ET})^{-1})]^{-1}, \quad (1)$$

$$k_{diff}/k_{ET} = 1-m \ln(1-p_{ET})^{-1} \quad (2)$$

of repeated collisions in the cage. Frenkel related m to a simple combination of Arrhenius–Andrade parameters of viscosity (η) in the form of Eq. 3:

$$m = \exp(E_\eta/RT) = \eta/A_\eta. \quad (3)$$

Viscosity was measured using the Ubbelode viscosimeter. In the ranges of $30 < T < 60$ °C and $10 < [\text{diphenylmethane}] < 85\%$, experimental η value varies from 0.44 to 1.23 cP, the calculated m grows from 45 to 130 and the rate constant k_{ET} fits Eq. 4 derived from Eq. 2:

$$T/k_{ET} = \eta/a - (A_\eta/a)[\ln(1-p_{ET})]^{-1} \quad (4)$$

Eq. 4 represents a linear function in coordinates T/k_{ET} versus η . From the slope, we obtained the value $a = 6.0 \times 10^5$ P L mol⁻¹ grad⁻¹ s⁻¹ (*i.e.* $a = 8R/1200$ instead of the above mentioned and widely used values). The intercept and the measured $A_\eta = 9.7 \times 10^{-5}$ P yielded $p_{ET} = 0.0083$ which is close to the rate constants of triplet-triplet energy transfer from some donors including benzophenone acquired in the *gas-phase* experiments.

Conclusion

The Frenkel kinetic theory of liquids has been used for the interpretation of interaction of excited molecules with energy acceptors and quenchers. A simple model of bimolecular reactions in a solvent cage has been put forward and applied to studying the energy transfer from the triplet ketone to the rare-earth complex. A “*gaseous-phase*” elementary probability has been obtained in a *liquid-phase* experiment.

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A Rigorous Foundation of the Diffusion-Influenced Bimolecular Reaction Kinetics

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1. Introduction

The rates of bimolecular reactions occurring in solutions can be influenced by the molecular transport processes that bring the reactant molecules into close proximity to one another. Hence one has to consider the transport equation of reactant molecules to predict the rates of fast reactions, and various approaches have been developed to incorporate the effects of the reaction events into the transport equation. In particular, Wilemski and Fixman incorporated the reaction sink function in the transport equation of reactant molecules. The reaction sink function, denoted by $S_{AB}(\Lambda)$, represents the reaction rate at a set of relative phase-space coordinates Λ of two reacting molecules, A and B. A major advantage of this approach is the capability of handling the reactions that may occur at a range of distance. In the appropriate limits, this approach reproduces the same results as the boundary condition approach.

For an irreversible reaction $A+B \rightarrow P$, the rate coefficient appearing in the usual rate equation, $-d[A]_t / dt = k_f [A]_t [B]_t$, is given by

$$k_f(t) = \int d\Lambda S_{AB}(\Lambda) \rho_{AB}(\Lambda, t). \quad (1)$$

Here $\rho_{AB}(\Lambda, t)$ is a nonequilibrium pair correlation function; $[B]_t \rho_{AB}(\Lambda, t) d\Lambda$ represents the number of B molecules in a volume element $d\Lambda$ around an A molecule, with the relative phase-space coordinates Λ . It is normalized as $\int d\Lambda \rho_{AB}(\Lambda, t) = V$, where V is the volume of the reaction vessel.

Then the next task is to find a proper reaction-transport equation governing the time-evolution of $\rho_{AB}(\Lambda, t)$. A useful, but nonrigorous practice has been to assume a phenomenological evolution equation of the form

$$\frac{\partial}{\partial t} \rho_{AB}(\Lambda, t) = \mathcal{L}(\Lambda) \rho_{AB}(\Lambda, t) - S_{AB}(\Lambda) \rho_{AB}(\Lambda, t). \quad (2)$$

For example, if $\Lambda = r = |\mathbf{r}_B - \mathbf{r}_A|$, the usual choice for $\mathcal{L}(\Lambda)$ is the Smoluchowski operator. Else if $\Lambda = (|\mathbf{r}_B - \mathbf{r}_A|, \mathbf{v}_B - \mathbf{v}_A)$, the choice for $\mathcal{L}(\Lambda)$ may be the Fokker-Planck-Kramers operator, and so on.

However, a rigorous approach is to start with the Liouville equation governing time evolution of the full phase-space probability density function for both reactant and solvent molecules. This gives a set of hierarchically connected reaction-transport equations for the reduced distribution functions of reactant molecules. A well-known fact revealed from such a rigorous approach is that when the concentrations of reactants are high, $\mathcal{L}(\Lambda)$ involves the effects of reaction events due to the coupling of reaction dynamics among many reactant pairs. On the other hand, it is less known that even in the low concentration limit, in which the many-particle effects can be neglected, $\mathcal{L}(\Lambda)$ cannot be independent of the reaction events in general. This aspect was addressed previously by Northrup and Hynes and by Cukier *et al.*, but no satisfactory account was given.

2. Results

We have shown that one can bypass the difficulty of finding the proper evolution equation for $\rho_{AB}(\Lambda, t)$, but that it is still possible to derive a formally exact expression for the bimolecular reaction rate coefficient without recourse to any approximation. Starting from the classical Liouville equation for all reactants and explicit solvent molecules, we derived a formally exact expression for the bimolecular reaction rate coefficient in the low reactant concentration limit. It was shown that the reaction rate can be related to the dynamics of repeated encounters of reactant molecules in a hypothetical system in which the encounters do not lead to reaction.

The derivation first led to the Noyes's rate formula with an exact molecular expression for the Noyes's h function, generalized to the case with an arbitrary nonlocal sink function. However, a direct perturbative approach based on the Noyes's rate formula fails in the case with large inherent reactivity. We thus provided a rate expression in a renormalized form with better convergence behavior. The well-known Wilemski-Fixman rate expression is reproduced as a lowest order approximation from it.

We examined the general properties of the rate coefficient. When the reaction-transport equation is given by Eq. (2) and Λ , which includes the internal degrees of freedom of reactant molecules as well as their relative position, undergoes arbitrary stationary Markovian process, it was shown by Kipriyanov and Doktorov that the asymptotic expression of $k_f(t)$ is given by

$$k_f(t) \xrightarrow{\text{large } t} k_f(\infty) \left[1 + \frac{k_f(\infty)}{4\pi D \sqrt{\pi D t}} \right], \quad (3)$$

where D is the relative diffusion coefficient of a reactant pair. We generalized this result to the cases with a broader class of $\mathcal{L}(\Lambda)$, involving non-Markovianity and anomalous diffusion. We also presented the expressions for the upper and the lower bounds to $k_f(t)$ that can be successively improved.

For reactions involving a long range sink function, the effect of the non-Markovianity of the repeated encounter events of a reactant pair becomes significant, and either the

Noyes theory or the Wilemski-Fixman theory fails. We provided an approximate, but practical, rate expression for such reactions that improves significantly on the Wilemski-Fixman theory. Numerical results calculated for the energy and electron transfer reactions will be compared with the exact results from available analytic rate expressions and direct numerical solutions of Eqs. (1) and (2).

Some other applications of the general theory are under progress, and some preliminary results will be presented.

Multiparticle $kA \rightarrow 0$ Reaction in Small Volumes

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1. Introduction

The distinct feature of the cell dynamics, when compared to in vitro experiments, is that biochemical reactions are well organized in space [1]. The living cell is not a bag of enzymes where all molecules are lumped together. Intracellular reactions occur in finite volumes that can be rather small. For example, the diameter of a reaction volume ranges from few nm (Golgi apparatus, ribosomes) towards micrometers (cytoplasm). The basic transport mechanism in the living cell is diffusion. There are other mechanisms but the diffusion is the most frequent one. Thus understanding of the diffusion limited kinetics of few reactants in small volumes is of considerable interest.

In the reactions in restricted geometries context, there have been more studies of binary than non-binary reactions. Perhaps, the main reason is that non-binary reactions are rare in the cell cytoplasm. The likelihood of many particles meeting in the vicinity of each other at the same time is rather small. However, there are many instances where sequential reactions appear to be multiparticle like due to strong cooperativity effects [2]. From that point of view, the study of multiparticle reactions in small volumes should be relevant for understanding the living cell biochemistry.

The talk will discuss the basic features of diffusion controlled reactions in infinite and finite (small volumes), emergence of anomalous kinetics (breakdown of mean field equations). An example of the breakdown of the mean field equations will be shown [3,4] that render the mean field equation qualitatively wrong. Finally, the results of a recent study of a multiparticle reaction model [5] will be presented.

2. Multiparticle reaction model and Method

The model is defined as follows. Particles A react in clusters of size k with the reaction rate that depends on the positions of particles in a well defined way. Particle are spatially extended objects (not points) with radius a . The goal will be to investigate kinetics for varying degree of cooperativity k , and the size of the particles a . For a given reaction instance the reaction rate is not zero if all reacting particles in the cluster are close enough. It is sufficient that one of the particles is far away from the cluster and the reaction instance will not proceed to the completion.

The model has been solved analytically using the formalism of a field theory. The master equation has been mapped onto the corresponding quantum field theory using the standard techniques, and the equations of motion for many-particle density functions have been derived. To do the calculations the formalism described in Ref. [4] was used heavily.

The (infinite) hierarchy of equations has been solved by truncating the hierarchy at the level of the $(k + 1)$ -density function. The expression for the time dependent effective reaction rate has been found in an approximate form.

3. Conclusion

The equations of motion differ significantly from the ones that describe binary reactions. The average particle number decays exponentially for large times. All scales in the problem combine non-trivially into the effective decay rate, and it is hard to identify the scales that control onset of the exponential behaviour. An analytic expression for the decay rate will be given.

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Diffusion-Controlled Reactions in Crowded Environments

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1. Introduction

Diffusion-limited reactions are commonly found in biochemical processes, such as enzyme catalysis, protein aggregation or complexation in cells. The simplest model of diffusion-limited encounter has been introduced by Smoluchowski a century ago under the hypothesis of infinite dilution and chemically isotropic spherical reactants. The Smoluchowski framework has been widely used to describe reactions occurring *in vivo*. However, biological environments are crowded: the cells cytoplasm, for instance, contains a large number of proteins, nucleic acids, and other smaller molecules that can occupy up to 30÷40 % of the available volume. Thus, crowding effects are expected to impact considerably on the thermodynamics and kinetics of biological processes occurring within the cell.

2. Results

We propose a first extension of the Smoluchowski framework that incorporates excluded-volume effects, adapting Event-Driven Brownian Dynamics to the particular configuration of an absorbing sink located at the center of a spherical bounding box and substrate spherical particles that diffuse around and get absorbed. The simulation scheme is designed to enforce constant flux toward the sink through particle injection at the spherical boundary. For large absorbers, the density dependence of the encounter rate obtained from the simulations can be explained in terms of a finite-pressure correction to the Smoluchowski value. However, reducing the sink-to-particle size ratio, the encounter is substantially depressed at intermediate packing until it becomes non-monotonic. Concomitantly, a peculiar ordering of the diffusing particles occurs in the vicinity of the absorbing center, with the appearance of stationary density waves. A mean-field analysis confirms that these phenomena are the result of the increasing competition among the diffusing particles when approaching a sink of smaller size. Finally, we show how the addition of an infinitesimal amount of non absorbing impurities can also slow down dramatically the reaction.

General Theory of the Single-File Multi-Particle Diffusion in Narrow Pores

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1. Introduction

The narrow nanoscale pores, which conduct ions or other small molecules, constitute a significant challenge for physical modeling. The particles in very narrow nanoscale pores cannot pass by each other (single-file motion). The pore can also be long enough to accommodate more than one particle at the same time. The examples of such nanopores, which are very important for practical applications, are the ion channels of biological membranes [1-3] and carbon nanotubes [4, 5]. The macroscopic flux of the permeating particles through these objects is of great importance for practical applications.

Despite the fact that the narrow pores with multiple occupancy are known for many years, there is no universally accepted dedicated physical theory of these objects. The goal of this work is development of the general theory of the multi-particle single-file diffusion in non-equilibrium conditions based on the very basic principles of non-equilibrium statistical physics and the theory of probability.

2. Outline of the theory

The main difficulty of describing the system under study is that the number of particles in the channel is variable, while all conventional dynamic equations and relations of the statistical physics, which describe non-equilibrium systems, operate with a fixed number of particles. The idea of our theoretical development is to present the distribution function of our system as a series in discrete channel occupancies. The outline of the theoretical development is the following:

1. The N -particle distribution function of the whole system $F(x_1, \dots, x_N; t)$ is constructed taking into account the properties of the reservoirs. Hereafter x_1, \dots, x_N are the coordinates of particles, t is the time.
2. The probabilities w_n of the occupancy states with n ions inside the channel are found ($0 \leq n \leq M$), where M is the maximal occupancy of the channel.
3. The partial distribution functions $f_m^{(n)}(x_1, \dots, x_m; t)$ of m ($m \leq n$) particles in the channel, which contains n particles are found. All quantities of the reservoirs except the external concentrations $c_{1,2}$ and the membrane potential ψ vanish at this step after transition to the thermodynamic limit.

4. It is shown that any property of the channel can be obtained as a series in channel occupancies. They depend on unknown n -particle distribution functions inside the channel $\phi^{(n)}(x_1, \dots, x_n; t)$.
5. It is shown that the distribution functions $\phi^{(n)}(x_1, \dots, x_n; t)$ are the solution of the hierarchical set of partial differential equations, which is obtained from the Langevin equation of motion of the ions inside the channel.

3. The super ions

The general theory of the single-file multi-particle diffusion in narrow pores [6] can be greatly simplified in rather wide class of specific bell-like shapes of the single-ion energy profiles, which are often observed in real ion channels. In such potentials the ions move in highly concerted manner, which corresponds to the existence of narrow and deep groove in the energetic landscape. The motion of multiple ions can be reduced to the motion of single quasi-particle (the super-ion), which moves in one-dimensional effective potential along the groove. It is shown that effective potentials of the super-ions, which correspond to the conducting occupancies of the channel, are essentially flat. This explains the phenomenon of the barrier-less conduction in the channels with multiple occupancy in very elegant way. The approximation of the super-ions also reduces the computational complexity of the problem dramatically in comparison with the generic computational procedure.

4. Conclusion

We developed a general analytical framework which describes single-file diffusion of multiple strongly interacting particles in non-equilibrium conditions. The model takes into account the external potential action on the diffusing particles and the fluctuations of the number of particles due to their exchange with external reservoirs. The model is constructed in a bottom-up manner from the very basic principles of statistical physics and probability theory. It is shown that the problem can be reduced to a hierarchical system of elliptic partial differential equations of increasing dimensionality, which can be solved numerically. Our framework allows us to compute any macroscopic characteristics of the single-file multi-particle diffusion, including the current and the occupancy probabilities. It is shown that the occupancy probabilities and the current are rational functions of external concentrations.

The theory is tested on a model of the narrow pore inspired by the selectivity filter of biological ion channel. The macroscopic characteristics of the model channel are obtained in a wide range of parameters. Obtained data correlate very well with the data of earlier studies performed on the same model, which serves as a validation of our theoretical framework.

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Driven Diffusion in a Periodically Compartmentalized Tube: from Homogenization to Intermittency

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1. Introduction

The problem of diffusion in a tube of varying cross-section arises in various contexts, including particle transport in porous solids, translocation of ions through channels in biomembranes, and development of technologies for controllable transfer on the nanoscale. The essential physics of the problem is associated with a spatial dependence of the diffusing particle entropy, induced by a variation in the tube cross-sectional area along the propagation direction. The most common approach consists in reducing the essentially 3D (or 2D) geometrically restricted Brownian motion to an effective 1D diffusion along the tube axis. The resulting kinetic equation for the effective 1D distribution is known as the Fick-Jacobs equation, which is the Smoluchowski equation with the entropic potential that accounts for changes in the space accessible for the diffusing particle [1]. The conventional approach is applicable to systems with smooth enough variations in the confining cross-section, but fails at strong forcing.

We study drift and diffusion of a point particle moving under the action of uniform force F in a tube of radius R , with periodic zero-thickness partitions dividing the cylindrical tube into identical compartments of length l . Each partition bears a circular opening of radius a , through which the particle can go from one compartment to the other. With this setup, the Fick-Jacobs approach is inapplicable.

The focus is on the dependence of the effective mobility μ and diffusivity D on the driving force F . We find, and this is our main result [2], that the behavior of $\mu(F)$ and $D(F)$ is *qualitatively different* from that previously reported in studies of driven transport

in tubes and 2D channels of varying cross-section (see Ref. [3] and references therein): (i) $D(F)$ monotonically decreases with F , while usually it grows between two limiting values; (ii) $D(F)$ diverges as $F \rightarrow \infty$, while usually it remains finite. Thus, entropic effects in diffusive transport in the tube with orthogonal cross-walls are enhanced with the driving force.

2. Two scenarios of the particle motion

Our consideration is based on two different scenarios, which are deduced from the analysis of statistics of the particle's transition times between neighboring openings, using Brownian dynamics simulations. At zero or small F , a transition from one compartment to the next one is a rare event in the sense that the passage time is much greater than all other characteristic times of the problem. This scenario, which we call *homogeneous*, suggests using a coarse-grained approach, making the problem analytically treatable. With this approach, 3D motion of the particle in the tube is mapped onto a 1D continuous-time random walk and then the approximation called “boundary homogenization” is invoked.

At strong forcing, one gets a new hierarchy of times. In particular, the time characterizing the overwhelming majority of intercompartment transitions is much smaller than all other characteristic times. In addition there are very rare, slow transitions associated with the particle diffusive motion along the partition wall, which are however very significant due to their dominating contribution to the transition time average. In other words, the driving force induces intermittency [4] in the particle transitions between neighboring compartments, which is manifested most clearly in a progressive growth of the corresponding statistical moments with respect to their order. Thus in this regime, an alternative scenario for the particle motion occurs, which we call *intermittent*.

3. Results for the effective mobility and diffusivity

Based on the qualitative picture of the two opposite scenarios, homogenous and intermittent, the limiting small- F and large- F behaviors of the effective mobility and diffusivity are derived analytically. In particular, we have shown that $D(F)$ diverges like F^2 as $F \rightarrow \infty$. The formulas obtained are in a good agreement with Brownian dynamics simulations, which are also used to find $\mu(F)$ and $D(F)$ at intermediate values of the driving force for various compartment lengths and opening radii. Our results clearly show that the particle transport through a tube formed by identical compartments may be qualitatively different depending on the compartment shape.

Acknowledgments

Yu.A.M. and V.Yu.Z. acknowledge support by RFBR (Grant No. 10-03-00393). Yu.A.M. was partially supported by DFG (Grant 436 RUS 113/722). A.M.B. was supported by the Intramural Research Program of the NIH, Center for Information Technology. L.V.B. was partially supported by a Leverhulme Research Fellowship.

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Atomistic Simulation of Self-Heating Reactions in Al-Coated Ni Nanoparticles

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1. Introduction

In practice, the synthesis of bulk nickel aluminides is usually achieved by using conventional coarse-grained powders where the grain sizes are of the order of micrometers [1]. However, distinct advantages have been reported by using nanometer size particles to synthesize NiAl [2]. It has been shown [2] that due to the physical and chemical characteristics of nanoparticles (especially their high stored energy and therefore high chemical activity) the reaction mode and mechanism are distinctly different from those where conventional coarse-grained powders are used. In particular, it was demonstrated [2] that using nanoparticles can dramatically decrease the ignition temperature of the reaction process. Furthermore, mixtures of nano-sized reactant nanoparticles of Ni and Al that undergo an exothermic reaction can be considered as promising nano-energetic materials for a wide range of advanced applications such as localized heat sources for chemical and bio neutralization and disease treatment, environmentally clean primers and detonators, welding, ultrafast fuses, and smart thermal barriers [3].

In this work we focus on molecular dynamics simulation with an embedded-atom method potential [4] of formation by alloying reaction of nanoparticle of *B2*-NiAl of diameters of ~ 4.5 nm and ~ 9.5 nm with goal to analyze in details phase and structure transformations accompanying of alloying reactions that start from Al-coated Ni precursor nanoparticles with equi-atomic fractions and then to explore the effect of nanoparticle size on the alloying reaction. These systems can be considered as useful models for a highly compacted mixture of Ni and Al nanoparticles or a powder blend which can be approximated by an ensemble of identical Ni spherical nanoparticles surrounded by a continuous Al matrix [5].

2. Discussion and Conclusions

It is found that the alloying reaction in the nanoparticle of diameter of ~ 4.5 nm is accompanied by solid state amorphization of the Al-shell and Ni-core in the vicinity of the interface region. The large driving force for alloying of Ni and Al promotes the solid state amorphization of the nanoparticle because it makes intermixing of the components more

probable compared with the crystalline state. A fraction of Al atoms remain segregated to the surface of the nanoparticle since Al has a lower surface energy than Ni. This is followed by the crystallization of the Ni-Al amorphous alloy into the B2-NiAl ordered crystal structure at ~ 900 K. The heat of the transformation of the initial Al-coated Ni nanoparticle into the B2-NiAl ordered nanoparticle can be estimated as ~ - 0.46 eV/at. The B2-NiAl ordered nanoparticle melts at a temperature of ~ 1500 K. The adiabatic temperature for the alloying reaction in the initial Al-coated Ni nanoparticle can be estimated to be below the melting temperature of the B2-NiAl ordered nanoparticle. It is shown that very rapid intermixing and Ni-Al amorphous alloy formation with a reaction self-heating rate ~ 1 K/ps may occur when the reaction is ignited. It is proposed that this takes place before any formation of the Ni-Al interfacial layer. In this case, the ignition temperature can be as low as ~ 100 K. The alloying reaction will be limited by the degree of pre-heating within the system, which if insufficient, will reduce the interdiffusion rate and hence promote interfacial intermixing. The formation of a thin Ni-Al layer at the interface will produce a strong interfacial diffusion barrier, slowing the alloying reaction within the nanoparticle.

The alloying reaction in the nanoparticle of diameter of ~ 9.5 nm demonstrates the possibility of the formation of a hollow B2-NiAl nanoparticle. In this case, the following stages of the transformation can be observed: intermixing between the f.c.c. Al-shell and f.c.c. Ni-core; amorphization of the shell and then intermixing between the amorphous Al-rich shell and f.c.c. Ni-core; crystallization (in the shell) of the Al-rich amorphous alloy into an Al-rich B2-NiAl and then intermixing between Al-rich B2-NiAl shell and f.c.c. Ni-core. Taking into account that B2-NiAl is a triple-defect compound [6], it is verified that deviation from the exact stoichiometric composition toward the Al-rich composition in the B2-NiAl shell of the nanoparticle is predominantly accommodated by vacancies on the Ni sublattice. Therefore, under certain conditions, interdiffusion between an Al-rich B2-NiAl shell and a f.c.c. Ni-core in such a nanoparticle may result in a flux of the vacancies from the shell into the core and then eventually to form a hollow B2-NiAl nanoparticle.

Acknowledgements

This research was supported by the Australian Research Council through its Discovery Project Grants Scheme. One of us (E.V.L.) wishes to thank the University of Newcastle for the award of a University Fellowship.

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Computer Investigations on the Kinetics of Simple Bimolecular Reactions

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1. Introduction

This Kinetics of simple bimolecular reactions in 3D liquids is investigated by large scale computer simulations. For most simulations the method of prerecorded trajectory (called also the method of periodic expansion) [1, 2] is applied, which enables us to consider systems of over 10^8 particles and attain desired accuracy. The irreversible reactions of two kinds have been investigated:

- (1) the trapping reaction: $A + B \rightarrow C + B$;
- (2) the annihilation reaction: $A + A \rightarrow B + B$, $A + A \rightarrow D$ (where D is a dimer).

2. Results and Conclusions

The main goal for (1) was to investigate the influence of the concentration of B on the reaction rate coefficient [3-5]. The simulation has shown that the excess in the rate coefficient is a result of two effects of opposite signs: the interparticle interactions (positive) and the fluctuations in concentrations of reagents (negative). The resulting cumulative effect is weak, except for the ionic systems [5] for which, due to long range B - B repulsion, the excess is positive and over two orders in magnitude higher than for non-ionic liquids. It is shown, by analyzing simple analytical model, that the positive contribution to the excess is strictly correlated with the liquid structure (via. two particle B - B correlation function).

In the second part the long time behavior of the rate coefficient for (2) obtained from the simulation is compared to the rate coefficient predicted within the classical Smoluchowski approach. The deviations are analyzed and compared to the analogous deviations for the trapping process (1). The influence of change of the liquid structure due to dimerization (the second scheme) on the reaction rate is also investigated.

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Structural Macrokinetics of Biomimetic Processes in Artificial Cells

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1. Introduction.

It is known that all cytophysiological processes occur on the cell ultrastructure, which is a heterogeneous (heterophase) medium. So the kinetics of metabolic processes should be considered as a structural macrokinetics of this partially ordered medium (soft matter). A macrokinetic approach is applied to a number of phenomena in which the reaction is synchronized with the diffusion, heat and mass transfer and charge transport, which include metabolism as a special case of processes in distributed active systems. However, the formation of non-equilibrium distribution of the reagents in the cell's ultrastructure is supported by the diffusion-limiting membranous structures, which are a special case of soft matter, together with the functionally similar colloidal systems. In this case, it is possible to simulate the structural macrokinetics of cytophysiological processes using heterogeneous distributed active medium (soft matter) as a carrier, reproducing the ultrastructural organization of the cytoplasm.

2. Materials and methods

The basis of the formation of stationary spatially inhomogeneous cytoplasmic distribution of reagents is the process of ultrastructural self-organization in distributed systems. Therefore, in cytophysiological modeling we used the method of photoinduced self-organization in a heterogeneous active medium (nanodispersed system) instead of the common methods of assembly, based on the forced association. The advantage of this method is that in the active medium under irradiation the formation of biomorphic dissipative structures and initiation of photoinduced metabolic processes on them occur simultaneously.

The structures obtained were investigated by the analytical SEM, TOF MS, X-ray phase microanalysis and the methods of chemical kinetics and mathematical morphology.

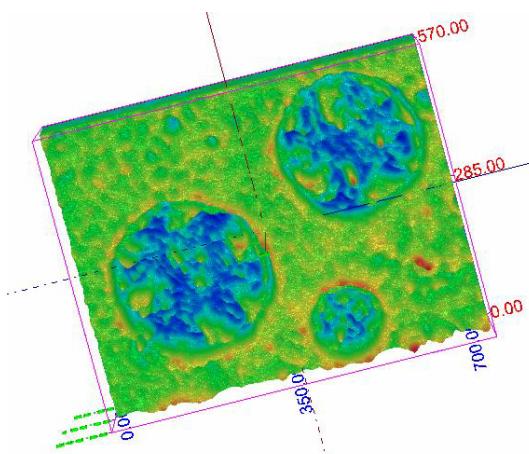


Fig. 1: Artificial Cells. 3D-view.

3. Results

From the data obtained it was found that the microstructures formed have a non-equilibrium distribution of concentrations, evolving in time and space, show oscillatory modes of reactions, possess distinct dynamics (pacemakers, standing waves) and reactivity to the external physical and chemical factors. Finally they are similar to the biological cells at the ultrastructural level due to the same physico-chemical mechanisms of an abiogenic origin. In other words, the self-organized biomimetic structures reveal structural macrokinetic behavior close to the biophysical one.

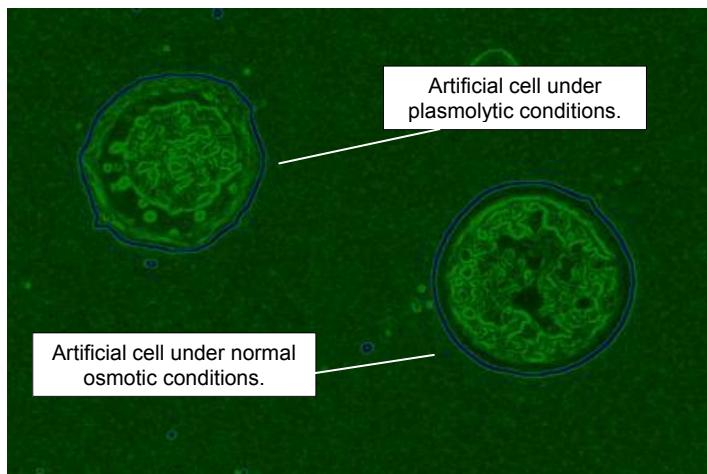


Fig. 2: Osmotic conditions model, based on the structural-kinetics cell's model.

4. Conclusion

Our model reproduces the structural-macrokinetic aspect of a number of metabolic phenomena, based on the physico-chemical analogies with the biological cell. Thus, the semi-permeability of bioorganic membranes is simulated by semiconductive polymer inorganic dynamic membranes, exergonic chemoosmotic redox processes are equivalent to cellular respiration, biomimetic self-oscillating reactions are analogues of oscillatory metabolic processes and finally the structure formation in these models is also provided by reaction-diffusion mechanisms.

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Dynamics of Friction Dependent Processes at Liquid Interfaces

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1. Introduction

Liquid interfaces (air/liquid, liquid/liquid) play a crucial role in many areas of sciences and technology, going from the origin of life to chemical extraction. In the bulk liquid phase, molecules are randomly oriented and the liquid properties can be characterised by isotropic values such as viscosity or dielectric constant. The situation is totally different at liquid interfaces, where the asymmetry of forces leads to an anisotropy of molecular orientation and hence to totally different properties. Therefore, the photochemistry at interfaces can be expected to differ from that in bulk phases. However, the measurement of the dynamics of photoinduced processes at interfaces is a problematic task, because the spectroscopic response originating from this very thin region, typically 1-2 nm, is totally buried in those arising from the bulk phases.

One of the best ways to circumvent this difficulty is to probe a property that is only non-zero at the interface. This is the case of the second-order nonlinear optical susceptibility, $\chi^{(2)}$, that vanishes in centro-symmetric media, like bulk liquids. Therefore, second-order nonlinear optical phenomena, such as second harmonic generation, takes place upon irradiation of a liquid interface. Moreover, the intensity of the generated signal is enhanced if the fundamental and/or the second harmonic frequency is in resonance with an optical transition of the molecules at the interface [1].

2. Results

We are investigating the excited-state dynamics of various dyes at different liquid interfaces using time-resolved surface second harmonic generation (TRSSHG). By comparing the interfacial dynamics with that measured in bulk solutions, novel information on interfacial properties can be obtained, the dyes acting as local probes.

For example, we have measured the excited-state lifetime of Malachite Green (MG) at air/water, alkane/water and alkane/water-glycerol interfaces (Fig.1). The S_1 state of MG is known to undergo a non-radiative decay to the ground-state through large amplitude motion of the phenyl substituents. Therefore, its lifetime depends strongly on the local viscosity, η , and follows

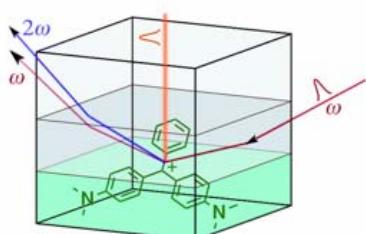
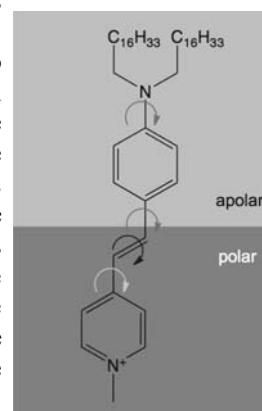


Fig. 1: TR-SSHG at a liquid/liquid interface with Malachite Green.

a η^α dependence, where $\alpha=0.6$. We have measured a S_1 lifetime of MG of 550 fs in bulk water and of 1.1 ps at air/water interface [2]. This shows that the friction exerted by interfacial water is substantially larger than that experienced in bulk water. When going from air/water to alkane/water interfaces with alkanes of different lengths, we found that the S_1 lifetime of MG is independent of the viscosity of the alkane below about 2 cP, but increases significantly with viscosity above this value [3,4]. This indicates that large amplitude motion of the non-polar phenyl substituent (sitting in the non-polar phase) also plays a role in the excited-state dynamics of MG, contrary to previous claims [5].

By varying the macroscopic viscosity of the polar phase in alkane/water-glycerol interfaces, we found that the interfacial S_1 lifetime of MG is always longer than in a bulk solution of the same viscosity, but that the α value is substantially smaller ($\alpha\sim 0.4$). This points to a different composition of the water-glycerol mixture at the interface [3]. Moreover, at a specific water-glycerol mixture, the S_1 lifetime departs totally from the η^α dependence and becomes very large. The origin of this spectacular effect is not understood yet.

Measurements at liquid/liquid interfaces can also be used to deduce information on the deactivation pathway of an excited molecule. This has been done for example with an hemicyanine (Fig.2), whose S_1 state decays non-radiatively through large amplitude motion. In order to find out which coordinate is responsible for this deactivation, the viscosity dependence of the excited-state lifetime of this dye at liquid/liquid interfaces has been performed. Whereas the lifetime is independent of the viscosity of the polar phase, a substantial viscosity dependence of the non-polar phase has been measured, indicating the involvement of a mode localised in the apolar part of the molecule.



3. Conclusion

Ultrafast spectroscopy at liquid/liquid interfaces is still in its infancy and is a challenging area for both experimentalists and theoreticians.

Fig. 2: hemicyanine at liquid/liquid interface.

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A “Cage Complex” Method in Chemical Reactions Theory in Solutions and its Application to the Consideration of Multistage Reactions

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1. Introduction

A variety of methods for the derivation of kinetic equations of physicochemical processes in liquid solutions, and calculations of the kinetics of different elementary reactions are now available in the literature. At the same time, multistage reactions are not adequately explored. For example, it is generally accepted that the mechanism of multistage reaction (a combination of successive and parallel elementary reactions) unambiguously specifies the form of the set of kinetic equations of formal chemical kinetics based on the use of the law of mass action. In gases commonly considered in the framework of the Collision Theory the kinetic law of mass action represents the fact that reactants in free walk (the mean time of which exceeds significantly the mean collision time) are spatially (and chemically) uncorrelated; this is expressed via the product of bulk concentrations of reactants involved in collision. The efficiency of such a collision (the reaction rate constant value) is determined by inelastic scattering cross-section upon collision. As in gases, in dilute solutions the reactants are almost all the time in the process of free random walks at the distances too short for the elementary event of chemical conversion to occur. The only difference is in the character of motion of reactants due to a solvent (commonly such a motion is treated as continual diffusion). However, it is essential that the change in the character of the relative motion of reactants affects the course of chemical conversion on the approach of reactants.

2. Results

The paper presents the analysis of different approaches to the examination of elementary stages of bimolecular reactions in liquid solutions. As is shown, most clear physical interpretation of their course is provided by the Encounter Theory (the prototype of the Classical Collision Theory). However, unlike reactions in gases, in solutions the reactants that came into contact resulting in chemical conversion event do not escape from the cage when the contact is over by virtue of the cage effect, but can make re-contact; and this leads to further chemical transformation. Only after a series of re-contacts the reactants move apart; this corresponds to the escape from the cage, i.e., the products begin walking freely. Thus the process that in a gas is considered as collision, in solution is treated as residence in the cage – the encounter of reactants consisting of re-contacts

(analog of “scattering”). Exactly for this reason the theory based on representing a solution as a “gas” of reactants has received the name the Encounter Theory.

Using the so-called kinematic approximation for the calculation of rate constants of reactions proceeding near the immediate contact of reactants, it is shown that consideration of both elementary and multistage reactions may be reduced to quasi-stationary solutions of the equations that correspond to a simple kinetic scheme (widely employed in formal chemical kinetics) with appropriately defined kinetic parameters. This approach that forms the basis of the “cage complex” method is clearly physically interpreted in the framework of the Encounter Theory. With this method, manifestations of the cage effect on the encounters of reactants are treated theoretically with elementary and multistage reactions of step-by-step catalysis in liquid solutions as an example.

3. Conclusions

The cage effect is shown to give rise to some essential effects not inherent in reactions in gases or reactions in solutions proceeding in the kinetic regime. Among such effects, the change in multistage reaction mechanism showing itself as new reaction channels and the corresponding transformation rate constants of reactants is most important. This substantially affects experimental kinetic evidence processing in determining rate constants of multistage reaction elementary stages.

Acknowledgement

Authors thank Russian Foundation of Basic Research (project 09-03-00456) for financial support.

Non-Markovian Effects in Kinetics of Quantum Tunneling Reactions Proceeding in Condensed Phase

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1. Results

The reformulation of the standard golden rule approach considered in this work for treating reactive tunneling reduces the computation of the reaction rate to a derivation of band shapes for energy levels of reactant and product states. This treatment is based on the assumption that the medium environment is actively involved as a partner in the energy exchange with the reactive subsystem but its reorganization effect is negligible. Starting from the quantum relaxation equation for the density matrix, the required band shapes are represented in terms of the spectral density function, exhibiting the continuum spectrum inherent to the interaction between the reactants and the medium in the total reactive system. The simplest Lorentzian spectral bands, obtained under Redfield approximation, proved to be unsatisfactory because they produced a divergent rate expression at low temperature. The problem is resolved by invoking a refined spectral band shape, which behaves as Lorentzian one at the band center but decays exponentially at its tails. The corresponding closed non-Markovian rate expression is derived and investigated taking as an example the photochemical H-transfer reaction between fluorene and acridine proceeding in the fluorene molecular crystal. The kinetics in this reactive system was thoroughly studied experimentally in a wide temperature range [1]. Our earlier studies on the theme of the present report [2-4] are supplemented by recent low-temperature calculations for this process.

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Effect of Cucurbit[7]uril on the Primary Photoprocesses of Fluorescent Dyes

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1. Introduction

Photophysical properties of aqueous solutions of 3,3'-diethyl-thiacarbocyanine iodide (**dye 1**) (Fig. 1) and of styryl (**dye 2**) (Fig. 2) were studied in the presence of

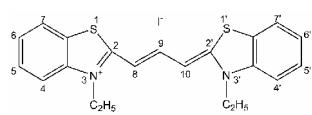


Fig. 1: Cyanine dye.

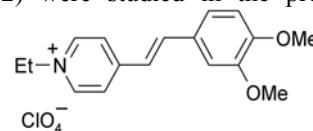


Fig. 2: Styryl dye.

cucurbit[7]uril (CB[7]) (Fig. 3) by means of fluorescence spectroscopy. Pumpkin-shaped macrocycle of CB[7] has a rigid cavity (the internal and external diameters are 5.4 Å and 7.3 Å, respectively, the height, 9.1 Å [1]) that allows including either of dyes as the guest-molecule.

2. Experimental results

The encapsulation of **dye 1** by CB[7] results in changing absorption spectrum and in a 5-fold

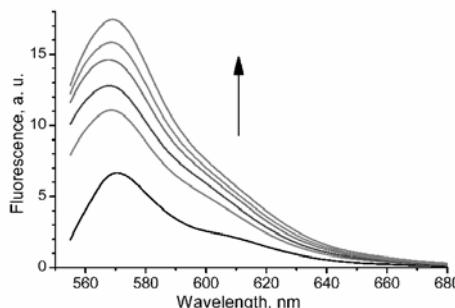


Fig. 4: The fluorescence spectra of cyanine dye for various concentrations of CB[7].

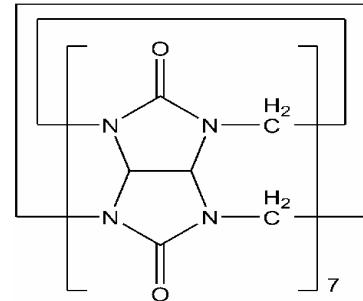


Fig. 3: Cucurbit[7]uril.

increase of its fluorescence quantum yield (Fig. 4).

It was also found that lifetime of **dye 1** fluorescence increases from 0.12 ns in homogeneous aqueous solution to 1.07 ns in the presence of CB[7]. The binding constant of 1:1 complexes of **dye 1** with CB[7] has been determined to be K=2.8E4

M^{-1} . The comparison of the absorption and fluorescence-excitation spectra of **dye 1** [2] gives the absorption spectrum of its non-fluorescent cis-isomers, (curve 3, Fig. 5).

The encapsulation of **dye 2** in CB7 results in shift of maximum of absorption spectrum to long-wavelengths from 383 nm to 406 nm and in a significant increase in the fluorescence of **dye 2** upon increasing the CB7 concentration from 0 to 1.6×10^{-5} M (Fig. 6).

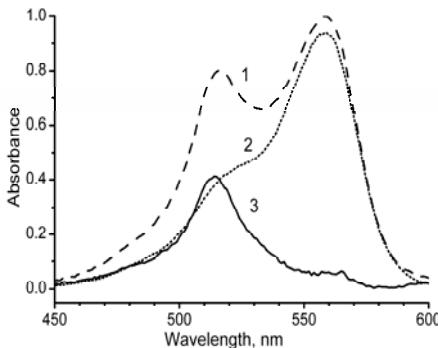


Fig. 5: Absorption (1) and fluorescence excitation (2) spectra of **dye 1** in the presence of 0.15 mM CB[7]; curve (3) corresponds to absorption spectrum of its cis-isomer.

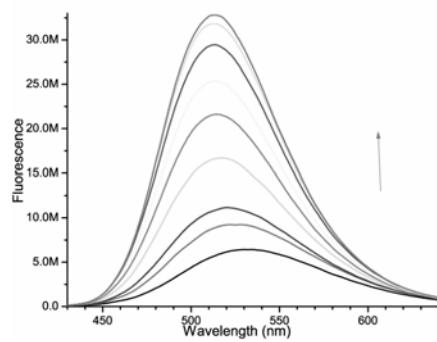


Fig. 6: The fluorescence spectra of styryl dye for various concentrations of CB[7].

The dependence of the fluorescence intensity of solution on the concentration of CB[7] allows the estimation of the binding constant (assuming 1:1 complexes **dye 2 + CB[7]**), that is $10^5 M^{-1}$.

The fluorescence lifetime of **dye 2** was measured by TCSPC and streakcamera techniques. The fluorescence decay of **dye 2** is the biexponential function with a main short component. Upon the addition of CB[7] the lifetime notably increases.

| | Decay, ns | Ampl. % |
|---------------|-----------|---------|
| Dye 1 | 0.11 | 92 |
| | 0.34 | 8 |
| Dye 1 + CB[7] | 0.26 | 90 |
| | 1.15 | 10 |

Fig. 7: The fluorescence lifetime of styryl dye

3. Conclusion

The encapsulation of the studied fluorescent dyes by CB[7] results in the stabilization of their cis-form and in a significant increase of the fluorescence.

Acknowledgments The work was supported by the Russian Foundation for Basic Research and the Russian Academy of Sciences.

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Advances in NMR Diffusion Measurements

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1. Introduction

Translational diffusion is the most fundamental form of transport in the solution state and it is directly linked to the size and shape of a diffusing species via the Einstein-Sutherland (or Stokes-Einstein) equation. Consequently, diffusion is a natural probe for molecular association (e.g., protein-protein self-association or drug-protein binding). Further, if the timescale of the measurement is such that the diffusing molecules have time to interact with any boundaries (e.g., diffusion in a porous medium or biological cell), then the diffusion measurement will also provide information on the characteristic distances of the geometrical restrictions. Of the available methods for measuring diffusion, pulsed gradient spin-echo (PGSE) NMR diffusion measurements (also commonly referred to as DOSY or NMR diffusometry) are now widely used due to their wide applicability, efficacy, information content and non-invasive nature [1]. At present, under ideal conditions the PGSE technique has a lower limit of $\sim 10^{-15} \text{ m}^2\text{s}^{-1}$. When used to probe porous media PGSE NMR is sometimes referred to as *q*-space imaging.

2. Improved NMR diffusion measurement techniques

To extract maximum information, the measurement technique must be accurate, precise and robust. Recent work in my laboratory has involved developing versatile PGSE NMR pulse sequences and associated analysis that address the relevant problems. For example, better solvent suppression allows measurements at lower solute concentrations without the need for deuterated solvents (Fig. 1).

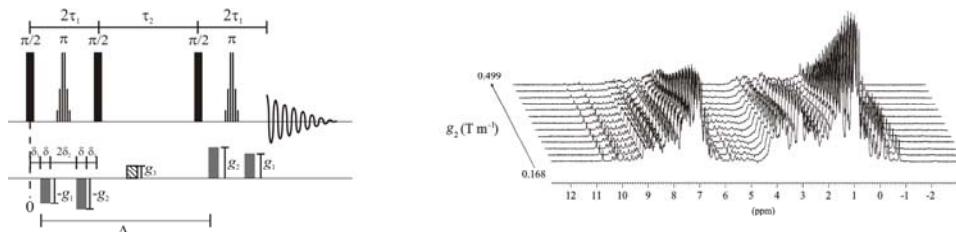


Fig. 1: The PGSTE-WATERGATE pulse sequence (left) and PGSE spectra (right) of 2 mM lysozyme in water (10:90 D₂O/H₂O). The water resonance is almost completely removed. Adapted from Ref. [2].

Accurate PGSE measurements require high signal-to-noise ratios and, ideally, that the sample is subject to strictly homogeneous magnetic gradients. The reality is often thwarted by the effects of J -evolution and the presence of susceptibility-induced background gradients resulting from the magnetically heterogeneous nature of the sample and also limitations of the gradient generation system (including its calibration). Recent work has also addressed these issues [3-5].

3. Conclusions

This lecture will detail some recent advances in NMR diffusion measurements and the type of modelling needed to analyse the resulting data. The talk will be illustrated with data drawn from a number of experimental studies ranging from biological to chemical.

Acknowledgement

This research was supported by a NSW BioFirst Award from the NSW Ministry for Science & Medical Research.

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A Theoretical and Experimental Studying of NMR Contrasting Properties of Nanocomposites Based on Ferric Oxides Stabilized by Arabinogalactan Matrix

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1. Introduction

Nanosized materials combining ferromagnetism and high solubility in a variety of solvents are of great interest as perspective contrast agents for Magnetic Resonance imaging (MRI). In particular compounds based on nanoparticles of magnetic ferric oxides (magnetite Fe_3O_4 and maghemite $\gamma\text{-Fe}_2\text{O}_3$) stabilized by an arabinogalactan (AG) matrix show promise for medical applications of MRI. Convenience of using these compounds consists also in wide accessibility of arabinogalactan and harmlessness of the two components [1]. The aim of the present work is to study relaxational properties of ferroarabinogalactans (ferroAG) both theoretically and experimentally.

2. Two models of ferroAG structure

Two models of ferroAG structure were considered by means of the stochastic perturbation theory. The first one supposes homogeneous distribution of ferric oxides inside a spherical polysaccharide matrix, while the second one - a single ferromagnetic core in the centre of the sphere. Diffusion both outside and inside the AG coat was taken into account. The two models were examined by measuring of the dependence of the spin-spin relaxation time T_2 on the viscosity of aqueous solutions of ferroAG (3.5%),

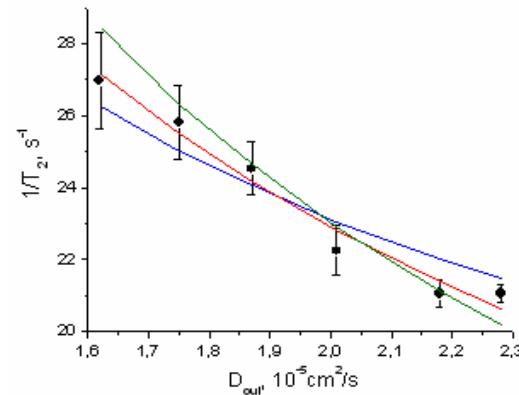


Fig. 1: Experimental (circles) and theoretical (lines) dependences of $1/T_2$ on D_{out} , magnetization of ferroAG (3.5%) powder is $96.6 \text{ Gs cm}^3/\text{g}_{\text{Fe}}$, $D_{in}=5 \cdot 10^{-6} \text{ cm}^2/\text{s}$. The homogeneous magnetized sphere model (blue line): $R=13.0 \text{ nm}$, $N=7000$. The central core model (red line): $R=9.0 \text{ nm}$, $R_c=6.5 \text{ nm}$, $N=44000$. Hwang-Freed model [2] (no AG coat, green line): $R_c=11.4 \text{ nm}$, $N=97000$.

$n(Fe)=0.1$ mM/l at 4.8 T (Fig. 1) and measuring of the magnetic field dependence of the spin-lattice relaxation time T_1 of the same samples (Fig. 2).

3. Conclusion

In the course of the fitting the following parameters were considered: the granule radius R , the ferromagnetic core radius R_c and the number of ferric atoms per a granule N , outer and inner diffusion coefficient D_{out} and D_{in} respectively. It follows from the analysis that the central ferromagnetic core model more adequately describes the experimental data on viscosity dependence of T_2 of the solutions examined, while the magnetic field dependence does not give a clear answer, what model is realized in practice.

Acknolegments

This work was supported by RFBR grant No. 09-03-00091, President grant for supporting the Leading Scientific Schools (3604.2008.3) and the Division of Chemistry and Material Science of RAS grant No. 5.1.1.

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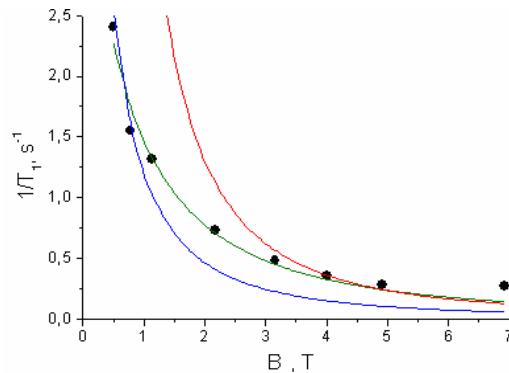


Fig. 2: Experimental (circles) and theoretical (lines) magnetic field dependences of $1/T_1$. Previously found parameters for the central core model (red line): $R=9.0$ nm, $R_c=6.5$ nm, $N=44000$. The best fit (green line): $R=R_c=4.8$ nm, $N=7000$ (the two models give the same parameters). Hwang-Freed model [2] (blue line) at $R_c=11.4$ nm, $N=97000$. The rest of parameters are the same as in Fig. 1.

Experimental Observation on Non-Markovian Effects: Quenching under Strong Light and the Relevance of the Liquid Structure on Bimolecular Reactions

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1. Introduction

In this communication we will present our latest experimental results on the study of fluorescence quenching by bi-molecular electron transfer in liquid solution.

2. Results

We will first revise the dependence on the viscosity, concentration and driving force of quenching, studied both by steady-state and time resolved fluorescence spectroscopy [1-3]. The combined analysis of the experiments leads to conclude that the influence of the liquid structure must be taken into account in order to coherently explain them in the frame of the Differential Encounter Theory [4].

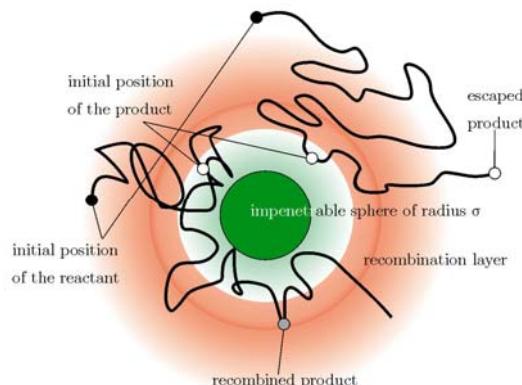
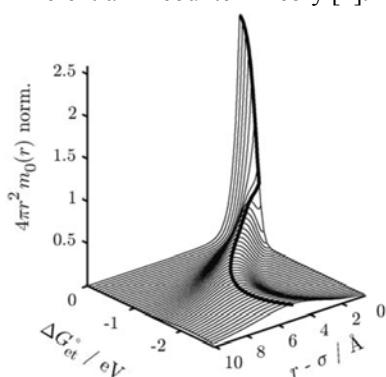
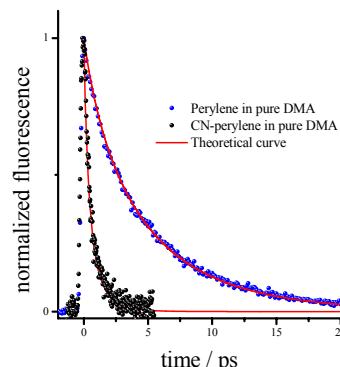


Fig. 1: Plot of the normalised initial ion distribution, $4\pi r^2 m_0(r)$, as a function of the free energy of electron transfer, ΔG_{et} , and the interparticle distance, $r-\sigma$, at a quencher concentration of 5×10^{-3} M.



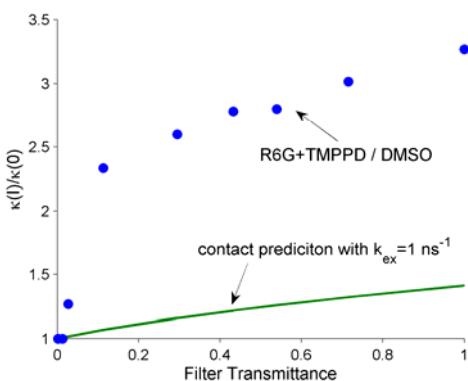
The second part of the talk will be devoted to the dynamics of quenching in highly concentrated media.



By comparing systems of similar characteristics but of different dipole moment on the fluorophore, we could establish how the surrounding medium orients and reacts in each case. The influence of this orientational modulation by dipole-dipole interaction extends to very low quencher concentrations, denoting the need of considering the molecular geometry in a wide range of bi-molecular reactions [5].

The final section of this talk will be dedicated to quenching experiments performed

under strong light excitation. It was theoretically predicted some years ago [6] that under such conditions the rate of quenching should increase respect to the usual laboratory conditions. We have indeed observed such an effect in the measurements and observed the expected results though the prediction was somehow short: the rate increases even more [7]. The origin of the effect will be explained in some detail in the context of the Encounter Theories [4, 6, 7].



Acknowledgements

These works have been done in collaboration with Günter Grampp, Arnulf Rosspeintner, Daniel Kattnig, Asim Mansha, of the Technical University of Graz (Austria), Eric Vauthey, of the University of Geneva (Switzerland), and Alejandro Cuetos, of the University Pablo de Olavide of Seville (Spain).

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Emitting Species in Conjugated Polymers for Photo- and Electro-Luminescence

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1. Introduction

Conjugated polymer chain has its backbone composed of alternative single and double bonds, in which π -electrons can delocalize along the chain. Upon excitation by light or electric field, the chain is able to emit fluorescence and phosphorescence light, due to its radiative decay process of molecule from its singlet excited state to singlet ground state and from its triplet excited state to the singlet ground state, respectively. For hydrocarbon materials, due to the spin forbidden transition of phosphorescence, the phosphorescence lifetime is typically microseconds to seconds, which is longer than fluorescence lifetime ($\sim 0.1\text{--}100$ ns) and is usually observed at low temperature. However, through the incorporation of heavy atoms (such as Pt) in the polymer backbones, the emission from the triplet excited state is visible at room temperature. Here, we focus on polyarylenes, from which only fluorescence can be observed at room temperature. In the bulk collection of chains, intrachain or interchain interactions exist and can inevitably change their photoluminescence (PL) and electroluminescence (EL) spectra as compared to those of their corresponding non-interacting isolated chain (i.e., no intrachain or interchain interaction acting on it) emissions by generating new emission peaks. This occurrence is usually not desirable for most optical and optoelectronic applications. Therefore, in addition to the non-interacting isolated chain (a non-interacting emitting species), it is important to understand the structural characteristics and optoelectronic properties of emitting species formed by intrachain or interchain interactions [1].

2. Single chain and chain ensemble fluorescence spectroscopy

For investigation of emission from non-interacting isolated chain, single-molecule spectroscopy measurement on a single individual chain was carried out. It was found that energy transfer between different conjugation length segments within a single polymer can occur. Energy transfer in rodlike polymer is very inefficient, since there is no path for three-dimensional exciton migration within it. However, in long-chain polymer, close packing of polymer segments in the core region allows efficient three dimensional energy transfer to funnel energy from short conjugation segment to the long conjugation length segment. In the extended region, greater separation of adjacent segments results in relatively inefficient one-dimensional energy transfer along the polymer backbone [2, 3]. For interacting emitting species in an ensemble of chains, the intrachain and interchain

interactions between lumophores result in the formation of excimer, exciplex, and aggregate, leading to a generation of new peak with featureless structure on the longer wavelength side in the fluorescence spectrum and usually to a lowering in PL quantum efficiency (PLQE). The excimer and exciplex only exist in excitation state, but aggregate is a ground-state emitting species. Many conjugated polymers are reported to form excimer (such as poly(2-methoxy-5-(2 -ethylhexyloxy)-1,4-phenylene vinylene (MEH-PPV) and poly(9,9-di-noctylfluorene (PFO)) or exciplex. Also, aggregates happens on many conjugated polymers such as MEH-PPV or dialkyl-substituted distyrylbenzene polymer. Aggregates in MEH-PPV and PFO can act as hole traps (also as electron traps for MEH-PPV). In addition, the presence of aggregate in MEH-PPV film can cause a lowering of hole mobility [4, 5].

On the other hand, β phase of PFO is a more coplanar chain segments (average backbone torsion angle is 160°) with an extended conjugation length of about 30 repeat units (UV-vis absorption peak at 430 nm) and can exhibit an emission spectrum with fine vibronic structure. Electron-trapping (a trap depth of 0.12 eV) and promoted hole mobility are two special functionalities of β phase. With the presence of few amount (1.32%) of β phase in PFO film, the device performance can be largely enhanced and its EL emission can be a pure and stable blue light. Note that excimer, exciplex, aggregate, and β phase can be observed in both PL and EL spectra [6].

In addition, electroplex is an electronically excited emitting species, which forms only under an electric field by cross-recombination of electrons in the acceptor (N) and the holes in the donor (M) molecules (or segments). If M and N are of the same kind of molecule (or segments), the complex pair is termed electromer. Electroplex and electromer are only visible in the EL spectrum, but not in the PL spectrum. The presence of electroplex and electromer leads to a red-shift of the emission relative to the pure individual material. The lifetimes of electroplex and electromer are about several hundred nanoseconds [7].

Acknowledgement

We thanks the Ministry of Education (Project 91E-FA04-2-4A) and the National Science council (Project NSC94-2216-E-007-034) of ROC for the financial support.

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Diffusional Charge and Exciton Transport in Long Conjugated Molecules: "Molecular Wires" for Photovoltaics?

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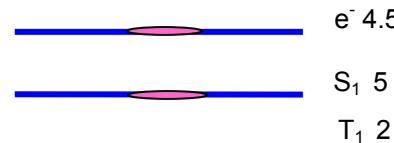
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1. Introduction

Long, conjugated molecules can act as semiconducting “molecular wires.” They have enormous potential for development of inexpensive solar photovoltaics. A field called “plastic solar,” has created solar cells having efficiencies reaching ~7% [1]. We will argue that popular methods make little use of the potential of conjugated molecules to act as “wires,” due in part to our limited understanding of what that potential is. Past difficulties with transport confines peoples’ thinking. Limitations on transport, particularly for excitons, are almost seen as absolute, although no fundamental basis is known for such a belief.

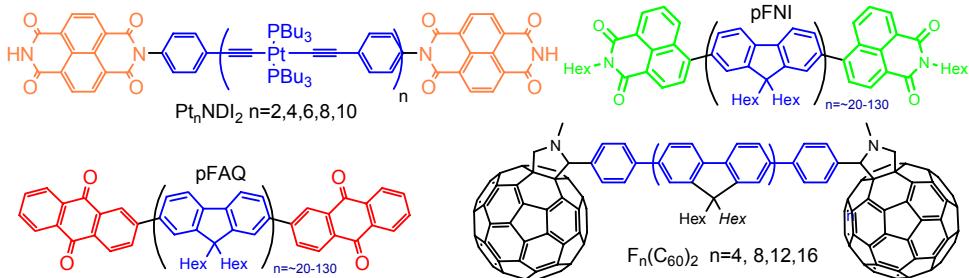
2. Results

Experiments described here seek to understand the natures of charges and excitons in conjugated molecules, and to determine how fast they move. The experiments also seek to understand the nature of charges in these “wires,” obtaining evidence that they are polarons, which may move along the wires by one-dimensional diffusion. Experimental results suggest that electrons or holes in polyfluorenes spread over lengths of 4.5 repeat units [2]. Singlet excitons are slightly longer and triplet excitons are much shorter as illustrated to the right. For singlet exciton experiments in our laboratory recently found transport to be much faster than previously believed [3].



We seek experimental answers to the question of what distances can they move without trapping. The experiments inject electrons or photoexcite long, conjugated molecules having charge or exciton traps at the ends using Brookhaven’s Laser Electron Accelerator Facility (LEAF) [4].

The measurements determine electron and exciton transport in polymers and oligomers having end-cap traps. Structures of molecules under study are shown below and others are in progress.



The charges are created in organic solvents by ionization of the solvents. Diffusional processes are also involved in attaching charges to the wires. Electrons created in a solvent relax to become “solvated electrons.” For long molecules unusual aspects of the diffusion of these electrons contribute to the electron attachment [5]. Understanding of these processes benefits from theoretical progress on diffusion-controlled reactions with extended objects [6]. Additional observations show that electrons may attach to solutes before relaxation to enhance our time resolution.

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Kinetic and Direct Computer Multiparticle Models of the Processes in Photosynthetic Membrane

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1. Introduction

The system of the processes in photosynthetic membrane is one of the most thoroughly investigated subcellular system, its structural organization and some kinetic parameters are known from independent experimental data. The paper presents the results of the work on kinetic and multiparticle computer modelling performed at the Department of Biophysics, Biological faculty MSU.

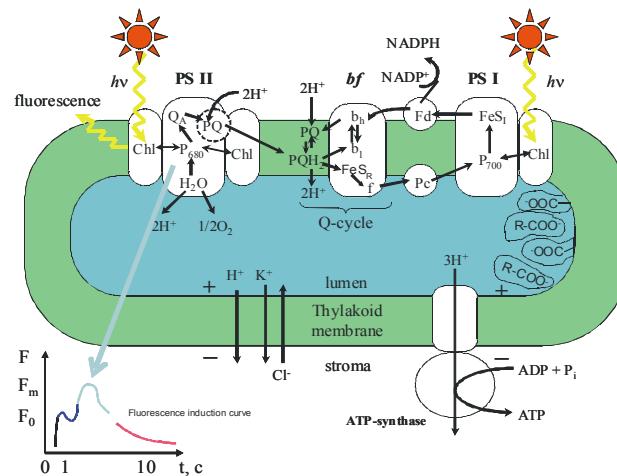


Fig. 1: Flowchart for the general kinetic model of primary photosynthetic processes. PSI, PS II – photosystems I and II; Chl – antenna chlorophyll; P680 and P700 – pigments of the PSII and PS I reaction centers; QA – primary quinone acceptor of PSII; FeSI – acceptor complex of PSI; Fd – ferredoxin; PC – plastocyanin; bf – cytochrome b/f complex; b_h and b_l – high and low potential hemes; FeSR – Rieske iron-sulfur center; PQ – plastoquinone, PQH_2 – plastoquinol; R-COO⁻ designate buffer groups. Signs (+) and (-) on the membrane indicate that the thylakoid lumen is charged positively and the chloroplast stroma is charged negatively in the course of photosynthetic processes. Zigzag arrows denote quanta of incident light and fluorescence. Common arrows indicate the direction of electron transfer along the chain and the ion fluxes across the thylakoid membrane upon the onset of the illumination.

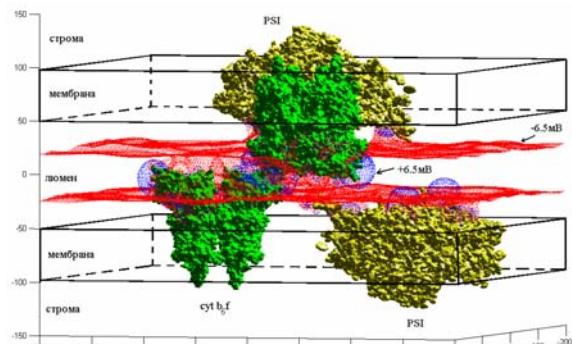
2. Kinetic models

The general kinetic model of the primary photosynthetic processes in a thylakoid membrane (Fig. 1) is based on the system of ordinary differential equations, describing the processes in multi-enzyme complexes of Photosystem I, Photosystem II and Cytochrome b_6f complex, coupled to transmembrane proton and other ions transport and generation of transmembrane electrochemical potential. This model simulates kinetics of different variables, including concentrations of electron carriers at different redox states, electrical and electrochemical potential values; it adequately simulates a set of fluorescence induction curves experimentally recorded at different light intensities under continuous illumination and after a short laser flash.

3. Direct computer multiparticle models

The direct multiparticle computer model describes processes proceeding in the simulated membrane “scene”, which includes stroma, lumen and intramembrane compartments constructed according to structural data. Motions of individual mobile electron carriers are described by the formalism of Brownian dynamics taking into account the electrostatic interactions. The direct model allows us to follow not only the kinetics, but, it also mimics the visual image of the behavior of electron carriers. The model reveals the role of complex geometry of the interacting proteins and spatial organization of photosynthetic membrane.

Fig. 2: The “scene” of the direct multiparticle model. Equipotential surfaces (6.5 mV) in lumen of chloroplast thylakoid, $pH=7$, ion strength $I=100$ mM, surface charge $\sigma = -47.5 \text{ mQ/m}^2$.



4. Conclusion

Kinetic and multiparticle computer models allow us to evaluate the parameters of photosynthetic processes which can not be determined experimentally and reveal physical mechanisms of regulation of photosynthetic electron transport and coupled processes of energy transformation.

Acknowledgements

The work was supported by grants of the RFBR 2000-2010 (now grant # N 08-04-00354) and Russian Ministry of Education, pr. P-2213.

Semi-Analytical Approach to Time-Dependent Trapping Model of Diffusion-Controlled Reactions

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1. Introduction

Consider the classical trapping model (TM) of diffusion-controlled reactions when particles B diffuse in a medium doped with static traps (sinks) A and react after they encounter. It is well known that despite its simplicity this model finds many important applications in physics, chemistry and biology (see, e.g. Ref. [1] and references therein). However a number of theoretical problems concerning the TM with N sinks is still unsolved. This caused first of all by rather complicated geometry of domain outside the sinks mathematically corresponding to a 3D periphaptic domain with N disconnected boundary. For the transient reactions occurring in periphaptic domains with $N \geq 2$ it is not feasible to separate or R -separate variables in the relevant diffusion equation and therefore this problem is not tractable exactly [2]. So monopole approximation [2], finite-difference computations and the method-of-images [3], generalization of the Wilemski-Fixman-Weiss decoupling approximation [4] were suggested. In terms of the Laplace transform with respect to time with the aid of relevant addition theorem the problem was investigated in Refs. [5, 6]. However a grand problem due to Laplace space inversion has arisen in earlier proposed methods [4-6].

2. Statement of the problem

The boundary value problem (BVP) corresponding to the TM reads

$$\partial u / \partial t - D \nabla^2 u = f \quad \text{in } Q_T := \{(\mathbf{x}, t) : \mathbf{x} \in \Omega^+, t \in (0, T)\}; \quad (1)$$

$$u(\mathbf{x}, 0) = u_0(\mathbf{x}), \quad u(\mathbf{x} \in \partial\Omega_i, t) = u_i(\mathbf{x}^*, t); \quad (2)$$

where $\Omega^+ = R^d \setminus \bigcup_{i=1}^N \overline{\Omega}_i$ is a domain outside N sinks regions Ω_i and $d \geq 1$, D is the diffusion coefficient of particles B .

The primary task for the theory of diffusion-controlled reactions is the derivation of the absorption rate, i.e., the total flux of B particles into the i th sink

$$\Phi_i^{(N)} = -D n_0 \int_{\partial\Omega_i} (\mathbf{n}_i \cdot \nabla u) |_{\partial\Omega_i} dS. \quad (3)$$

Here $u = 1 - n_B/n_0$, n_B and $n_0 = \lim_{|\mathbf{x}| \rightarrow \infty} n_B$ are the local and bulk concentration of particles B , respectively, and $\partial\Omega_i$ is the surface of i th sink.

2. Elucidation of the approach

Our approach is based on the known Rothe method [7]. Divide the domain Q_T into temporal layers by planes: $t = m\tau$ such that $[0, T] = \bigcup_{m=1}^n I_m$, where $I_m = [(m-1)\tau, m\tau]$,

$m = \overline{1, n}$ and $\tau = T/n$ is the step in time. Substituting the time derivative in Eq. (1) by its backward difference derivative approximation we obtain the following system of n elliptic differential equations

$$(v_m - v_{m-1})\tau^{-1} - D[\sigma \nabla^2 v_m + (1-\sigma) \nabla^2 v_{m-1}] = f_m,$$

where $v_m := u(\mathbf{x}, m\tau)$, $f_m := f(\mathbf{x}, m\tau)$ and $\sigma \in [0, 1]$ is a subsidiary parameter to improve the convergence and stability of the computational scheme. It is clear that if we pose the following initial and boundary conditions

$$v_0(\mathbf{x}) = u_0(\mathbf{x}) \quad \mathbf{x} \in \Omega^+, \quad v_m(\mathbf{x}^*) = u_i(\mathbf{x}^*) \quad \mathbf{x}^* \in \partial\Omega_i$$

the functions $v_m(\mathbf{x})$ are approximate solutions of Eq. (1) given on the mesh at issue. If one defines the following functions

$$u_n(\mathbf{x}, t) = \sum_{m=1}^n \{v_{m-1}(\mathbf{x}) - [v_m(\mathbf{x}) - v_{m-1}(\mathbf{x})](m-1-t/\tau)\} \chi_{I_m}(t),$$

where $\chi_{I_m}(t)$ is the indicator function of the segment I_m one has at the mesh points

$$u_n(\mathbf{x}, (m-1)\tau) = v_{m-1}(\mathbf{x}) \quad \text{for } \forall m = \overline{1, n}.$$

In this way for different values of n we obtain the functional sequence $\{u_n(\mathbf{x}, t)\}_1^\infty$ of approximate solutions for BVP (1), (2) such that $u(\mathbf{x}, t) = \lim_{n \rightarrow \infty} u_n(\mathbf{x}, t)$.

Proposed here semi-analytical approach to time-dependent BVP (1), (2) allows us to achieve approximate solution of the same accuracy considerably faster than known in literature methods [3-6].

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Reaction Kinetics Constrained by Multi-Scale Protein Mobility: the Ultrametric Diffusion Approach

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1. Introduction

Over 25 years ago Hans Frauenfelder (CNLS, Los Alamos) discovered that, as long as the protein conformation rearrangements limit the enzymatic reaction, a heavy kinetic tail follows a power law or the stretched exponent [1]. In order to explain this fact, he supposed that the protein energy landscape (EL) consists of great number of local minima corresponding to the protein conformational substates (CSs). With respect to the transitions between CSs, the local minima were assumed to be clustered into hierarchically embedded basins of minima: the smaller basins separated by smaller barriers are pooled into larger basins that are separated by higher barriers. In other words, the protein CSs do exhibit a tree-like order: the distances between the CSs are satisfied the strong triangle inequality. Since that, the protein CS-space is an ultrametric (non-Archimedean) space, and the fluctuation-induced protein mobility can be interpreted as the ultrametric diffusion - a homogeneous Markov process propagating over the ultrametric space. However, up to the end of the 90-th, no description of the rebinding kinetics based on the ultrametric idea had been realized. The state of things moved forward when the p -adic master equation of ultrametric diffusion was introduced in the following form (see Ref. [2]):

$$\frac{df(x,t)}{dt} = \int_{Q_p} w(|x-y|_p) [f(y,t) - f(x,t)] d_p y. \quad (1)$$

Here the field Q_p of p -adic numbers describes the protein CSs, $f(x,t)$, $x \in Q_p$, $t \in R_+$, is the probability density to find a protein in a state x at the instant t , $w(|x-y|_p)$ is the rate constant to jump over the ultrametric distance $|x-y|_p$ in the CS-space, and $d_p y$ is the Haare measure on Q_p . Then, using the ultrametric (p -adic) equations of the reaction-diffusion type, it was shown [3] that, indeed, the power tail of the ligand-rebinding kinetics can be understood on the basis of Frauenfelder's idea.

Roughly at the same time, Josef Friedrich (MTU, Munich) studied the spectral diffusion in deeply frozen proteins and was found oneself in the situation similar to the rebinding kinetics. The spectral diffusion is established by monitoring the burnt spectral hole (its width, σ) in the absorption spectrum of chromophore markers implanted in

protein molecules. Such measurements have been done in deeply frozen proteins with respect to the waiting time (t_w) and the aging time (t_{ag}) on many time scales, and it was found that the spectral diffusion broadening and the spectral diffusion aging both obey the power laws, $\sigma(t_w) \sim t_w^a$ and $\sigma(t_{ag}) \sim t_{ag}^b$, with characteristic exponents $a = 0.25 \div 0.30$, $b \approx -0.07$ (see Ref. [4]). Note, that the spectral diffusion broadening exponent much less than 0.5, characteristic for familiar diffusion. Again, these observations produced many contradicting views on spectral diffusion in frozen proteins, all without any relation to the ligand-rebinding kinetics, despite of the fact that scale-invariant behavior of the spectral diffusion and the rebinding kinetics are both constrained by the protein motions.

2. Results

Unlike these theories, we have shown that the spectral diffusion in deeply frozen proteins can be understood on the basis of ultrametric description of protein mobility, which we developed before for the rebinding kinetics. In the case of spectral diffusion, a key point is the relationship between the protein fluctuation dynamics in the CS-space, which trajectories we model by a random walk over ultrametric space, and the spectral diffusion propagating along the frequency straight line. We advance the arguments that the spectral diffusion, itself, is due to rare events occurring in the midst of the transitions in the protein CS-space. Such rare events can be associated with hitting very particular CSs related to rearrangements of the marker neighbors; hence, the time intervals between random changes of the marker absorption frequency are modeled by the first passage times for ultrametric random walk [5]. Such approximation gives an excellent agreement with the Friedrich's experimental data [6].

Thus, we have exploited ultrametric diffusion as a unique background for description of fluctuation-induced protein mobility in both the ligand-rebinding kinetics and the spectral diffusion. In fact, for small ligands or absorption markers, a protein molecule is the nano-scale surroundings with complex multi-scale behavior. Hence, the ultrametric diffusion approach may commonly work for rate processes in condensed surroundings, which fluctuation characteristics are similar to the protein motions.

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Diffusion Model of Photoaligning in Azo-Dye Layers

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1. Results

A model of the rotational diffusion of the azo-dye molecules under the action of a polarized UV light was used to explain the formation of the photoinduced order in azo-dye layers. A diffusion mechanism was proposed that does not involve photochemical or structural transformation of azo-dye molecules. The model uses the diffusion equation with the specific potential, which characterizes the interaction of the molecule and the activated light [1].

In the model the azodye molecules are identical and do not interact with each other azodye molecules are elongated rods with the absorption oscillator (chromophore) parallel to their long axes inertial contribution to the effect of molecular rotation is negligible potential of the interaction, i.e. the azodye molecular alignment tends to be perpendicular to the light polarization $\theta = \pi/2$ azodye molecular distribution f is symmetric and the initial alignment at time $t = 0$ is random, i.e.

$$f = f(\theta, t) = \rho(u, t)/4\pi, \quad u = \cos \theta, \quad \rho(-u, t) = \rho(u, t), \quad \rho(u, 0) = 1.$$

In equation of the rotational diffusion

$$\nabla^2 f + \nabla \cdot (f \nabla \omega) = D^{-1} \partial f / \partial t$$

$\omega = (A/2) \cos^2 \theta$ is the potential of the interaction between the chromophore unit and electric field of the light E that are oriented at an angle θ between each other, $A = I\alpha V_m \tau / k_B T$ is relative energy of activated UV-light, I is light intensity, V_m is molecular volume, α is absorption coefficient, τ is characteristic time of the molecular reorientation after light absorption, D is coefficient of the rotational diffusion of the azodye molecule, k_B is Boltzmann constant, T is absolute temperature.

Both approximations of negligible and strong molecular interaction during the process of the reorientation under the action of a polarized light are considered. A certain critical temperature phase transition T_c was predicted: for $T < T_c$ the order parameter of the azo-dye layer relaxes to a nonzero value when the light field is switched off.

In case of negligible intermolecular interactions the relative order parameter is presented in view as follows:

$$s \approx (2/15) A [1 - \exp(-t/\tau_{rise})].$$

The response (rise) time is equal to:

$$\tau_{rise} = 1/6D \approx \pi \eta a_m / k_B T,$$

where D is a diffusion coefficient, η is viscosity, a_m is the characteristic size of the molecule or molecular cluster.

The rate of the induced order parameter is directly proportional to the relative intensity of the activated light:

$$\left. \frac{ds}{dt} \right|_{t=0} \approx \frac{2A}{15\tau_{rise}} = \frac{4}{5} AD.$$

To find nonzero values of the order parameter of the azodye layer after relaxation, an approximation of the frozen potential has been used, which “remembers” the final value of the averaged order parameter at the moment when the light is switched off. A good agreement with observed experimental data was found (Fig. 1). A diffusion model of azo-dye reorientation in polymer matrix is in progress.

An approach that takes into account photochemical reaction is also developed.

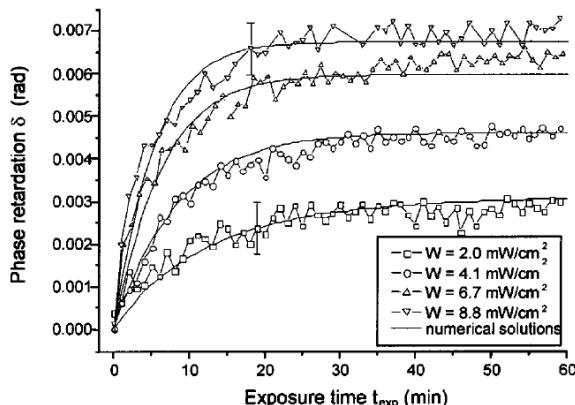


Fig. 1: Dependence of the photoinduced phase retardation d on exposure time t_{exp} for various powers W of the activated UV light. Solid lines indicate the numerical solution of the diffusion model.

Acknowledgements

This research was partially supported by RGC Grants HKUST6004/01E and HKUST6102/03E.

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Model of Diffusion Kinetics in Heterogeneous Medium

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1. Introduction

The paper is devoted to consideration of diffusion processes in heterogeneous mediums. Originally the approach was oriented for description of spatial effects in biological population dynamics, taking into account chemical interaction of specimens and their environment [1]. It was shown that diffusion (directed by gradients in a heterogeneous space), accompanied with point chemical reactions, can give quite special nonlinear equilibrium distribution of reagents [2]. In the case of ecological interpretation, the carriers of reagents were specimens of amphibians, which diffuse in some areal. It is known, that the skin of lake frogs and their tadpoles excretes metabolites, which bind heavy metals – dangerous pollutants. Such type of ecosystems can be used for biological purification of environment, polluted by the industrial waste.

Really, the scheme is much more universal. The carriers of reagent can have not biological, but chemical or physical nature. Directed distribution of reagents in heterogeneous medium is very actual topics in the field of reaction kinetics; corresponding models can have both medical and technological applications [3].

2. Mathematical model

Let us consider a linear area with various conditions in different points and time cycles, initiated from outside. The reagent carriers are divided into N groups and pass step-by-step from one group to the next one. The dynamics of i -th group is described by the diffusion equation:

$$\frac{\partial x_i}{\partial t} = \frac{\partial}{\partial l} \left[\eta_i(t, l) \frac{x_i(t, l)}{X_i(t, l)} \frac{\partial x_i}{\partial t} \right] - \frac{\partial}{\partial l} [\varsigma_i(t, l) g(t, l) x_i] - \frac{S_i(t, l)}{X(t, l)} x_i^2 \quad (1)$$

where $x(t, l)$ is the density of the carriers at point l ; $X(t, l)$ is their characteristic density. Carriers' movement is directed by the temperature gradient $g(t, l)$; η_i is the diffusion intensity, S_i is the coefficient of reagent reproduction, $t \in [t_0, t_k]$ for $i = 2, \dots, N$, where t_0 is the beginning of the period of the regent activity, and t_k is the end of the activity. For $i=1$, $t \in [t_R, t_k]$, where t_R is the reproduction time. The boundary conditions are taken as follows

$$\frac{\partial x_i}{\partial l}(t, 0) = 0, \quad \frac{\partial x_i}{\partial l}(t, L) = 0, \quad i = \overline{1, N}; \quad x_0(t_R, l) = \sum_{i=1}^N R_i(l) x_i(t_R, l) \quad (2)$$

Here L is the area length, $R_i(l)$ is the i -th species reproductive ability at the point l .

If $i \neq 1$, $x_i(t_0, l) = \varphi_i(l)$ for the first stage, and further

$$\begin{aligned} x_i(t_0, l) &= V_{i-1}(x_{i-1}(t_k, l)), \quad l \in [0, L_1] \\ x_i(t_0, l) &= 0, \quad \quad \quad l \in [L_1, L] \end{aligned} \quad (3)$$

where L_1 is the length of a pure zone, x_i is obtained from the previous step, V_i is the ‘survival’ coefficient of i -th carrier during passing from their group to the next one.

3. Results

Computer simulation of the model (1)-(3) was based on quite crude grid algorithm, included explicit scheme of Euler-type by the time coordinate and symmetrical scheme by the space one:

$$\begin{aligned} x_{k+1,j} = x_{k,j} + \Delta t &\frac{(\eta_{k,j+1} / X_{k,j+1})x_{k,j+1}(x_{k,j+1} - x_{k,j}) - (\eta_{k,j} / X_{k,j})x_{k,j}(x_{k,j} - x_{k,j-1})}{\Delta l^2} - \\ &- \Delta t \frac{\zeta_{k,j}x_{k,j}(G_{k,j+1} - G_{k,j}) - \zeta_{k,j-1}x_{k,j-1}(G_{k,j} - G_{k,j-1})}{\Delta l^2} - \Delta t \frac{S_{k,j}}{X_{k,j}} x_{k,j}^2 \end{aligned} \quad (4)$$

As shown the realisation of the scheme (4) (and taking into account evident discrete character of the process), it give sufficient level of accuracy. All the calculations were realised in the courses of two cycles: big (by time) and small (by space) ones. A stable state of the model is investigated; a criterion of stability is small difference of initial conditions between two consecutive years. The fact of convergence is guaranteed by the presence in the model of the ‘factor of self-restriction’.

Computer simulation has been carried out for different reasonable values of coefficients. Particularly, it is shown that effectiveness of the reaction depends on size of the rehabilitation ‘pure’ zone (Fig. 1).

4. Conclusion

The model illustrates possibilities of computer simulation of complex kinetic reactions in homogenous media. Combination in one model a description of such effects as diffusion, its dependence of environment homogenous (temperature, external periodic changes, etc.), peculiarities of the base chemical reaction makes the system of differential equations quite perspective tool for practical researches.

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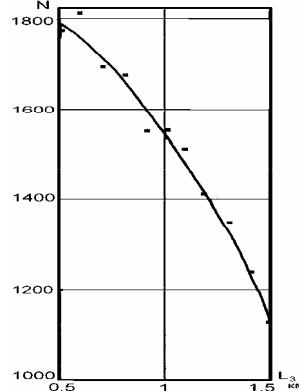


Fig. 1: Dependence of stable concentration of the reagent depending the length of the ‘pure’ zone

Ultrafast Kinetics of Charge Transfer Reactions. Problems of the Reaction Mechanism Recovering from Experimental Kinetics

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1. Introduction

Traditional chemical kinetics considers rates of the chemical reactions as functions of elementary rate constants. But for ultrafast reactions these rate constants occur to be variables dependent on the distance between molecules, time, etc. There are two kinds of approaches to the reaction kinetics in such a case: (1) time-dependent rate constants $k(t)$ and (2) distribution of rate constants $P(k)$. In the first case kinetic curves can be described as $N(t) = F(0) \exp(-k(t)t)$. This approach can be illustrated by Smoluchovski equation $k_{\text{Diff}}(t) = 4\pi\sigma D[1 + (\sigma^2/\pi D t)^{1/2}]$, used for diffusion controlled reactions [1]. Second approach uses Laplace transform $N(t) = \int_0^\infty P(k) \exp(-k t) dk$ for representation of the reaction kinetics. This approach is useful when one considers the reactions, which rates depend on the distance between reactant molecules.

Traditional approximation of the experimental kinetics $N(t)$ as a sum of several exponential terms is reasonable when one deals with slow reactions, which kinetics can be described by some combination of the rate constants. Unfortunately inverse Laplace transform of a sum of exponential functions is a sum of δ -functions and this representation cannot be used for proper description of ultrafast reactions concerned with a continuous distributions $P(k)$. On this reason the approximation of $N(t)$ as a sum of several other functions, having continuous inverse Laplace transforms is necessary in such a case.

2. Results

The use of the distribution $P(k)$ approach for analysis of experimental kinetics of some excited-state electron transfer reactions is considered. Electron transfer reactions of excited perylene with tetracyanoethylene (TCNE) in concentrated acetonitrile solutions, perylene derivatives (PeX) in neat N,N-dimethylaniline (DMA), and Coumarins with electron-donating solvents are discussed. Available kinetic data were represented in the form $N(t) = \sum_m a_m b_m^2 / (t + b_m)^2$, corresponding to the distribution $P(k) = \sum_m a_m k \exp(-b_m k)$.

Experimental kinetics of the excited perylene decay at various concentrations of TCNE [2] can be presented as $N(t) = a_1 b_1^2 / (t + b_1)^2 + a_2 b_2^2 / (t + b_2)^2$. Term $a_1 b_1^2 / (t + b_1)^2$ corresponds to almost identical $P(k) = a_1 k \exp(-b_1 k)$ with amplitudes a_1 proportional to [TCNE]. This term can be attributed to electron tunneling from excited perylene to

practically immobile TCNE molecules located around ($t < 10$ ps). Second term corresponds to the diffusion controlled reaction ($t > 20$ ps) and $b_2 \approx 1/(4\pi\sigma D[\text{TCNE}])$.

Kinetics of the excited perylene derivatives decay in neat DMA [3] can be described by a single term $b^2/(t + b)^2$, corresponding to the distribution of $P(k) = ak \exp(-bk)$ or spatial distribution of an electronic coupling $P(V^2)$.

Kinetics of the excited Coumarine 152 decay in neat electron donating solvents [4] can be described by two terms $N(t) = a_1b_1^2/(t + b_1)^2 + a_2b_2^2/(t + b_2)^2$, corresponding to more complex distribution $P(k) = a_1k \exp(-b_1k) + a_2k \exp(-b_2k)$ and spatial distribution of electronic coupling $P(V^2)$ inherent to these more complex donor and acceptor molecules.

These examples show that the distribution of rate constants $P(k)$ can be used successfully for description of ultrafast electron transfer kinetics. Vivid demonstration of the features of rate constants distributions in various systems and evaluation of electron transfer parameters can be obtained directly from experimental kinetics by application of inverse Laplace transform.

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Photoinduced Electron Transfer in Solid Films in the Presence of External Electric Fields

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1. Introduction

Excited-state dynamics of molecules and molecular assemblies is influenced by application of external electric field, depending on the electronic structure of the excited state; excitation dynamics can be controlled by external electric fields in some cases. The information about the structure and dynamics of the electronically excited states in the presence of external electric fields is also essential for design and development of materials having novel photoconductive property, nonlinear optical property or electroluminescence (EL) property, and such information can be obtained from the measurements of the electroabsorption (E-A) and electrophotoluminescence (E-PL) spectra, i.e., plots of the electric-field-induced change in absorption intensity and photoluminescence (PL) intensity, respectively, as a function of wavelength.

2. Results

In the present talk, electric field effects on PL of electron donor (D) and acceptor (A) pairs which show photoinduced electron transfer in solid films will be introduced. Electric field effects on PL of π -conjugated polymers will be also introduced. Not only the steady-state E-A and E-PL spectra but also field-induced changes in PL decay profile as well as time-resolved E-PL spectra have been measured with particular attention to the following topics:

- 1) applied electric field direction dependence;
- 2) D-A pair dependence, i.e., dependence on the free energy gap of reaction;
- 3) D-A distance dependence;
- 4) temperature dependence;
- 5) photoexcitation energy dependence;
- 6) synergy effects with application of electric field and magnetic field.

Diffusional Effects on the Reversible Excited-State Proton Transfer. From Experiments to Brownian Dynamics Simulations

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1. Introduction

Proton transfer is arguably the most important reaction in nature, since the vast photosynthetic and photoresponsive electron-transfer machinery exists largely to create a proton gradient. Our specific objective is the development of rigorous photochemical and photophysical probes for elucidating the *structural* and energetic requirements for proton transfer, including the initial solvation, nuclear motion within the transition structure, charge separation, and diffusional recombination. On a broader level, this will facilitate progress in a myriad of areas in which proton transfer is required, including “green” solvents such as supercritical fluids, gas-phase clusters, and in biochemical reaction mechanisms. Over the last several years, we have developed a number of “super” photoacids that allow proton transfer to be examined on an ultrafast timescale and in a variety of objects, greatly expanding the range of systems with which to push the limits of theory [1].

The modern theory describing the kinetics of the reversible excited-state proton transfer (ESPT) is largely based on works of Huppert, Pines, and Agmon. They analyzed the geminate-recombination reaction of photoacids in terms of the diffusion model, in which the diffusion of a dissociated geminate proton is considered as a random motion in the field of the charged anion and the diffusion equation is therefore generalized to the Debye-Smoluchowski equation (DSE) [2]. In most cases no analytical solution exists and the set of coupled DSEs describing the time evolution of the excited photoacid and its conjugated anion can be solved numerically using the Spherically Symmetric Diffusion Problem (SSDP) application [3]. We have utilized this approach successfully for various photoacids in a wide-array of solvents [4], microheterogeneous systems, and even for the Green Fluorescent Protein.

2. ESPT dynamics in 6-hydroxy-*N*-methylquinolinium

6-hydroxy-*N*-methylquinolinium (MHQ) salts are the strongest photoacids known to date [5]. We have found that the reversible excited-state proton transfer dynamics from this class of molecules are much more complicated than those that govern naphthol-type photoacids. The time-dependent charge interaction between the excited MHQ zwitterion (Z^* , Fig. 1) and the proton is not trivial. The force field of a system is (i) dynamic owing to a moving counterion, and (ii) anisotropic due to the strong dipole nature of the conjugate base. Because of the high anisotropy of the system, it is not possible to account

for forces in a manner similar to that used for spherically-symmetric static Coulomb potential for an ion pair geminate recombination [1, 2]. To construct a suitable model system we have developed a coarse-grained geometrical model that accounts for the main features of the spatial structure and the force field of the system. We were able to adequately fit the experimental kinetic data with the results of these extremely long-span (up to 10 ns) Brownian dynamics simulations (Fig. 1). Moreover, our preliminary results demonstrate that the anisotropy of the potential force can be taken into account after adapting this force for the use in the SSDP. We have demonstrated that moving counteranion ($C_4F_9SO_3^-$) modulates the time-dependence of the Z^*-H^+ interaction potential and slows down the diffusion of a proton. Finally, using the rate constants of photoinduced deprotonation and reprotonation we calculated the pK_a^* (ca. -7 in water).

3. Conclusion

Using Brownian dynamics simulations and analytical methods we developed a method that adequately describes the ESPT of highly asymmetrical “super”photoacids. We revealed the role of the counteranion on the dynamics of the diffusion-limited protolytic photodissociation. Our computational package can be utilized in the analysis of diffusion-influenced reversible fast excited-state reactions in solutions.

Acknowledgement

This work was supported by the U. S. National Science Foundation (CHE-0809179 to L.M.T. and K.M.S.).

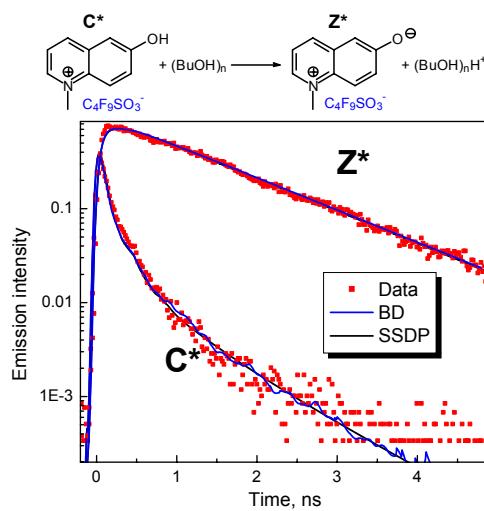


Fig. 1: Fluorescence decay of MHQ in butanol measured at the cationic and the zwitterionic bands. Solid lines are the results of straightforward Brownian dynamics simulation, and the fitting using SSDP package. The calculation results were convoluted with the instrument response function.

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Radiation Induced Fluorescence Decay as a Visualization Tool for Studies of the Kinetic Processes Involving Radical Ions in Solution

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1. Introduction

Delayed fluorescence is a typical response of matter exposed to ionizing irradiation. In weakly polar organic solution, the irradiation results in the creation of an ensemble of radical ion pairs (RIPs). Within the ensemble, the charge recombination is very frequent event and it reasonable to consider it as taking place at every moment. If the recombination is accompanied by a fluorescence photon emission from the excited states of the recombination products, it allows monitoring the evolution of the ensemble with high temporal resolution.

The purpose of this presentation is to draw the attention of physical chemists, both theoreticians and experimentalists, how much understanding of the processes involving the RIPs could come from the analysis of the kinetics of the radiation induced recombination fluorescence excited by a radiation pulse.

2. Principles of an approach

With short-lifetime luminophore, the delayed fluorescence decay $I(t)$ can be approximated by the product of the RIPs recombination rate $R(t)$, the probability to find a RIP in the singlet spin state immediately before its recombination $\rho_{ss}(t)$, and the mean fluorescence quantum yield $\varphi(t)$ of the excited states formed at the moment:

$$I(t) \propto R(t) \cdot \rho_{ss}(t) \cdot \varphi(t).$$

In weakly polar solutions, these factors are considered independent ones, and these can be affected by external fields or scavengers. The possibility of an additional modulation of the fluorescence intensity decay is very important for reaching definite conclusions about the studied system. Particularly, the time dependence of any diffusion-controlled process is universal one, and mobility of the recombining charge carriers cannot be determined relying on the $I(t)$ decay without additional experiments.

This presentation focuses on the so called “scavenger problem”, specifically, on kinetic studies of the irreversible reactions between geminate ions and scavengers that result in the change of the $\varphi(t)$ value. Several examples of the electron transfer reactions from organic radical anions to haloalkanes are given. As an illustration, Figures 1a and 1b demonstrate the dramatic change in fluorescence decays when additional electron

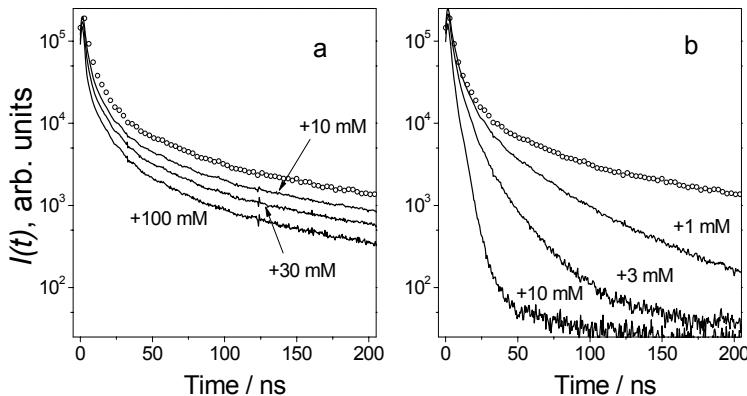


Fig. 1: The experimental fluorescence decay curves obtained at 293 K for the solutions of 10 mM diphenylacetylene in *n*-dodecane (curves shown by circles in both plots) on a semilogarithmic scale. Other fluorescence decays were obtained with the addition of 1-bromohexane (a) and 1,2-dibromoethane (b) in the concentrations as specified in the corresponding plots. The curves are normalized approximately to the same irradiation dose.

scavengers not only compete in excess electron scavenging (Fig. 1a) but participate in reactions with secondary radical ions, too (Fig. 1b).

Using data on the diffusion coefficients of the reactants involved the values of the effective reaction radii were obtained and interpreted within the theory of the distant electron transfer reactions.

3. Conclusion

The analysis of the relative changes in the fluorescence intensity decay caused by a small amount of scavengers can serve as an effective approach to kinetic studies of the scavenging reactions involving geminate radical ions, especially in combination with the methods of time-resolved electric and magnetic field effects.

Acknowledgments

This work was supported by the Council for Grants of the President of the Russian Federation for State Support of Leading Scientific Schools (Grant no. NSh-4249.2010.3).

Transient Exciplex vs. Marcus and Radiationless Transition Mechanisms of Electron Transfer Reactions

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1. Introduction

New approach to kinetics of the excited-state electron transfer reactions has been developed recently, which takes into account substantial decrease of the barrier in contact pairs of reactants, due to strong electronic coupling (concatenated mechanism), and implies transient formation of an exciplex [1-3]. In contrast to conventional approaches to these reactions [4], which consider them either in terms of the transition state theory, as a preliminary thermally activated reorganization of the medium and reactants necessary for degeneration of electronic levels in molecules of reactants and products (Marcus mechanism) or in terms of radiationless quantum transitions, which requires no preliminary activation and occurs in exergonic region, this transient exciplex formation mechanism provides natural explanation for many well known important features of ET reactions, being contrary to another two theories, and the new possibilities to control their rates and quantum yields.

2. Results

There are two important features that distinguish this mechanism: (1) a very small energy barrier, caused by the strong electronic coupling, which decreases the activation energy and (2) a competition of the formation of final products (radical ions) with efficient radiationless decay in a transient exciplex, caused by its relatively long lifetime ($\sim 10^{-8} - 10^{-11}$ s), in contrast to the transition state ($\sim 10^{-13} - 10^{-15}$ s). Radiationless decay in transients can decrease the products quantum yield substantially.

Several features of the excited-state ET reactions inherent to the concatenated mechanism and contradicting common Marcus and radiationless transition mechanisms are discussed using numerous experimental data on their kinetics.

- 1) Nonexponential fluorescence decay of parent M^* .
- 2) An absence of an exciplex emission cannot testify against the transient exciplex formation since many exciplexes have much smaller emission rate constants and lifetimes than parent excited molecules and exciplex emission spectra can overlap significantly with parent reactant fluorescence.
- 3) Sublinear dependence of τ_0/τ on the quencher concentration in contrast to the linear dependence of fluorescence quantum yields.
- 4) Non-Arrhenius (bell shape) dependence of quenching constant on inverse temperature.
- 5) Negative values of apparent activation enthalpy of quenching.

- 6) Weak solvent polarity effect.
- 7) Quenching of singlet excited states is not frequently followed by the decrease of the triplet state yield.
- 8) The dependence of apparent activation free energy $\Delta G_{\text{ET}}^{\ddagger}$ on ΔG_{ET}^* frequently does not follow either Marcus equation or Weller equation and has rather small slope at $\Delta G_{\text{ET}}^* > 0.3 \text{ eV}$.
These features arise due to equilibrium formation of transient exciplex and can be used for clarification/elucidation of actual mechanism of electron transfer in particular cases.

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Spectroscopic Signatures of Proton Transfer Dynamics in the Complexes with Strong-Short Intermolecular O–H...N Bond in Aprotic Solvents

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1. Introduction

The present study deals with strong (short) intermolecular O–H...N bonds in the 1:1 hydrogen bonded complexes formed by benzoic acids and phenols with pyridines. In the gas phase the bridging (shared) proton is always located near oxygen and the only state without proton transfer (HB state) exists. In the condensed phase the bridging proton shifts along the hydrogen bond (H-bond) towards the base. In the extreme case the proton transfer state (PT state) is formed. The latter state can appear as a local or the global minimum on the potential (free) energy surface only as a result of the environment effect. The adducts of 3-methylpyridine with 2,6-dichloro-4-nitrophenol (Py–Ph) and 2,4,6-trimethylpyridine with 3,5-dinitrobenzoic acid (Py–BZA) are considered in the present study. The structure and IR spectra of these 1:1 complexes with strong (short) intermolecular H-bond were studied in the condensed phase where proton transfer was observed [1, 2]. The effect of the external electric field on geometry of H-bond is taking into account using the Polarizable Continuum Model (PCM) model [3]. In this approach the strength of the external electric field is proportional to the dielectric permittivity of the media ϵ . The latter has been varied from 2.4 (toluene) to 36.6 (acetonitrile). The overall aim of the study is to inspect the spectroscopic properties of the PT state in the considered 1:1 complexes. For these purpose it is necessary: (i) to identify the PT state as a local or the global minimum on the potential (free) energy surface; and (ii) to investigate the effect of proton transfer on the frequency and IR/Raman intensity of the bridging proton vibrations.

2. Results and discussion

Calculations have been done in the B3LYP/6-31G** approximation. According to the B3LYP-PCM computations of Py-Ph and Py-BZA, the PT state appears as a local minimum on the potential (free) energy surface at $\epsilon > 4$ (diethylether). This estimation agrees with the available experimental data [1]. Proton transfer causes strong changes of the geometry of the O...H...N fragments and the lengths of the adjacent bonds [4]. As a result the IR spectra of the HB and PT states differ strongly. The HB state for both the Py-Ph and the Py-BZA complexes is characterized by the only one band in the 3000 - 1800 cm^{-1} region, which is associated with the OH stretching vibration. While the PT state of the both complexes is characterized by a band in the $\sim 2100 - 1700 \text{ cm}^{-1}$ region.

The PT state manifests itself most noticeably in the region below 1000 cm⁻¹ [4]. This is due to a strong coupling of shared proton vibrations to other vibrations [5]. As a result, several IR intensive bands associated with the stretching motion of the bridging proton appear in the PT state of the both complexes in the considered region. Similar situation was observed for the KH maleate crystal (see Table 1 in Ref. [6]) characterized by a strong-short quasi-linear intramolecular H-bond.

An accurate computation of the H-bonded potential in the complexes in aprotic solvents requires the consideration of a three-dimensional free energy surface based on the bridging proton coordinate, the O...N distance and the medium coordinate [7]. Calculation procedures accounted for the medium coordinate feasible to describe proton transfer in a polar solvent were developed. It can be done either using the molecular dynamics [8] or the continuum approximation [9]. Both procedures are quite cumbersome and have not ever been applied for computations of the potential barrier in such big systems, as complexes of substituted pyridines with benzoic acid and phenol derivatives.

3. Conclusions

According to the B3LYP-PCM computations, a stable structure with proton transfer (the PT state) appears at $\epsilon > 4$ for the 1:1 complexes of Py–Ph and Py–BZA. The PT state has a distinct band which locates in the 2100 – 1800 cm⁻¹ region. Its IR intensity decreases with the decrease of its frequency. The nature of the band is different in the Py–Ph and Py–BZA complexes. In Py–BZA it is the stretching vibration of the HN⁺ group, while in Py–Ph it is the specific vibration of the bridging proton. Raman scattering activity of the OH stretching in the HB state is at least one order of magnitude bigger than that of any other vibration in the PT state. This feature can be helpful when the state without proton transfer is present in a small mole fraction.

Specific feature of the PT state of Py–Ph is an intense IR band near 600 cm⁻¹ associated with an asymmetric stretching vibration of the O⁻...HN⁺ fragment. The intensity of this band is reciprocally proportional to the O...N distance, which is proportional to the H-bond energy. The presence of this band can be used as an additional criterion of the formation of the PT state in complexes of pyridines with phenols.

Acknowledgement

This study was supported by Russian Foundation for Basic Research (grant 08-03-00515).

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Magnetic Field Effects on Reaction of Hydrocarbons Oxidation in the Liquid Phase

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1. Introduction

It is well-known that sometimes in non-equilibrium processes even small perturbations can have serious consequences for nonlinear systems where reverse relations are of great importance. This is because of the disturbance of the state stability which leads to the change of the process regime [1]. One can assume that in some chemical or biochemical systems rather strong effect of weak magnetic fields is also caused by the disturbance of steady states stability and the change in the behavior of the system (or part of the system) [2-4].

2. Reaction system

We considered a reaction of hydrocarbons oxidation in the liquid phase and treated it theoretically. The reaction system under discussion is a flow reactor to the inlet of which hydrocarbon is constantly delivered in the mixture with an inhibitor under oxygen saturation conditions; the reaction mixture constantly flows from the chamber at the same rate. The present contribution covers the specific features of the manifestation of magnetic interactions in reactions involving radical pairs in conditions of stability disturbance for the system.

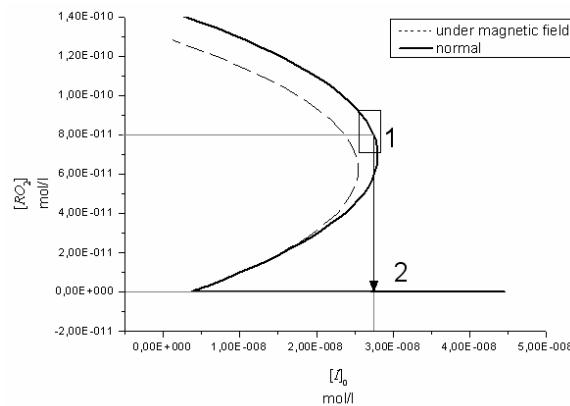


Fig. 1: The dependence of stationary concentration of peroxy radicals on the concentration of inhibitor delivered into the reactor in the presence and in the absence of external magnetic field.

3. Conclusion

The possibility of strong effect of weak magnetic fields of the order of several oersted in hydrocarbon oxidation reactions in the liquid phase is theoretically predicted. It is

shown that under certain conditions in this reaction system three steady states may arise two of which are stable and the third state is unstable. Varying rate constants of radical reactions by means of external magnetic field, one can disturb the steady state stability and cause a non-equilibrium phase transition in the system between the two stable steady states. It is similar to the phase transition of the first kind, and will be accompanied by an abrupt change in the concentration of reacting substances.

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Nonequilibrium Phenomena in Electron Transfer Reactions

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1. Introduction

Photoexcitation of a molecular system by a short laser pulse creates a nonequilibrium nuclear state. Such a state is usually visualized as a wave packet far removed from the excited state free energy minimum. If in the course of relaxation the wave packet passes through the reactant and product term crossing areas then the hot transitions can appear to be of primary importance.

Chemical reactions themselves can create nonequilibrium states. For example, photoinduced electron transfer proceeding in the vicinity of the term crossing of the excited and the ionic states produces a localized state that is far away from the product free energy surface minimum. The relaxation of such a state can also result in hot back transitions to the ground state.

Here we present an overview of the nuclear nonequilibrium effects produced by both the photoexcitation [1,2] and chemical reaction [3] for a number of real chemical systems.

2. Hot electronic transitions

The charge recombination dynamics of excited donor-acceptor complexes in polar solvents has been investigated within the framework of the stochastic point-transition approach. The model involves the excited state formation by the pump pulse and accounts for the reorganization of a number of intramolecular high frequency vibrational modes, for their relaxation as well as for the solvent reorganization following nonexponential relaxation. The hot transitions accelerate the charge recombination in the low exergonic region and suppress it in the region of moderate exothermicity that results in straightening the dependence of the logarithm of the charge recombination rate constant on the free energy gap to the form that can be fitted to the experimental data. The model provides correct description of the nonexponential charge recombination dynamics in excited donor-acceptor complexes, in particular, nearly exponential recombination in perylene-tetracyanoethylene complex in acetonitrile. It appears that overwhelming majority of the initially excited donor-acceptor complexes recombine in a nonthermal (hot) stage when the nonequilibrium wave packet passes through a number of term crossings corresponding to transitions toward vibrational excited states of the electronic ground state in the area of the weak and moderate exothermicity.

The charge recombination dynamics of excited donor-acceptor complexes consisting of hexamethylbenzene (HMB), pentamethylbenzene (PMB), and isodurene (IDU) as electron donors and tetracyanoethylene (TCNE) as electron acceptor in various polar

solvents have been investigated. All electron transfer energetic parameters have been determined from the resonance Raman data and from the analysis of the stationary charge transfer absorption band, while the electronic coupling has been obtained from the fit to the charge recombination dynamics in one solvent. It appears that nearly 100 % of the initially excited donor-acceptor complexes recombine in a nonthermal stage. The main conclusions are: (i) the model provides a globally satisfactory description for the IDU/TCNE complex although it noticeably overestimates the spectral effect, (ii) the solvent effect is quantitatively well described for the PMB/TCNE and HMB/TCNE complexes but the model fails to reproduce their spectral effects, (iii) the positive spectral effect observed with the HMB/TCNE complex can not be described within the framework of two-level models and the charge redistribution in the excited complexes should most probably be taken into account.

The charge recombination in a photoexcited donor-acceptor complex comprising of 1,2,4-trimethoxybenzene (electron donor) and TCNE (electron acceptor) in polar solvents is demonstrated to occur predominantly on hot stage in parallel to nuclear relaxation. The recombination dynamics of the photoexcited complex in acetonitrile have two-stage character, the first stage was very fast with effective timescale of 30 - 80 fs, and the second, slow with effective time longer than 100 ps. In more viscous solvents, the reaction terminated at the fast stage [4]. These regularities are well described by the considered here model that is a strong argument in favour of the nonadiabatic model. Two-step charge recombination dynamics is unique so far. There are at least two reasons for its rarity. Firstly, in the area of low exothermicity, $-\Delta G_{CR} < E_m$, exciplexes can dominate. The exciplexes are characterized by strong electronic coupling and by quite different regularities. Secondly, the charge recombination can terminate at the hot stage what is the reason of unobservability of the second thermal stage.

The intramolecular charge separation from the second singlet excited state of directly linked Zn-porphyrin-imide dyads and following charge recombination into the first singlet excited state presents one more important example of the crucial role of hot transitions. In this case the charge recombination proceeds in the Marcus normal regime and its free energy can be even positive. This is additional argument in favor of the generality of the statement that the charge recombination predominantly proceeds on the hot stage if the energy gap is smaller than the medium reorganization energy.

The perspectives of photochemistry of second excited states are discussed.

Acknowledgments This work was supported by the Ministry of education and science of the Russian Federation (contract P1145) and the Russian foundation for basic research (Grant No. 10-03-97007).

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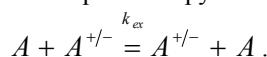
MARY – Spectroscopy: Application to Electron Transfer Reactions

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1. Introduction

The electron self-exchange, sometimes called degenerate electron exchange, between a neutral molecule and its radical, either neutral or charged, can be measured by linebroadening effects within ESR-spectroscopy



2. Electron self exchange rate constants measured by MARY-spectroscopy

If such a redox couple is part of a spin-correlated radical ion pair, see Fig. 1, it gives rise to line width effects in the fluorescence-detected MARY (magnetic field effect on reaction yield) spectrum similar to those observed in EPR spectroscopy [1-4]. An increasing self-exchange rate (i.e., a higher concentration of the neutral molecule) leads to broadening and subsequent narrowing of the spectrum. Along with a series of MARY spectra recorded for several systems (the fluorophores pyrene, pyrene-*d*₁₀ and *N*-methylcarbazole in combination with 1,2- and 1,4-dicyanobenzene) in various solvents, a theoretical model is developed that describes the spin evolution and the diffusive recombination of the radical pair under the influence of the external magnetic field and electron self-exchange, thereby allowing the simulation of MARY spectra of the systems investigated experimentally [5].

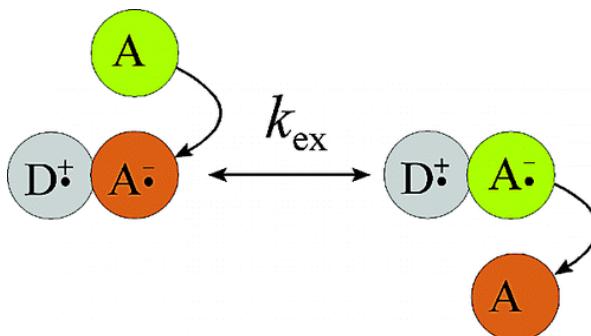


Fig. 1

The spin evolution of the radicals in the pair is calculated separately using spin correlation tensors, thereby allowing rigorous quantum mechanical calculations for real spin systems [6]. It is shown that the combination of these simulations with high resolution, low noise experimental spectra makes the MARY technique a novel, quantitative method for the determination of self-exchange rate constants. In comparison to a simple analytical formula which estimates the self-exchange rate constant from the slope of the linear part of a line width vs concentration plot, the simulation method yields more reliable and accurate results.

3. Discussion

Electron Self Exchange rate Constants can be measured using MARY-spectroscopy. The correctness of the results obtained by the MARY method is proved by a comparison with corresponding data from the well-established EPR line broadening technique. With its less stringent restrictions on radical lifetime and stability, the MARY technique provides an alternative to the classical EPR method, in particular for systems involving short-lived and unstable radicals.

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Determination of the Mass Diffusion Coefficient in Melts Using the Light Scattering Method

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1. Introduction

Earlier it was found that the light scattering intensity by the borate melts subjected to a stationary temperature gradient was increased [1]. This enhancement of the intensity was connected with the arising of non-equilibrium concentration fluctuations in the binary system induced by Soret effect. Based on the theory of light scattering by the non-equilibrium liquids subjected to a stationary temperature gradient [2], the value of the mass diffusion coefficient was determined in the lithium borate melt containing 1.6 mol % Li₂O at the temperature 407°C [3]. The purpose of the present study was to obtain the mass diffusion coefficient in this melt at the temperature 450°C.

2. Results

The experimental procedure was the same as described in [3]. We measured the time-dependence of the scattered intensity for the temperature difference $\Delta T \approx 80^\circ\text{C}$ at the temperature 450°C. The analysis of the experimental results showed that the data obtained were satisfactorily described by the equation $I(t) = \Delta I [1 - \exp(-t/\tau)] + I(0)$, where $\Delta I = I(0) - I(\infty)$, $I(0)$ was the scattered intensity at the initial moment of the time, $I(\infty)$ was the stationary intensity after the relaxation process, t was the time, and τ was the relaxation time. It was found that the relaxation time τ was about 510 sec, that was approximately by six times lower compared with the relaxation time at the temperature 407°C [3]. Based on the theory [2] we found the value of the diffusion coefficient $D(q)$ at the temperature 450°C, which was $5.9 \cdot 10^{-14} \text{ cm}^2 \text{ s}^{-1}$.

3. Conclusion

It was shown that the light scattering method gave the opportunity to obtain the reliable data on the mass diffusion coefficient in the high viscosity melts.

Acknowledgements This study was carried out based on the financial support by the RFBR according to the project N 10-03-00705.

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Kinetic Equations and the Phenomenon of Spatial Structurization for Local Concentrations of Reactants in Spatially Inhomogeneous Solutions

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1. Introduction

Traditionally the irreversible reaction in spatially inhomogeneous liquid solution is described using the additivity of contributions from the mobility of reactants and chemical reaction between them. The influence of chemical reaction on the additional mobility of reactants is ignored. So the force interaction determined by the approach of reactants on the encounter may affect essentially the trajectory of their motion. This gives rise to new physical effects in spatially inhomogeneous systems. Correct account of such changes in the ensemble of reactants may be taken solely by consistent many-particle theory.

2. Results

Spatially inhomogeneous dilute solutions of reactants placed in a continual solvent (Wait approach) are examined. The Markovian kinetic equations taking into consideration the force action of reactants on each other due to binary encounters in solution during reactant macroscopic displacement were obtained for the first time on the basis of the familiar non-Markovian equations of the Integral Encounter Theory. It has been shown that the value of “collision integral” of reactants determined by their stochastic motion is small as compared to the “collision integral” with the solvent molecules in the frame of the binary approach to the description of the solvent evolution. Nevertheless, taking account of the encounters of reactants with each other may turn out to be of primary importance, since it results in new physical effects.

The phenomenon of spatial structurization due to the encounters of different species of reactants in two-component spatially inhomogeneous solution is considered as an example of the above effect. It is described using the kinetic equations derived by the authors for weak chemical reaction.

3. Conclusion

Thus the solution derived serves to treat theoretically the spatial structurization phenomenon, and to evaluate characteristic times of the effect observed.

Acknowledgements Authors thank Russian Foundation of Basic Research (project 09-03-00456) for financial support

Kinetics of Reversible Reactions between Metastable Reactants in Viscous Solutions

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1. Introduction

Over the last 20 years reversible diffusion-influenced reactions have been the subject of particular interest to the researchers [1-6]. A variety of approximate approaches to the many-particle problem have been used to describe the kinetics of the elementary reactions such as:



This kinetics shows a rather complicated behavior. At long time it passes to power law asymptotic with the amplitude specific for each particular set of the reaction parameters (diffusion coefficients of reactants, their concentration, etc.)

It turns out that, unlike the above reactions (1), the reactions between the excited reactants such as



proceed primarily by a universal manner.

2. Results

This contribution presents analytical solutions describing markovian reaction kinetics (2) in a single way. It is shown that the specific character of the reaction determined by the form of the integral equation kernel manifests itself solely at the intermediate stage, while at the final stage the reactions show universal behavior depending only on the combination of equilibrium concentrations and intrinsic lifetimes of excited reactants. Problems of the kinetics description refinement at the intermediate stage by the modification of the kernels of kinetic equations for reactant concentration are discussed.

Acknowledgements

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Fluctuation Effects in the Solid Phase Kinetics of Diffusion Controlled Processes: A Monte Carlo Simulation

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1. Results

The recombination of free radicals was modeled for three types of events: the generation (homogeneous and inhomogeneous), migration, and recombination of particles of the same type in a cubic lattice for various time scales. A simple formula was proposed to describe this kinetics with an inhomogeneous initial distribution. This model was used to describe experimental data on the recombination of free radicals in a real γ -irradiated system. Reasonable values were obtained for the characteristic spur radius and diffusion coefficient. An approach was developed to the analysis of fluctuations in a steady state chemical process to obtain useful information on the elementary events that form the basis of this process. It was found that the fluctuation noise of total number of particles in the system depends on the mechanism of elementary processes occurring in this system; consequently, it can be a source of information on process parameters. This is also true for other steady state processes, which can also be simulated by the Monte Carlo method, for example, the formation of nano-particles in composite materials. For these processes the developed procedure can be applied to determine fundamental kinetic rates responsible for the observed fluctuation kinetics.

2. Conclusions

Therefore, fluctuation kinetics can be a source of information on process parameters. The problem is to reveal a relationship between the parameters of noise and the elementary rates that operate the noise. Computer simulation using the Monte Carlo technique is a useful tool to solve the problem.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, projects nos. 08-03-00029 and 09-03-92474-MNKS.

Manifestation of Macroscopic Correlations in the Kinetics of Elementary Irreversible Reactions in Liquid Solutions

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1. Introduction

The kinetic theory of reactions in solutions is commonly based on the concepts of the Encounter Theory (ET) (the prototype of Collision Theory in gases). The Encounter Theory, just as the Collision Theory and former theories of reactions in liquid solutions based on the concept of independent pairs, gives differential (rate) kinetic equations corresponding to the notions of independent pair encounters. The specific feature of reactions in liquid solutions as compared to reactions in gases is cage effect that results in long-range space-time correlations. From this point of view, the notion of independent pair encounters of reactants and so of the applicability of the Encounter Theory concepts for reactions in liquid solutions is questionable.

2. Results

Using an modern many-particle method for the derivation of non-Markovian binary kinetic equations, we have treated theoretically the applicability of the Encounter Theory concepts to the widely known diffusion assisted irreversible elementary bulk reactions $A+A \rightarrow \text{Product}$, $A+B \rightarrow \text{Product}$ and (for example, radical reaction) in dilute solutions.

3. Conclusion

The method shows that the agreement with the Encounter Theory is observed when the familiar Integral Encounter Theory (IET) is employed which in this method is just a step in the derivation of kinetic equations. It allows for two-particle correlations only, but fails to take account of correlation of reactant simultaneously with the partner of the encounter and the reactant in the bulk. However, the next step leading to the Modified Encounter Theory (MET) under transformation of equations to the Regular Form both extends the time range of the applicability of ET rate equation (as it was for reactions proceeding with one of the reactants in excess), and gives the equation of the Generalized Encounter Theory (GET). In full agreement with physical considerations, this theory reveals macroscopic correlations induced by the encounters in the reservoir of free walks. This means that the encounters of reactants in solution are correlated on a rather large time interval of the reaction.

Though any non-stationary (non-Markovian) effects manifest themselves rather weakly in the kinetics of the bimolecular reaction in question, just the existence of the revealed macroscopic correlations in the binary theory is of primary importance. In particular, it means that the well-known phenomena which are generally considered to be

associated solely with correlation of particles on the encounter (for example, Chemically Induced Dynamic Nuclear Polarization (CIDNP)) may be induced by correlation in the reservoir of free random walks of radicals in solution.

Acknowledgements

Authors thank Russian Foundation of Basic Research (project 09-03-00456) for financial support.

Electrodiffusion with Adsorptive Boundary Conditions

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1. Introduction

This paper deals with a particular model of electrodiffusion of ions: we consider the electrolyte solution in the vicinity of the negative electrode and study the formation of the diffusive boundary layer in the Li-ion battery. Density evolution of ions in electrolyte and other electrodiffusion phenomena are described by the Nernst-Planck-Poisson (NPP) parabolic-elliptic system [1-3]. During the last thirty years different variants of NPP have been studied in details [4-6]. Still the situation when the availability of free electrode surface is the limiting factor [7-8] has not been properly investigated.

We suppose that the concentration of negative ions in the considered region is negligible and therefore we study only the diffusion and migration of positive ions Li⁺. Our model takes into account the variation of the electric potential and the surface processes – adsorption, desorption and charge transfer – that simultaneously take place at the electrode surface. In these assumptions we obtain the NPP system with adsorptive boundary conditions. We construct exact steady state solutions to this system, then solve it numerically and study the attraction of its time-dependent trajectories to the stable steady state solutions.

2. The model

Let t be time and let x be the distance measured from the electrode surface. Let $\theta=\theta(t,x)$ be the concentration of Li⁺ ions in the electrolyte, $\sigma=\sigma(t)$ is the fraction of the occupied electrode surface and $\varphi=\varphi(t,x)$ is the electric potential. Then the proposed model looks as follows:

$$\begin{aligned} \theta_t &= D(\theta_x + \alpha\theta\varphi_x)_x, \quad t > 0, \quad 0 < x < \delta; \\ \theta(t,0) &= \Theta(\sigma); \quad \theta_x(t,\delta) = 0; \\ \varphi_{xx} &= -\beta\theta, \quad t > 0, \quad 0 < x < \delta; \\ \varphi(t,0) &= \varphi^*; \quad \varphi_x(t,\delta) = 0; \\ \sigma_t &= k_a \cdot \theta(t,0) \cdot (1 - \sigma) - (k_d + k_e) \cdot \sigma. \end{aligned} \tag{1}$$

Here $\delta=1.0E-06$ m is the thickness of the diffusive layer. Let $\alpha=zF/RT$ and $\beta=zF/\epsilon_0\epsilon$, where $z=1$ is the ion charge, $F=9.6485E+04$ C/mol is the Faraday constant, $R=8.3145$

$J/(K \cdot mol)$ is the universal gas constant, $T=300$ K is the temperature, $\varepsilon_0=8.85E-12$ F/m is the electric constant and $\varepsilon=2.25$ is the relative permittivity of electrolyte.

The NPP equations with respect to θ and φ , that describe the diffusion and migration, are coupled with the O.D.E. with respect to σ , which models adsorption, desorption and discharging. The concentration of ions at the electrode surface ($x=0$) is supposed to be a function $\Theta(\sigma)$ of the surface coverage [8]. The values of the adsorption, desorption and discharging rate constants $k_a \approx 1.0E+01$ sec $^{-1}$, $k_d \approx 1.0E+02$ sec $^{-1}$, $k_e \approx 2.0E-02$ sec $^{-1}$ and the diffusion coefficient $D=1.0E-09$ m 2 /sec are taken from [7-9]. We assume that they do not depend on σ , θ and φ .

3. Results

Theorem. Let $\Theta(\sigma)$ be an arbitrary smooth positive function. Let σ^* be the solution to the algebraic equation: $\sigma^* = k_a \cdot \Theta(\sigma^*) / (k_a \cdot \Theta(\sigma^*) + k_d + k_e)$ and $\theta^* = \Theta(\sigma^*)$. Let $\gamma^2 = \theta(\delta) > 0$, $0 < \gamma \leq (\theta^*)^{1/2}$. Then if $2\alpha\beta\delta^2\gamma^2 < \pi^2$ then the sought classical steady state solution to (1) exists and looks as follows:

$$\theta(x) = \gamma^2 \left(1 + \tan^2 \left(\gamma \sqrt{\frac{\alpha\beta}{2}} (\delta - x) \right) \right); \varphi(x) = \varphi^* + \frac{1}{\alpha} (\log(\theta^*) - \log(\theta(x))). \quad (2)$$

Computational experiments demonstrate that the steady state solution (2) is stable: all time-independent solutions to (1) reach a vicinity of (2) in less than 10^4 seconds regardless of the initial distribution. We study numerically the behavior of the time-dependent solutions to (1) with the right hand function $\Theta(\sigma) = \kappa\sigma(1-\sigma)^l \exp(-\sigma/2)$, $\kappa=const$ from Ref. [8] for various initial distributions of the ion concentration $\theta(0,x)$ and the electric potential $\varphi(0,x)$; we obtain $\sigma(0)$ by solving: $\Theta(\sigma(0)) = \theta(0,0)$.

Initially uniform graph of $\theta(x)$ exhibits a sharp break at the left end of the interval. At this point the concentration of ions quickly descends and reaches the minimal value. Then the concentration in the points to the right from this minimum starts falling down, proceeding like a wave from left to right. The boundary layer extends up to $1.0E-07$ m. The electric potential doesn't form the boundary layer at the left end of the interval. Instead it undergoes a rapid increase at the right side and then exhibits a slow decrease to the level just slightly higher than the initial. The potential distribution reaches the steady state (2) simultaneously with the distribution of the ion concentration.

4. Conclusion

The proposed mathematical model of electrodiffusion with adsorptive boundary conditions demonstrates the stability of its spatially non-uniform steady state solution. This solution is of the diffusive concentration boundary layer type.

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Random Search Strategies

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1. Introduction to search processes

Search processes are ubiquitous among physical, chemical, and biological systems. Representative examples include diffusion-limited encounter of molecules involved in a chemical reaction; the dynamical or stochastic search for a global minimum in a complex energy landscape, relevant to systems such as glasses, protein (folding), and others; oil recovery from mature reservoirs; proteins searching for their specific target sites on DNA in gene regulation; animal foraging; survival at the edge of extinction due to low availability of energetic resources; automated search of registers in high-capacity databases, search engines (e.g., "crawlers") that explore the internet, and even pizza delivery in a jammed traffic system of a medium-size town.

The search for a desired target may depend on a variety of conditions. Targets may be sparse, hidden, difficult to detect even when found. The targets may be mobile or immobile, they may try to avoid searchers, there may be one target or many. They may have a finite life-time and vanish before they are detected. Searchers may search "blindly", detecting the target only upon encounter, or may perceive distant targets and adjust their motion accordingly. They may have no memory of previously visited areas, or they may avoid such areas. The searchers may act individually or in swarms, optimizing their search efficiency by exchanging information. Finally, the "efficiency" of a search may be judged by a variety of measures, including the time to reach a target or targets, the number of encounters of searchers and targets per unit time, or the exploration range of space per unit time. In general, for each specific situation different search strategies may be appropriate. The quest for optimal strategies has motivated a great deal of work in the past and currently represents one of the most rapidly growing fields of research.

Although the applications are diverse, the underlying physical mechanisms are often the same. Moreover, the inherent complexity of the problem, the abundance of ideas and methods found in this interdisciplinary, innovative field of research is studied in many areas of physics. In particular, the concepts and methods of statistical mechanics are particularly useful to the study of random search. On the one hand, it centers on how to find the global or local maxima of search efficiency functions with incomplete information. This is, naturally, related to the long tradition in physics of using different conceptual and mathematical tools to optimize relevant quantities, e.g., energy, entropy, and action. Such ideas and approaches are very important to solve computationally

complex problems involving optimizations in very high dimensional energy landscapes, e.g., in protein folding. On the other hand, random search can also be studied from the perspectives of diffusion and transport properties, stochastic processes, Lévy walks and flights, complex systems and fractal geometry. Some important questions in random search, especially in the case of discrete landscapes, are also associated with graph theory, random lattices, and complex networks.

The highly innovative character of the subject stems from a cross-fertilization of approaches, ideas and fruitful synergies between condensed matter and statistical physics, quantitative biology and mathematics. In particular, analyzing the data gathered by biologists on the trajectories of lizards, fish, or birds searching for food, one introduces random search strategies, based either on Lévy-type or on intermittent random motion, (in which slow search phases alternate with fast relocations), which explore most of the available space within a minimal time, with minimal oversampling and having the best chances of success. As one important outcome, one may introduce more efficient computer algorithms for the search for global minima in nonconvex (multiple extrema) energy landscapes by simulated annealing – it appears that a random search with Lévy-type jump-length distributions allows for a faster cooling scheme, and hence, for a considerable reduction of computer time, than standard algorithms (Boltzmann machine) based on a nearest-neighbor exploration. An observation that in reality a protein finds a specific binding site on a DNA 10^3 times faster than it is predicted by conventional chemical kinetics, prompted a very deep understanding of the role of non-specific parts of the DNA. Being inert with respect to the reaction, they act as very efficient antennae reducing the overall search time, essentially in the same way as cell bound glycoproteins, extending in the extracellular medium, enhance the efficiency of chemoreception by capturing the ligands and facilitating their transport to the cell bound receptors. A straightforward impact of this analysis is a design of microporous cathodes for PEM fuel cells by choosing the materials with an optimal particle-surface affinity, which will greatly enhance the reaction rates.

2. The main goal of the talk

The main goal of our talk is to describe a recent progress in understanding and quantifying random search algorithms in diverse areas, to present novel results and to discuss growing synergies between the problems arising in condensed matter and statistical physics, quantitative biology, and mathematics.

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Asymptotic of Homogeneous Gaussian Process

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1. Introduction

Consider an evolution of the model of a physical system in a spatial-temporal homogeneous medium. That is the all statistical characteristics of a medium are invariant under the translation in the space-time. The evolution process is due to two main mechanisms, namely, diffusion (dissipation) and self-organization (e.g., under the action of external fields). The effect of the medium on the evolution process is described here using a spatially and temporally homogeneous random field $V(\mathbf{q}, t)$, $\mathbf{q} \in \mathbf{R}^d$, $t \in \mathbf{R}^+$ (hereafter d is the dimension of the Euclidean space \mathbf{R}^d) where $V(\mathbf{q}, t)$ the continuous and lower bounded function on $\mathbf{R}^d \otimes \mathbf{R}^+$. Moreover the distribution of the variate V is Gaussian with a zero mean $\mathbf{E}V = 0$, and the correlation function $W(|\mathbf{q} - \mathbf{q}'|, |t - t'|) \equiv \mathbf{E}[V(\mathbf{q}, t)V(\mathbf{q}', t')]$. In this case all characteristics of the field $V(\mathbf{q}, t)$ are expressed in terms of the correlation function $W(r, t)$, which is bounded and integrable, together with its derivative, on $\mathbf{R}^d \otimes \mathbf{R}^+$. Furthermore the function $W(r, t)$ is assumed to tend to zero sufficiently fast as $(r/L) \rightarrow \infty$ and $(t/T) \rightarrow \infty$, where L and T are the characteristics scales of length and time. Let $\rho(\mathbf{q}, t; \mathbf{q}_0)$ denotes a certain "density" of the system (e.g., mass density). The temporal evolution of the system is described by the equation

$$\frac{\partial \rho}{\partial t} = D \Delta_d \rho - V(\mathbf{q}, t)\rho, \quad (1)$$

with the initial condition $\rho(\mathbf{q}, 0; \mathbf{q}_0) = \delta(\mathbf{q} - \mathbf{q}_0)$, where $\delta(\mathbf{q})$ is the delta-function, Δ_d is the d -dimensional Laplacian and D is the diffusion coefficient. The parabolic partial differential equation describes the superposition of diffusion and branching (birth-death) processes. Using the known Feynman-Kac formula [1-3], we can write the solution to Eq. (1) vanishing as $q \rightarrow \infty$ in the form

$$\rho(\mathbf{q}, t; \mathbf{q}_0) = \lim_{N \rightarrow \infty} (4\pi D \tau)^{-Nd/2} \int_{\mathbf{R}^d} \dots \int_{\mathbf{R}^d} \exp \left(-\sum_{n=1}^N \left[\frac{(\mathbf{q}_n - \mathbf{q}_{n-1})^2}{4D\tau} + \tau V(\mathbf{q}_n, t_n) \right] \right) \prod_{n=1}^{N-1} d\mathbf{q}_n$$

where $\tau = t/N$, $t_n = n\tau$, $n = \overline{1, N}$, $\mathbf{q}_n = \mathbf{q}(t_n)$, $\mathbf{q}_0 = \mathbf{q}(0)$, $\mathbf{q} = \mathbf{q}(t)$. For different applications the most important function is the "mean of density" $G(r, t)$ defined by

$$G(r, t) \equiv \int_{\mathbf{R}^d} d\mathbf{q} \delta(\mathbf{q} - \mathbf{q}_0 - \mathbf{r}) \mathbf{E} \rho(\mathbf{q}, t; \mathbf{q}_0). \quad (2)$$

Here we investigate mainly the asymptotic behavior of this function, as $(r/L) \rightarrow \infty$ and $(t/T) \rightarrow \infty$. It is worth noting that formula (2) involves two independent types of functional integration: the first, over the space of the trajectories $\{\mathbf{q}: \mathbf{R}^+ \rightarrow \mathbf{R}^d\}$ and, the second, over all realization of the random potential V .

2. Results

In this paper we treat the function φ obtained by a twofold integral transformation under G . This function obeys the integral equation of the well-known Dyson equation form [4]. That is invariant with respect to a continuous group so called the renormalization transformations (RG). This allows definition the invariant spectral parameter B connected directly with the function φ . Due to this property the value B satisfies the Lie differential equation, which is convenient to find an asymptotic behavior of the function $G(r, t)$ as $(r/L) \rightarrow \infty$ and $(t/T) \rightarrow \infty$ [5]. To realize the proposed approach we use a factorization of the correlation function: $W(r, t) = \omega(r) T^{-2} \exp(-t/T)$, where the function $\omega(r)$ is assumed to be absolutely integrable on \mathbf{R}^d along with its derivative $d\omega/dr$. Hence in the case of small and large values of $\bar{\omega} = \sup_{r \geq 0} \omega(r)$ this leads to the asymptotic estimate at issue for $1 < d < 4$. The

asymptotic estimate of $G(r, t)$ is obtained in the case $\bar{\omega} > 1$ as the both variables (r/L) and (t/T) tend to infinity under the condition that their ratio (rT/tL) remains constant and small. Because of a cumbersome form of the asymptotic expression for $G(r, t)$ when $1 < d < 4$ we present here the result in the cases $d = 2$ and $d = 3$ only

$$G(r, t) = \frac{c_2 T^2}{u_2 t^2} \left[\frac{r^4 T^2}{u_2 D t^3} \right]^{1/3} \exp \left(E_2 t + \frac{\kappa_2 r^4 T^2}{u_2 D t^3} \right) [1 + O(T/t)], \text{ when } d = 2, \quad (3)$$

$$G(r, t) = \frac{c_3 T^2}{u_3 t^2} \left[\frac{r^5 T^2}{u_3 D t^3} \right]^{1/12} \exp(E_3 t) \left\{ \cos \left[\kappa_3 \left(\frac{r^5 T^2}{u_3 D t^3} \right)^{1/2} + \frac{\pi}{4} \right] + O(T/t) \right\}, \\ \text{when } d=3, \quad (4)$$

where $c_d, k_d, E_d, u_d = \int_{\mathbf{R}^d} \omega(r) d\mathbf{r}$ are positively defined constants. The cases $d = 1$ and

$d = 4$ are special and require a separate study. It follows from formula (3), that for $d = 2$ the behavior of the function $G(r, t)$ as $(t/T) \rightarrow \infty$ is defined mainly by the exponentially increasing factor. However, at $d = 3$ the asymptotic function of $G(r, t)$ contains (see Eq. (4)), not only $\exp(E_3 t)$, but the periodic factor too. Starting from a given moment of time and at the fixed small values of (rT/tL) this factor leads to a decrease of the main asymptotic term in $G(r, t)$ with increase of (t/T) . However for large enough values of (t/T) it is impossible to assert that the first term in (4) gives the main contribution to the asymptotic formula. The point is that the other expansion terms may be nonzero at the point, where the periodic factor vanishes.

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Narrow Escape Problem in 2D: Boundary Homogenization Approach

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1. Introduction

The narrow escape problem deals with a particle diffusing in a confined domain which contains a small absorbing spot on its otherwise reflecting boundary. This problem arises when analyzing diffusive transport in compartmentalized systems, such as nerve cell synaptic membranes, dendritic spines, porous media, to mention just a few.

The quantity of main interest in the narrow escape problem is the mean first passage time (MFPT) of the particle to the spot. Because of non-uniform boundary conditions it is rather difficult to find an analytical solution for the MFPT. Asymptotic behavior of the MFPT in the limiting case of small spot size has been found (see Refs. [1, 2] and references therein). The results for two- and three-dimensional domains are quite different. The leading term of the MFPT to a circular spot of radius a on the surface of a sphere of radius R ($a \ll R$), is given by $\pi R^3/(3Da)$, where D is the particle diffusion coefficient. In two dimensions the leading term of the MFPT to an absorbing arc of length l on the boundary of a circular disk of radius R ($l \ll R$), is $(R^2/D) \ln(R/l)$.

2. Results

Here we study a particle diffusing in a circular disc with non-overlapping identical absorbing arcs on the boundary and extend earlier rigorous results in several respects (see Ref. [3] and references therein).

(i) We suggest an approximate formula for the MFPT to one absorbing arc of arbitrary length ($0 < l \leq 2\pi R$). The known asymptotic behavior is recovered from the formula as $l \rightarrow 0$.

(ii) The formula with $n = 1$ is a special case of a more general result, which gives the MFPT to one of n non-overlapping identical arcs of length l ($0 < l \leq 2\pi R/n$), evenly spaced along the disc boundary.

(iii) Another result is the formula for the MFPT to one of the two non-overlapping arcs of length l ($0 < l \leq \pi R$), arbitrarily located on the disc boundary.

The formulas were tested against the MFPT found numerically by solving the 2D diffusion equation with non-uniform boundary conditions (BCs) by the finite difference method. Comparison shows that the formulas predict the MFPT with relative error less than 2%.

3. Discussion

A key step of our approach to the problem is a replacement of the non-uniform BCs at the disc boundary by an effective uniform radiation BCs with properly chosen trapping rate. Such a replacement, called boundary homogenization (BH), is based on the fact that sufficiently far away from a patchy non-uniform boundary the fields of the steady-state fluxes and concentrations become uniform in the lateral direction. As a consequence, one cannot distinguish between uniform and non-uniform boundary only by analyzing the flux, which is the main quantity of interest in this problem. BH is applicable when the domain near the boundary is relatively small, namely the domain where the fields are non-uniform because they keep memory of the real boundary conditions. Therefore, it is far from obvious that BH is applicable to our 2D problem. Nevertheless, we show that BH-based formulas for the MFPT in 2D work surprisingly well in spite of the absence of the hierarchy of the length scale.

Acknowledgements

We are grateful to Yurii Makhnovskii, Stas Shvartsman, and Vladimir Zitserman for useful discussions. A.M.B. was supported by the Intramural Research Program of the NIH, Center for Information Technology.

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Diffusion Kinetics of Regent Carrier in the Case of its Continuous Aging

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1. Introduction

A diffusion model of ecological kinetics for the case of continuous aging of biological objects, which play role of carriers of some chemical reagents, has been proposed in [1]. A modification of the model, which is a variety of diffusion-influenced reactions have [2] is considered. The modification is oriented for the case of diffusion reagent transportation, discrete working cycles and carriers' aging.

2. Model

Let a spatial organisation of a chemical reaction is shown in Fig. 1. The reagent, which is in use for the process in the area L_3 is transported from the area L_1 by some carriers. Similarly to the ecological system in [3], the system can be described by the differential equations:

$$\frac{dx}{dt} + \frac{dx}{d\tau} = \frac{d}{dl} \left[\eta(t, \tau, l) \frac{x(t, \tau, l)}{X(t, \tau, l)} dx \right] - \frac{\partial}{\partial l} [\zeta(t, \tau, l, G)x] - S(t, \tau, l) \frac{x(t, \tau, l)}{X(t, \tau, l)} x$$

where $x(t, \tau, l)$ is a density in of carriers of the 'age' τ in the point l in the moment t .

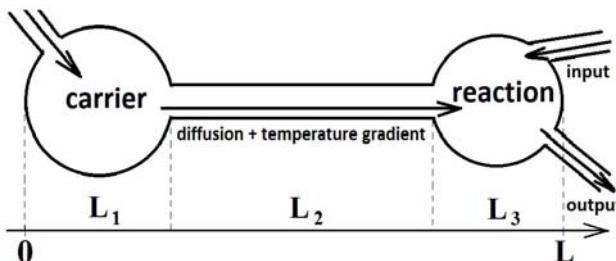


Fig. 1: Structure of the system.

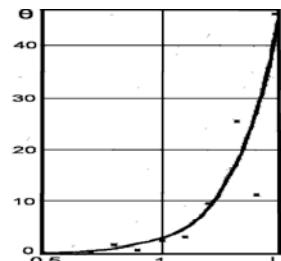


Fig. 2: Effectiveness of the reaction.

3. Results

As an illustration of usage of the model, let us give in the Fig. 2 the dependence of effectiveness of the reaction from the area L_1 size.

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Mobility of Molecules Oriented around Polymer Chains

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1. Introduction

The rate of reactions proceeding in condensed matter depends on the mobility of reactants molecules. For reactions of macromolecules with small molecules only molecules being in the immediate contact with a polymer chain react with it. It is known, that in polymer solutions the solvent molecules disposed in the first monolayer near a macromolecule are oriented in respect to the polymer chain. Properties of this monolayer differ essentially from those of the rest solvent.

2. Results

To elucidate the change of mobility of molecules being in the first monolayer surrounding polymer chains we have studied the fluorescence polarization of fluorescein (sodium salt) (F) and acridine orange (AO) in water and in oriented systems: polyvinyl alcohol – F – water, polyvinyl alcohol – AO – water, polyethylene oxide – F – water, polyethylene oxide – AO – water. Orientational correlation between polymer and dye molecules was characterized by the linear IR dichroism of electron absorption spectra in the oriented polymer matrix. The obtained results point out an increase of relaxation time of rotational diffusion of dye molecules more than by two orders of magnitude comparing with that in their aqueous solutions.

Direct Computer Simulation of Ferredoxin-FNR Interaction in Solution

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1. Introduction

In the photosynthetic electron transport chain transfer of an electron with high potential from one acceptor to another creates an electrochemical gradient. Plant and algae cells utilize this difference of potentials to synthesize ATP. The ultimate step of the linear electron transport is the reduction of ferredoxin:NADP⁺-reductase (FNR) with ferredoxin (Fd). For the electron transfer to occur two proteins must come close and acquire appropriate orientation which is determined by their shape and surface charge distribution. We have developed a direct multiparticle simulation method which allows describing kinetics of protein approach and complex formation in restricted space of biological compartments and in solution.

2. Method of simulation

In the model a few hundreds of proteins diffuse in a 3D reaction volume. The proteins are subjected to random Brownian force and electrostatic force which is created by charged amino acid residues on protein surface. Electrostatic field around the proteins is calculated according to Poisson-Boltzmann equation (Fig. 1). This allows to take into account ionic strength and pH of the solution. When two proteins come close they align against each other according due to electrostatic interactions. If the distance between certain atoms of the protein cofactors (C8M atom on FNR

and Fe1 on Fd) is less or equal to a model parameter r the proteins form a complex with probability p . The program calculates the dependence of number of formed complexes upon time which allows to calculate the rate constant of the reaction.

In the model we use the following scheme of the reaction:

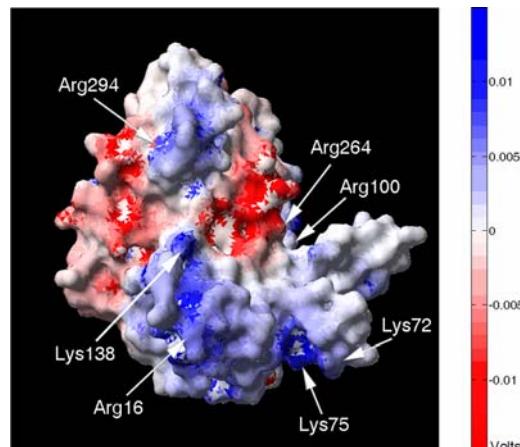
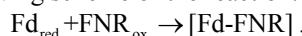


Fig. 1: Surface electrostatic potential of FNR.

3. Results

The second order rate constants obtained using the model are in good agreement with the experimental data [1] for the wild type proteins and mutants of FNR [2]. Also we have obtained ionic strength dependencies for these proteins (Fig. 2). The results of our simulations allow us to divide charged amino acid residues on FNR surface into two groups according to their contribution in the electrostatic attraction of ferredoxin. We have shown that ionic strength dependencies of these two groups of residues show different behavior: slightly impaired mutants and wt FNR show non-monotonic behavior with maximum value at 200 mM due to formation of tight non-productive complexes at low ionic strength, while second-rate constants of highly impaired mutants decrease monotonically with ionic strength. These results are in good agreement with the experimental data.

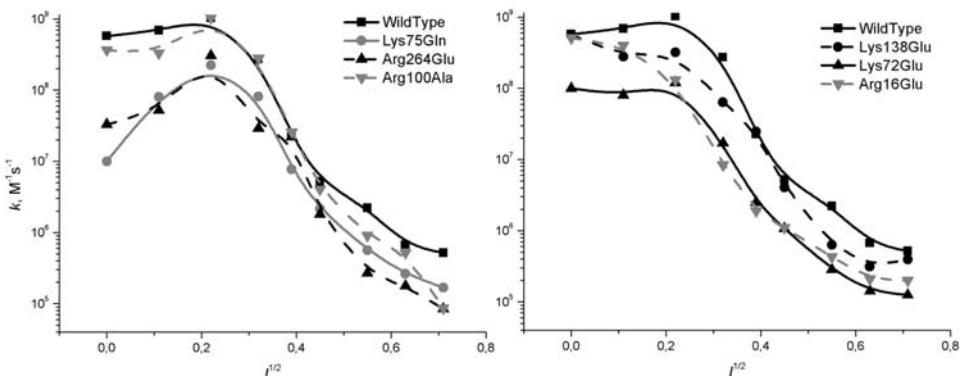


Fig. 2: Second-order rate constant k dependence on the root square of the ionic strength I for the wild-type and mutant FNR and Fd: simulation results.

4. Conclusion

Our model allows to simulate kinetics of protein binding taking in account shape of the molecules and electrostatic interactions between them.

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The Composition of the Protein Affects Its Shape in Supramolecular Structures

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1. Introduction

All amino acid residues composing the polypeptide chain is conventionally divided into two groups: nonpolar (hydrophobic) and polar (hydrophilic). The formation of a hydrophobic core in proteins is crucial for their activity. Proteins with their huge molecular weight have relatively compact structure, primarily due to hydrophobic interactions [1-3]. In 1964 Fisher [1] found out that, knowing the total number of amino acid residues in the nucleus and the ratio of polar residues to nonpolar ones, may be predicted the shape of the globule. Under the assumptions that (i) the protein is covered with a monomolecular layer of polar residues of thickness $h \sim 4\text{-}5\text{\AA}$, (ii) all residues have identical volumes and (iii) the form of globules is nearly spherical, the relative hydrophilicity of the protein b (the ratio of the polar (« p ») and nonpolar (« n ») residues) is the ratio of the volume of a spherical layer of V_p and V_n central core, i.e.

$$b_s = V_p / V_n = 3h / (r_0 - h).$$

Consequently, the smaller r_0 , the greater should be b . Strictly speaking, globule can be spherical only at $b = b_s$. If $b > b_s$, i.e. the number of polar residues in the protein more than is needed to cover the hydrophobic core of a hydrophilic layer, the globule is extended in the form of an ellipsoid and has a larger surface area than in the case of a sphere. When $b \gg b_s$ fibrillar structure arises; if $b < b_s$, hydrophilic residues are not fully cover the hydrophobic core and hydrophobic interaction between these open areas leads to protein aggregation and the emergence of supramolecular structures.

Let us assume that:

(a). Protein is composed of a hydrophobic core and hydrophilic shell. We introduce the dimensionless form factor $F = V^2 S^{-3}$ (S is square, V is volume). One can see that F possesses the maximum for a sphere: $F_{\max} = (36\pi)^{-1}$. Let $\delta_p = b / (1 + b)$ be the volume fraction of the polar residues. Using the relation $Sh = \delta_p V$, we obtain $F = h^3 / \delta_p^3 V = h^3 / \delta_p^3 Mv$, where v is a specific volume (for proteins usually we have $v \approx 1.3 \text{ sm}^3/\text{g}$).

(b). Approximate protein by a prolate ellipsoid of revolution with major semiaxis b and minor semiaxis a so we can use the known formulae [4]

$$S = \pi \frac{a^2}{\cos^2 \alpha} (1 + \cos 2\alpha) \left(1 + \frac{2\alpha}{\sin 2\alpha} \right), \quad V = \frac{4\pi a^3}{3 \cos \alpha},$$

where α is angular eccentricity, i.e. $a = b \cos \alpha$. For constant density δ_p coincides with the mass fraction of M_p/M (the ratio of polar residues to the total number was used in Ref. [1]).

2. Results

1. Under the assumptions (a) we derived the following formula

$$\xi = \frac{\delta_p a}{3h} = \frac{1}{2} \left(\cos \alpha + \frac{\alpha}{\sin \alpha} \right) \equiv f(\alpha) \quad (1).$$

It is worth noting that $f(\alpha)$ is a slowly varying monotonically decreasing from $1/\pi/4$ function (see Fig. 1).

2. Under the assumptions (a) and (b) for supramolecular structures (such as dimers, trimers, etc.) we showed that the parameter ξ in formula (1) tends to $\pi/4$, α tends to $\pi/2$ with the increasing of the subunits number, i.e. structure gets a cylindrical shape with constant diameter.

Acknowledgements

Author thanks Russian Foundation of Basic Research (project 0.9-0.3-00469) for financial support.

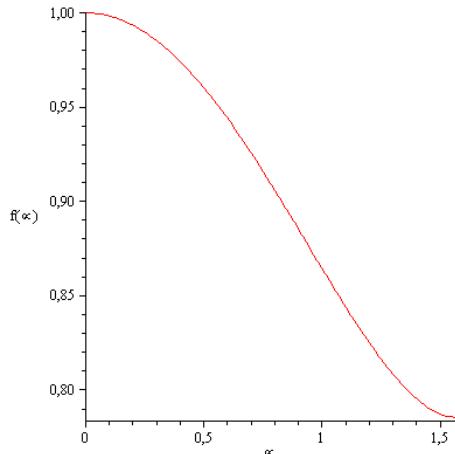


Fig. 1: Dependence of function $f(\alpha)$.

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Monte Carlo Simulation of Hollow Sphere Formation by the Kirkendall Effect in a Core-Shell Diffusion Couple with an Ordering Tendency

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1. Introduction

Hollow nanoparticles have attracted much attention as large surface area and low density advanced materials for a wide range of applications. One of the techniques for production of hollow nanoparticles is based on the Kirkendall effect occurring in interdiffusion. It works as follows: in the presence of concentration gradients among the atomic components of a diffusion couple, vacancies prefer to exchange their positions with atoms having a higher jump frequency. If there are not enough vacancy sinks on the fast component side then an excess of vacancies should precipitate into a void there. The void nucleation should be especially favoured in spherical or cylindrical samples when the faster component is encapsulated by the slower component. Experimental progress in the synthesis of hollow nanoparticles by means of the Kirkendall effect in interdiffusion has motivated theoretical studies of the problem [1-3].

Recently, we have applied a Monte Carlo based modelling approach to study the formation of a hollow nanosphere by solely entropy-driven interdiffusion in an initially A-core-B-shell binary random alloy system [3]. The used model can be described as an A-B binary Ising lattice gas with three pair-interaction energies ϕ_{AA} , ϕ_{AB} and ϕ_{BA} (for random alloy model $\phi_{AA}=\phi_{AB}=\phi_{BA}$) and a self-generated vacancy composition through exposed to vacuum surface. In particular, it was shown that at a temperature which provides an equilibrium vacancy composition $\sim 10^{-4}$ in pure A and B as well as in a binary A-B random alloy, then void nucleation can be observed if the atomic jump frequency ratio is of the order of 10^3 .

2. Discussion and Conclusions

In this work, we demonstrate that the formation of a hollow nanosphere by interdiffusion in an initially A-core-B-shell binary alloy system with an A_3B ordering tendency requires a much smaller value of the atomic jump frequency ratio at the same value of the equilibrium vacancy composition for pure A and B (the equilibrium vacancy composition for the A-B alloy is even lower). The atomic jump frequency ratio is of the order of 10 above the order-disorder temperature and can be as small as 2 below the order-disorder temperature. In all our simulations with the nearest neighbour interactions between atoms that provide the equilibrium vacancy composition $\sim 10^{-4}$ or lower, we have observed only single void formation followed by its growth. However, it is noted that an

increase of the equilibrium vacancy composition in the model (especially for the faster component in the core) up to 10^{-3} - 10^{-2} results in the formation of multiple pores and then their later agglomeration into a single void. This occurs because the vacancy composition in the core under supersaturation during initial stage of interdiffusion is high enough to supply the vacancy clustering and, as a result, the void nucleation problem is avoided. Then, the vacancy clusters simply grow owing to the vacancy flux during a further stage of interdiffusion imitating the formation of multiple pores. This observation is also in accord with recent Monte Carlo simulation results [2].

Acknowledgements

This research was supported by the Australian Research Council through its Discovery Project Grants Scheme. One of us (E.V.L.) wishes to thank the University of Newcastle for the award of a University Fellowship.

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Positive Spectral Effect in Charge Recombination Dynamics of Excited Donor-Acceptor Complexes in Viscous Solvents

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1. Introduction

Recently the charge recombination (CR) dynamics of the excited donor-acceptor complexes (DACs) consisting of hexamethylbenzene (HMB), pentamethylbenzene (PMB), and isodurene (IDU) as electron donors and tetracyanoethylene (TCNE) as electron acceptor have been studied by using transient absorption (TA) [1]. The TA signal was measured at 400 nm in the series of polar solvents: acetonitrile (ACN), valeronitrile (VaCN), and octanenitrile (OcCN) after excitation at 620 (red) and 480 (blue) nm. The effective time of the TA signal decay identified with CR time constant was shown to decrease markedly with the diffusive relaxation time of the solvent. In viscous solvents, the effective CR rate constant was found to depend on the excitation pulse frequency. This phenomenon was called the spectral effect [2]. In VaCN, the spectral effect measured between 480 and 620 nm was negative (the CR rate decreases with increasing excitation pulse frequency) with IDU/TCNE, positive with HMB/TCNE, and vanishingly small with PMB/TCNE [1].

All previous theoretical investigations of the spectral effect had been carried out under the assumption that the observed signal is proportional to the excited state population [2 - 4]. Such models predict the positive spectral effect only for ultrafast charge recombination proceeding in the low exothermic region (the free energy gap is smaller than the medium reorganization energy). However the transient absorption and transient grating experiments uncovered the positive spectral effect for HMB/TCNE complex in valeronitrile where the charge recombination occurs in the high exothermic region [1]. This observation cannot be explained by current theories of the spectral effect even at the qualitative level that may indicate the observed signal to differ noticeably from the charge transfer dynamics. To examine this assumption, the TA theory accounting for the excited DAC evolution in viscous medium should be derived.

2. The inversion of the spectral effect sign in the high exothermic region

Making use an approximation of well separated short pulses in a second order perturbation theory for pump and probe stages, applying the sweeping approximation at the recombination stage we have obtained a factorized expression for the transient absorption difference signal, ΔA , depending on the specified wavelength of the pump and probe pulse and a time delay between pulses. The expression is partitioned into two factors: (f1) describes the signal evolution due to the motion of the wave packets in the ground and excited states, (f2) results from the excited state depopulation. In the

framework of the three-level model the total signal includes the bleach, ΔA_{BL} , the stimulated emission, ΔA_{SE} , and the excited-state absorption, ΔA_{ESA} . For the excited-state absorption there is an angle, θ , between the directions of the reaction coordinates corresponding to electronic transitions at the pump and the probe stages.

A difference between the normalized ΔA signal and the excited state population dynamics is shown in Fig. 1. In calculations we adopted the parameters of the DACs, which are typical for the complexes consisting of methyl-substituted benzene and tetracyano-ethylene. The energetic parameters for the first excited state can be derived from the steady-state absorption and the resonance Raman spectra of DAC in the viscous solvent (VaCN). However there is extremely limited information about the higher excited states of DACs, so that the angle θ and the energy of the third level are the free parameters. When either the angle θ is equal to $\pi/2$ or the reorganization energy of a medium E_{r23} is zero, the TA difference signal is identical to the charge recombination dynamics and the spectral effect in the high exothermic region is always negative. A minor alteration of the energy gap between second and third levels leads to quantitative changes of the signal evolution.

The spectral effect for the measured ΔA signal can be positive in contrast to the excited state population kinetics (compare the dashed and solid lines). The angle θ as well as other energetic parameters of the DAC play a key role in the spectral effect sign inversion.

Acknowledgements

This work was supported by the Ministry of education and science of the Russian Federation (contract P1145).

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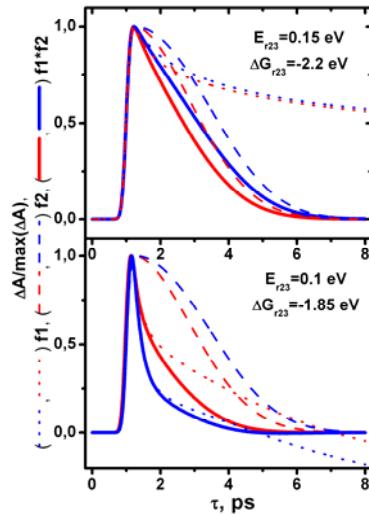


Fig. 1: The normalized ΔA signal, $f_1 * f_2$, and the excited state population decay, f_2 , after pumping at 480 nm (blue) and 680 nm (red).

Photoinduced Biomimetic Self-Oscillatory Processes in Biopolymer-Immobilized Silver Halides

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1. Introduction.

There are known oscillatory reactions induced by photo-chemical [1] and radiochemical [2] agents. This phenomenon of optochemical control is essentially a formation of phase wave under the transition from a dark cycle of reaction to the stage of irradiation. Since the phases formation is photochemically controlled, it is possible to form patterns of predetermined shape in an optically-controlled autowave processes. One can select such an active medium, in which oscillatory reactions will occur driven by physical factors of the medium response on the radiation (photoelectron emission, photovoltaic effect, Kikoin effect etc). Feedback mechanisms of an input signal can increase the process.

The authors studied mechanisms of self-oscillatory processes in an active medium based on the substrate with a multi-factor response, such as spectrally sensitized disperse inorganic semiconductors (AgHal) in polymer immobilization. The mechanisms for multi-factor response in such medium include: photosensitivity, charge injection, thermal diffusion etc. Such semiconductors ionize under irradiation and hence reveal the presence of multistability, charge accumulation and charge interactions (transfer) between the particles, so they appear to be active media. Multistability is provided by photoreduction of metallic silver, alternating with the solarization process. The phase transitions observed are both transitions of the type of sol-gel and an dielectric-conductor. This phenomenon is similar to a switching autowave between high impedance and low impedance states in semiconductor films occurring when either heating or irradiation. In this connection the controlled formation of heterogeneous dissipative structures based on dispersed semiconductors of such chemical composition is rather possible [3].

2. Method & materials

In this work we used colloidal Gel-



Fig. 1: Dissipative structures in AgHal-GIM.

immobilized AgHal media, in which the structuring was carried out by means of interacting micelles and dynamic membranes. Irradiation was performed with a mercury UV emitter and HeCd-tunable lasers with a wavelength in the UV spectral range. Detection of the medium parameters was carried out by measuring the redox potential and photometrically. We used a specially mounted installation to collect electrochemical information including a bidirectional (reversible) counter and an automated digital nanovoltammeter. The samples in the course of the reaction were observed under the microscope.

3. Results

Under irradiation of the active media one can observe self-organization of wave packets, anti-pacemakers and localized Turing patterns and oscillons [4] as in the BZ-reaction. It was shown that the excitation occurs in a hard mode: phase portraits of the excitation period include both stable and unstable limit cycles, as well as a stable equilibrium state. Subsequently the phase portrait transforms into a focus, invested into limit cycles. Further measurements revealed charge oscillations in the electrical double layer of micelles and showed oscillations of the coefficient of nonlinear distortions. Computer data processing led to the discovery of strange attractors, indicating the highly nonlinear nature of the process.

4. Conclusion

In the specific system described above the formation of dissipative structures is provided by a number of simultaneously working and interacting mechanisms, such as: photo-induced oscillatory redox reactions, noise-induced non-equilibrium phase transitions, electrohydrodynamic instability and convection in liquid crystals, phase transitions caused by the generation-recombination processes, convective mechanism similar to the cells formation in Rayleigh-Benard convection etc.

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Photoinduced Self-Oscillatory Processes in Hydrolyzed Ferric Chloride Solutions

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1. Introduction

Feedback is an important regulatory mechanism of metabolic processes in living organisms, ensuring consistency of matter and energy flows in nonequilibrium conditions. One of the feedback mechanisms in the reaction system is autocatalysis that contributes to the transition of the whole system into the oscillating mode. Herewith the combination of chemical oscillations with diffusive transfer ensure the formation of stable spatial structures in active medium due to the inhomogeneous distribution of reagents and intermediates in the reaction volume [1]. This paper concerns photoinduced oscillatory processes which follow the formation of dissipative structures in an inorganic active medium.

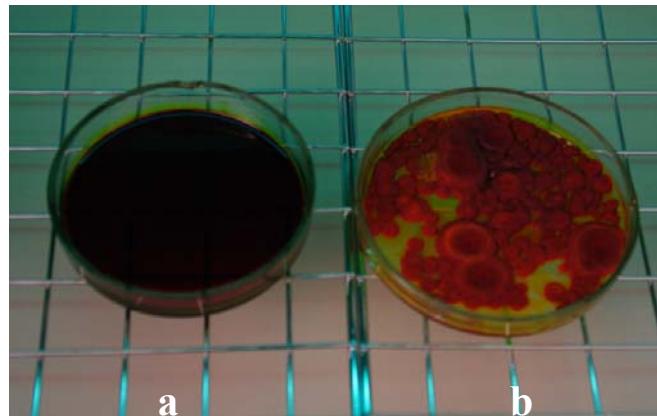


Fig. 1: Macroscopic dissipative structures (b)
and the result of a check experiment (a).

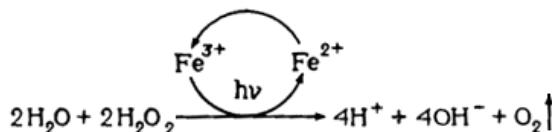
2. Method of simulation

It is known that self-oscillatory reactions occur in non-equilibrium distributed kinetic systems with a diffusion transport. Accept the widespread Belousov-Zhabotinsky media there is a number of other active media, including almost inorganic ones, potentially capable of self-oscillation mode of chemical reactions. An example of the latter is the substrate in the Bray-Libavsky reaction, demonstrating oscillating mechanism of oxidation-reduction of the iodate ion by hydrogen peroxide. It is also known that self-oscillations in active kinetic systems can be initiated by external influence, in particular, by irradiation [2]. The authors studied kinetic regimes in active media based on the products of ferric chloride hydrolysis. This substrate possesses semiconducting properties

and photosensitivity in the UV range, as well as the ability to form nanoscale positively charged aggregates with a large specific surface, providing heterogeneous redox catalysis [3].

3. Results

In the system studied concentration oscillation and the oscillations of electrochemical potential and mechanical characteristics of the medium occurred both under irradiation and after the structuring of the precursor during the subsequent autonomous functioning of the structures obtained. However, in a limited volume of the reaction system, one can observe only damped oscillations. The latter occur due to photoinduced redox processes on the surface of semiconductor particles providing charge separation, and membranous structures that facilitate the spatial separation of redox semi-reactions. UV-C radiation initiates radical chemical processes in the substrate followed by the accumulation of peroxide intermediates, in particular, H₂O₂. The latter induces autocatalytic reactions, maintaining acid-base balance and the balance of concentrations of oxidized and reduced forms of iron. During the formation of dissipative structures periodic fluctuations of pH and the followed periodic precipitation of insoluble products in the local space around the growing particles also occur with the participation of hydrogen peroxide and peroxide intermediates in the autoxidation-photoreduction of iron cations [4].



Electrochemical potential oscillations in the substrate can be caused by uncompensated molecular fluctuations on the surface of semiconductor nanoparticles of ferric hydroxide and magnetite in electrocatalytic processes. In general, the phase segregation of the structures obtained in conjunction with the autocatalytic processes in them allows adequately simulating of biological processes.

4. Conclusion

It is possible to initiate photoinduced self-oscillatory processes in the active inorganic nanodispersed semiconducting medium through autocatalysis in the kinetic modes of chemical reactions.

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Application of Electron Paramagnetic Resonance to the Study of Thermal In-Diffusion in Crystals and Ion Exchange in Glasses

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1. Introduction

Lithium niobate is a widely used material in integrated optics due to its electro-optical, acousto-optical, and nonlinear properties. Single crystals of LiNbO₃ are used to realize efficient electro-optical integrated devices for telecommunications. Thermal in diffusion of thin films is the most common technique used realize optical waveguides in LiNbO₃. This process takes place at high temperatures (up to 1000 °C) and requests long processing times (up to 100 h). The ion exchange is very attractive method due to the fact that is performed at relatively low temperature and short processing time. The ion exchange is widely used in the case of glasses as a suitable technique fabricating optical waveguides with graded refractive index, too. This process has been extensively described in the case of alkali, silver or copper ions as dopants. The aim of this work is to study the evolution of states of transition elements (Fe and Cu) introduced into LiNbO₃ by means of thermal diffusion, and the states of transition ions (Mn,V,Cr,Co,Cu) in ion-exchanged silicate glasses as it can be derived from EPR data.

2. Results

The copper ion-exchange process in silicate soda-lime (SL) glasses is experimentally studied by means of electron paramagnetic resonance analysis. Ion exchange was carried out by dipping glass plates into molten eutectic salt CuSO₄:Na₂SO₄ at different temperatures and processing times. The other transition elements (TM) were added to eutectic mixture as TM(SO₄) in the amount 50% TM/Cu.

EPR spectra (recorded in the temperature range from 77 K to 473 K) exhibit anisotropic features with partially resolved hyperfine structure (HFS). The total concentration of Cu²⁺ ions estimated from EPR spectra for SL sample is $(2.8 \pm 7) \cdot 10^{17} \text{ cm}^{-3}$ for glass (without dopants) immersed at 585°C for 20 min. Computer simulation of EPR spectra indicates the nonuniform distribution of Cu²⁺ ions throughout the diffusion layer. From the parameters of spin Hamiltonian follows that in the interior of the diffusion layer of SL glasses the local environment of Cu²⁺ ions is similar to that inside silicate glasses. Based on the comparison of experimental EPR spectra of Cu²⁺ ions in cells of PVA gel [2] with those contributing to the best-fit-computed EPR spectra, the depth profile of Cu²⁺ ions concentration was calculated. It is found that more than 80% of total concentration of

Cu^{2+} ions are accumulated in the first 4 μm of the soda-lime plate. Depth profiles of Cu^{2+} ions concentrations are well approximated by exponential functions $c(x) = c_0 \exp(-ax)$, where c_0 is the surface Cu^{2+} concentration and x is expressed in μm . For the SL sample we found $c(x) = 1.2 \exp(-0.43x)$. Thermal treatment of these glasses at 620 °C for 1 h leads to the increase in the intensity of EPR signals. At the same time the band of optical absorption at 560 nm appears. This band can be ascribed to the formation of nanoparticles of metallic copper.

Dopants are also distributed uniformly throughout diffusion layer. Thermal treatment at 600°C for 30 min leads to the formation of nanoparticles colloid metallic Co and Cu, crystals VO_2 , CrO , Cr_2O_3 and MnO . The composition of crystals was determined on the base of temperature dependence of intensity and the width of EPR lines in diffusion layer and comparison those of crystals with known dependence at phase transitions.

Copper ion exchange has been performed in LiNbO_3 single crystals. Cu ions migrate into LiNbO_3 and replace Li. Its incorporation induces a re-ordering of the matrix due to the $\text{Cu}^{2+} - 2\text{Li}^+$ exchange. The majority Cu^{2+} ions are accumulated in thin surface layer, where these ions are coupled by strong spin-spin exchange which is responsible for single line. A small portion of Cu^{2+} ions are located on well-defined sites and lead to orientation dependence.

Single crystals LiNbO_3 were doped with Fe by means of thermal diffusion. The study of magnetic resonance shows that Fe forms ferromagnetic phases and some portion of Fe^{3+} are located on sites in isolated states and exhibits the orientation dependence.

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Application of Photocatalytic Oxidation for Determination of Chemical Oxygen Demand Using a Nano-TiO₂

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1. Introduction

Chemical oxygen demand (COD) and biological oxygen demand (BOD) are two main indexes in environmental monitoring. COD has the advantage of speed and simplicity over BOD, however, this procedure is time-consuming, and it demands high-quality personnel and expensive (Ag_2SO_4) and toxic (HgSO_4) reagents. In recent years, the photochemical degradation of pollutants using nano-TiO₂ as catalysts has received considerable attention [1]. This photo-catalytic method is built on the reactive properties of electron–hole pairs generated in the semiconductor particles under illumination by light whose energy is greater than the semiconductor bandgap; these electrons and holes can recombine or reach the particles surface and react with species in solution with suitable redox potentials [2]. Therefore, when organic and inorganic compounds are both in the solution, both oxidation and reduction reactions can take place simultaneously, avoiding the possibility of recombination of the electron–hole pairs and these two processes influenced synergically. It has been reported that many inorganic compounds such as O₂, Cr(VI), and S₂O₈²⁻ were used as electron scavengers, which inhibits the recombination of electrons and holes, and enhance the rate of photocatalytic degradation of organic compounds. It is known, that Cr(VI) can easily accept photo-excited conduction band electrons and enhance the rate of photocatalytic degradation of organic compounds [3]. Reactant (Cr₂O₇²⁻) and product (Cr⁺³) both can be determined by a colorimetric method. This indicates that the COD of a given sample can be assessed by monitoring the change of Cr(III) concentration produced by the photocatalytic reduction of K₂Cr₂O₇.

2. Results

Here, a novel COD measurement method using a TiO₂ is investigated in which a change of Cr(III) concentration of a given sample is measured during photocatalytic oxidation of the organic compounds therein. The values obtained can reliably be correlated with the COD values obtained using the conventional methods.

P-25 TiO₂ was obtained from the Degussa Corp. A bath reactor system was used to perform the photocatalytic reaction in TiO₂ powder aqueous suspensions. The reaction mixture inside the reactor was maintained in suspension by means of a magnetic stirrer. A UV irradiator with a 9W lamp (Osram), in the center of the reactor, was used as the UV source and the reactor was equipped with a water jacket to maintain constant temperature.

The pH value of the solution was maintained at a desired level with KOH and H₂SO₄ and monitored by pH-meter (experiments was implement with pH 0,5). The total volume of reaction solution was maintained at 50 ml for each experiment. When the UV lamp was turned on ($\lambda_{\text{max}} = 253,7 \text{ nm}$), photocatalytic oxidation of the organic compounds began to occur, accompanying an increase of Cr(III) concentration produced by the photocatalytic reduction of Cr(VI). After 20-25 min irradiation reaction, the aqueous samples were filter using a 0,22 μm membrane filter to remove TiO₂ particles. The absorbance of Cr(III) was determined colorimetrically at 590 nm with a KFK-2 photometer, according to with the COD values of samples were obtained. All measurements were repeated three times.

For preparing a COD calibration, an appropriate volume of glucose standard solution was stepwisely added to the reactor to determine the corresponding absorbance of Cr(III). The COD calibration graph was made by the standard COD value and the absorbance of Cr(III). It indicates that the oxidation rate of organic compounds increases with increasing TiO₂ dosage, up to 4 g·l⁻¹; the increase seemed gradually to approach a limiting value for higher dosages of TiO₂. This can be explained by the high TiO₂ dosage decreasing the penetration of light, and thus reducing the effectiveness of the photocatalytic oxidation. The absorbance of Cr(III) increases with increasing Cr(VI) concentration up to 0,01 mol·l⁻¹, the increase seemed to change more slowly for higher Cr(VI) concentration. It is notable that the absorbance of Cr(III) increases with increase of temperature. At very high temperatures, because of evaporation, the reproducibility decreases. Therefore, 80 °C was selected for further experiments.

Artificial samples of wastewater were analyzed by the present method. The results show that COD values obtained using the proposed method are within ±10 % of those given by the conventional COD method.

The results were checked by incorporating known amounts of a standard substance in the wastewater samples and determining the COD values. Good recoveries of the standard substance added were obtained.

3. Conclusion

IA photocatalytic method for the determination of chemical oxygen demand (COD) using a nano-TiO₂ is described. The measuring principle is based on direct determination of the change of Cr(III) concentration resulting from photocatalytic oxidation of organic compounds and simultaneous photocatalytic reduction of stoichiometrically involved K₂Cr₂O₇ in the solution.

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Theory of Diffusion-Influenced Reactions of Particles with Several Active Sites

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1. Introduction

It is well known that sterically specific liquid-phase reactions in the case where one of the reactants has several active sites play an important role for many applications in chemistry and biology [1-4]. As it is known from the literature, in diffusion-controlled regime such reactions exhibit rather unusual dependence on the steric factor f , namely, they are proportional to \sqrt{f} but not to f , as it is intuitively expected (see, e.g., [5] and references therein).

2. Results

In the present work a more complicated case of reactants with several active sites characterized by different steric factors f_i were considered. We derived compact general formulas for partial rate constants of individual active sites that are valid at arbitrary geometries of reactants and their active sites as well as at any distance between different sites. Formulas have universal and vivid appearance and the rate constants are expressed via the kinetic rate constants and convolutions of the free Green functions over reaction zones. Effects of mutual influence of the active sites were studied, which reveal themselves in dependence of the partial rate constants for different active sites on the inter-site distances. Possible applications of our results in photochemistry are discussed.

Acknowledgements

This work has been supported by RFBR (project No. 09-03-91006, 08-03-00539), President Grant for supporting the Leading Scientific Schools (3604.2008.3), Program of Division of Chemistry and Material Science RAS (project No. 5.1.1).

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Influence of Diffusion of Components of H_3BO_3 Solutions Through Dubbed Membranes on Adsorption Properties of Such Membrane Films

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1. Results

Membrane processes are based on advanced penetration of one or a few components of a fluid or gaseous mixture as well as a colloid system through the separation membrane. In our paper a separation of the mixtures with similar properties namely purification of boric acid solutions is considered.

Solid and liquid, organic and inorganic materials have been used as initial layers. In comparison with usual stock membranes dubbed selective membranes (SM) have been used. The upper layer has been formed separately, it was coated as a ready film.

The SM studied have high selection ability. Membrane films with ion-exchange films have the best water diffusion properties and H_3BO_3 selectivity.

In some cases there is no dependence of the SM diffusion properties on some layers penetration ability.

Following SM parameters have been measured: thickness, moisture and sorption capacity.

The moisture capacity value is proportional to the SM diffusion properties. For the membranes of the same nature such thickness dependence is inversely proportional. For other cases such dependence was not observed.

An increase of the sorption capacity improves both diffusion properties and selectivity.

Translational and Rotation Self-Diffusion in Polymeric Systems Including Photo- and Thermo-Polymerized Systems by an Interference-Holography Method and a Method of Photo-Induced Optical Anisotropy

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1. Introduction

Structural modification of polymer materials is made by both variation of polymers chemical structure and adding of different plastifizing additions. They change molecular mobility as well as relaxation processes which determine the entire complex of the polymer's physical and mechanical properties.

The kinetics of structural transformations and properties of network systems resulting in photo- and thermo-solidification depend strongly on ability of reacting particles and products of their reactions to translational and rotational movements. At deep stages the reaction becomes sharply slow and even stops owing topology and diffusion limitations. Therefore in the polymer there is a sufficiently big rest (up to 5% and more) of functional groups which did not take place in the reaction. They plastify the material and sometimes worsen technical and exploitation performances of the materials processed.

Therefore a problem of investigation of relaxation processes and their influence on reaction ability of both macro- and micromolecules is timely and important.

2. Experimental

Rapid rotational movements of the molecules are investigated successfully by dielectric [1], NMR [2] and EPR [3] methods. Investigation of slow rotational diffusion with relaxation time 10^1 – 10^6 s is possible by using a method of square electrochromism [4] based on the Stark effect. However its practical application is difficult owing to necessity of measuring of small changes of optical density ($\sim 10^{-4}$ – 10^{-5}).

Simple methods like an interference-holography and a method of photo-induced optical anisotropy have been used to investigate both translational and rotation diffusion (mobility) in polymeric systems.

The translational mobility has been studied by the interference-holography method. The object investigated was irradiated by two mutually coherent laser beams that resulted in forming a diffraction grating. Special photosensitive substances (spyropiranes or SP) have been added into photo-solidified compositions. In this case the diffraction gratings have been formed by using a He-Ne laser with emission wavelength $\lambda=632.8$ nm. After

preliminary solidification of the layer by UV irradiation an observing a dark relaxation of the recorded diffraction grating allows a determination of the translational mobility kinetics dependent on composition components, grating period, solidification conditions.

In the case of high viscosity (solid films) when the translational mobility in the layer is almost excluded the method of photo-induced birefringence (PIB) has been used to investigate the molecular motions with relaxation time from 1 s to 10^5 – 10^8 s [5].

3. Results obtained

The PIB induction mechanism in the layer is owing to orientation selective excitation of photochemically stable dye, local heating of the medium in the molecule's vicinity during process of dissipation of energy of the absorbed light quantum, and orientational transstructuring of the molecule absorbed this quantum as well as the molecule's vicinity.

After termination of the activating radiation dark relaxation processes take place. They are determined by the intensity of molecular relaxation mobility in the medium investigated [6].

A dependence of rotational mobility on chemical nature of components of thermosolidified compositions on the base of oligourethaneacrylate as well as on solidification regime (power of the light source, time, temperature) has been measured.

Rotational mobility in plastified layers of photo-sensible polymer has been measured. There is no need in adding special azo dye probes as the macromolecule comprises spectrochromophore groups sensitive in the near UV range. Adding of dibutylphthalate as a plastifier enhances the rotational motion and the relaxation rate.

The results can be used for development of new photo-aligning and photo-refractive polymers.

Acknowledgements

The work is supported by Russian Foundation for Basic Researches, grant #10-03-90028-Bel_a and Ministry of Education and Science of Russian Federation, State Contract #02.740.11.5218.

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Energy Transfer Kinetics in Molecular Nanostructures with Fluctuated Configuration Parameters

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1. Introduction

In solving the problems of the design of functional nanodevices, the macromolecular chain in the cavity of a porous adsorbent just as well on the surface of a dispersed nanoparticle is frequently considered [1, 2]. One of the promising nanosystems of this kind is a linear polymer molecule that contains photoactive centers in its structure and is adsorbed on nanocavity walls. Specially derived spatial density distributions of units of the polymer chain adsorbed by the surface of a nanosized spherical or cylindrical cavity (particle) were used to describe the kinetics of the bimolecular reaction of radiationless energy transfer and cross annihilation of electronic excitation in nanoporous media (colloidal solutions). The cases of marked attraction of the chain units by cavity walls (particle surface) and the lack of the attraction were considered.

2. Kinetics of bimolecular reactions in nanosystems

We have shown that the detailed description of the kinetics of bimolecular reactions proceeding in nanosystems with the aforementioned structure requires that the formed radial profile of polymer units and, hence, the profile of reaction centers, should be taken into account in an explicit form. Conformation dynamics of the adsorbed macrochain was presented by randomly walk in an effective potential $V(r)$ with simplest symmetry. Thus, a change in the radial distribution of the density of macrochain units and random displacements of links entails the appearance of the corresponding response in the kinetic regime of the bimolecular reaction in the nanopore, with the character of the response being sensitive not only to the size of the nanoreactor but also to its form.

The effective radial-time rate $U_{\text{eff}}(\rho, t)$ of the radiationless energy transfer by the restricted motion in the r_m -area with diffusion coefficient D and Forster's radius R_F of an separated macrochain link has the following form ($(r_m / r)^2 \ll 1$)

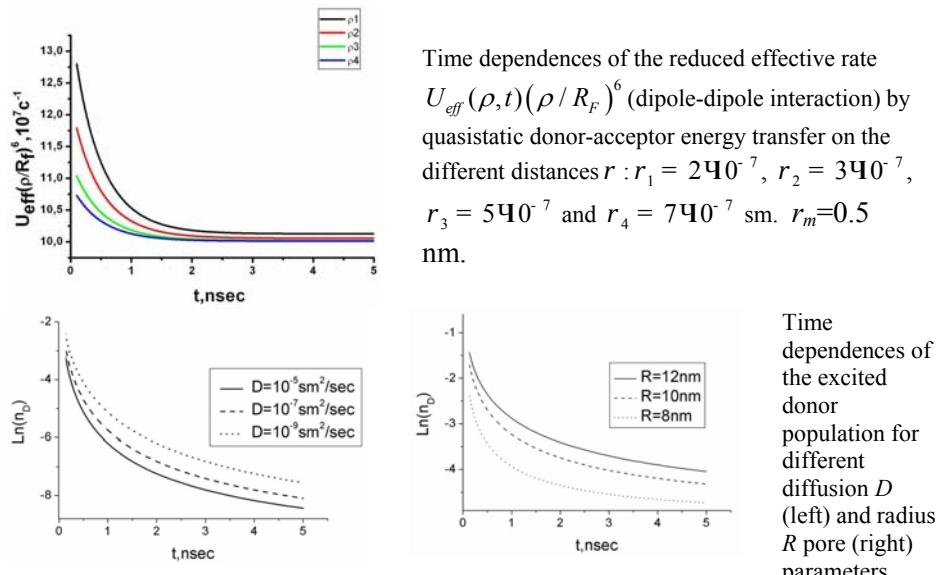
$$U_{\text{eff}}(\rho, t) = U_0 \left(\frac{R_F}{\rho} \right)^6 \left[1 + 3 \left(\frac{r_m}{\rho} \right)^2 + 20 \sum_{k=1}^{\infty} \left(1 + \lambda_k^2 r_m^2 \right) \frac{\cos \lambda_k r_m}{(\lambda_k \rho)^2} \exp(-\lambda_k^2 D t) \right]$$

λ_k are positive roots of the equation $\operatorname{tg}(\lambda_k r_m) = \lambda_k r_m$.

Population donor kinetics $n_D(t)$ in the case of the quasistatic energy transfer to N_A quenchers and acceptor radial distribution function $f(r)$ corresponds to such time dependence

$$n_D(t) = n_0 \exp \left[-\frac{t}{\tau_D} - N_A \int_0^R f(r) \left[1 - \exp \left(-\int_0^t U_{eff}(\rho, t') dt' \right) \right] 2\pi r^2 \sin \theta dr d\theta \right],$$

$\rho = \sqrt{R^2 + r^2 - 2Rr \cos \theta}$, $0 \leq \rho \leq 2R$, R is spherical pore radius, τ_D is lifetime of the excited donor state.



3. Conclusion

In this work we have compared the kinetic regimes of energy transfer bimolecular reactions in nanopores of different shapes containing macrochains with activated reaction centers for cases of different density distributions of chain units along the radius. We taken into account an inhomogeneous distribution of polymer chain links and restricted random displacements of reaction centers. In addition, molecular dynamics simulation of the formation of the radial density profile of the units of a 70-unit lysozyme segment was performed for the purpose of comparison with the model analytical relationships.

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Numerical Research of Perturbed Advection-Diffusion Problems in Environment with Thin Heterogeneities

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1. Introduction

A large number of topical physical and chemical problems of microelectronics, biology, medicine, environmental protection include researches of reactions and also heat and mass transfer in heterogeneous environments with complex structures characterized by the fact that they contain features as thin layers or channels with different properties from the main environment. Such environments can contain inclusions that size is not significantly different from the other components of the environment, and inclusion, where one, two or even all three dimensions are significantly smaller than the others. To find solutions of problems of the first type usually use traditional analytical and numerical approaches. Objectives of the second type require development of special mathematical models and corresponding numerical schemes [1].

2. Mathematical models and numerical schemes

We present mathematical models of heat and mass transfer based in advection-diffusion equations, which takes into account small thickness of curved channels by lowering dimensionality of mathematical relations in the thin inclusion [2]. This approach avoids many difficulties related to discretization of different field scale parts, to reduce computing costs.

We suppose that the physical and chemical properties of the environment and inclusions can be different. The mathematical model that is presented, predicts that in the main environment is available diffusion-dispersion transfer and in a thin layer inclusions additionally we have advective transfer. Heterogeneity of the proposed mathematical model is not only due to complex structure of environment or different nature of phenomena, but the use of different dimension relations in built system of key equations. This leads to application of modified schemes of finite element method.

There are also aware that obtaining numerical solutions of advection-diffusion problems with a significant predominance of advective transfer processes over diffusion (i.e. for large Peclet numbers) is connected with considerable difficulties engendered unstable numerical schemes of the finite element method or finite differences.

For the advection-diffusion problems with dominant advection we propose a new scheme to stabilize the finite element solutions (Fig. 1) using the concept of residual-free

bubbles [2]. The proposed numerical scheme involves the use of hierarchical basis [3] to solving local problems.

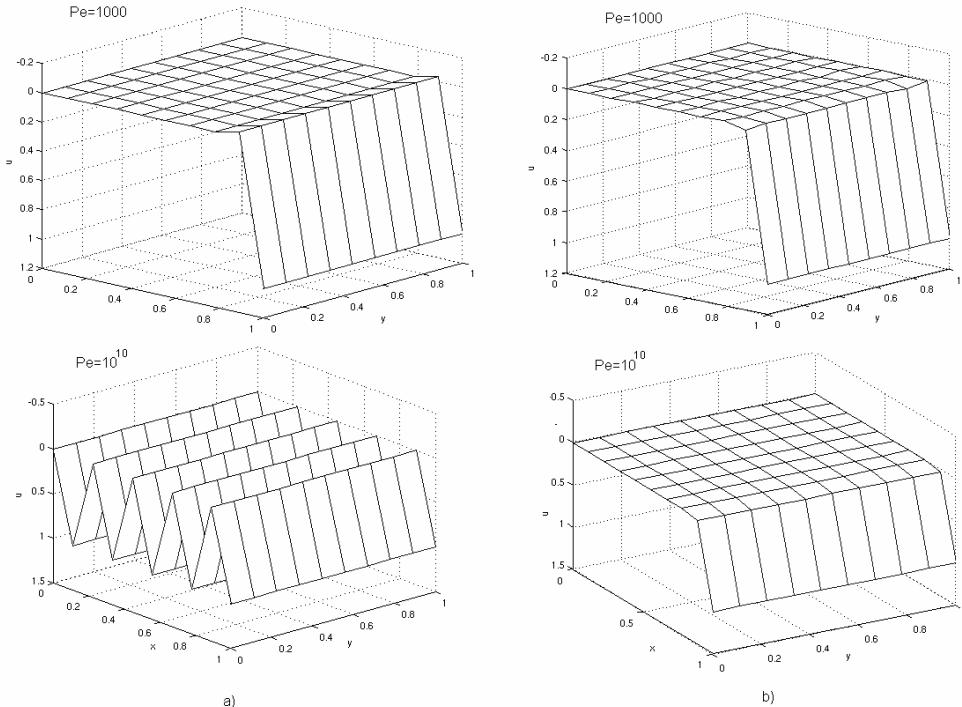


Fig. 1: Numerical results obtained by a) the FEM with hierarchical basis; b) new modified residual-free bubbles method.

3. Conclusion

As a result we obtained a method that has a high resistance to oscillations for large Peclet numbers, good performance and simplicity in computation parallelization to solve advection-diffusion problem in environment with thin inclusions.

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On Diffusion Regimes of Nonequilibrium Chemical Reaction with Closed Stream Lines

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1. Introduction

On the basis of the asymptotical theory at large Reynolds numbers and small relaxation parameters the chemical nonequilibrium gas recirculating problem is investigated. The distributions of thermodynamic and thermochemical parameters in the recirculation reaction region are calculated. The principal feature of problem in question is the constancy of concentration values for every closed stream line. Moreover these values in principal approach of asymptotical method are unknown. In order to determine the concentration values it necessary to consider the next approximation. In this approximation the diffusion of mixture components across closed stream lines is a limiting process in recirculation region.

2. The recirculation region with chemical reactions

In order to study the problem of nonequilibrium chemical reaction with closed streamlines it is necessary to take into account a considerable number of relaxation parameters. These parameters (G_k , where k is the mixture component, $k=1,\dots,N$, N is the full number of components) denotes the ratio of characteristic value of chemical reaction rate to characteristic value of gas dynamic rate. The most interesting case in practice is $Re^{-1} < G_k \ll 1$, where Re is the Reynolds number. Also in the limit $Re^{-1} \rightarrow 0$, $G_k \rightarrow 0$, $Re G_k = \xi_k = const$, where ξ_k is the Damkohler number, which is the ratio of characteristic rate of chemical reaction to characteristic rate of binary diffusion. The characteristic values of ξ_k are:

- a) $\xi_k \gg 1$ – in this case it is necessary to take into account the thin layers of chemical relaxation;
- b) $\xi_k \ll 1$ – the frozen gas phase of chemical reaction with homogeneous distribution of component concentration across the closed streamlines;

$\xi_k \sim 1$ – unhomogeneous distribution of component concentration across the closed streamlines.

3. Conclusion

The asymptotical analytical model considerate above is properly the fluid chemical reactor. Therefore it must have a large practical application including, for example, both radiowave propagation in plasma and new nanomaterials production.

Consistent Description of Kinetics of Degenerate Electron Exchange and Dimerization Reactions and Their Effects on MARY Spectra

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1. Introduction

Degenerate electron exchange (DEE) reactions



have been studied for a long time already by various ESR techniques [1, 2] as they are ubiquitous for radical ions formed photo- or radio-chemically. Model description of DEE effects on ESR spectra has always been based on the concept non-correlated jumps of the electron spin over hyperfine structure components of the radical ion. The frequency of these jumps has been identified with that of diffusional encounters between radical ions $A^{\star+/-}$ and neutral molecules A . However, such model does not take account of DEE reversibility and numerous repeated contacts of $A^{\star+/-}$ and A during their encounter in solution. Collisions of $A^{\star+/-}$ and A lead to electron transfer between them and result in additional modulation of HFI during the encounter of the two reactants.

2. Discussion and Conclusions

In the present work we have investigated effects of DEE on spin dynamics in low magnetic fields and on Magnetically Affected Reaction Yield (MARY) spectra. Case of a radical ion with one magnetic nucleus has been studied in detail in the situation where $a\tau_d \sim 1$ and the conventional approach are no longer valid. We have studied the manifestation of diffusion-controlled DEE in the electronic spin evolution of the radical ion with one magnetic nucleus. Additionally, DEE effects on MARY spectra have been investigated.

We also have considered effect of dimerization reaction on MARY spectra when one of radical or radical pair has few equivalent magnetic nuclei. The dependence of $B_{1/2}$ width of MARY spectra on concentration of neutral molecules is calculated and comparison with the earlier made experiments have been performed.

Acknowledgements

This work has been supported by RFBR (project # 08-03-00539), President Grant for supporting the Leading Scientific Schools (3604.2006.3), Program of Division of Chemistry and Material Science RAS (Project # 5.1.1).

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Optimization of Magnesium Carbonate Chlorination Based on Study of Process Mechanism and Kinetics

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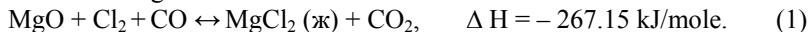
1. Introduction

The analysis of drawbacks of magnesite ($MgCO_3$) chlorination process, such as its low productivity, chlorine breakthroughs [1], etc., leads to the assumption that gasification of solid reductant in chlorinated feedstock followed by mass transfer of gaseous reagents (Cl_2+CO) to the oxide surface through the film of formed magnesium chloride are limiting process steps. To intensify the chlorination process, we have set aside reductant gasification as a separate process step.

2. Experimental investigation and results

To substantiate the process kinetics by a differential thermal analysis using the procedure of study into a solid-gas system, where gas was filtered through the layer of material under investigation, we have investigated the mechanism of natural magnesium carbonate (magnesite) interaction with chlorine and carbon oxide mixture. The reaction products were analyzed in copper K_α radiation using a DRON-0.5 diffractometer.

It has been found that chlorine starts its interaction with magnesium carbonate after a thermal dissociation of magnesium carbonate followed by chlorination of formed magnesium oxide according to the reaction



Endothermic effect of formed magnesium chloride melting $\Delta H=43.16 \text{ kJ/mole}$ is offset by reaction (1) heat, and the surface of caustic magnesite is filmed with molten magnesium chloride, skipping the step of solid-phase chlorination.

Study into the kinetics of chlorination process in a quartz vessel with a diameter of 40 mm ($T=1253 \text{ K}$) has demonstrated that carbon oxide and chlorine supplied to the reaction zone in an equimole ratio resulted in a low chlorine utilization and is thus inappropriate. Fast growth in the degree of chlorine utilization (Fig. 1, curve 1) takes place due to the increase in carbon oxide concentration, and, in gaseous phase within a range of ratios $P_{CO}/P_{Cl_2} = 3$ to 4, this parameter is as high 95 to 98 %. As far as carbon oxide concentration in the initial mixture grows, magnesium oxide chlorination rate (V_{MgO}) increases, reaching its maximum at a ratio $P_{CO}/P_{Cl_2} = 2$ (Fig. 1, curve 2).

It has been known that the processes of oxide chlorination in chloride melts are, as a rule, limited by the mass transfer of the reagents [2]. Within a boundary layer, the Stefan flow velocity does not depend on hydrodynamic conditions and is entirely governed by the conditions of diffusion and stoichiometry of reagent flows [3]. Therefore, if equimole

($\text{Cl}_2 + \text{CO}$) mixture is used, chlorine diffusion flow through molten magnesium chloride film towards magnesium oxide surface exceeds that of carbon oxide, resulting in low chlorine utilization.

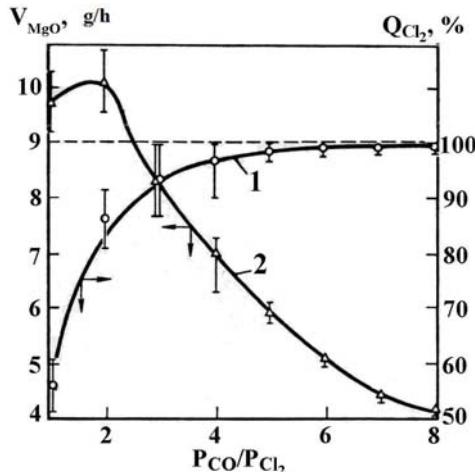


Fig. 1: Chlorine utilization factor Q_{Cl_2} (1) versus magnesite chlorination rate V_{MgO} (2) and ratio of Cl_2 and CO partial pressures in reaction gases

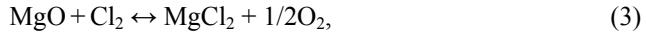
Based on the equations of Fick and Henry laws, we have obtained an equation for the calculation of chlorine and carbon oxide partial pressures in a gaseous phase that provide for an equimolecular delivery of the reagents to the interphase boundary

$$D_{\text{Cl}_2} K_{P\text{Cl}_2} (1-x)(1-P_{\text{CO}_2})\delta^{-1} = D_{\text{CO}} K_{P\text{CO}} x(1-P_{\text{CO}_2})\delta^{-1}, \quad (2)$$

Where $x = P_{\text{CO}}/(1-P_{\text{CO}_2})$, $1-x = P_{\text{Cl}_2}/(1-P_{\text{CO}_2})$.

Using known experimentally measured solubility constants and gas diffusion coefficients [4], as well as calculated data from Stokes-Einstein equation, after their corresponding insertion to (2), we have found chlorine-to carbon oxide ratio in gaseous phase that yields the parity of their diffusion flows through liquid chloride film to magnesium oxide surface: $P_{\text{CO}}/P_{\text{Cl}_2} = 3.35$. The calculated ratio fits the experimental relationship well (Fig. 1), this being the indicative of correctness of our diffusion model for the process.

In the course of further study into the process conducted in a pilot reactor with an internal diameter of 0.1 m, it has been found that, the longer the gases and the layer of material to be chlorinated contact each other, the lower is a partial pressure ratio in the initial mixture $P_{\text{CO}}/P_{\text{Cl}_2}$, resulting in the maximum chlorine utilization under given conditions. In such a case, diffusion stoichiometry is not observed, chlorine diffusion flow exceeds the flow of carbon oxide, resulting, due to reversibility of chlorination reaction



in equilibrium concentrations of chlorine and oxygen at the oxide surface [5]. Process rate and, therefore, the degree of chlorine utilization are in this instance governed by oxygen diffusion in the bulk of the melt followed by a homogeneous reaction of its interaction with dissolved carbon oxide



3. Conclusion

The established model of chlorination has allowed optimization of process parameters of its implementation in a pilot installation and a 3-fold growth in chlorination volume rate and vessel productivity, with actually full chlorine utilization.

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Monte Carlo Simulation in the Multibaric-Isothermal Ensemble on the Liquid-Solid Phase Transition of L-J Fluids

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1. Introduction

The liquid becomes the solid when it is cooled, and the solid becomes the liquid when it is heated up. The phase-diagram exhibits that the phase transition takes place with the pressure change. In the present study, we investigated the pressure-induced liquid-solid phase transition of the Lennard-Jones (L-J) fluid system by using the multibaric-isothermal Monte Carlo (MUBA MC) method [1].

2. Computational Method and Results

We put 108 L-J particles in the periodic cubic cell and performed the MUBA MC simulations under temperature $T^*=1.04$ by changing its pressure from $P^*=2.39$ into 7.16. The conventional MC simulations under $T^*=1.04$ for $P^*=2.63, 3.82$, and 5.25 were also carried out for comparison. The long production run, which was calculated by using the MUBA weight factor that we decided in the present study, implied the existence of two distinct configurational spaces.

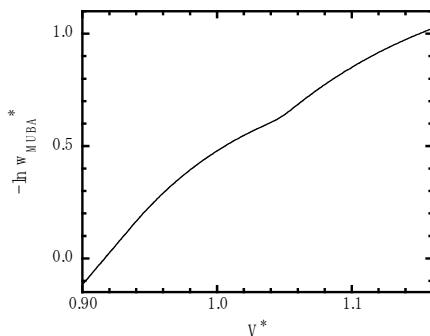


Fig. 1: The logarithm of the MUBA weight factor as a function of volume obtained by the MUBA MC production run.

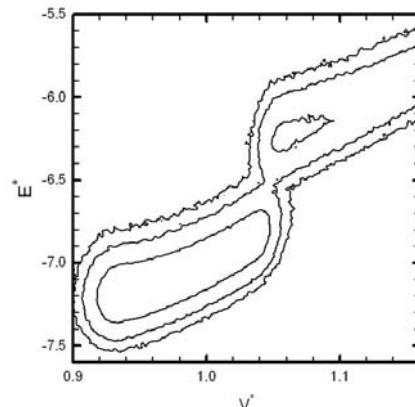


Fig. 2: The contour representation of the probability distribution $P_{\text{MUTH}}(V^*, E^*; T^*)$ in logarithmic scale.

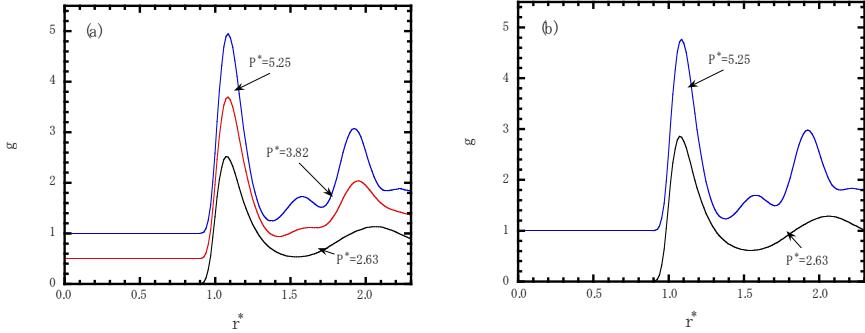


Fig. 3: The radial distribution functions at $P^*=2.63, 3.92, 5.25$ under $T^*=1.04$, which were obtained (a) from the MUBA MC production run by the reweighting techniques and (b) from the conventional MC calculations.

3. Conclusion

Thermodynamic quantities calculated from the MUBA MC production run by the reweighting techniques and the radial distribution functions for $P^*=2.63$ and 5.25 indicate that the phase transition between liquid and solid states takes place at $P^*=3.82$ under $T^*=1.04$, which is agree well with the transition temperature $T^*=1.04$ at $P^*=3.63$ obtained by the isobaric-multithermal Monte Carlo (MUTH MC) simulation [2].

Acknowledgements

This research was supported, in part, by Japan Society for the Promotion of Science (JSPS): Grant-in-Aid for Scientific Research (C), Grant No. 22540423.

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Diffusive Quasi-stationary Evaporation and Grows of Finite Arrays of Large Drops of Pure Liquids

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1. Introduction

It is known that evaporation or growth (EG) of liquid drops may be treated as a diffusion-controlled reaction. The present theoretical model describes EG of the dense array of F immobile large drops with arbitrary surface shapes S_f . EG occur in N component gas mixture with the relative vapor concentration of drops matter $c_i \ll 1$. When EG occurs without internal heat release and radiant heat exchange the distribution of the gas and particles temperature $T_e, T_i^{(f)}$ and relative concentration c_i are described by the set of non-linear boundary-value problems (1), (2):

$$\operatorname{div} \vec{q}_T^{(e)} = 0, \quad \operatorname{div} \vec{q}_T^{(f)} = 0, \quad \operatorname{div} \vec{q}_l = 0, \quad (1)$$

$$T_e|_{S_f} = T_i^{(f)}|_{S_f}, \quad c_i|_{S_f} = c_{1s}(T_i^{(f)})|_{S_f}, \quad (\vec{q}_{Tl}^{(e)} - U_l \vec{q}_{1l})|_{S_f} + L_i m_i \vec{q}_{1l}|_{S_f} = \vec{q}_{Tl}^{(f)}|_{S_f}, \quad T_e|_{\infty} = T_{e\infty}, \quad c_i|_{\infty} = c_{i\infty}, \quad (2)$$

where $\vec{q}_T^{(e)} = U_l \vec{q}_l - \chi_e \nabla T_e$, $\vec{q}_T^{(f)} = -\chi_i^{(f)} \nabla T_i^{(f)}$, $\vec{q}_l = -nD(\nabla c_i + K_T \nabla T_e / T_e)$ are the heat and vapor flux densities; $c_j = n_j / n$, $n = \sum_{j=1}^N n_j$; m_j , n_j are mass and concentration for j -th molecules; $U_l = m_l h_l + V_l (K_T / c_l)$, h_l is specific enthalpy of the vapor molecules; V_l is the coefficient included Duffer effect; $n = p_{\infty} / kT_e$, p_{∞} is the gas pressure; $K_T = K_T^{(1)} c_1$ is the thermal diffusion factors; L_i is the specific vaporization heat; $c_{1s}(T_i^{(f)})$ is the relative concentration of saturated vapor. The coefficient D is the effective coefficient of the diffusion of the first component, which may be found by Stefan-Boltzman equation. In case of three components gas ($N=3$). The coefficient D is $D = D_{12} D_{13} / (D_{13} c_{2\infty} + D_{12} c_{3\infty})$, where D_{12} and D_{23} are the binary diffusion coefficient. The coefficient χ_e is $\chi_e = \chi_e^{(0)} + \chi_e^{(1)} (c_l - c_{l\infty})$. The coefficients D , $\chi_e^{(0)}$, $\chi_e^{(1)}$, $K_T^{(1)}$ and function U_l depend on the outside temperature T_e .

2. Results and discussion

The solution to the Eqs. (1) is

$$c_1 = \{c_{1\infty} + B\psi_1(T_e)\}\exp(-\psi_2(T_e)), \quad \psi_3(T_e) = \psi_3(T_{i0})G(x, y, z), \quad T_i^{(f)} = T_{i0} = \text{const}, \quad (3)$$

where $\psi_1(T_e) = \int_{T_{e\infty}}^{T_e} [(\chi_e^{(0)} - \chi_e^{(1)}c_{1\infty})(a/nD\chi_e)\exp\psi_2(T_e)]dT_e, \quad \psi_3(T_e) = \int_{T_{e\infty}}^{T_e} adT_e, \quad a = \chi_e/[1-BU_1],$

$\psi_2(T_e) = \int_{T_{e\infty}}^{T_e} (K_T^{(1)}/T_e - B\chi_e^{(1)}a/(\chi_e nD))dT_e, \quad B = -[c_{1\infty} - c_{1s}(T_{i0})\exp(\psi_2(T_{i0}))]/\psi_1(T_{i0}).$ The value of T_{i0}

is the solution to the transcendental equation

$$\psi_1(T_{i0}) = (L_1 m_1 - U_1)[c_{1\infty} - c_{1s}(T_{i0})\exp(\psi_2(T_{i0}))] \Big|_{T_e=T_{i0}}. \quad (4)$$

Function $G(x, y, z)$ is the solution of the Laplace equation in the F -connected domain with Diriclet boundary conditions

$$\Delta G(x, y, z) = 0, \quad G|_{S_f} = 1, \quad G|_{\infty} = 0. \quad (5)$$

The relations for the corresponding fluxes of molecules and heat $\bar{q}_1^{(e)}, \bar{q}_T^{(e)}, Q_1^{(f)}, Q_T^{(f)}$ read

$$\bar{q}_1 = B\bar{q}_T^{(e)}, \quad \bar{q}_T^{(e)} = -\psi_3(T_{i0})\nabla G, \quad Q_1^{(f)} = BQ_T^{(f)}, \quad Q_T^{(f)} = -\psi_3(T_{i0}) \oint_{S_f} \nabla_{\perp} G dS_f. \quad (6)$$

Subscript “ \perp ” denotes projections of normal vectors to the surfaces S_f . It follows from formulas (3)-(4) that in absence of internal heat release and radiant heat exchange between drops and medium that: a) In quasi-stationary state interacting large drops either evaporate or grow simultaneously at identical temperature of the surface ($T_i^{(f)} = T_{i0}$); b) The steady-state evaporating or growth temperature T_{i0} is independent on distances between drops, their surface shape and sizes; c) The distributions of the gas temperature T_e depend on the geometrical properties of the assembly of drops.

3. Conclusions

When the distance between surfaces of the drops becomes much shorter than the size of the smallest drop and drops are highly heated by internal heat sources one can estimate the treated array of drops using the analytical formulae (3) and (6). In this case the particle surface temperatures are the same (i.e. $T_i^{(f)} = T_{i0}$). The dependence of the temperature T_{i0} and the particle sizes on time are governed by the system of the following differential equations

$$\sum_{f=1}^F Q_w^{(f)} = \sum_{f=1}^F (\gamma_p^{(f)} M_p^{(f)} dT_{i0}/dt + Q_r^{(f)} + (L_1 m_1 - U_1)|_{S_f} Q_1^{(f)} + Q_L^{(f)}), \quad dM_d^{(f)}/dt = -m_1 Q_1^{(f)}, \quad (7)$$

where $Q_w^{(f)}$ is total power of the heat sources; $M_d^{(f)}$ is the mass of f -th drop; $\gamma_p^{(f)}$ is the heat capacity of particles; $Q_L^{(f)}$ is heat flux due to the heat-exchange radiation. The equations (7) may be used to describe evaporation of a single particle of arbitrary surface shape.

Quasilattice Approximation of Statistical Systems with Strong Superstable Interactions: Correlation Functions

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1. Introduction

The main difficulty in mathematical description of continuous systems in Classical Statistical Mechanics is accumulation of a large number of particles in small volumes. The lattice gas model was invented to avoid these problems and describe some general characteristics of real systems. But in majority of works there was no parameter which in some sense restored systems to continuous media.

In this talk (see Refs. [1, 2]) we propose some intermediate approximation of continuous media, which is very close to lattice gases and all main characteristics of continuous gases (pressure, correlation functions in the fixed volume and correlation functions of infinite systems) can be obtained with help of limit transition.

Quasilattice approximation in Equilibrium Classical Statistical Mechanics was proposed in the article [1] for the investigation of infinite systems of interacting point particles with two-body strong superstable potentials. Let us split d -dimensional space R^d into non-intersecting cubes with an edge a and the center in $ar, r \in Z^d$:

$$\overline{\Delta_a} = \bigcup_{r \in Z^d} \Delta_a(r), \quad \Delta_a(r) = \left\{ x \in R^d \mid a(r^i - 1/2) \leq x^i < a(r^i + 1/2) \right\}.$$
The main

point of this approximation consists in the idea that in the expressions for the basic characteristics of the system integration is carried out not over all space of configurations but only over those configurations, which contain for the given partition of the space R^d into hyper cubes not more than one particle in each cube.

2. Partition functions, corresponding pressure and correlation functions in case of quasilattice approximation

Let us define basic quantities of approximated systems:

$$\rho_\Lambda^{(-)}(\eta; z, \beta, a) := \frac{z^{|\eta|}}{Z_\Lambda^{(-)}(z, \beta, a)} \int_{\Gamma_\Lambda} e^{-\beta U(\eta \cup \gamma)} \prod_{\Delta \in \Delta_a \cap \Lambda} \chi_-^\Delta(\eta \cup \gamma) \lambda_{z\sigma}(d\gamma) \quad \text{are}$$

correlation functions in the fixed volume Λ ,

$$Z_\Lambda^{(-)}(z, \beta, a) := \int_{\Gamma_\Lambda} e^{-\beta U(\gamma)} \prod_{\Delta \in \Delta_a \cap \Lambda} \chi_-^\Delta(\gamma) \lambda_{z\sigma}(d\gamma) \quad \text{is grand partition function,}$$

$\chi_-^\Delta(\gamma) = \begin{cases} 1, & |\gamma_\Delta| = 0 \vee 1, \\ 0, & |\gamma_\Delta| \geq 2 \end{cases}$; $\rho^{(-)}(\eta; z, \beta, a)$ are the correlation functions of infinite

systems; $\eta \in \Gamma_\Lambda$, Γ_Λ is the space of finite configurations in the volume Λ ; $\lambda_{z\sigma}$ is the Lebesgue-Poisson measure. An approximated pressure is defined in such a way:

$$p^{(-)}(z, \beta, a) = \frac{1}{\beta} \lim_{|\Lambda| \rightarrow +\infty} \frac{Z_\Lambda^{(-)}(z, \beta, a)}{|\Lambda|}, \quad \beta \text{ is the inverse temperature.}$$

The same functions of continuous systems $Z_\Lambda(z, \beta), \rho_\Lambda(\eta; z, \beta)$ are defined in a similar way without terms $\prod_{\Delta \in \Delta_a \cap \Lambda} \chi_-^\Delta(\gamma)$ and $\prod_{\Delta \in \Delta_a \cap \Lambda} \chi_-^\Delta(\eta \cup \gamma)$ respectively (see also Ref. [1]).

3. Main results

Interaction is called strong superstable (see Refs. [1, 2]), if there exist $m \geq 2, a_0 > 0$ s. t. for any $0 < a \leq a_0$ there exist $A(a) > 0, B(a) \geq 0$ s. t.:

$U(\gamma) \geq A(a) \sum_{\Delta \in \Delta_a : |\gamma_\Delta| \geq 2} |\gamma_\Delta|^m - B(a) |\gamma|$, for any $\gamma \in \Gamma_0$ (space of finite configurations).

Theorem. Let two-body interaction be strong superstable. Then the following holds:

1. $\lim_{a \rightarrow 0} \rho_\Lambda^{(-)}(\eta; z, \beta, a) = \rho_\Lambda(\eta; z, \beta)$ for any $\eta \in \Gamma_\Lambda$;
2. $\lim_{a \rightarrow 0} \rho^{(-)}(\eta; z, \beta, a) = \rho(\eta; z, \beta)$ for any $\eta \in \Gamma_0$ and sufficiently small z ;
3. $\lim_{a \rightarrow 0} Z_\Lambda^{(-)}(z, \beta, a) = Z_\Lambda(z, \beta)$.

4. Conclusion

Such an approximation helps to generalize some results in case of lattice gas on the case of classical continuous systems. It contains also the transition parameter, that is the length a of an edge of an arbitrary cube from the partition of the space R^d and ensures the connection between the lattice and continuous cases. It is especially important, because there are many results in the theory of lattice systems and very few for continuous ones.

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Hydrodynamic Effects for Propulsion of a Molecular Motor by Asymmetric Reaction in Fluids

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1. Introduction

Study of molecular motors that convert chemical energy to mechanical work is of great importance in many fields of modern nanotechnology. We investigate theoretically a model of self-propelling device in liquid driven due to chemically anisotropic reaction on its surface. This kind of molecular motor stems from the possibility of decorating of microparticles by special, enzymatic reactive sites. Chemically anisotropic reactions are investigated rather well (see Refs. [1, 2] and references therein).

Existing theory explains this motion by diffusiophoresis effects due to a nonuniform distribution of the reaction products in a vicinity of particle surface [3-5]. To the best of our knowledge the measured experimental value of the propulsion velocity is about $1 \mu\text{m/s}$, however theoretical estimates predict a much smaller velocity about 1 nm/s [3]. Moreover known experiments give for a particle not only higher velocity value but even different direction of motion which contrary to diffusiophoresis model is along the direction of the flux of reactants.

2. Statement of the problem

In our paper we propose a new, hydrodynamic explanation of this motion to eliminate the contradiction between theory and experiment. It has been shown that the time-dependent regime of reaction at issue is rather short [1]. So our treatment is based on the steady-state Stokes equation for an incompressible fluid. In order to calculate the propulsion velocity we assume that the value of the reaction product velocity \mathbf{v}_f is a constant within the whole cape like active site: $0 \leq \theta \leq \theta_0$.

Consider a small macroscopic spherical particle of radius R translating at velocity \mathbf{U} at a reference point placed into its center. The steady-state Stokes equation for an incompressible fluid around this sphere reads

$$\mu \nabla^2 \cdot \mathbf{v} - \nabla p = 0, \quad \nabla \cdot \mathbf{v} = 0, \quad (1)$$

where μ is the dynamic viscosity of the surrounding liquid. We solve the Stokes equation under appropriate boundary conditions

$$\mathbf{v}|_{r=R} = U \mathbf{e}_z + u(\theta_0) \mathbf{e}_r, \quad \mathbf{v}|_{r \rightarrow \infty} \rightarrow \mathbf{0}, \quad (2)$$

$$u(\theta_0) = |v_f| [1 - H(\theta - \theta_0)], \text{ for } \theta \in [0, \pi),$$

where $H(\xi)$ is the Heaviside step function, \mathbf{e}_z and $\mathbf{e}_r = \mathbf{r}/r$ are the unit vector in the axial and radial directions, respectively.

3. Results and conclusions

Solution of the boundary-value problem (1), (2) leads to we obtained the steady-state propulsion velocity of the spherical device

$$\mathbf{U}(\text{Re}_f) = \frac{1}{4} \sin^2 \theta_0 \left(1 - \frac{4}{3} \text{Re}_f\right) \mathbf{v}_f, \quad (3)$$

where $\text{Re}_f = R|v_f|/\nu$ is the Reynolds number of the reaction flow and ν is the kinematic viscosity of the fluid. Critical Reynolds number may be defined by the relation $\mathbf{U}(\text{Re}_f^c) = 0$, i.e. $\text{Re}_f^c = 3/4$. If viscosity ν decreases we get typical jet propulsion, i.e.

$$\mathbf{U}(\text{Re}_f) \sim -\frac{1}{4} \sin^2 \theta_0 \frac{4}{3} \text{Re}_f \mathbf{v}_f \quad \text{as } \text{Re}_f \rightarrow \infty.$$

Otherwise, if $\text{Re}_f < \text{Re}_f^c$, velocity of propulsion changes its direction becoming positive. This explains known experimental results [3, 4] at least qualitatively. Moreover it is worth noting that the predicted change in velocity direction may be experimentally verified.

Acknowledgement

The author expresses his sincere grateful to Prof. G. Oshanin who aroused my interest to this problem.

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