From atoms and molecules to new materials and technologies

Predictive Modeling of Advance Materials and Material Processing Based on Multiscale Simulation Paradigms

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Presented at International School on “Computer simulation of advanced materials”
MSU, Moscow
July 2012

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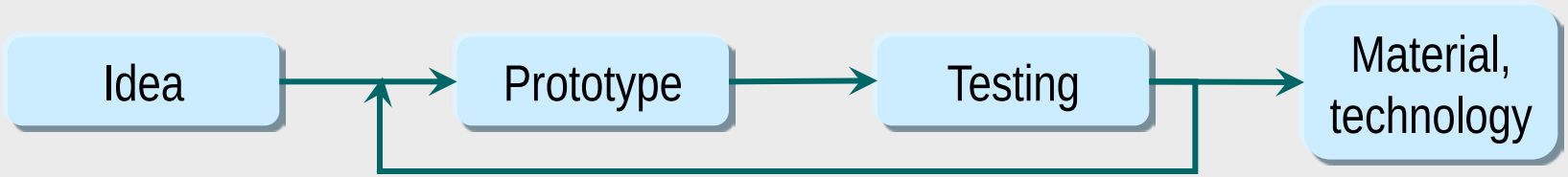
Approach

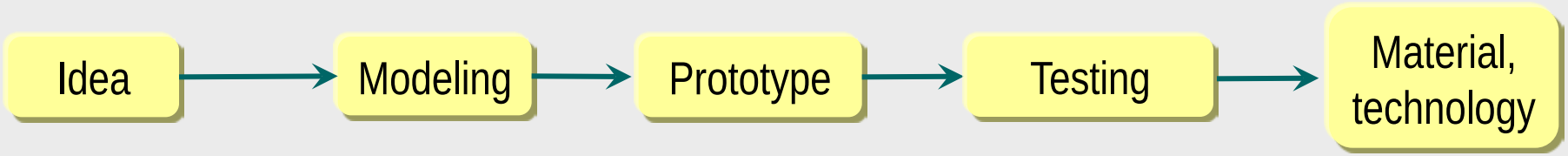
Standard approach to design of new materials and technologies: empirical search



ü Expensive ü Long time ü No assimilation of fundamental data

The role of modeling consists in description and extrapolation of experimental data using phenomenological models

Integrated approach, based on predictive modeling



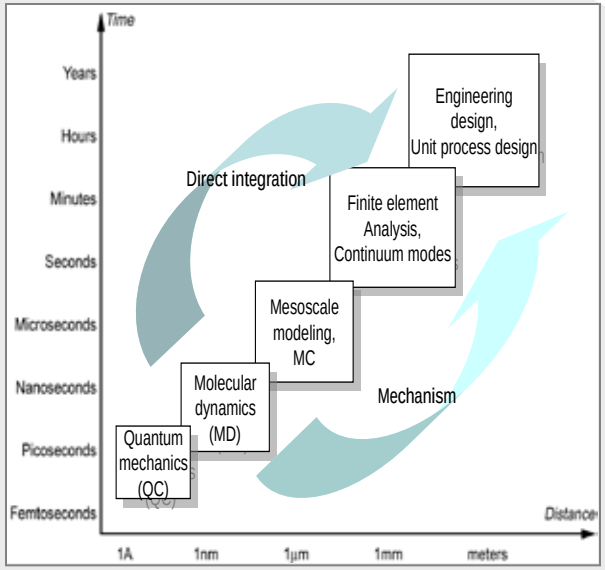
ü Reduced time and cost of development ü Reduced risks

A priory modeling, based on detail understanding of structures and mechanisms at atomistic level, before construction of prototype

Technologies and tools of predictive modeling

Problems

- ü Huge computers resources needed even for every single level
- ü Unfeasibility of direct integration of spatial and temporal scales
- ü No reliable integration methods
- ü Stochastic nature of multilevel modeling: models, data, properties
- ü Cognitive problems (data formats, computer languages etc.)
- ü No effective software tools for scales integration and collaborative work



Background for solution

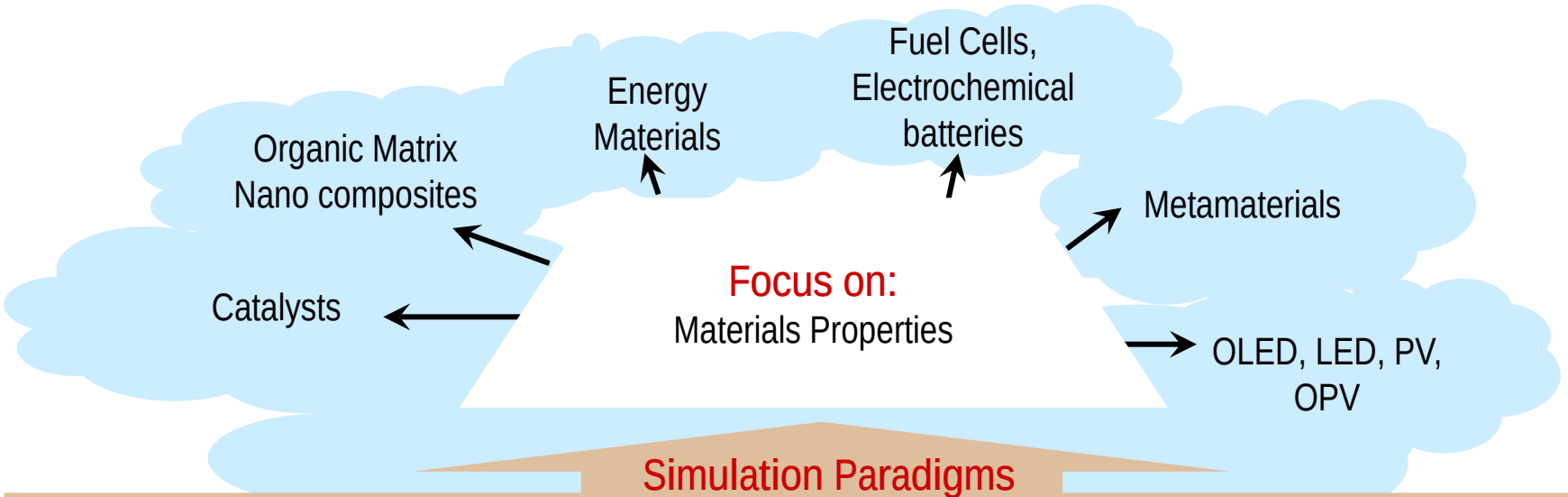
- ü Exponential growth of computer resources (Moore's law, HPC)
- ü Development of high-performance algorithms
- ü Development of predictive theoretical methods

Solution

Development of methods and tools for integrated multilevel modeling

Elaboration and use of High Performance Computing algorithms and systems

Multiscale Modeling for Advanced Materials



Simulation Paradigms

- Macro level : FE, FDTD for optics
- Mesoscale methods: DPD, Mean Field Models, MC
- Atomistic methods: quantum chemistry, molecular dynamics, DFT

High Performance Computing

- Code parallelization
- HPC Architecture choice
- Platform-specific Code Optimization (Tailoring)

Information Technologies for Cloud Computing & Distributed Collaboration

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Kintech Lab profile

KINTECH was founded in 1998 by scientists and engineers from and the NRC "Kurchatov Institute“, MIFI, and Moscow State University

ACTIVITY FIELDS:

- Conducting of inventive research and consulting for a wide range of applications
- Software development for multi-scale multi-physics modeling modeling and design in complete cycle
- Customer support in their own research activity using the advanced simulation capabilities of KINTECH's software

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Selected Kintech projects in energy and materials: materials & devices

- Multiscale modeling of thin high-*k* dielectric film deposition and the investigation of their properties
- First-principles modeling of defects at the SiC/SiO2 interface
- Multiscale modeling of the optic properties of metamaterials and the design of devices on their basis
- Multiscale modeling of semiconductor nanosensors and CdTe solar cells
- Multiscale modeling and screening of scintillator and phosphor materials
- Optimization of the fabrication of microelectromechanical (MEMS) devices
- Multiscale modeling of phase transition in ferroelectric materials
- Modeling of Nano Electro Mechanical systems (NEMS) based on carbon nanotubes
- First-principles modeling of catalysts for fuel cells
- Predictive modeling of carbon based materials

Selected Kintech projects in energy and materials :

- Multiscale modeling for PDE design
- Multiscale modeling of cold spay technology
- Multi-physics modeling of car exhaust cleaning
- Mechanistic modeling of depleted combustion processes
- Mechanistic modeling of coal gasification kinetic
- Plasma waste gasification modeling
- Industrial safety: explosions
- Multiscale modeling of chemically active plasma systems including PAC and plasma exhaust cleaning modeling
- Multiscale modeling of chemically active plasma systems
- Membrane gas separation modeling and system design
- First-principles modeling of catalysts for fuel cells
- Software development for environmental and industrial safety

Kintech selected customers

- ü General Electric since 2003
- ü Motorola (Freescale Semiconductor), 2000-2006
- ü Intel since 2007
- ü Siemens
- ü Daimler
- ü Qualcomm
- ü David System and Technology SL, Spain
- ü Scientific Utilization Inc. USA
- ü Renault, France
- ü Rhone Poulence, France
- ü TNO, Netherlands
- ü DLR (Germane Airspace Center), Germany
- ü Arvin Meritor Inc, USA.
- ü PlasmaSol Corp., USA
- ü Princeton University, USA

imagination at work

Launched by Motorola freescale semiconductor

SIEMENS

RENAULT

TNO

Key Parallel Software tools Developed at Kintech

Kintech Lab develops methods and special software tools for multilevel modeling in different engineering fields:

- Chemical Workbench – an integrated environment for the development and reduction of chemical mechanisms for combustion, plasma, etching, films growth
- FDTD-II – a tool for modeling the optical properties of metamaterials
- MD-kMC – an integrated environment for atomistic modeling
- EtchLab – a tool for modeling and optimization of MEMS fabrication
- TRACC - integrated package to solve 3D fluid dynamics problems with radiation transport using special software and a database

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Predictive multi scale modeling for energy and materials: specific projects

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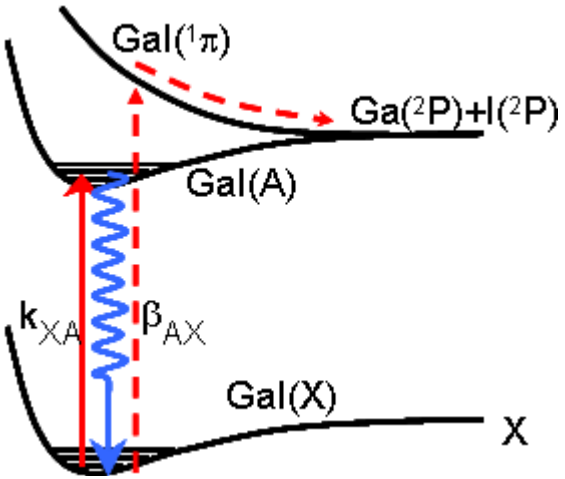
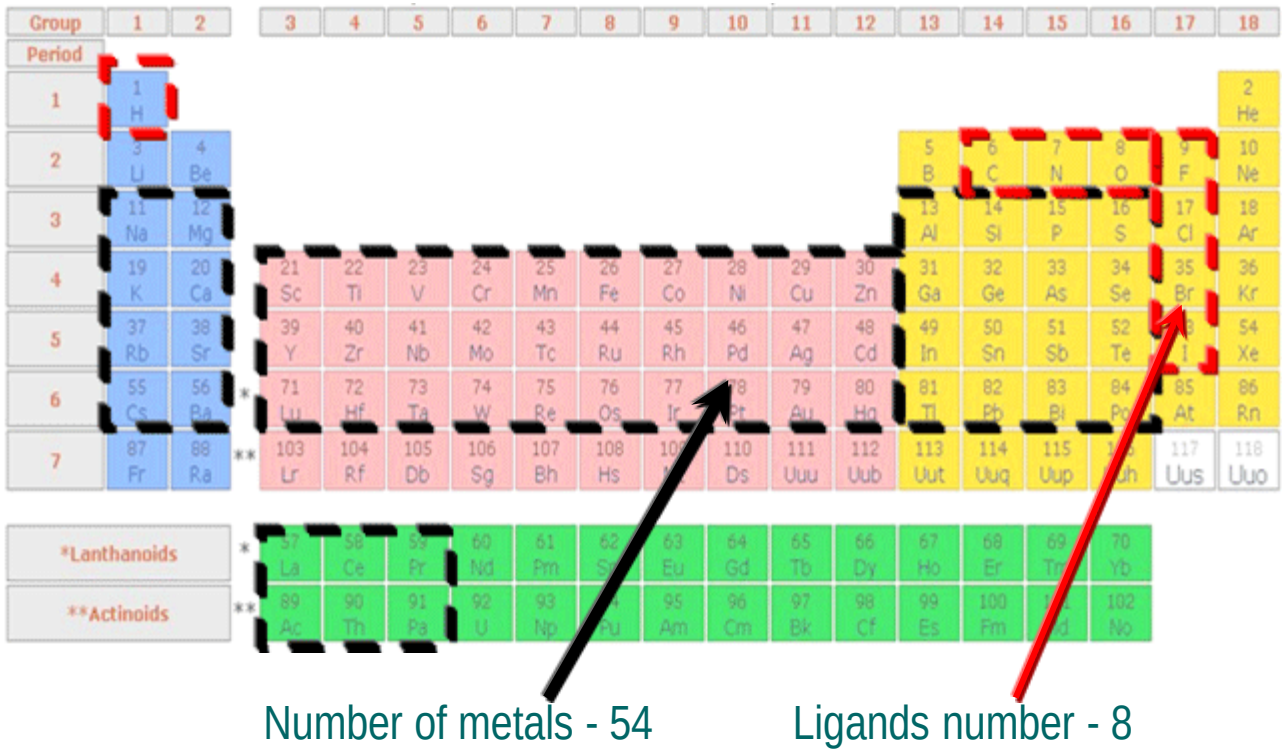
Advanced plasma light source

Theoretical Screening of Effective Emitting Substances in Fluorescent Plasma Light Sources

Goal: mercury free light source development



Emitting systems



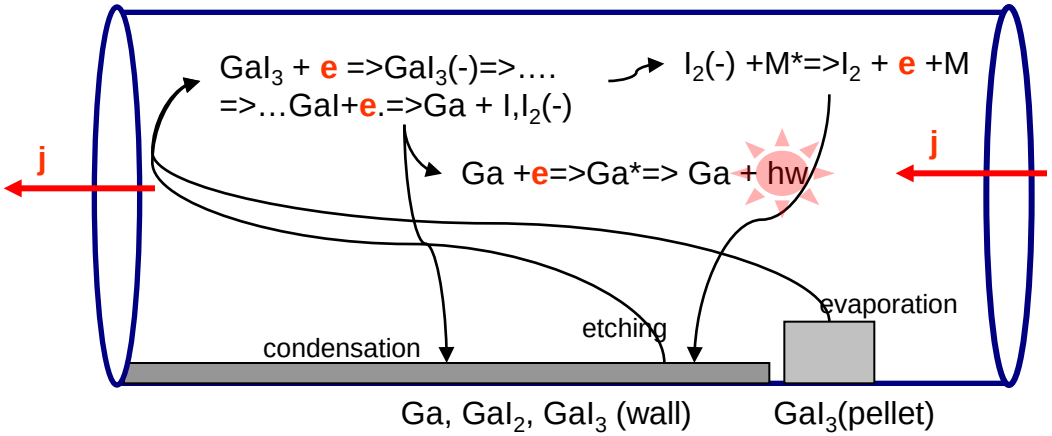
Problems

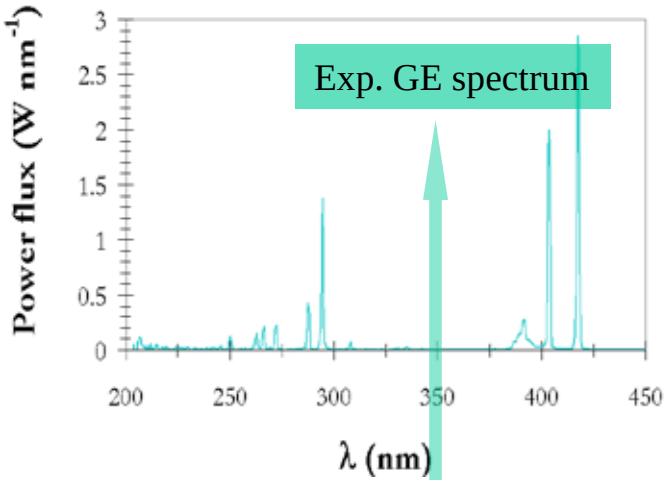
Large number of candidates

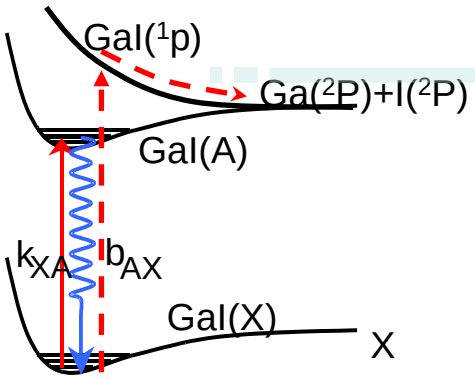
Number of system to explore: = 486

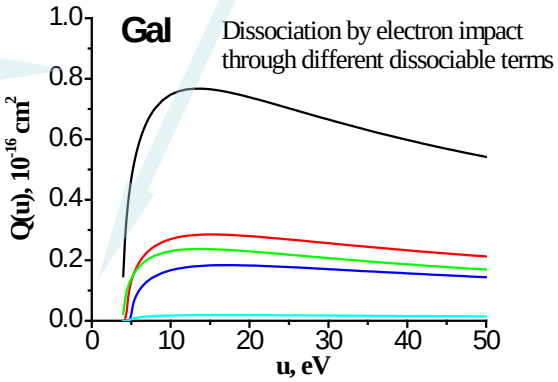
Advanced plasma sources of light

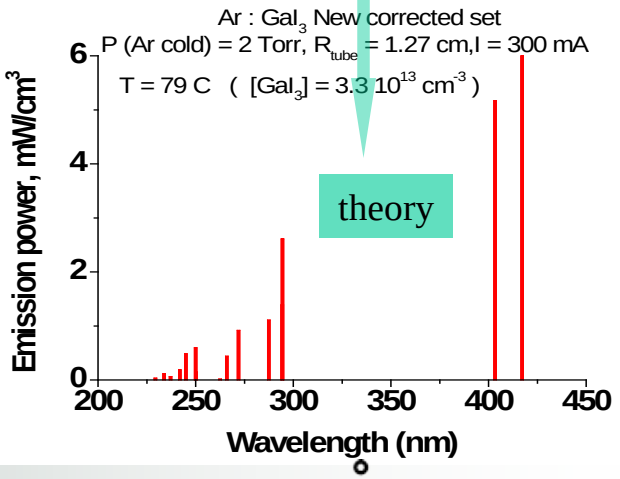
Hg-free lamps on metal halides non-equilibrium plasma











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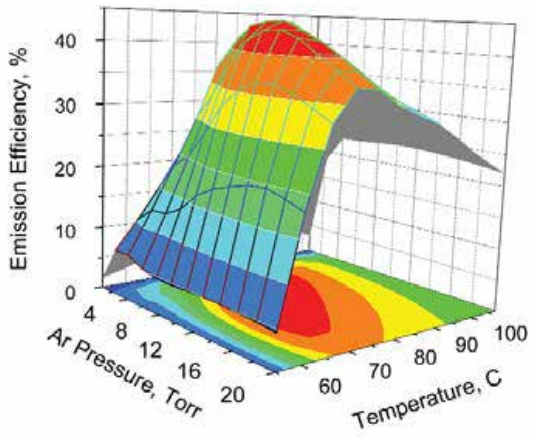
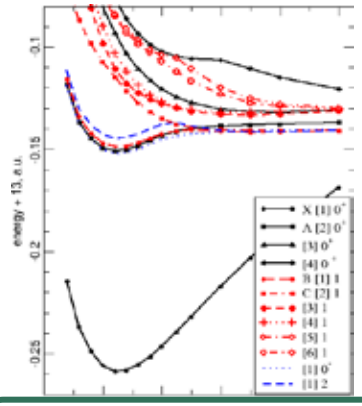
Non-empirical multi physics multi scale approach to calculation of the properties of chemically active nonequilibrium plasma



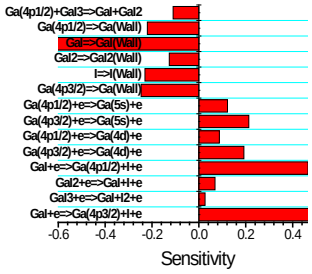
Recommendations

Plasma modeling for parameters optimization and processes control

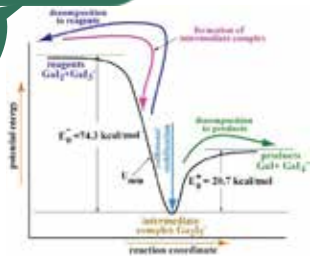
Construction and analysis of a physical - chemical mechanism



Evaluation of cross sections, rate constants, and radiation parameters



ab initio calculations of unknown parameters of atoms, molecules, and their interactions



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DATA ACQUISITION BY AB INITIO ELECTRONIC STRUCTURE CALCULATIONS

During the last decades computational electronic structure methods have become

- **competitive to experimental techniques in the accuracy of excited state energies (0.1 eV and better)**
- **often more accurate than experiment in transition probabilities, oscillator strengths**
- **reliable source of information on the states & transitions difficult for experimental studies**

Highly accurate but expensive *ab initio* methods (coupled-cluster like)

Intermediate accuracy approaches (e.g. multireference perturbation theories)

Roughly approximate methods (e.g. time-dependent DFT)

EXCITED ELECTRONIC STATES OF MOLECULES

Highly accurate but expensive *ab initio* methods

<table>
<tr><td>Approximate MultiReference Coupled Clusters = size-consistence corrected configuration interaction (MR AQCC, ACPF)
Columbus, Asec 3</td><td rowspan="3">Small (2-3 non-H atoms) molecules

Excitation energies:
< 0.1 eV errors

Oscillator strengths:
± 10-20 % and better</td><td>Exhaustive info on low-lying states of small light-element molecules</td><td></td></tr>
<tr><td>Response / Green function techniques
Dalton, Gaussian, Molpro
Cfour, Asec 3</td><td rowspan="2">Molecules with simple shell structure (closed-shell or one open shell)</td><td></td></tr>
<tr><td>Fock-space coupled cluster methods
Asec 3</td><td>Relativistic formulations for heavy-element compounds available</td></tr>
</table>

EXCITED ELECTRONIC STATES OF MOLECULES

Intermediate accuracy approaches

Multiconfiguration perturbation theories (PT): CASPT2 etc Molpro, Molcas Firefly, Games	Small & medium size molecules (~10^1 non-H atoms) Excitation energies: ~ 0.1 eV accuracy	Scanning of potential surfaces (fails in certain areas)	
Multireference (effective-Hamiltonian) many-body Perturbation Theory (PT): quasidegenerate PT (MCQDPT) multipartitioning PT Etc Efop	Oscillator strengths ± 10-30 % (MCQDPT, MPPT)	Scanning of potential surfaces & transition moments for states of any nature	Relativistic formulation of MPPT exists

EXCITED ELECTRONIC STATES OF MOLECULES

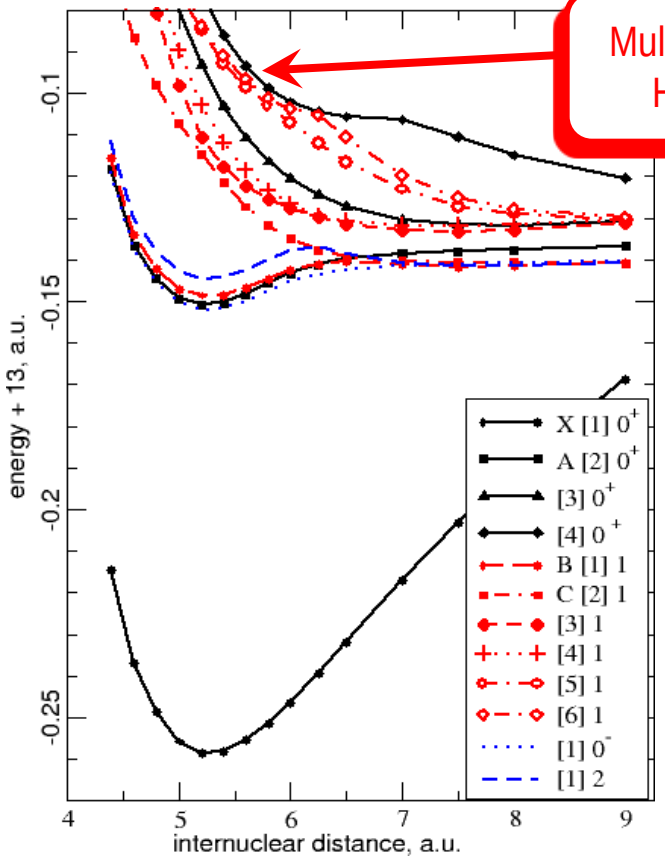
Roughly approximate methods

Time-dependent DFT Gaussian, ADF, etc	Medium size (MCSCF) and large (~10^1 non-H atoms) molecules Excitation energies: ~1 eV accuracy (TD DTF – often much better) Oscillator strengths: qualitative	Main way to study excitations for large molecules; useful for geometry optimization of excited states
Multiconfiguratinal Self Consistent Field (MCSCF) Gaussian, Molcas, Molpro		
Time-dependent Hartree-Fock (TDHF) CI / singles (CIS) All the codes		

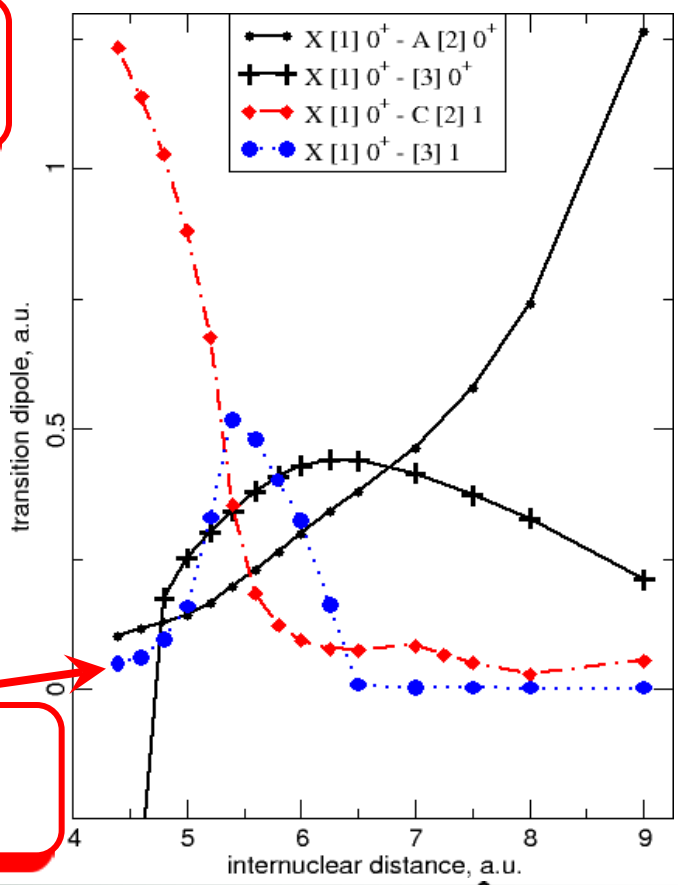
Theory & modeling highlights for electronically excited states

Accurate (< 0.1 eV) first-principles calculations of electronically excited states are feasible!

Example excited states and transition dipoles of InI



Multiple avoided crossings
High states densities



Dependence on R
is non-trivial !

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GROUND ELECTRONIC STATES OF MOLECULES

Highly accurate but expensive *ab initio* methods

Multireference singles + doubles configuration interaction (**MR SDCI**) method	Small & medium size molecules (about 10 atoms)	Transition state (**TS**) of chemical reactions (term crossing)	Scalar relativity through relativistic effective core potentials (**RECPs**) for heavy element compounds *Not for the right lower corner of periodic table.*
Fourth-order Moeller-Plesset (**MP4**) level of perturbation theory Coupled Cluster calculations (**CCSD, CCSDT, etc**) Gaussian, Molpro, etc	Barrier heights and heats of reactions: accuracy of 0.1 eV	Accurate calculations of potential energy surface (**PES**) only in the vicinity of its stationary points *Too expensive for surface scan!*	
Quasi Additive Compound Methods (**CBS -** - Complete Basis Set Extrapolation methods; **G1, G2, G3** - Gaussian - 1, 2, 3 methods etc) Gaussian	Barrier heights and heats of reactions with accuracy of 0.1 eV for molecules containing up to 20 atoms	Highly accurate estimates for energies of molecular processes by combining several different approaches. *The cheapest ! To be verified first !*	

GROUND ELECTRONIC STATES OF MOLECULES

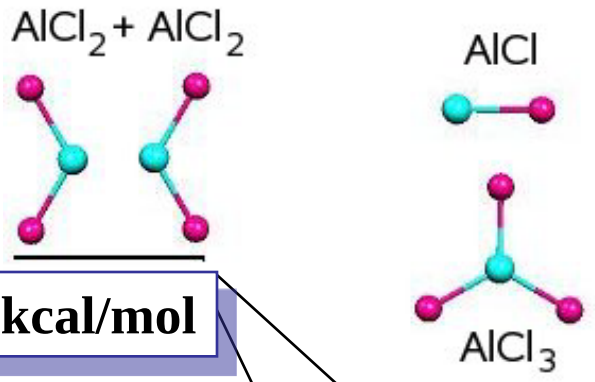
Intermediate accuracy approaches

<table>
<tr><td>Second-order Moeller-Plesset (MP2) perturbation theory
All the programs
Turbomol</td><td>Medium size molecules (10-100)</td><td rowspan="2">Scanning of PES & evaluation of various properties of molecules and chemical reactions
accuracy of 0.2 eV – 0.3 eV and can be less
For the Ga and In systems MP2 was proved to give 0.1 eV accuracy</td><td rowspan="2">Spin-orbit DFT method taking into account relativistic effects for adequate description of molecular parameters for heavy element compounds</td></tr>
<tr><td>DFT Methods (GGA and hybrid functionals)
All the programs
Accelrys</td><td>Medium size & large (hundreds of atoms) molecules</td></tr>
</table>

ACCURACY OF AB INITIO CALCULATED PROPERTIES OF MOLECULES AND CHEMICAL REACTIONS

Molecular property	Accuracy	
	Light element compounds (neglect the effects of relativity)	Heavy element compounds
Equilibrium interatomic distances	0.01 Å	0.01-0.05 Å
Bond angles	1 º	1 – 3 º
Vibrational frequencies	1 – 3 %	5 – 10 %
Dipole moments	0.1 *D*	0.2 – 0.5 *D*
Polarizabilities	10 %	10 – 30 %
Barrier heights and heats of reactions	1 - 2 *Kcal/mol*	5 – 10 *Kcal/mol*
First ionization potentials and electron affinities	0.1 *eV*	0.2 – 0.5 *eV*

EXAMPLE: ENTHALPY OF REACTION 2AlCl2 -> AlCl + AlCl3



0 kcal/mol

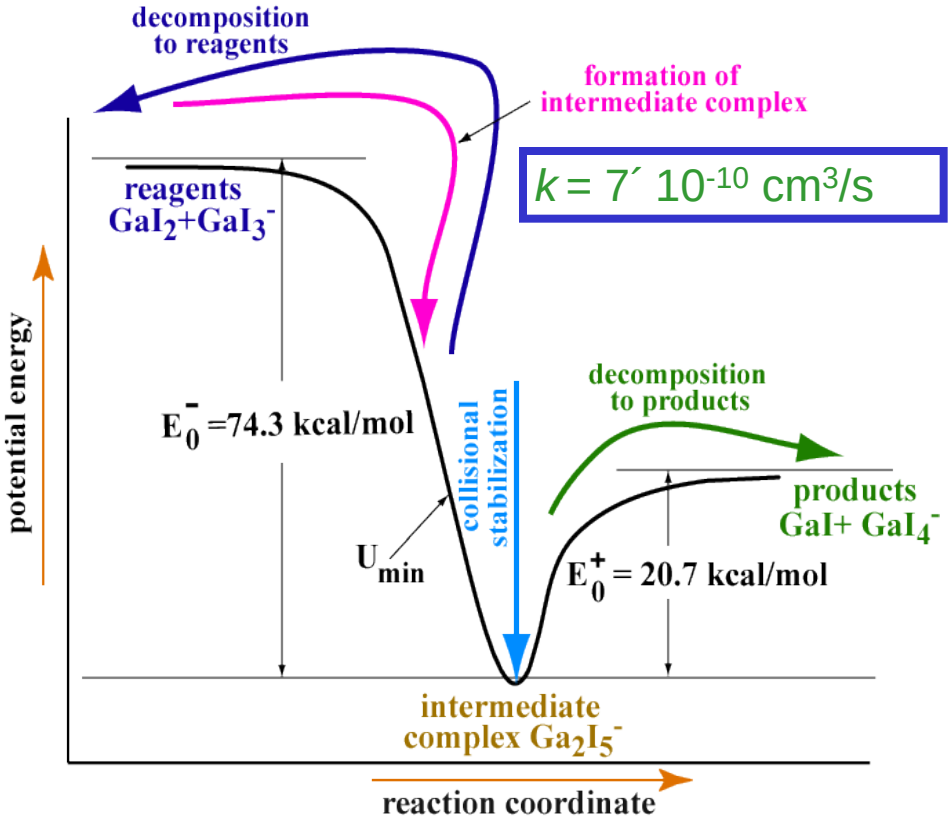
-18 kcal/mol (old experimental value, NIST)

-42 kcal/mol (our ab initio estimate)

- **$AlCl_2$ enthalpy of formation value was revised (-67.0 to -57.1 kcal/mol)**
- **New experimental estimate for reaction enthalpy -37 kcal/mol**

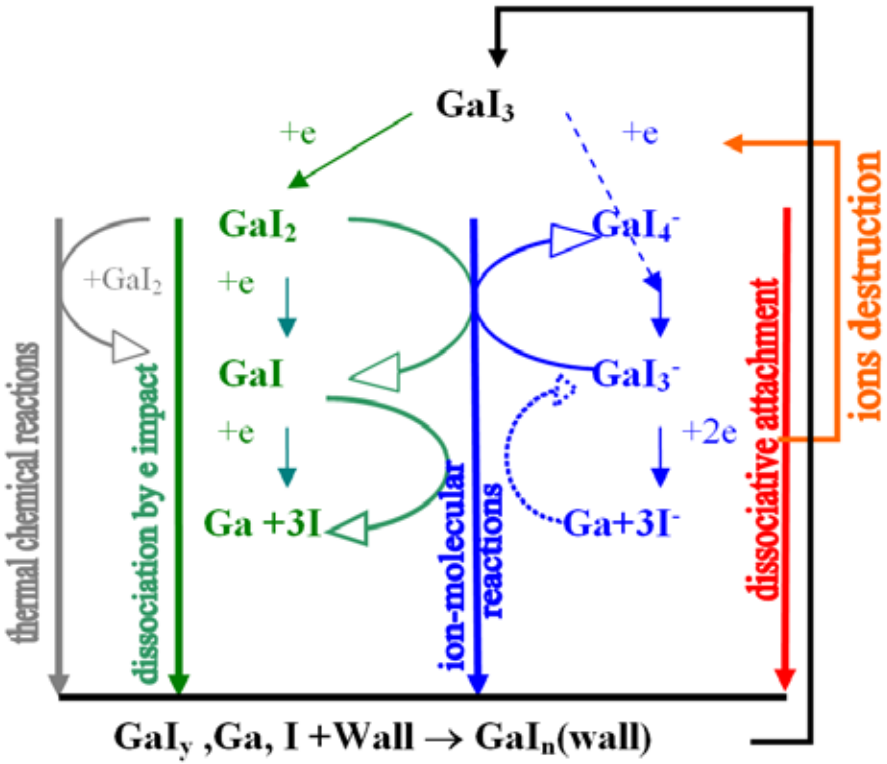
Calculation of reaction rates coefficient and kinetic mechanism build up

Reactions rate coefficients calculation



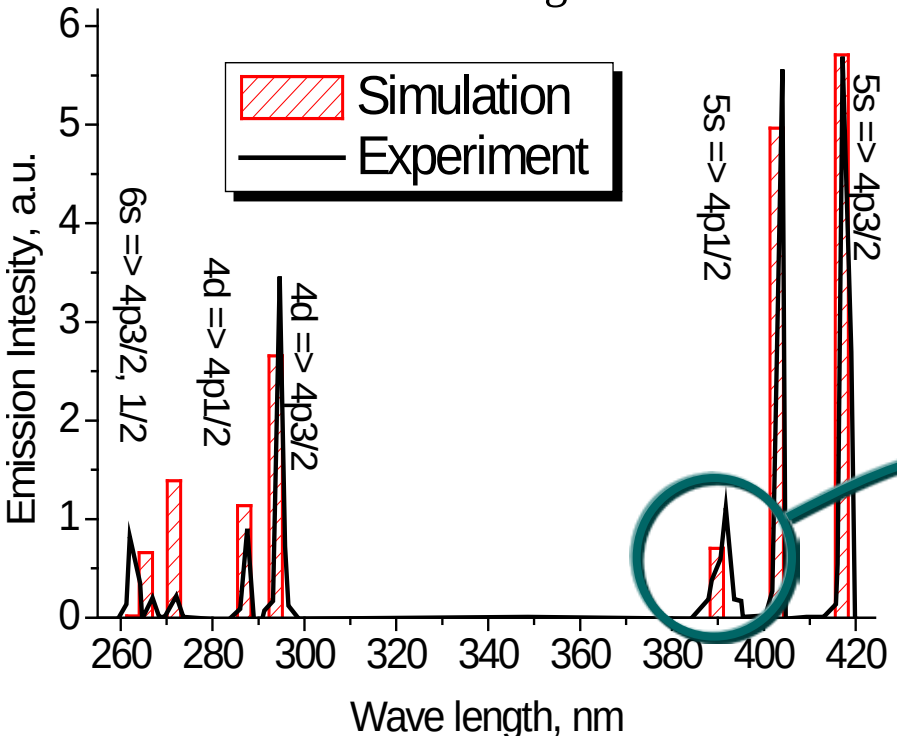
Reaction profile GaI_2+ GaI3$^-$ ® GaI + GaI_4^-

Mechanism development



Non-empirical approach to calculation of the properties of chemically active nonequilibrium plasma: validation

Atomic Emission Ar-GaI3 System
Glow Discharge



Molecular Emission Ar – GaI3 System
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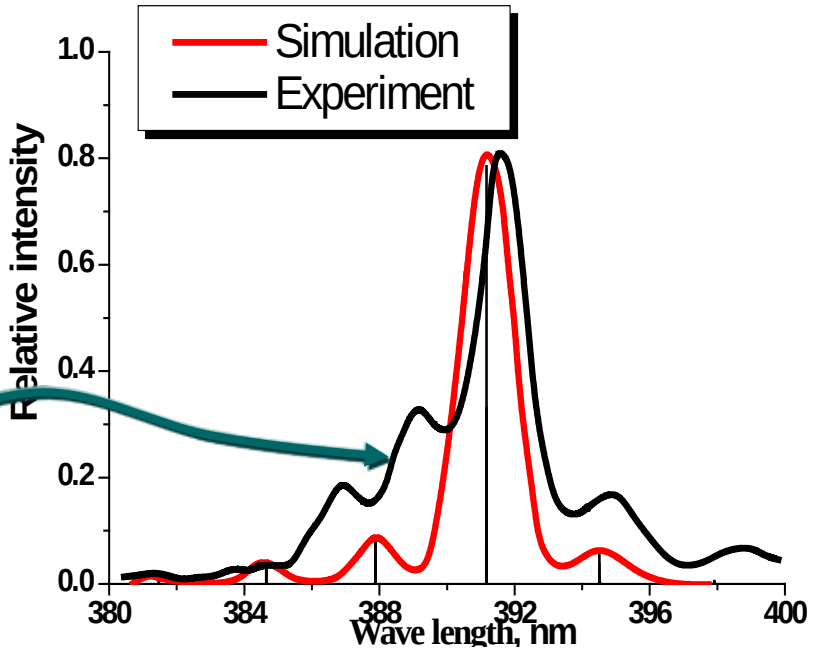

Predictive system models & understanding can be built up from first-principles estimates of underlying physical & chemical kinetics

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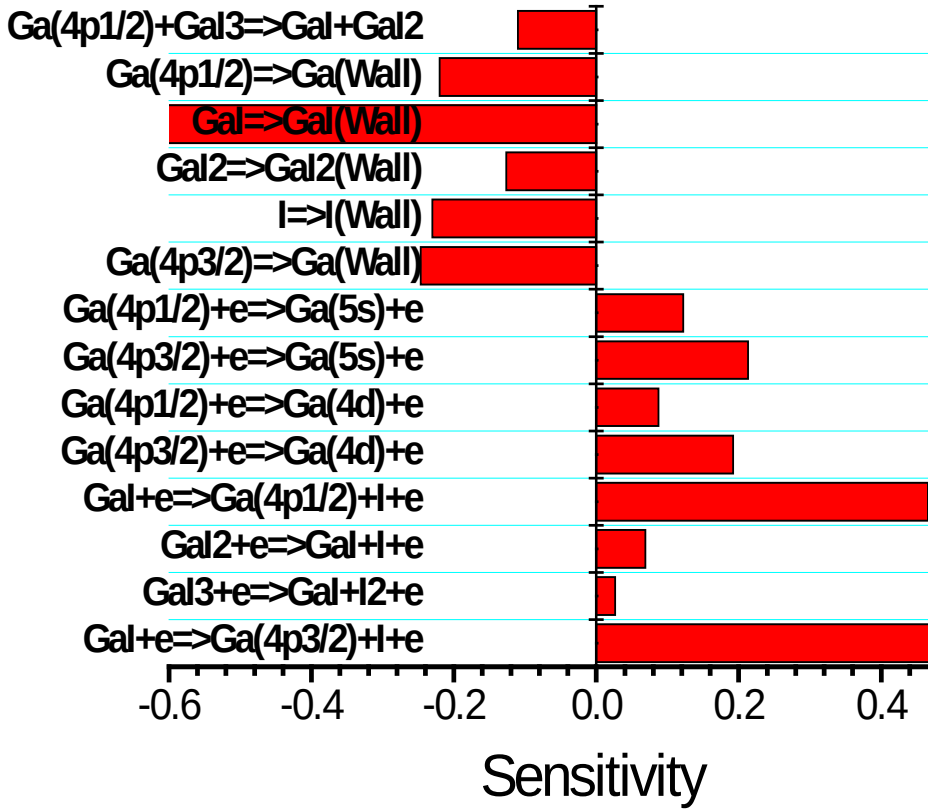
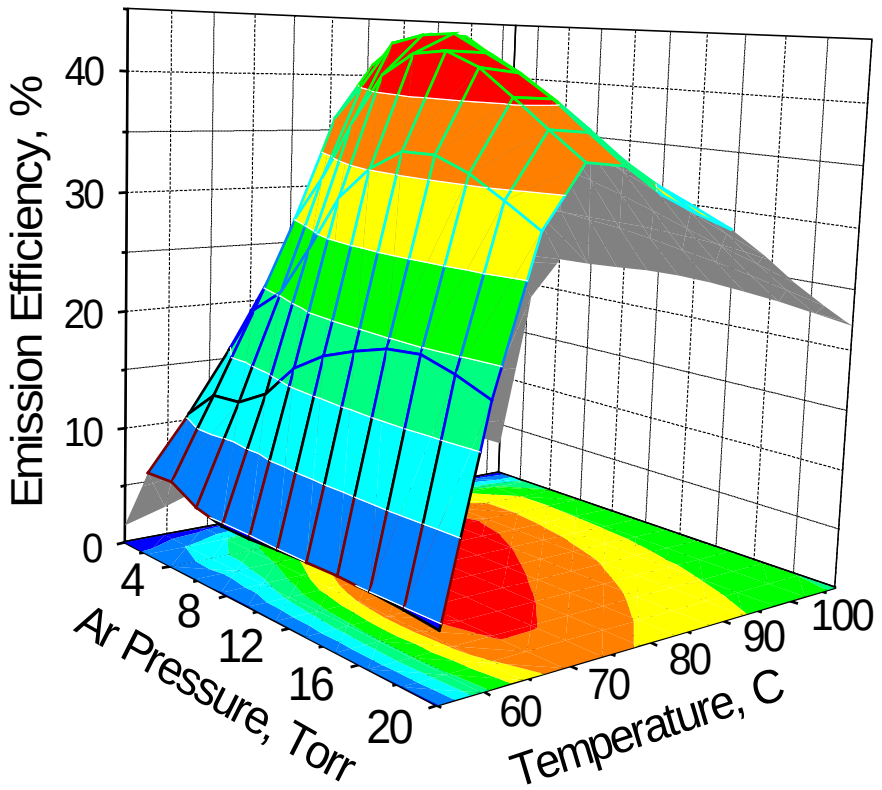
Sensitivity analysis and parameters optimization

Sensitivity analysis:
why calculation we can be predictive



Discharge parameters optimization



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Predictive multi scale modeling based on HPC for energy and materials: specific projects

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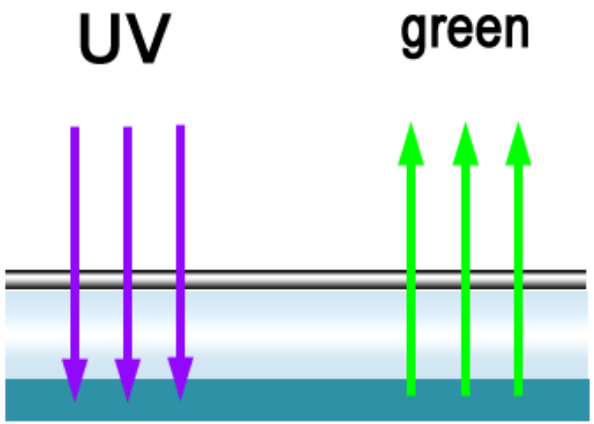
Theoretical screening of advanced phosphors

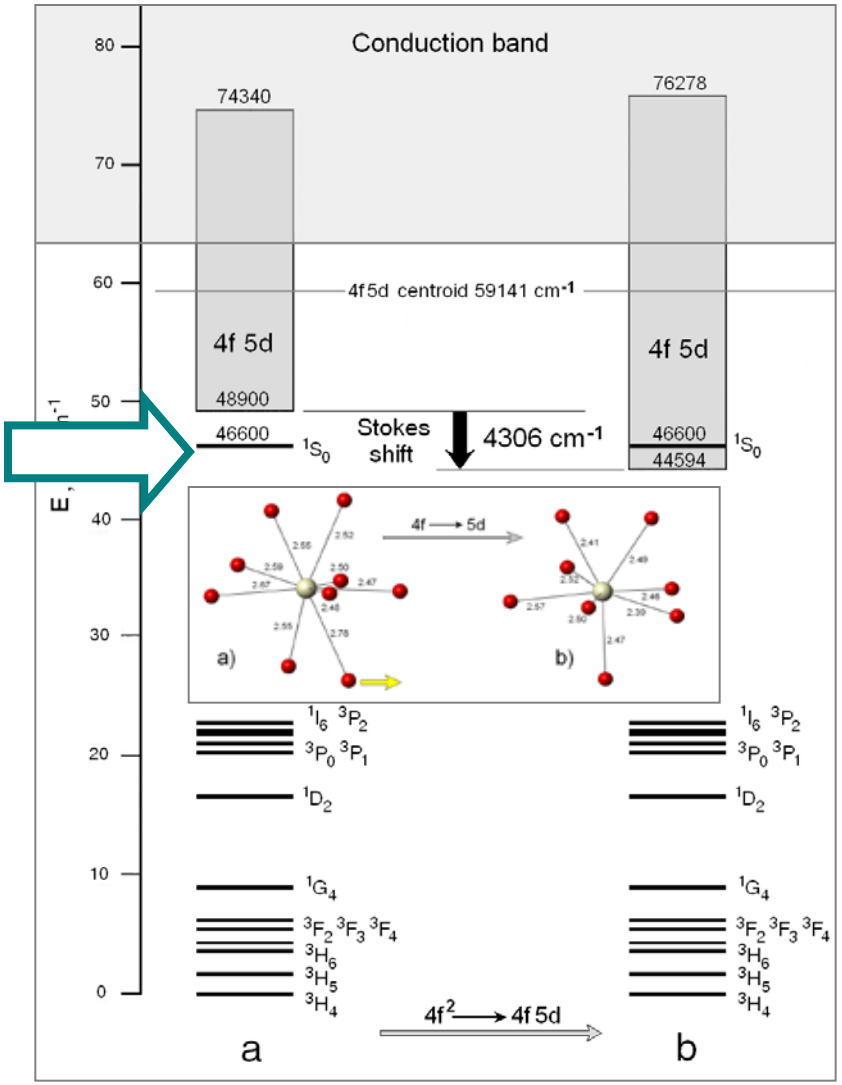
Modeling of phosphor properties

Optimization of conversion efficiency of phosphors

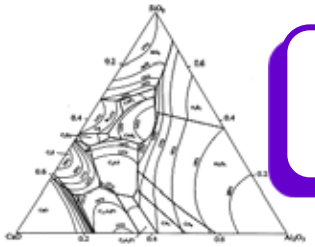
Search and selection of best phosphors with prescribed properties



Large Stockes shift of 5d states in the $LaPO_4:RE^{3+}$ and $YF_3:RE^{3+}$ phosphors is related to considerable changes in the coordination number of the rare-earth site upon the 4f ®5d excitation

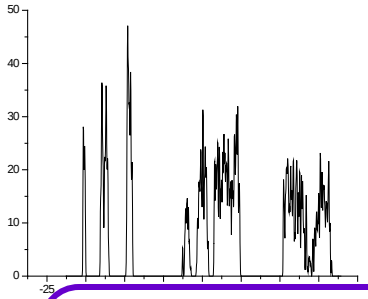


Modeling of phosphor properties

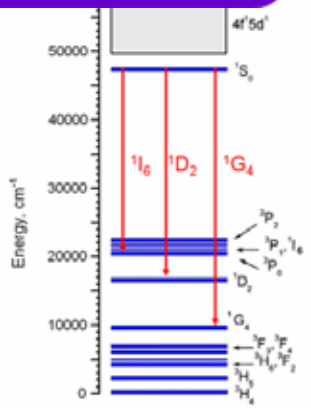


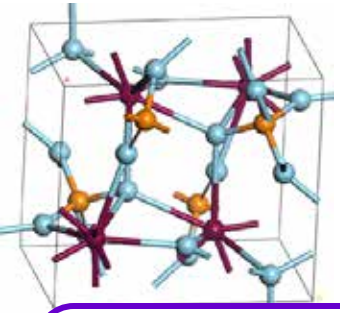
Термодинамический анализ материала

Расчет спектров поглощения и испускания, интенсивности и других свойств люминофора

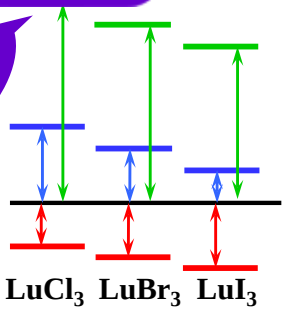


Расчет миграции и захвата возбуждений



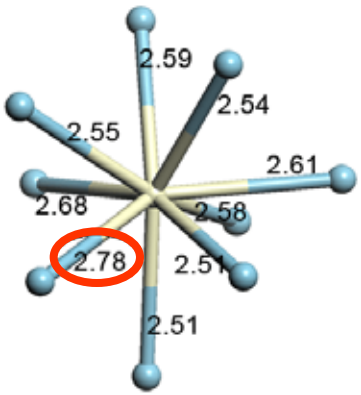


Первопринципный расчет электронной структуры материала

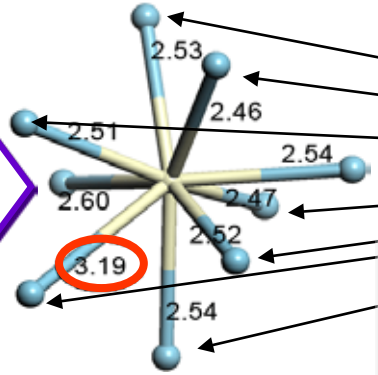


Восстановление структуры материала из дифракционных данных

Modeling of phosphor properties



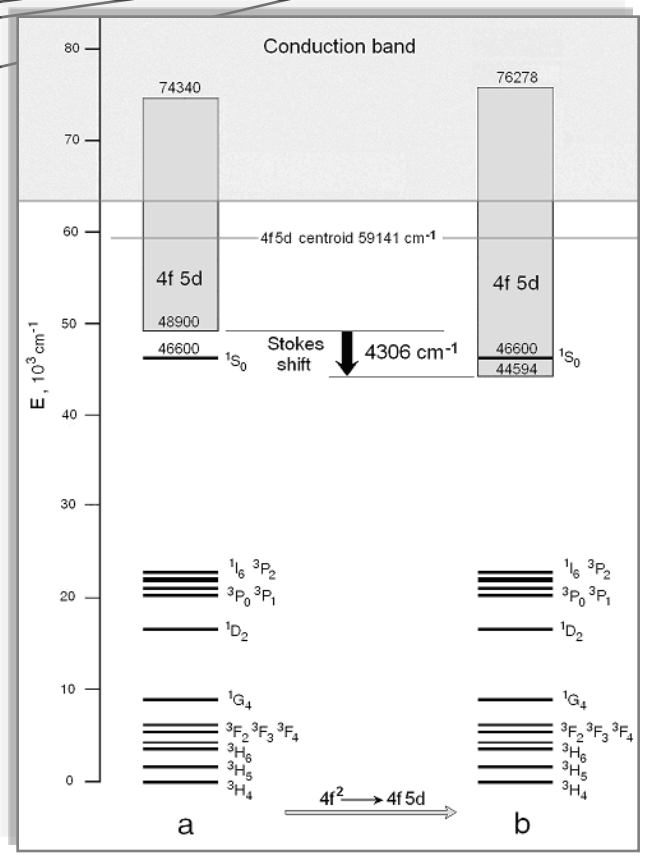
Coordination number of Ce in $LaPO_4$ changes from 9 to 8



$$V_{CF} = \sum_{k}^{ligands} v(k)$$

Calculated Stocks shifts

Host/dopant	Calc (cm^{-1})	Exp (cm^{-1})
$LaPO_4:Ce^{3+}$	5050	4884
$LaPO_4:Pr^{3+}$	4300	-
$YF_3:Ce^{3+}$	5100	5444
$GdF_3:Ce^{3+}$	5273	5567
$K_2GdF_5:Ce^{3+}$	2005	2227



KINTECH LABORATORY

Predictive multi scale modeling based on HPC for energy and materials: specific projects

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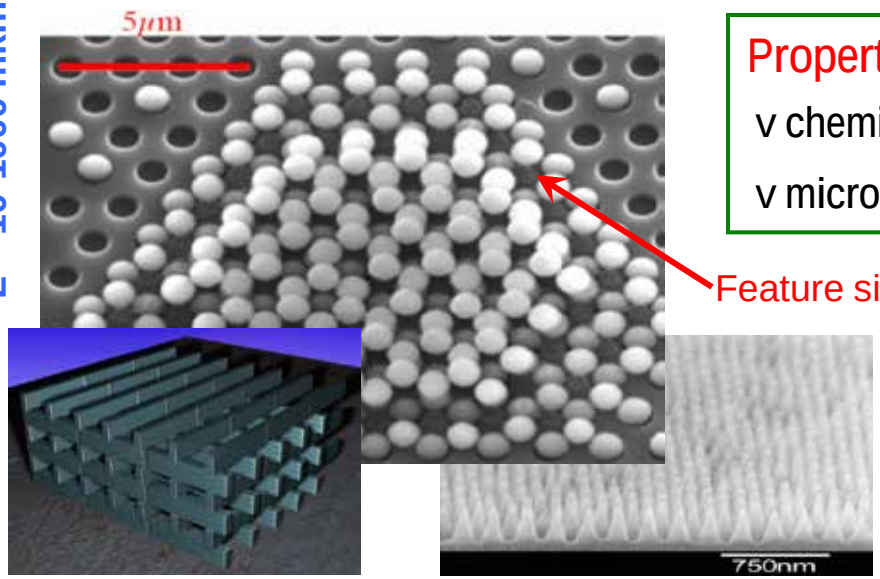
A priory design of Photonic Metamaterials

Photonic metamaterials

L ~ 10-1000 mkm



Feature size l ~ 100 nm

Properties of photonic metamaterials are defined by:

- v chemical composition
- v micro- and nano-scale geometry !

Photonic metamaterials:

- v Modify radiation/reflection pattern
- v Enhance reflection in forbidden bands
- v Enhance emission in allowed (transmission) bands
- v Reduce radiation in band gaps
- v Modify density of states

Applications:

- v New light sources emitting in controlled spectral region
- v Emission control for creation of new luminescent materials and device
- v Optoelectronics design of new nonlinear optical materials
- v Creation of new lasing media, photonic fiber laser
- v Mirrors, photonic waveguides, couplers and multiplexers
- v Beam shaping, new types of fibers
- v New elements for near field optics

$(L/l)^3 >> 10^6$: Parallel Code Development & HPC are of critical importance !

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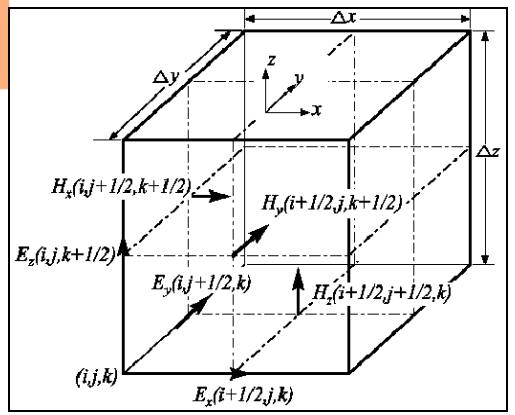
Parallel FDTD code for metamaterials design

Finite differences time-domain method (FDTD) & code

- Simulation of arbitrary geometry
- Simulation of materials with nonlinear material properties
- Simulation of E-M field distribution inside and outside the structure
- Simulation of oblique incidence on periodic structures
- Sensitivity analysis (modeling the impact of defects)

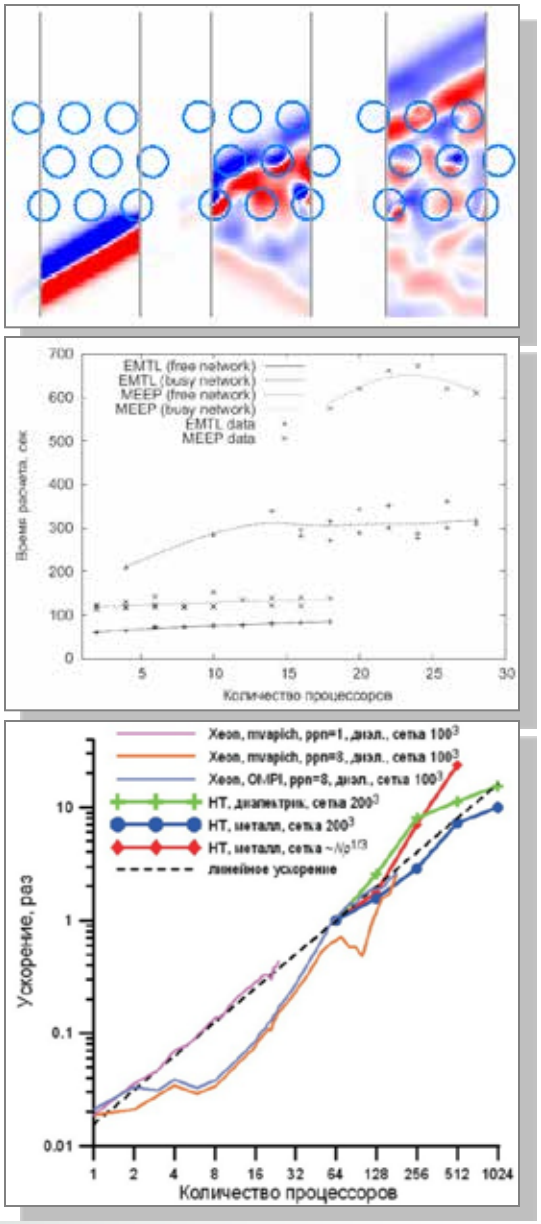


Applications

- New light sources emitting in controlled spectral region
- Emission control for creation of new luminescent materials
- Optoelectronics design of new nonlinear optical materials
- Creation of new lasing media, photonic fiber laser
- Mirrors, photonic waveguides, couplers and multiplexers
- Beam shaping, new type of fibers
- New elements for near field optics
- Creation of photonic materials with electrically or mechanically controlled characteristics
- New left handed materials

Electromagnetic Template FDTD Library underlining FDTD code

- Novel computational methods within FDTD in EMTL:
  - Subpixel smoothing for dispersive media, for reducing the staircasing affects of the media interfaces on a regular grid
  - Iterative technique for simulation of oblique plane wave incidence on a periodic structure
  - The method of calculation of the frequency transfer matrix by FDTD for simulation of optical properties of multi-layered periodic structures
- EMTL is a parallel library (MPI, Open MP)
- Cross platform
- High computational efficiency for arbitrary problem geometries is achieved by balanced domain decomposition
- Linear parallel scalability even for large numbers of processors



- *A. Deinega and I. Valuev, Optics Letters 32, 3429 (2007)*
- *I. Valuev, A. Deinega, and S. Belousov, Optics Letters 33, 1491 (2008)*
- *A. Deinega, S. Belousov, and I. Valuev, Optics Letters 34, 860 (2009)*
- *A. Deinega and I. Valuev, Computer Physics Communications, to be published (2010)*

Numerical methods and programs for optical properties modeling

2. Layered Korringa-Kohn-Rostoker method (LKKR):

for spectra calculations of ideal photonic crystals with finite width
+ for band structure of ideal photonic crystals calculations
+ for density of photonic states calculations of ideal photonic crystals
+ taking into account experimental dielectric function (real and imaginary part) for any material
+ high speed and convergence of the method for scatterers with spherical symmetry

4. Ray-tracing method

+ for modeling of light propagation through the medium structured on the big scale (much bigger than the wavelength). The numerical realization of geometrical optics case.

3. Plane wave expansion method (PW):

+ for band structure of ideal photonic crystals calculations (1D, 2D and 3D symmetries)
+ for density of photonic states and local density of states calculations of ideal photonic crystals
+ arbitrary shape of scatterers

5. Effective media method

+ for modeling of light propagation through the random inhomogeneous medium with small impurities (much smaller than the wavelength). Effective refractive index instead of complex structured medium.

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Predictive multi scale modeling based on HPC for energy and materials: Advanced Light Source

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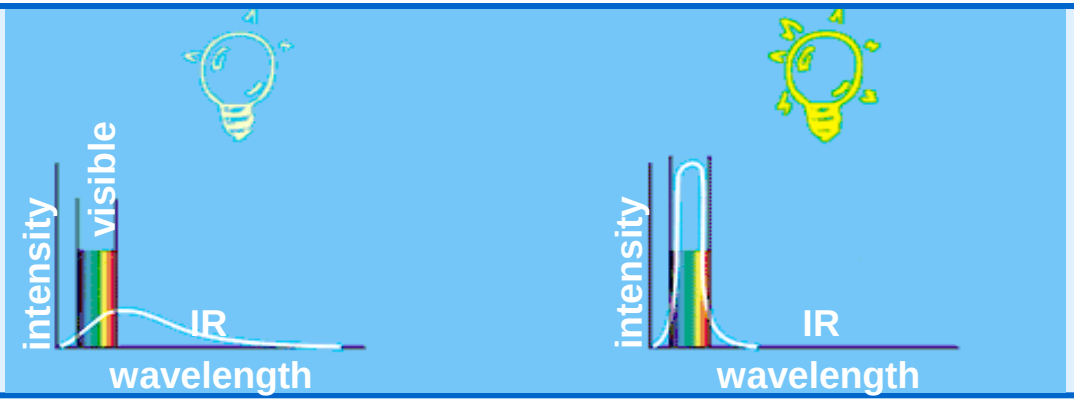
A priory design of Photonic Metamaterials

Computer aided design of advanced light sources based on photonic crystals

Motivation

Metallic photonic crystals offer a fine emission control – a way towards high efficiency light sources

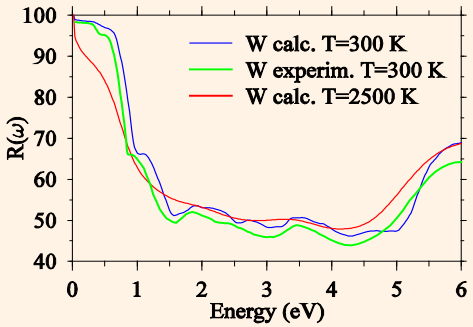


Problem to address

For maximizing efficiency of a light source optimizing photonic crystal material and geometry is of crucial importance. A priori modeling greatly reduces development time and costs. Modeling of photonic crystal optical properties combined with the first principle based modeling of material properties solves the problem.

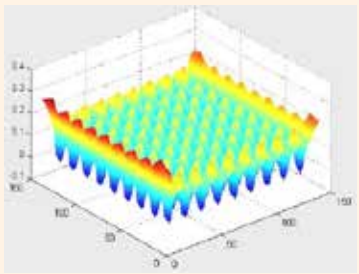
Solution

Kintech Lab and GE Global Research developed parallel FDTD code for CAD of materials and devices for nano-photonics and combined it with DFT method for material properties modeling.



First principle computation of material properties

Modeling and optimization of photonic crystal optical properties



imagination at work

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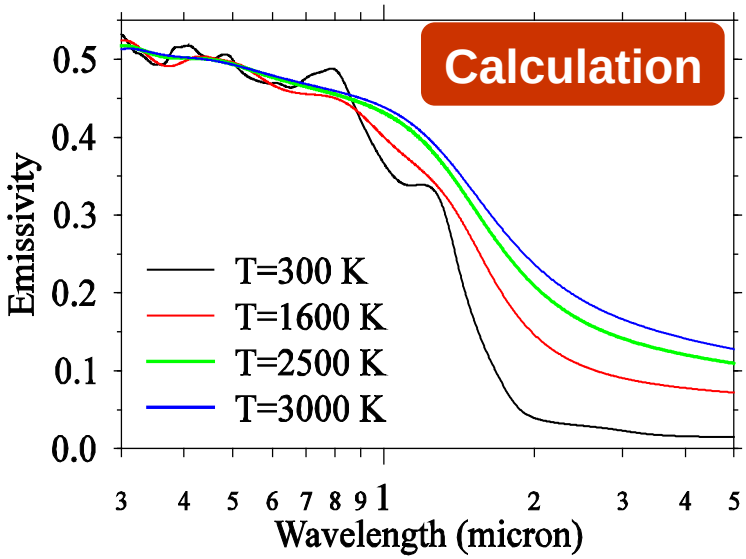
Calculation of material optical properties at high temperature

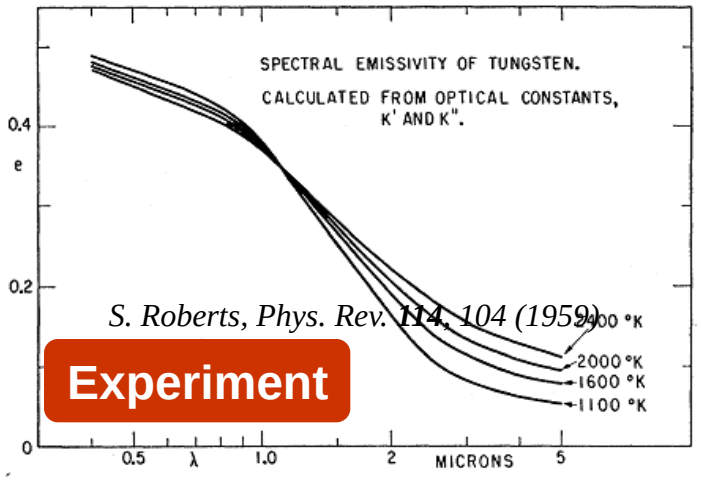
Modification of electron density function method (DFT)
(E. Maximov, UFN, 170, 1035 (2000))

Model takes into account:

- Ø Thermal expansion of solid bodies
- Ø Variations of electron occupation numbers with temperature
- Ø Interaction of electrons with
  - ü Lattice thermal vibration
  - ü Defects

1. Strong dependence of luminosity on the temperature
2. Good agreement with experimental data at high temperatures





S. Roberts, Phys. Rev. 114, 104 (1959)

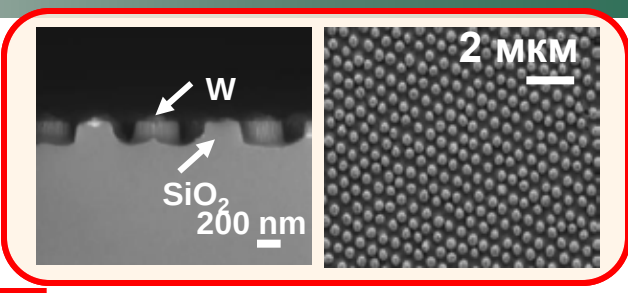
Computer aided design of advanced light sources based on photonic crystals

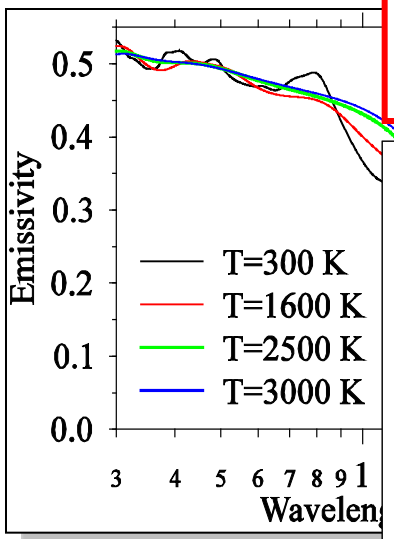
First principle computation of material properties

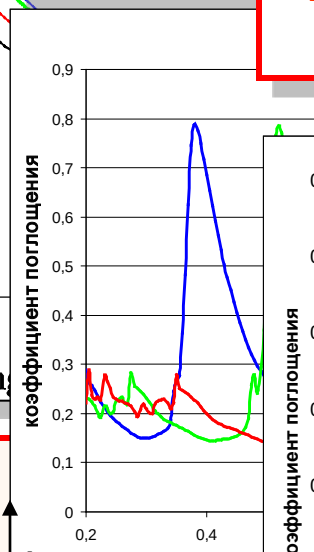
Modeling and optimization of photonic crystal optical

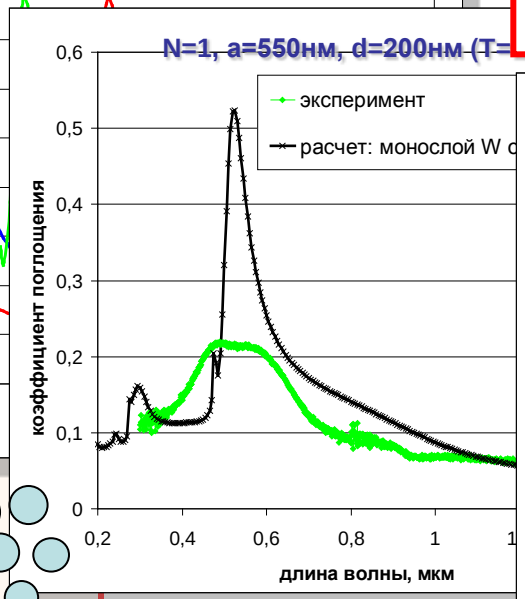
Taking into account defects of periodic structure

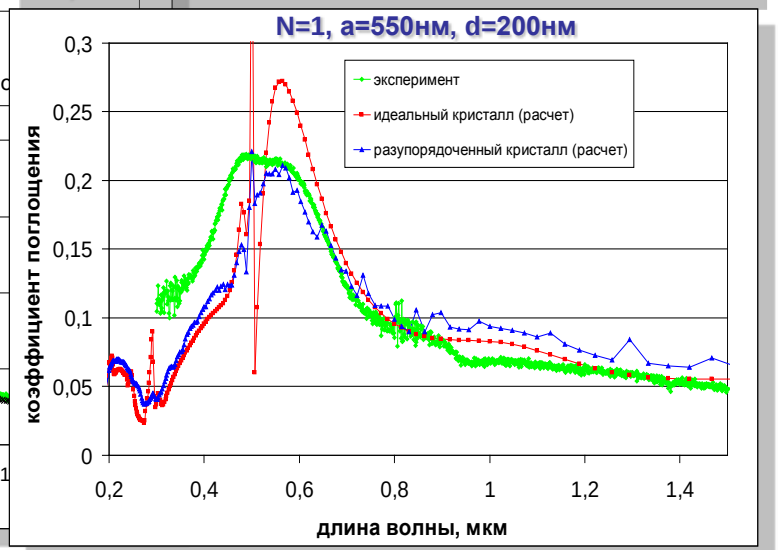
1. **Comparison to expt. data**
2. **Design rules**

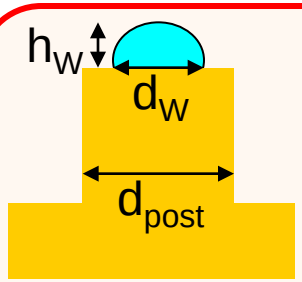


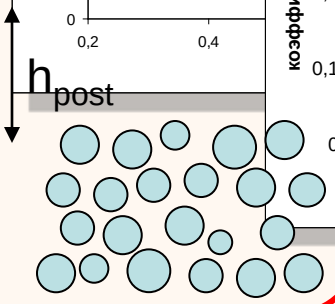












imagination at work

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Predictive multi scale modeling based on HPC for energy and materials: Antireflection Coating, OLED outcoupling

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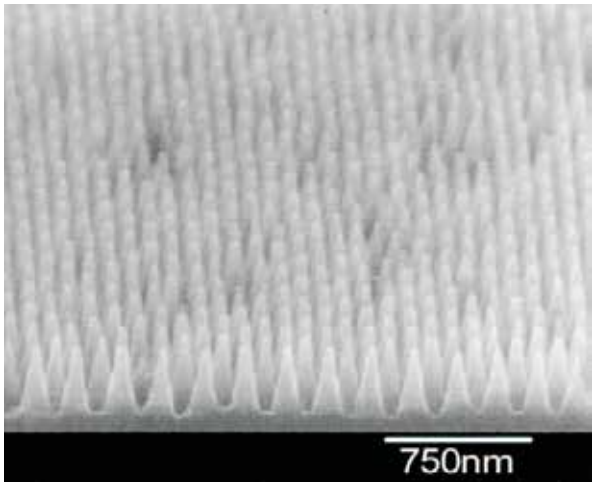
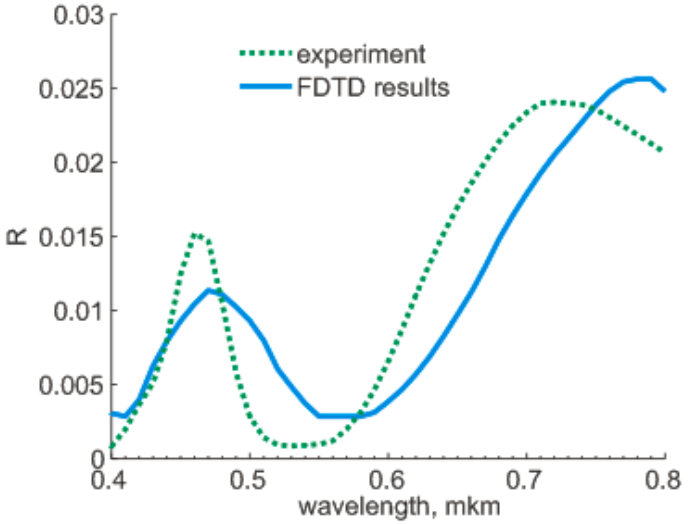
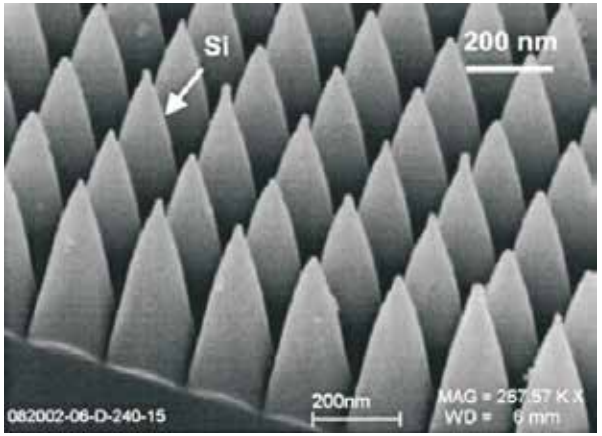
A priory design of Photonic Metamaterials

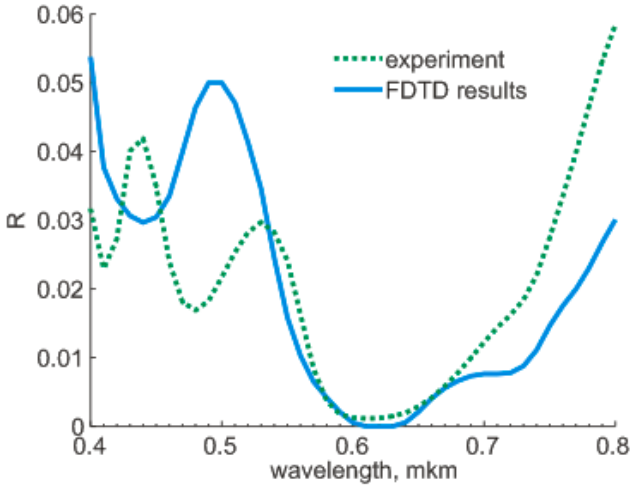
Numerical modeling and optimization of parameters for antireflection coating based on periodic surface nanostructured for solar batteries application





Y. Kanamori, M. Sasaki, and K. Hane, Opt. Lett. 24, 1422 (1999)





Zhaoning Yu er al., J. Vac. Sci. Technol. B 21(6), 2874 (2004)

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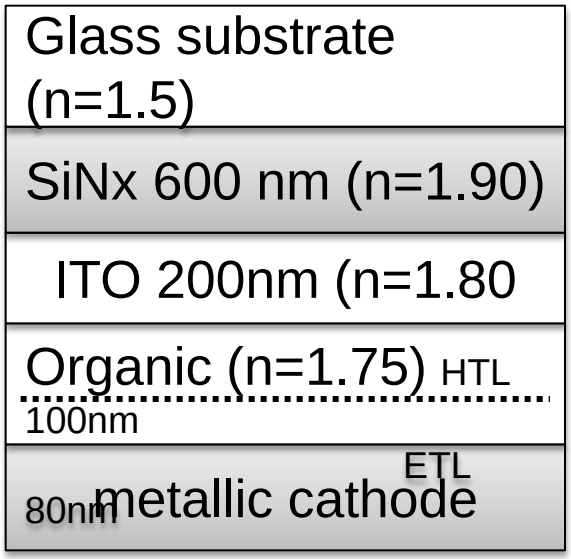
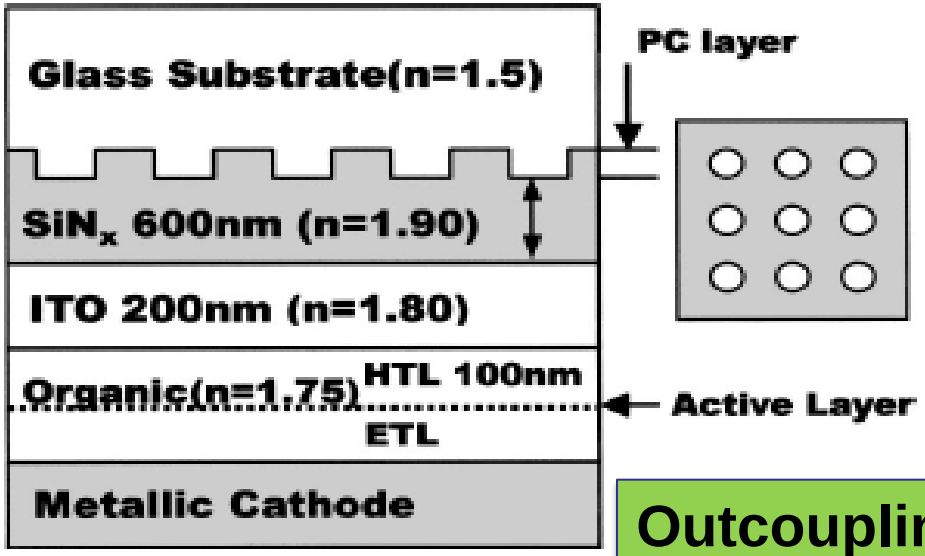
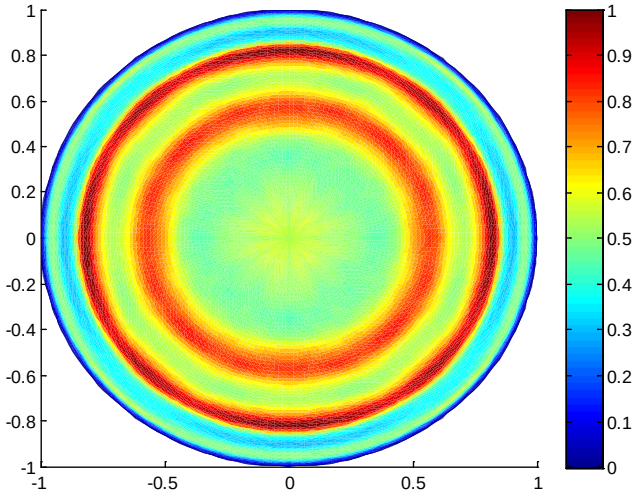
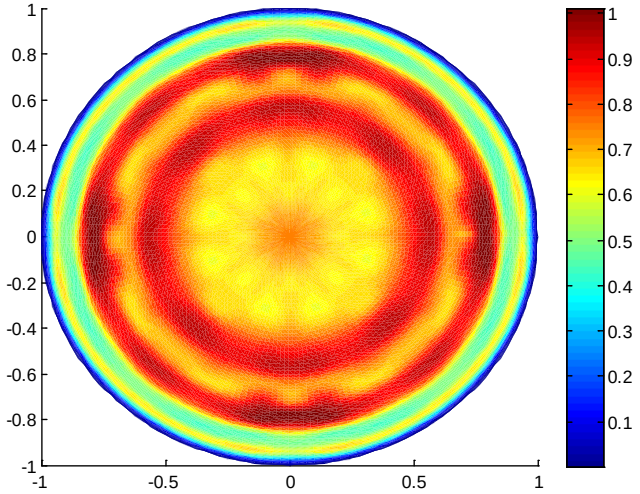
Modeling OLED outcoupling efficiency enhancement with 2D patterned PC structures

Far-field angular distribution of OLED structures





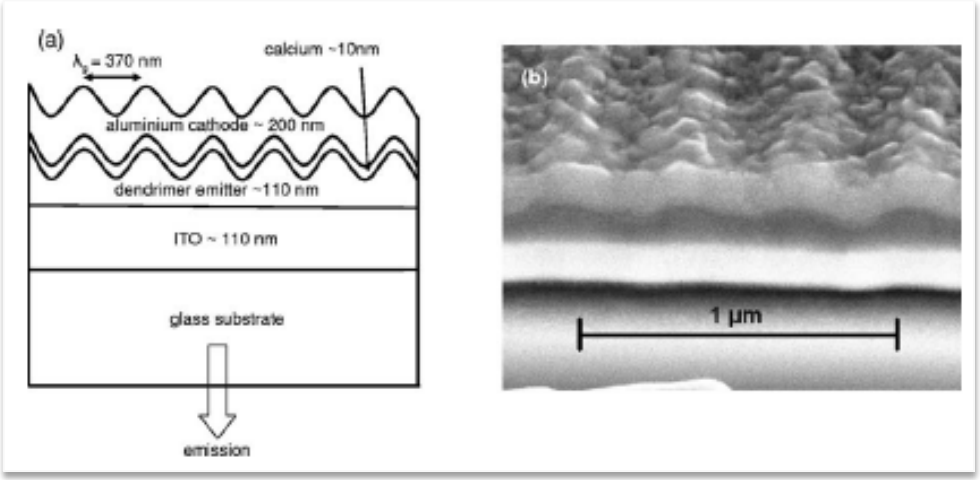




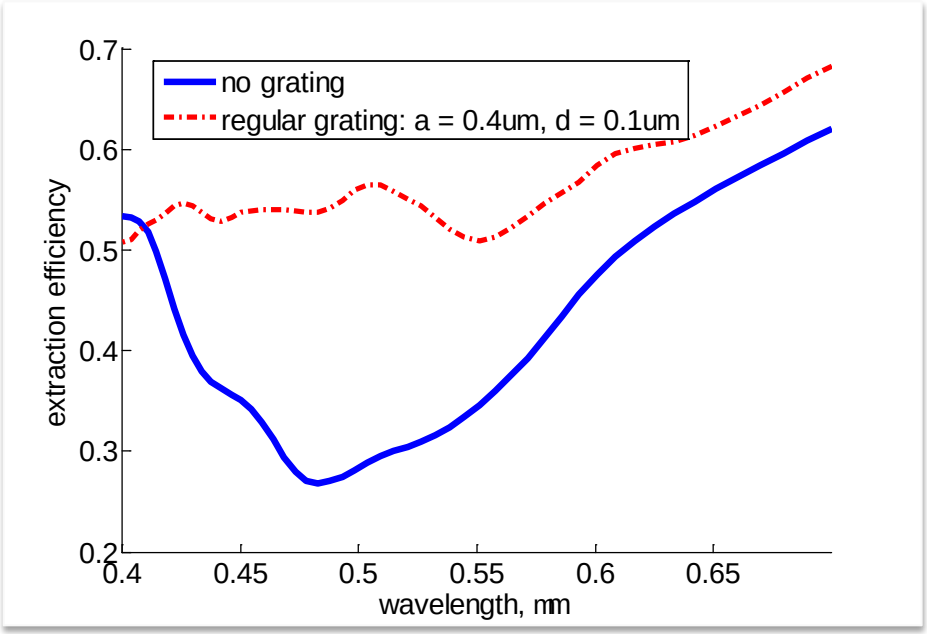
Outcoupling efficiency and directionality improvement!

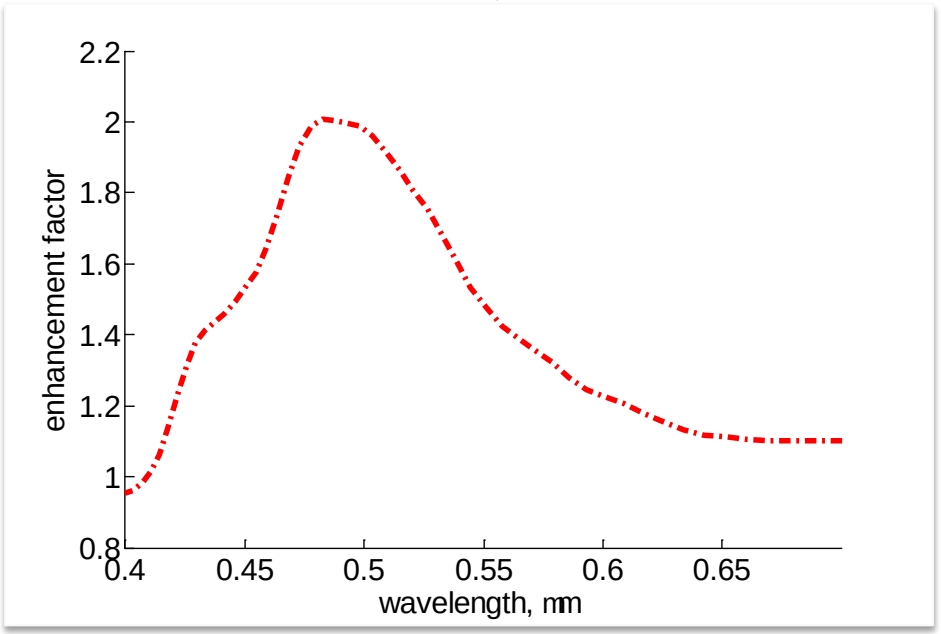
Ref: Y.-J. Lee et.al. "A high-extraction-efficiency nanopatterned organic light-emitting diode", Appl. Phys. Lett. 82, 3779 (2003)

Modeling OLED outcoupling efficiency enhancement with 1D cathode grating structures



Up to 2-3 times outcoupling efficiency enhancement





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Predictive multi scale modeling based on HPC for energy and materials: Optical Chemical Sensors

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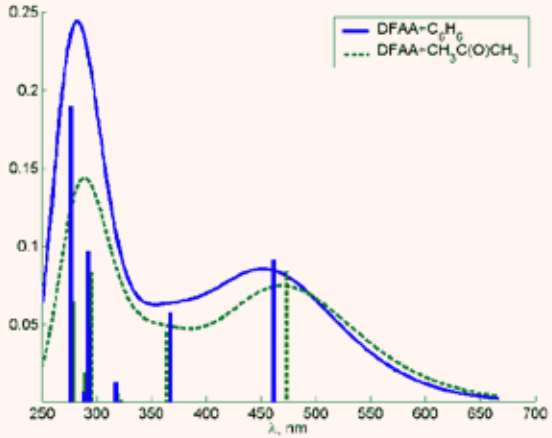
A priory design of Photonic Metamaterials

Photonic effects in chemical sensors

- Luminescence suppression and amplification on certain wavelengths with photonic band gap (PBG) and local density of state (LDOS) maxima in photonic crystals
- Local field enhancement in sensor layer
- Overall emission intensity enhancement due to effectively large surface area of a sensor layer
- Redistribution of the emitted light through the angles due to the scattering within nanostructured sensor layer
- Efficiency managing of the energy transfer between donor-molecule and acceptor-molecule
- Light entanglement effect for the absorption enhancement
- Photonic crystal based antireflection coating usage for pump radiation enhancement

- *W. Zhang et.al., Sensors and Actuators B: Chemical Vol.131, N1, p.279 (2008)*
- *H.J. Kim et.al., Sensors and Actuators B: Chemical Vol.124, N1, p.147 (2007)*
- *Z. Yang et.al., Optics Letters, Vol. 33, 17, pp. 1963-1965*
- *B. Kolaric et al, Chem. Mater. 19, 5547 (2007)*
- *K. Shibata et al, Colloid Polym. Sci. 285, 127 (2006)*
- *Carl Hägglund et al, Appl. Phys.Let. 92, 013113 (2008)*
- *L. Tsakalakos et al, Appl. Phys. Lett. 91, 233117 (2007)*

Chemical sensor: multiscale approach based on *Ab initio* Q-chemistry and electro-magnetic predictive modeling



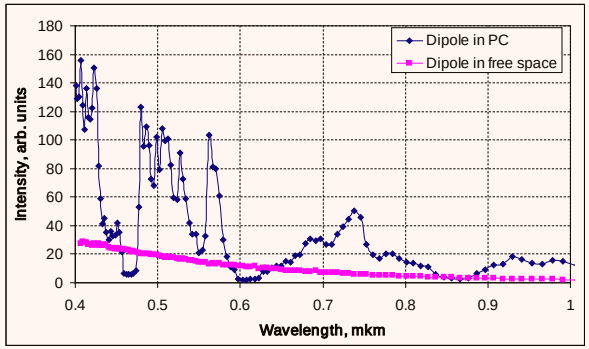
Absorption lines shape for definilaminoacredine complexes with acetone and benzol

Optical response of the sensor layer calculation

FDTD modeling of electromagnetic field distribution in sensor layer and calculation of supramolecular centers radiation within photonic crystal

Computation of absorption and fluorescence lines shape of molecular complexes

TDDFT computation of absorption and fluorescence lines of supramolecular centers

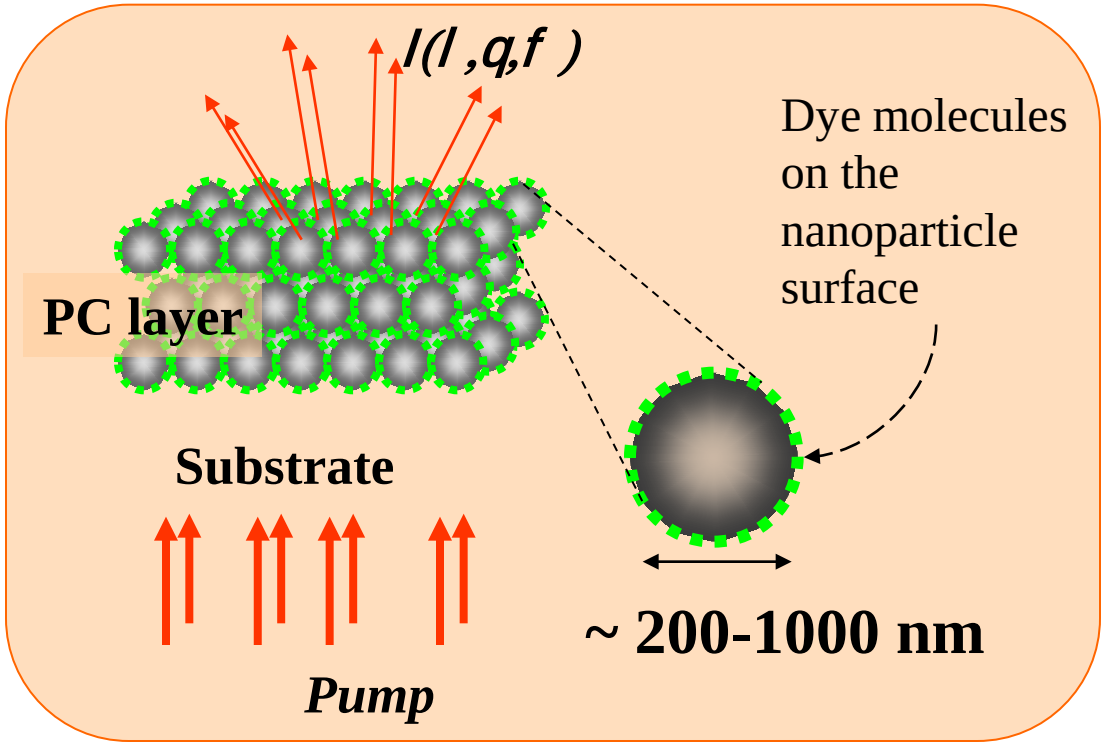


Fluorescence intensity of free molecule in vacuum and in photonic crystal

Chemical sensors: numerical modeling of the optical response

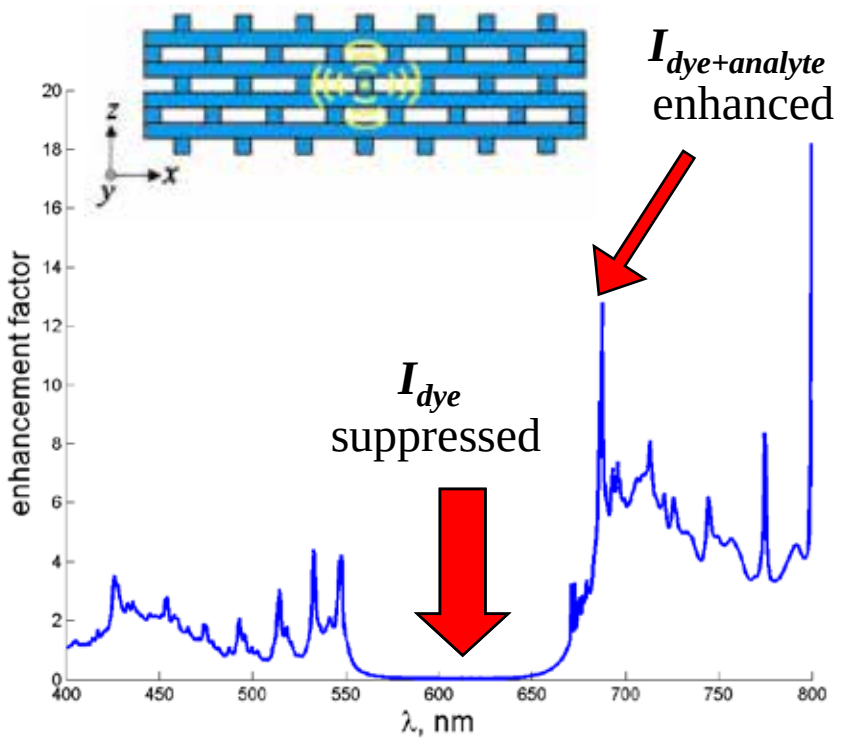
Model parameters:

- Structure geometry:
  - lattice type
  - size of elements
  - number of layers
- Material properties $\varepsilon(\nu)$:
  - elements optical properties
  - medium optical properties
  - substrate optical properties
- Dye molecules spectra
  - absorption
  - luminescence

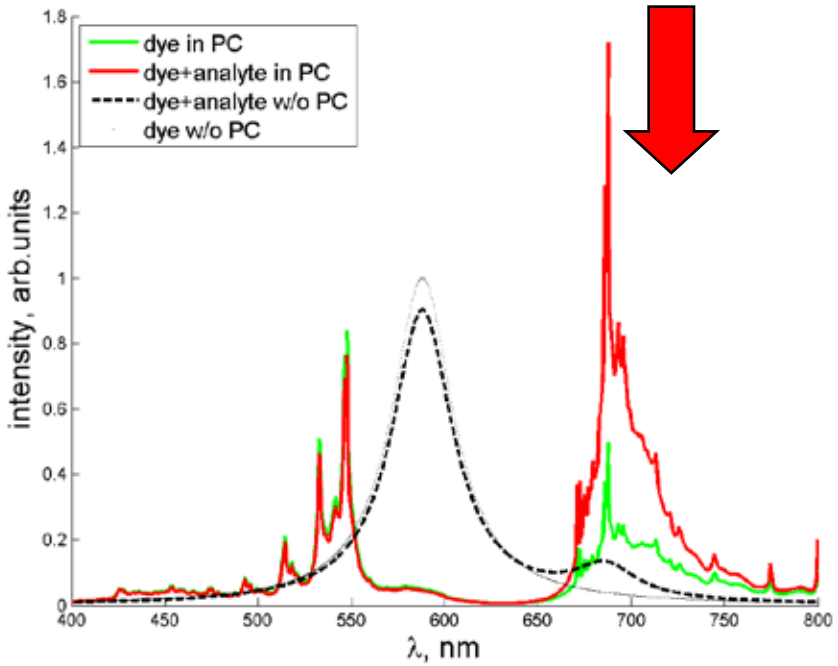


Setting parameters → Pump wave propagation → Excitation of supramolecular complexes proportional to the local field intensity → Luminescence in photonic crystal structure

Numerical modeling of the optical response in optical chemical sensors



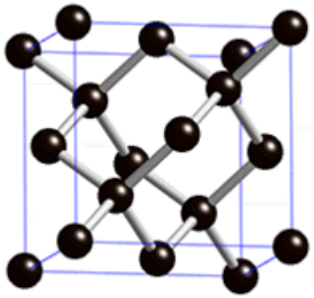
Response
enhanced >10 times



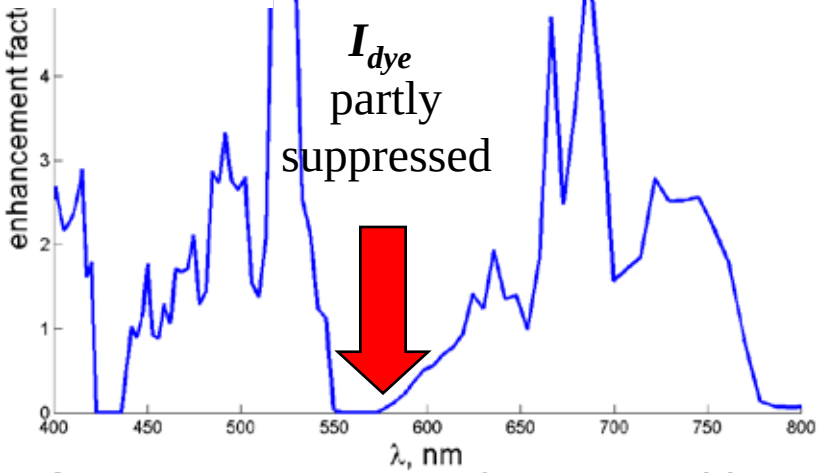
PC parameters: a = 279 nm, h = w = 69.77 nm

Log-piles: enhancing dye+analyte peak by band-edge resonance, suppressing free dye peak by PBG

Numerical modeling of the optical response in optical chemical sensors

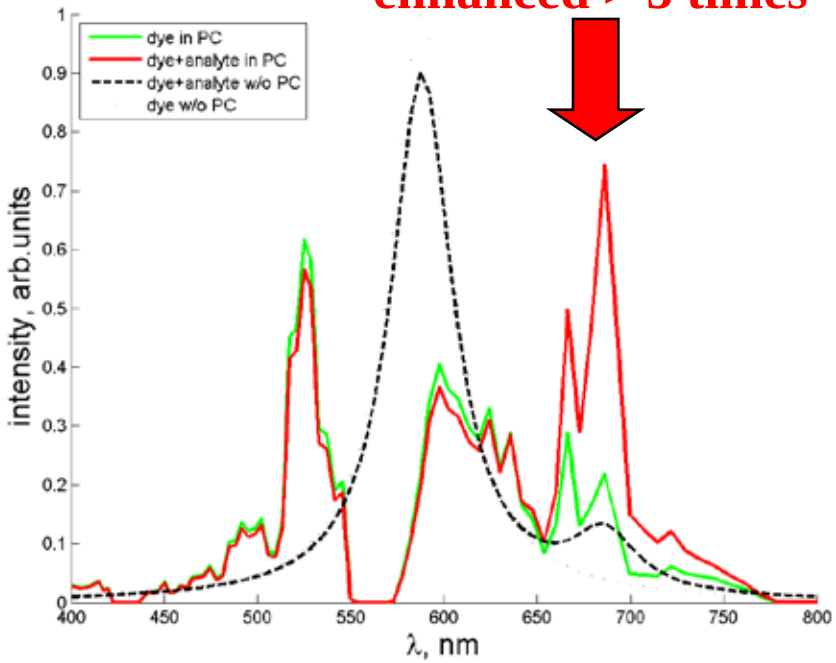


$e = 12.96$ $I_{dye+analyte}$ enhanced



I_{dye} partly suppressed

Response enhanced > 5 times



PC parameters: a = 416nm, r_{sph}= 88 nm (diamond close-packed case, f = 34%)

Diamond PC: enhancing dye+analyte peak, suppressing free dye peak by PBG

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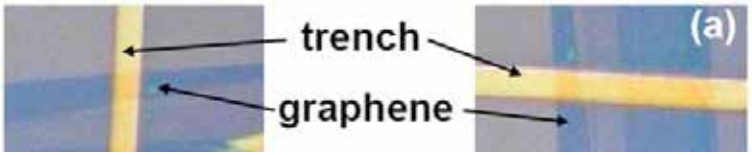
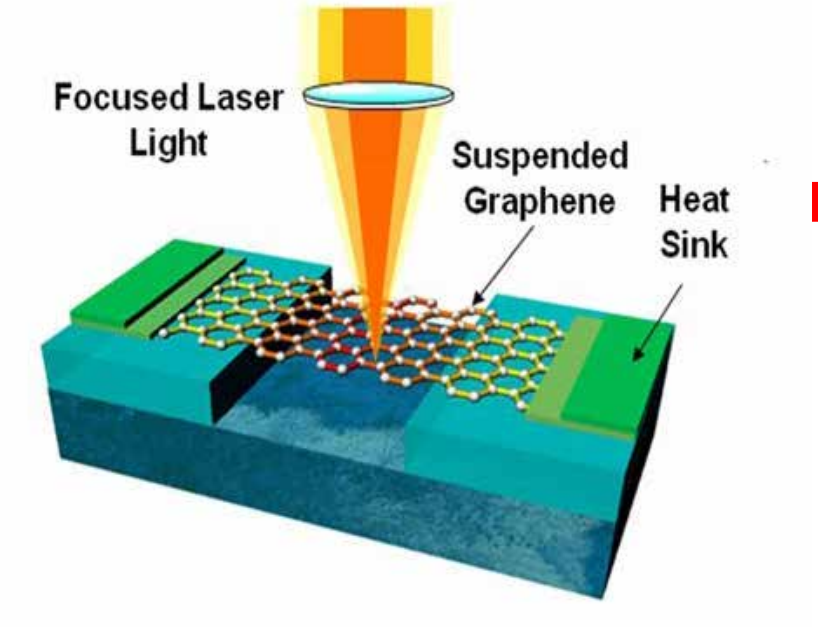
Investigation of thermal conductivity of graphene

Thermal conductivity of graphene

Thermal conductivity of supported graphene





S. Ghosh et al, APL **92**, 151911 (2008)

The extremely high thermal conductivity in the range of 3080–5150 W/m K and phonon mean free path of 775 nm near room temperature.

Exceeds graphite and CNT thermal conductivity (2000-3000 W/mK)

Experiment: thermal conductivity depends on the number of graphene layers

Theory: thermal conductivity of graphene increases with length

Mechanistic understanding and modeling prove is required to “believe” and to emply the effect for real graphene-based materials (e.g. graphene paper)

Thermal conductivity of graphene/graphite

Boltzmann Transport Equation theory

$$k = \frac{1}{4\pi^2 \hbar} \sum_j \int C(\omega,T)\,\tau(\omega,T)\,\frac{v}{u}\,\omega\,d\omega$$

Three-phonon scattering relaxation time:

P. G. Klemens, Journal of Wide Bandgap Materials7, 332 (2000)

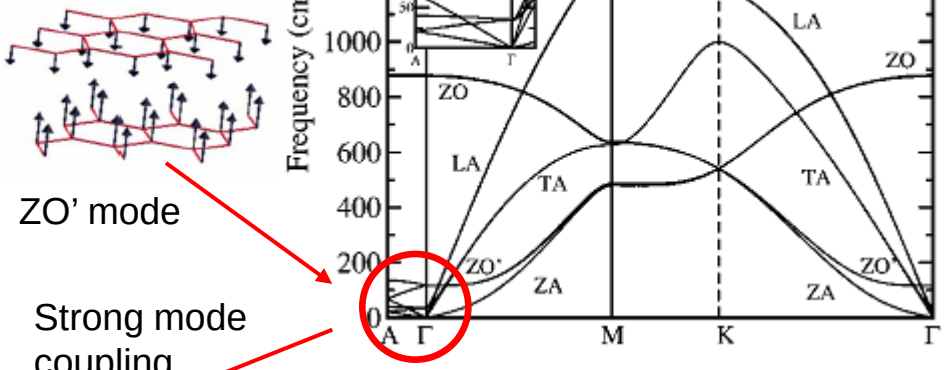
$$\frac{1}{\tau} = 4\gamma^2 \frac{kT}{Mv^2}\frac{\omega^2}{\omega_D}$$

at $\omega \to 0$

$$C(\omega) \to k_B,\ \tau(\omega) \to 1/\omega^2,\quad k \to \int d\omega/\omega = \ln(\omega) \to \infty$$

graphite

Minimum cutoff frequency is determined by inter-plane interaction



ZO' mode

Strong mode coupling

$\omega_{min} = \omega_{ZO'} \approx 2\pi \times 4\text{THz}$

Marzari et al, PRB 71, 205214 (2005)

graphene

Phonon mean free path is restricted by flake size:

$$l(\omega,T) = \frac{1}{2\gamma^2} \times v \times \frac{M \times v^2}{k \times T} \times \frac{\omega_D}{\omega^2} < L$$

$$\Rightarrow \quad \omega_{min} = \sqrt{\frac{1}{2\gamma^2} \times v \times \frac{M \times v^2}{k \times T} \times \frac{\omega_D}{L}}$$

Þ Graphene thermal conductivity should increase with flake size

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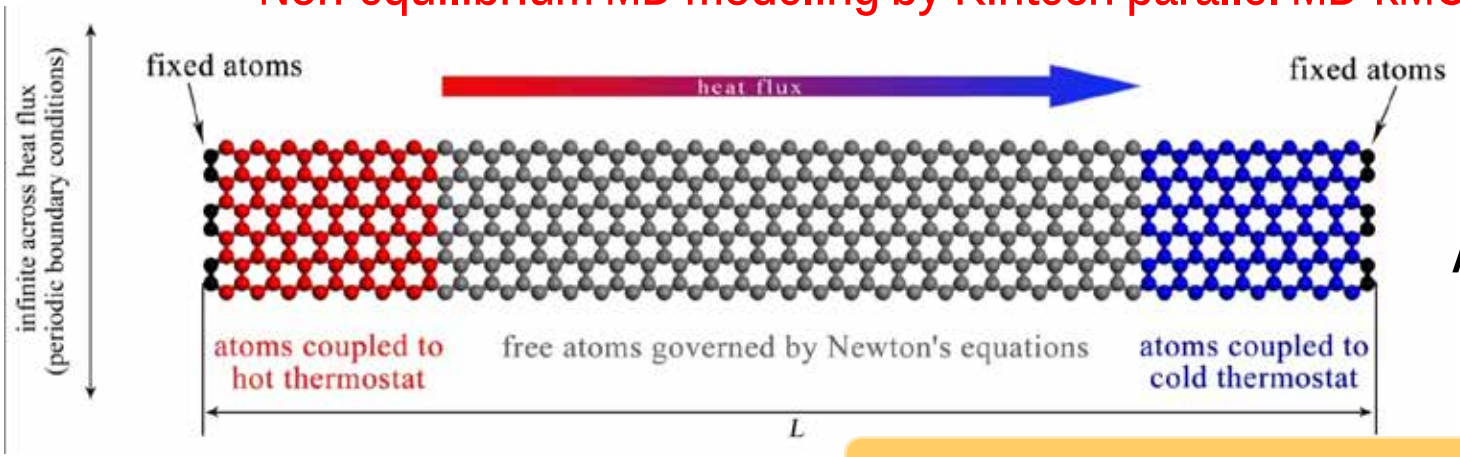
Thermal conductivity of graphene/graphite

Non-equilibrium MD modeling by Kintech parallel MD-kMC code



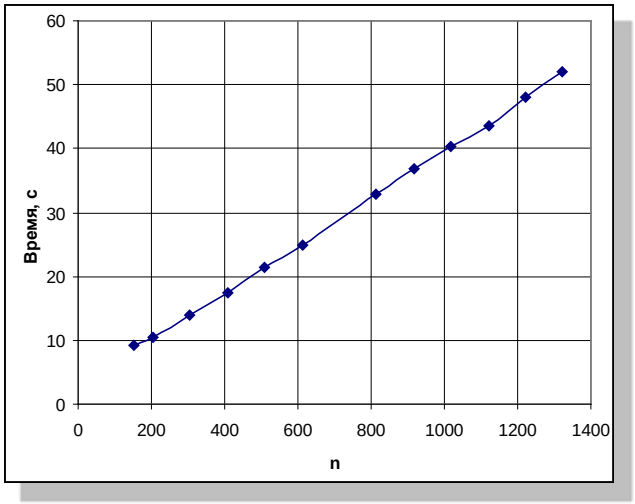
$$\lambda = -\frac{Q}{bd\tilde{N}T}$$

Linear scaling was proven up to 200 cores

- *High-performance molecular dynamics simulations should be used to model transport in real scale graphene flakes:*
- *Flake sizes: micron scale*
- *Number of atoms: > 100,000*

➡ *efficient parallel MD algorithms are required for many-body interatomic potentials (Tersoff, Brenner). One week run on 200 cores for 10^5 atoms.*

- *Domain decomposition method was adapted for NEMD calculations*



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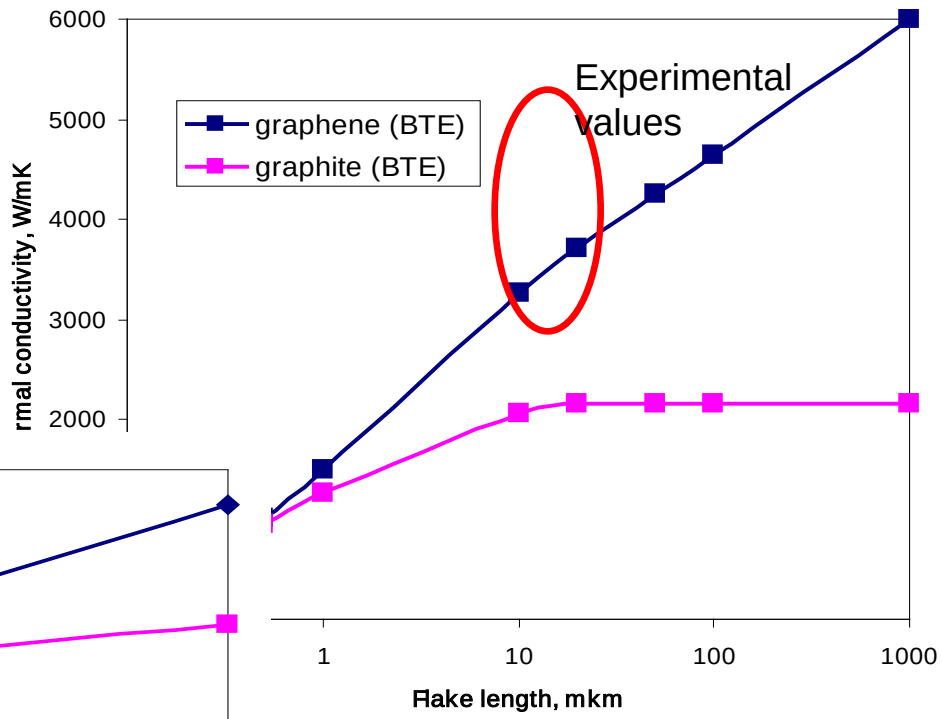
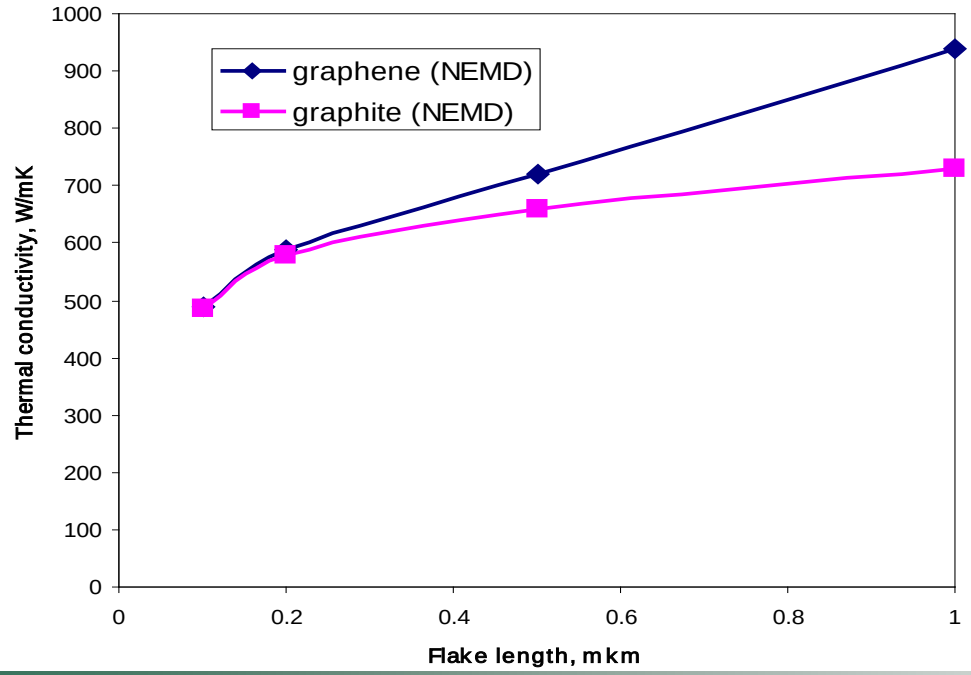
Thermal conductivity of graphene/graphite

Multi-scale modeling of thermal conductivity:

Boltzmann transport equation (BTE)



Non-equilibrium MD (NEMD) modeling



MD and BTE modeling prove that

1. *Graphene thermal conductivity increases with flake size*
2. *Interplane coupling in graphite limits thermal conductivity*

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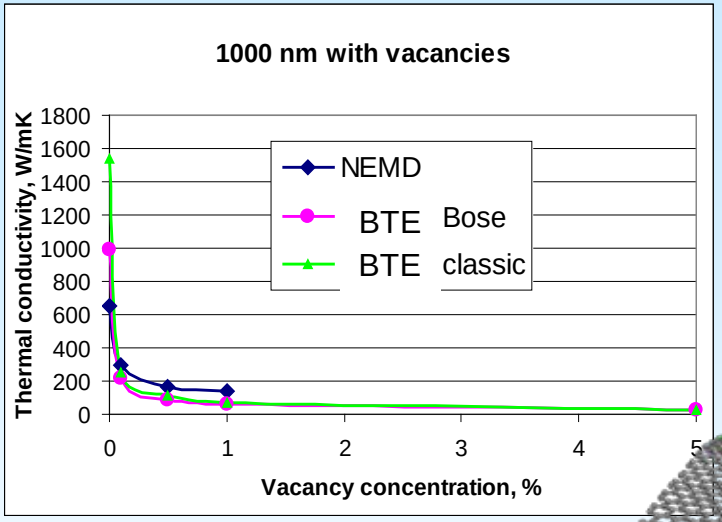
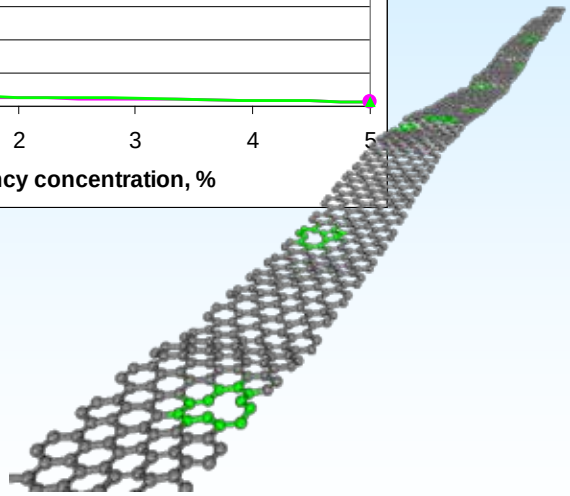
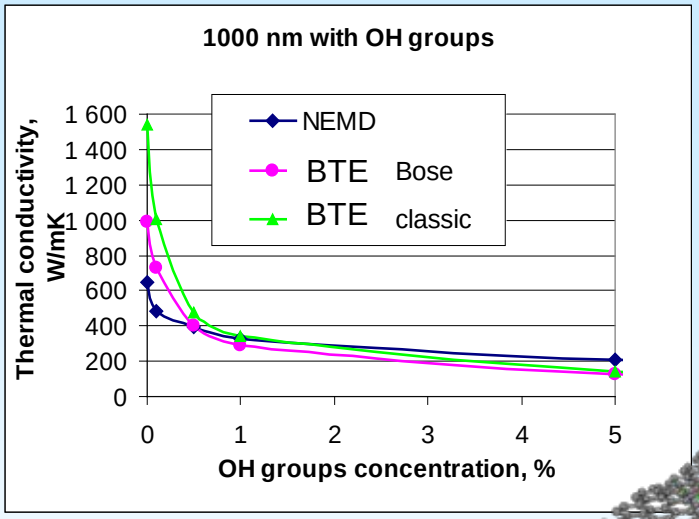
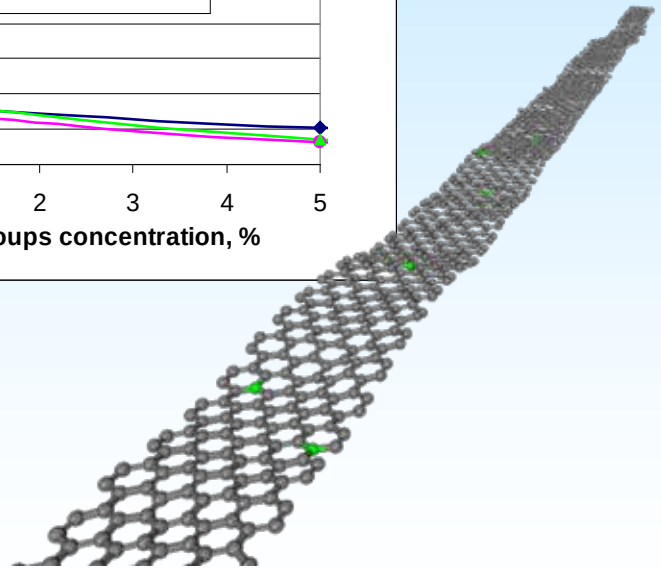
Thermal conductivity of graphene/graphite

Influence of defects on thermal conductivity of graphene









Significant reduction of thermal conductivity at vacancy density about 1%

Significant reduction of thermal conductivity at OH group density about 1%

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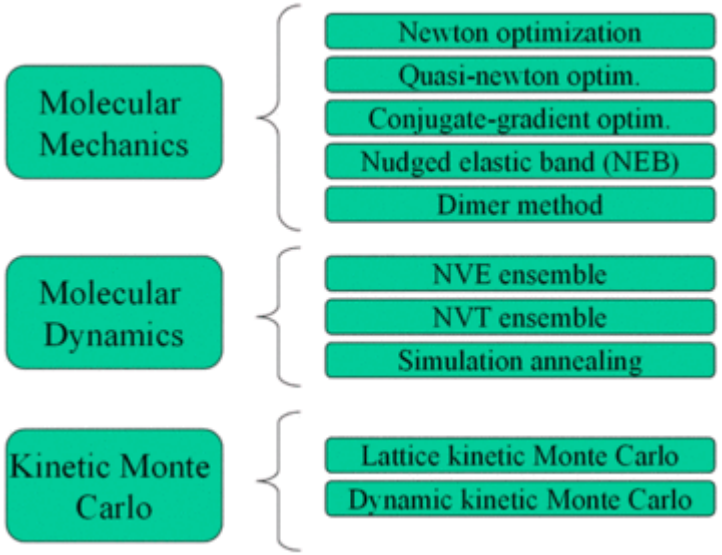
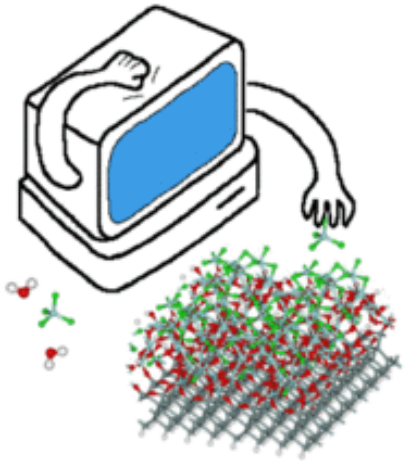
MD-kMC

MD-kMC code is an integrated environment for different atomistic simulations based on molecular mechanics, molecular dynamics, and kinetic Monte Carlo methods using a wide set of empirical and semiempirical energy functionals. Nonequilibrium molecular dynamics method implemented in MD-kMC allows to calculate phonon thermal conductivity.



MD-kMC library of potentials:

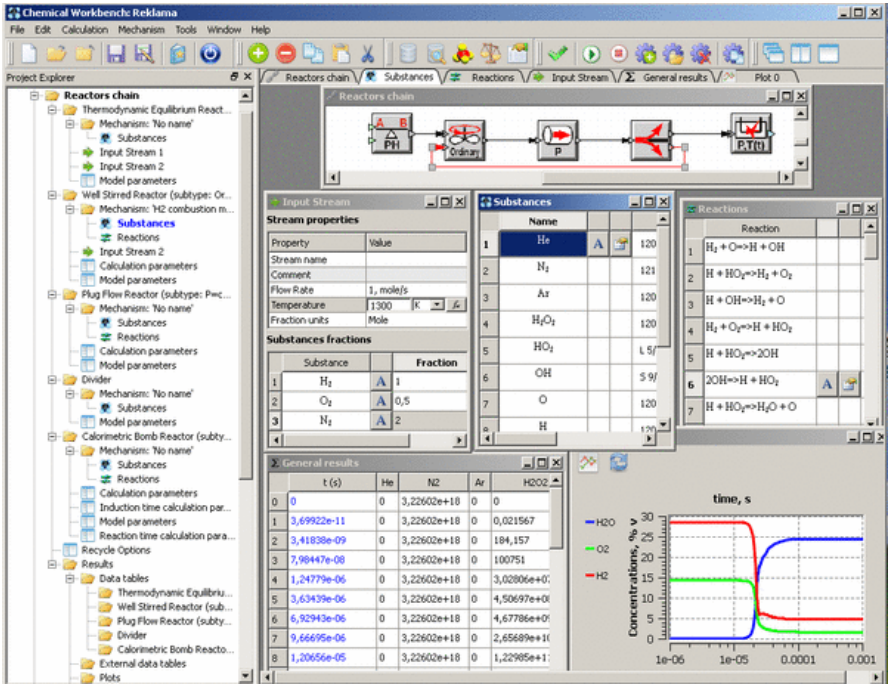
- Charge variable potentials (QEq charge equilization method)
- Environment-dependent potentials (Tersoff-type many body functionals (Tersoff, Brenner))
- (Modified) embedded atom (MEAM) potentials (Based on Baskes EAM and MEAM functionals)
- Tight Binding methods for spd orbitals (Orthogonal TB, Orthogonal self-consistent charge (SCC) TB, Non-orthogonal TB, K-point sampling)



http://www.kintechlab.com/products/md-kmc/

Chemical Workbench

Thermodynamic Models – a set of models for calculating the thermodynamic properties of multicomponent mixture,
Gas-Phase Kinetic Models – various models for general gas-phase kinetic modeling,
Flame model – premixed Flame reactor is a 1D model for calculation of laminar flame front velocity and structure,
Heterogeneous Kinetic Models – a set of models for surface chemistry modeling

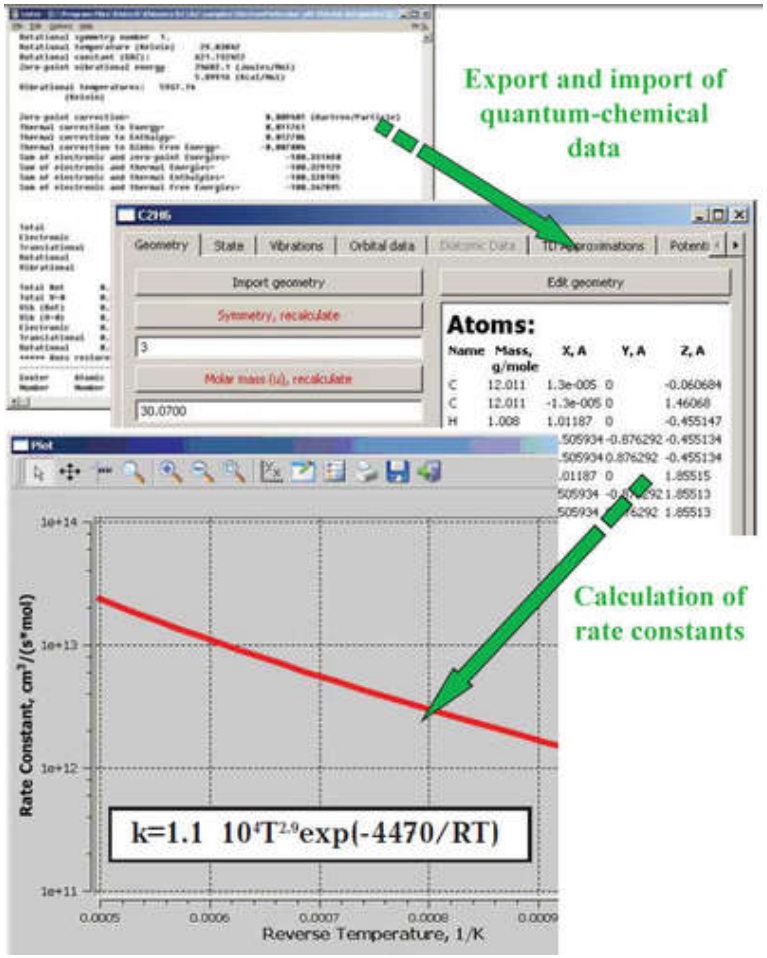


Non-Equilibrium Plasma Models – a set of comprehensive models for non-equilibrium plasma process,
Detonation Model – model for estimating of wave parameters and modeling of advanced propulsion systems,
Separators and Mixers – various tools to control reactor's streams, and a membrane reactor model for calculating separation characteristic of membrane unit,
Mechanism Analysis and Reduction – a tool set for kinetic mechanism analysis and reduction.

http://www.kintechlab.com/products/chemical-workbench/

Khimera

Khimera allows one to calculate the kinetic parameters of elementary processes and thermodynamic and transport properties from the data on the molecular structures and properties obtained from quantum-chemical calculations or from an experiment.
The molecular properties and the parameters of molecular interactions can be calculated using available quantum-chemical software (GAUSSIAN, GAMESS, JAGUAR, ADF) and directly inputted into Khimera in an automatic mode.



Khimera Models:

Chemistry of Heavy Particles
Surface Processes
Electron-Molecular Reaction
Vibrational Energy Transfer
Photochemical Reactions and Electronic Energy Transfer
Multicomponent Thermodynamic Properties Model
Multicomponent Gas Transport Properties Model

http://www.kintechlab.com/products/khimera/

intelligence everywhere™

Launched by Motorola freescale semiconductor

Drift-diffusion code (charge transport simulation)

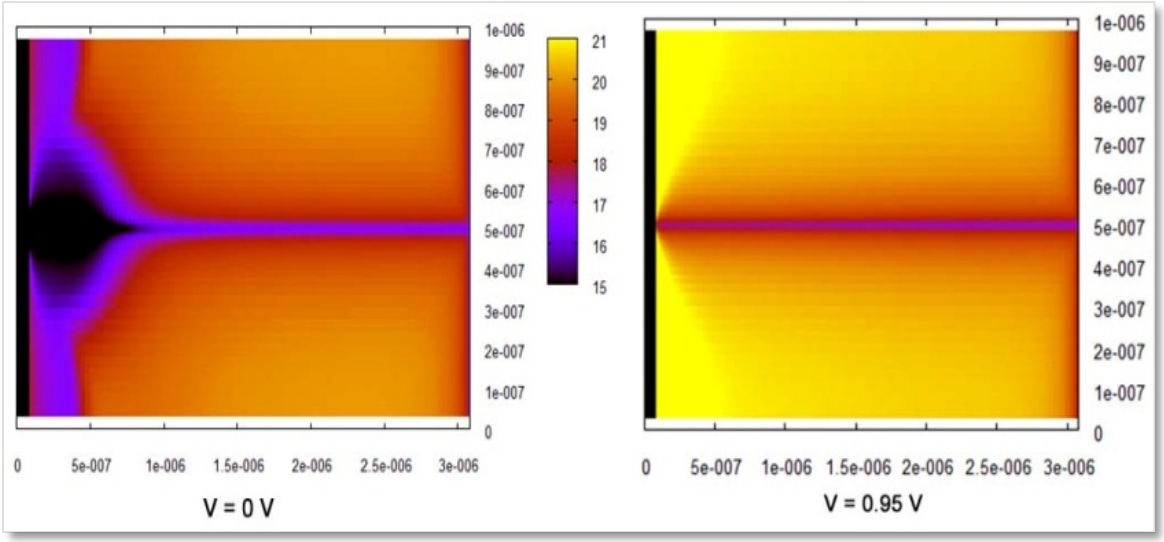
Solving Poisson and continuity equation for drift and diffusion of charge carriers

$$\nabla\varepsilon\nabla\psi + q(p - n + N_D - N_A) = 0$$

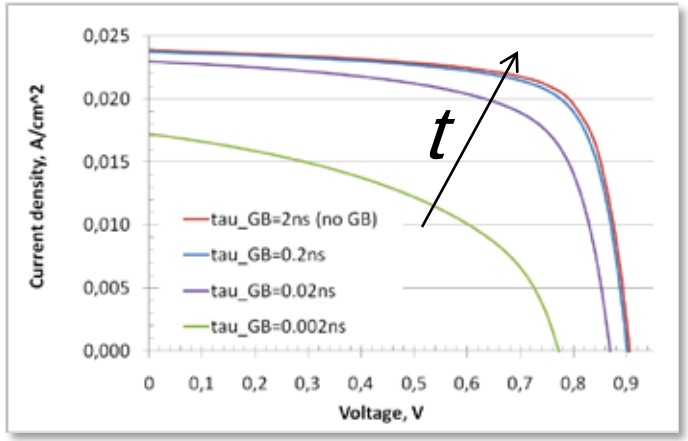
$$\frac{1}{q}\nabla J_n + G - R = \frac{\partial n}{\partial t} \qquad J_n = q\mu_n nE + qD_n\nabla n$$

$$-\frac{1}{q}\nabla J_p + G - R = \frac{\partial p}{\partial t} \qquad J_p = q\mu_p pE - qD_p\nabla p$$

- Inorganic 1D and 2D heterojunction structures
- Steady-state solution
- Shottky barrier or charge injection model at cathode/anode boundaries
- Organic multilayer structures
- Energy disorder
- Local mobility and diffusion coefficients



Distribution of the recombination rate near grain boundary in thin film solar sell



JV curves of cell with recombinative grain boundaries

KINTECH LABORATORY

Predictive multi scale modeling based on HPC for energy and materials: specific projects

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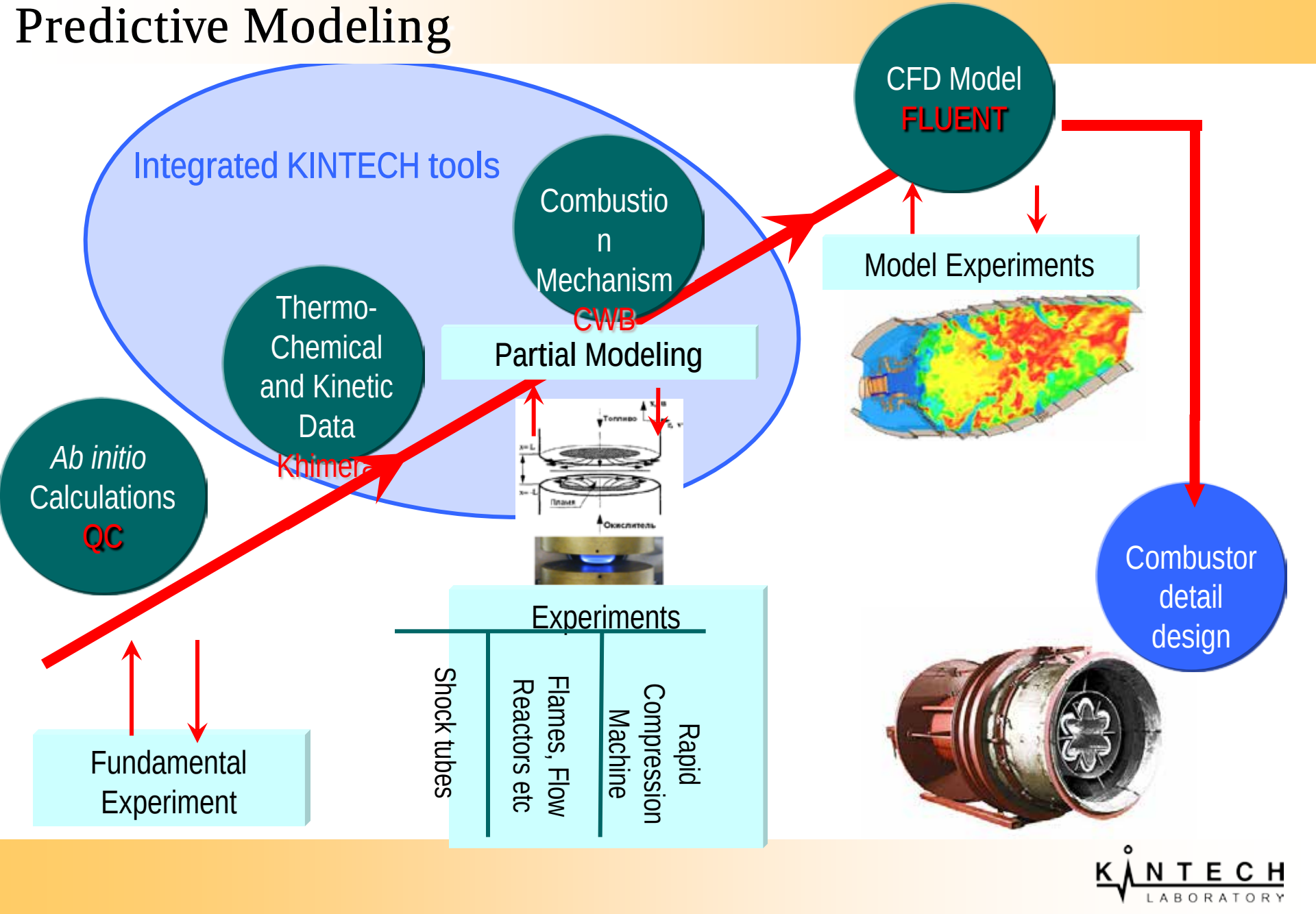
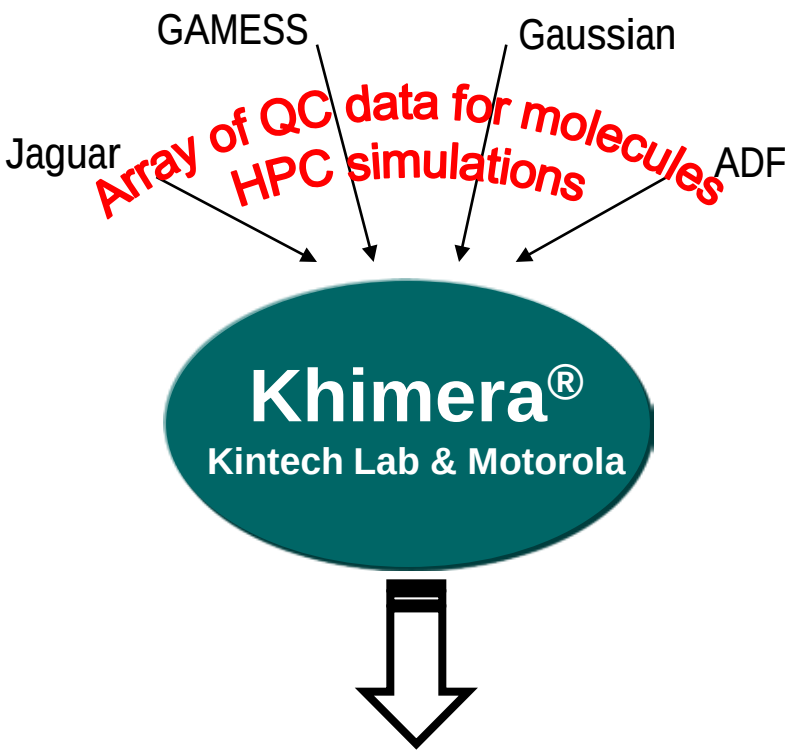
- info@kintechlab.com
www.kintechlab.com

A priory design of Combustion based Advanced Energy Systems

Development Cycle of Combustion Chamber Based on Predictive Modeling

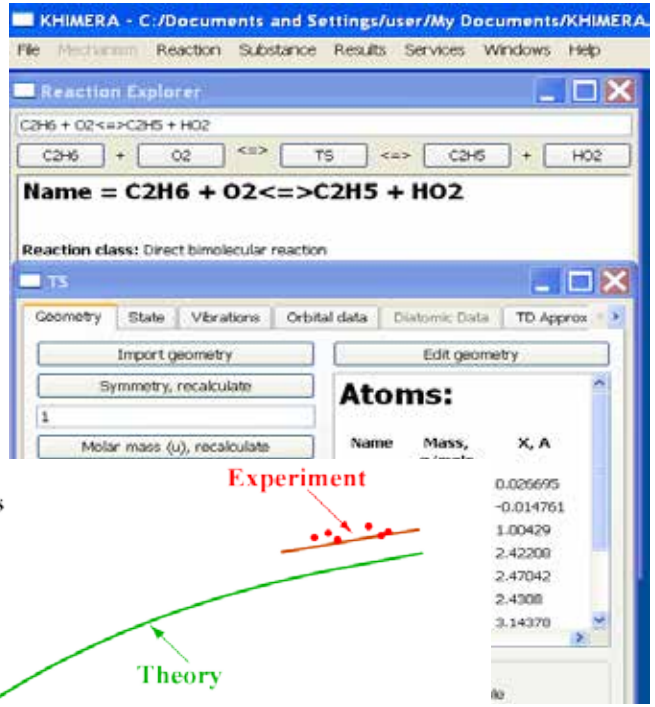


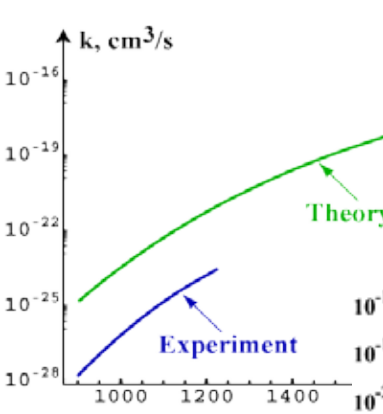
Software for development and reduction of the combustion mechanisms of real fuel: Data recovery with Khimera®

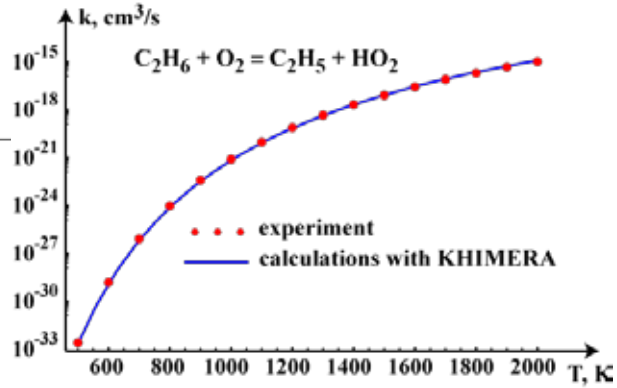


Relevant First-principles based physico-chemical data:

- Elementary processes in gas phase and plasma, at surface and in liquid phase
- Gas mixtures transport properties
- Thermodynamic data of individual substances





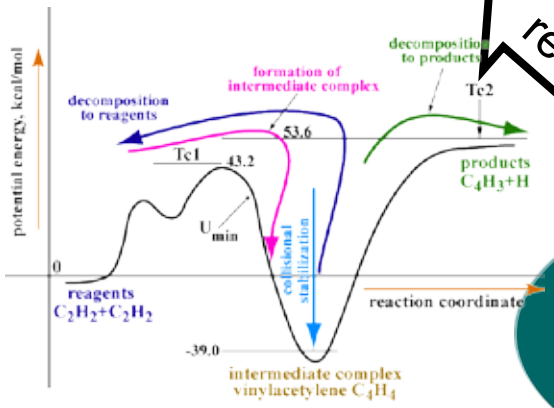


MOTOROLA

KINTECH LABORATORY

Software for development and reduction of the combustion mechanisms of real fuel: Mechanism generation software

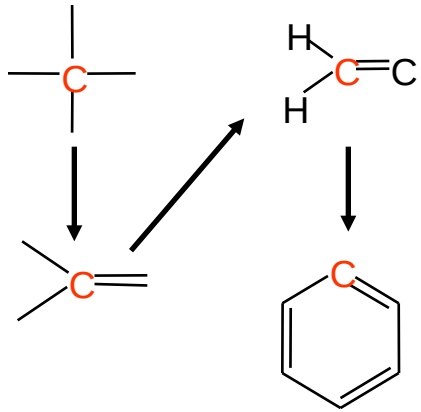
Khimera®
(Kintech Lab)



data recovery

mechanism elements

Elementary processes



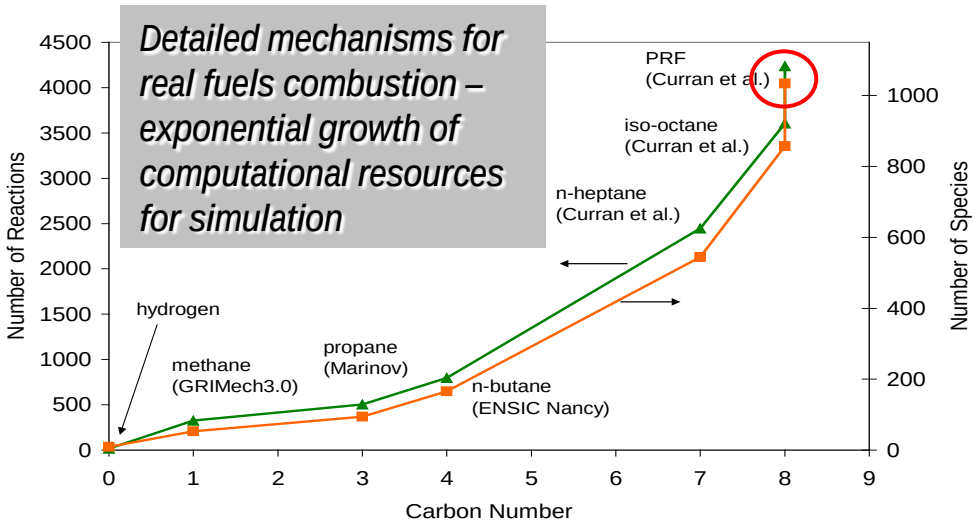
Generation and validation of detailed mechanisms for combustion in the frame of Chemical Workbench

Validated detailed kinetic mechanisms for reduction and CFD modeling

Method for mechanism generation was developed by multi-disciplinary collaborative team supported by RFBR grant:

RRC Kurchatov Institute (contractor), Semenov Institute of Chemical Physics RAS, Photo Chemistry Center RAS, Institute of Mechanics MSU, Kintech Lab

Software for development and reduction of the combustion mechanisms of real fuel: HPC and mechanism reduction

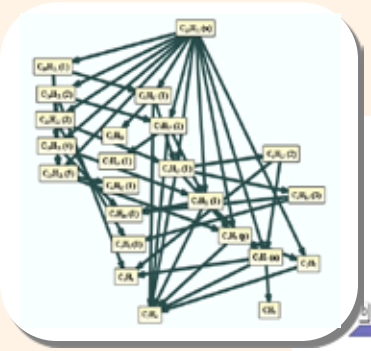


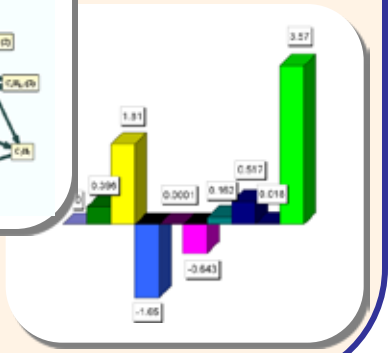
Mechanism Reduction

Chemical Workbench® - parallel code for kinetic mechanisms automatic reduction and multiple testing

Reduction methods

- Computational singular perturbation
- Principal component analysis
- Directed Relation Graphs
- Rate-of-Production analysis





Code Parallelization

Kintech Lab software Chemical Workbench® was parallelized and optimized by Intel CRT team and Kintech Lab experts for Intel architecture

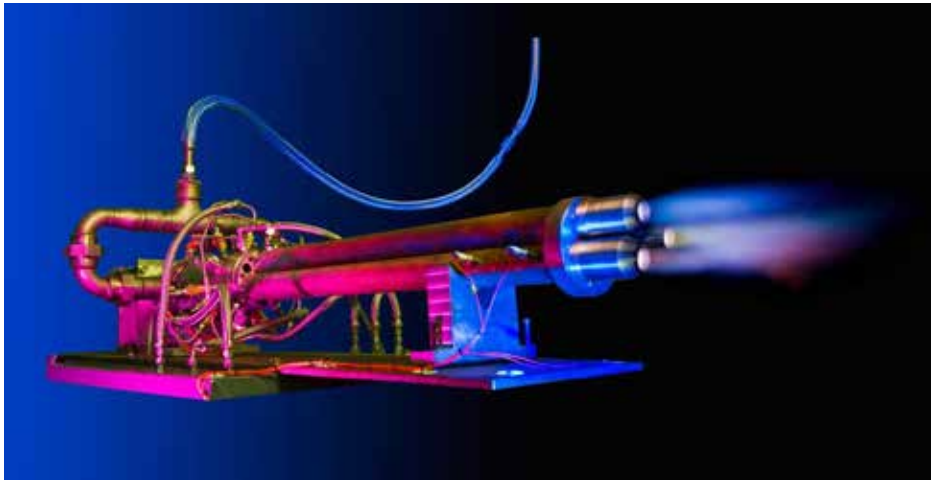
Iso-octane mechanism reduction runs 43 minutes instead of 24 hours with new parallelization algorithm. We have 2,27 times performance boost of our application with Intel Xeon 55xx vs. previous generation Intel Xeon 54xx.

intel

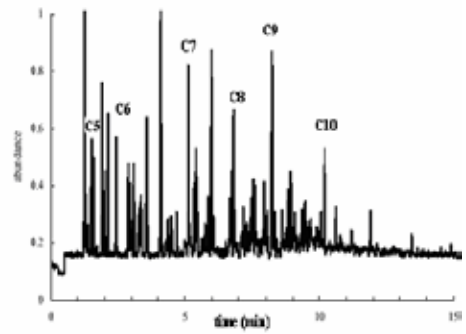
KINTECH LABORATORY

Predictive Modeling of New Generation Detonation Based Engine: Problem

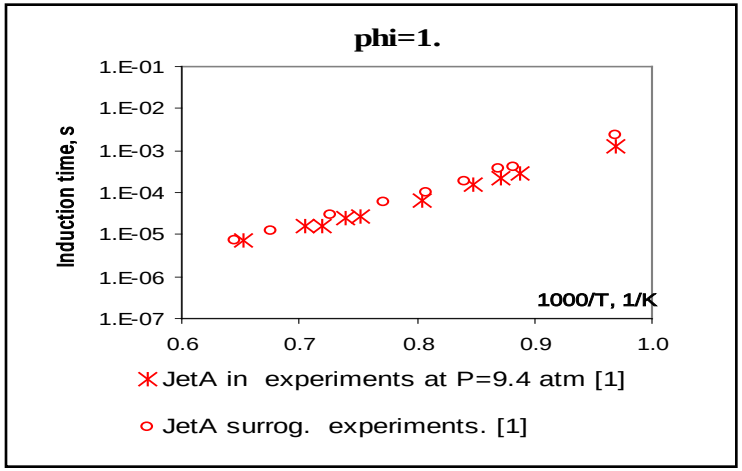
Pulsed detonation engine (PDE) at GE Global Research Centre



Surrogate of the aviation fuel



n-decane $C_{10}H_{22}$ - 72.7%
n-hexane C_6H_{14} - 9.1%
benzene C_6H_6 - 18.2%



Ignition delay time for aviation kerosene (GE GRC experiments)

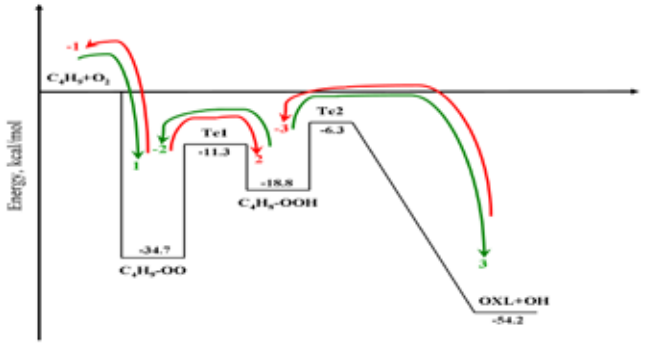
Problem:

Develop predictive CFD model for simulation of detonation initiation and propagation inside of the PDE, which is capable to operate with standard aviation fuel – aviation kerosene Jet-A

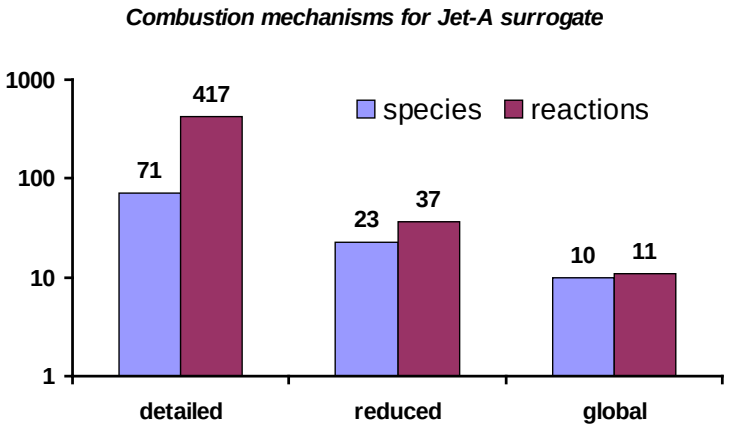
Predictive Modeling of New Generation Detonation Based Engine: Jet-A combustion mechanisms development

QC calculations for uncertain reactions

$C_6H_6+O_2 <=> C_6H_5/+HO_2$ $\quad k = 1.3\cdot10^{-20}T^{3.2}\exp(-61.45/RT)$



Mechanisms validation



Detailed mechanism reduction

Detailed mechanism (~ 400 rxn)

↓

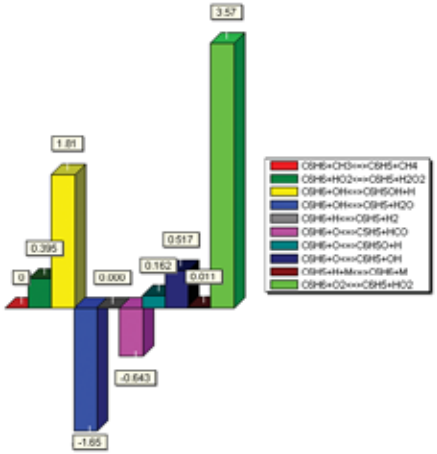
Skeletal mechanism (~ 100 rxn)

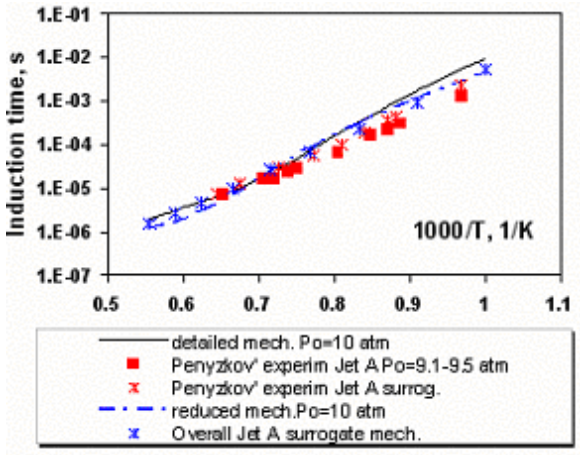
↓

Reduced mechanism (~ 30 rxn)

↓

Global mechanism (~ 10 rxn)

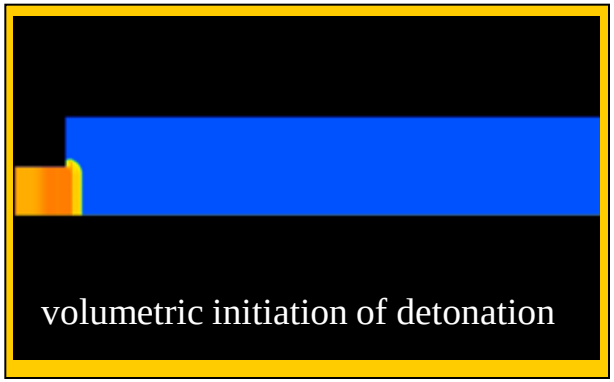


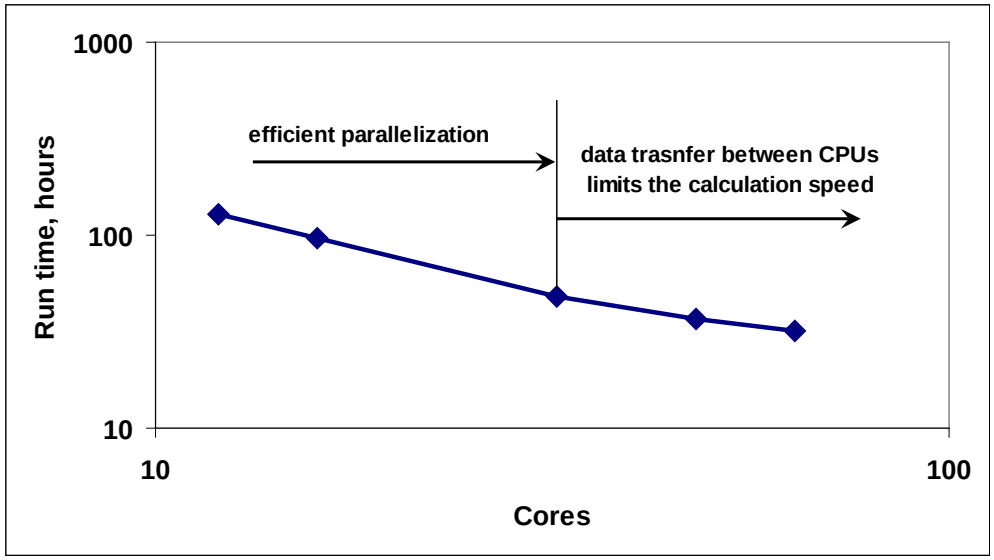


Predictive Modeling of New Generation Detonation Based Engine: parallel computations load balance for CFD

Parallel computations performance – case study for detonation simulations

- Unsteady detonation wave propagation
- Global mechanism of Jet-A combustion (10 species, 11 reactions)
- Intel Xeon CPUs
- Infiniband connection



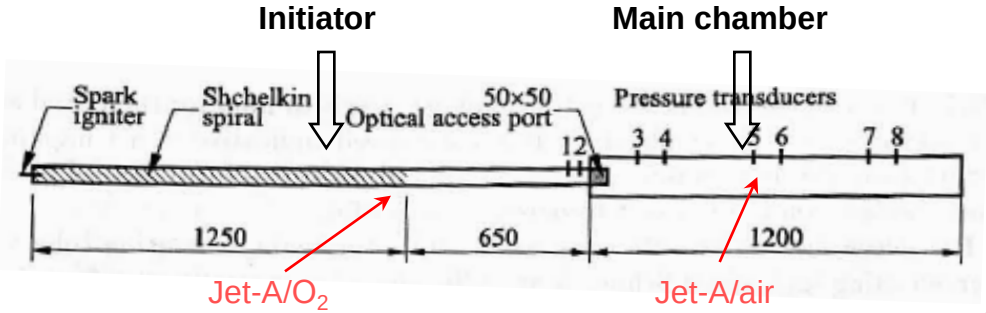


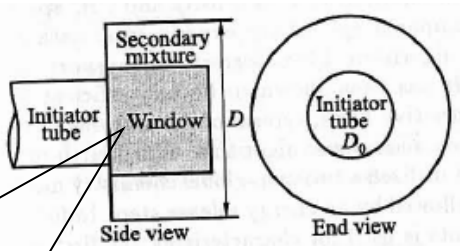
For available cluster configuration is was decided to limit the number of cores by 36

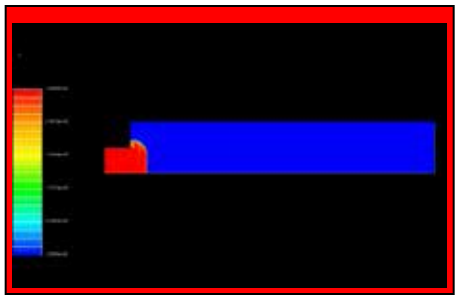
Different tasks with 36 cores were run simultaneously for efficiently use of computational resources

Predictive Modeling of New Generation Detonation Based Engine: Jet-A fuelled PDE ignition modeling

PDE







f = 0.3
(detonation quenching)

f = 0.4
(wall-induced detonation inittiation)

f = 0.6
(volumetric initiation of detonation)

Experiment
$f_{opt} \approx 0.4$

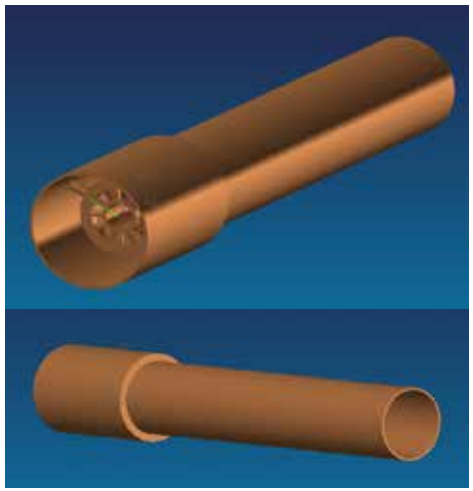
Predictive Modeling of NOx emissions from industrial GT burner

Natural gas-fired burner for industrial gas turbine

Goal: *develop predictive CFD model of NOx emissions from GT burner*

Effects to be included due to complex mixture composition

- *complex chemistry of methane combustion*
- *Radiative heat losses from burner to ambient*
- *NOx formation paths*



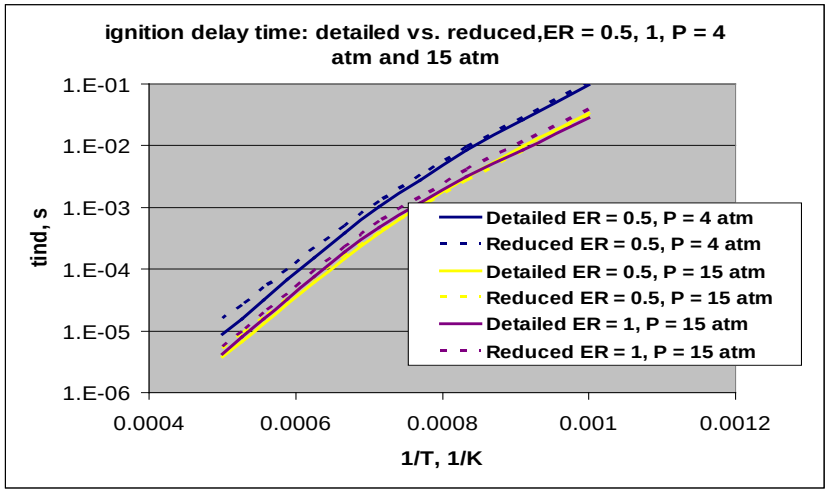
Chemistry models

Detailed and Reduced mechanism for CH_4

- 82 species and 191 reactions
- 17 species and 25 reactions
- reduced vs. detailed: maximum error in simulation of laminar flame velocity and ignition delay time 20%

NO formation mechanisms:

- thermal mechanism
- N2O path



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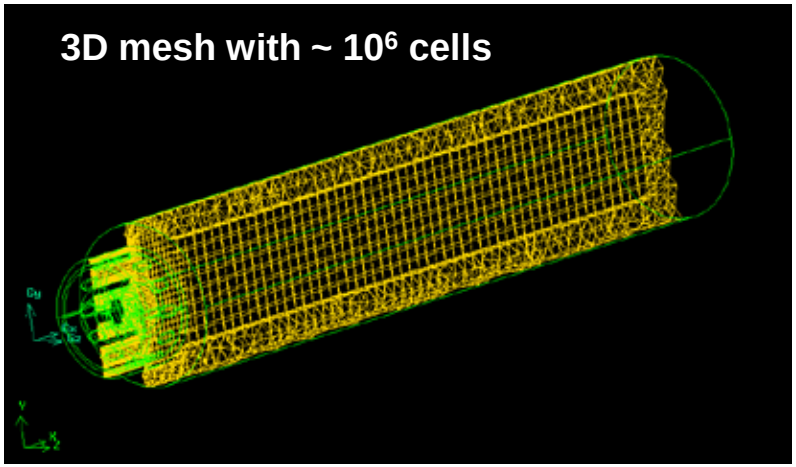
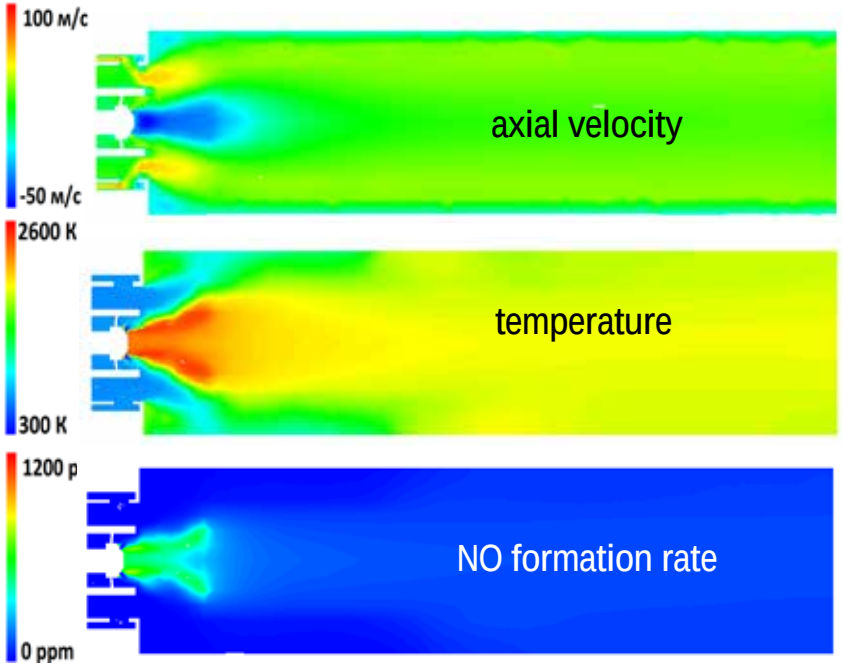
Predictive Modeling of NOx emissions from industrial GT burner





Average run time with reduced mechanism:

- 18 Intel Xeon Dual Core CPU (36 cores)
- Infiniband interconnect
- 20 - 24 hour to reach steady-state solution

NO, ppm@15%O_2	0.5*Full Power	0.8*Full Power	Full Power
Modeling	10 - 20	17 - 28	37 - 43
Experiment	23	27	33

Desired accuracy – 20% maximum error in NO concentration prediction – is attainable with reduced mechanisms of methane combustion

KINTECH LABORATORY

Thank you!

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