Multimillion Atom Simulations of Reactive Nanosystems

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Multiscale Modeling and Simulations of Hard and Soft Materials

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Outline

1. Collaboratory for advanced computing and simulations and multiscale algorithms
2. Chemical reactions: Oxidation dynamics and flash heating of an Al/Al_2O_3 nanoparticle
3. Chemical reactions: Isothermal heating of a chain of three Al/Al_2O_3 nanoparticles
4. Research in Progress

   Molecular dynamics with non-adiabatic transitions

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- **Dual-degree students:** (PhD in material science or physics + MS in computer science)

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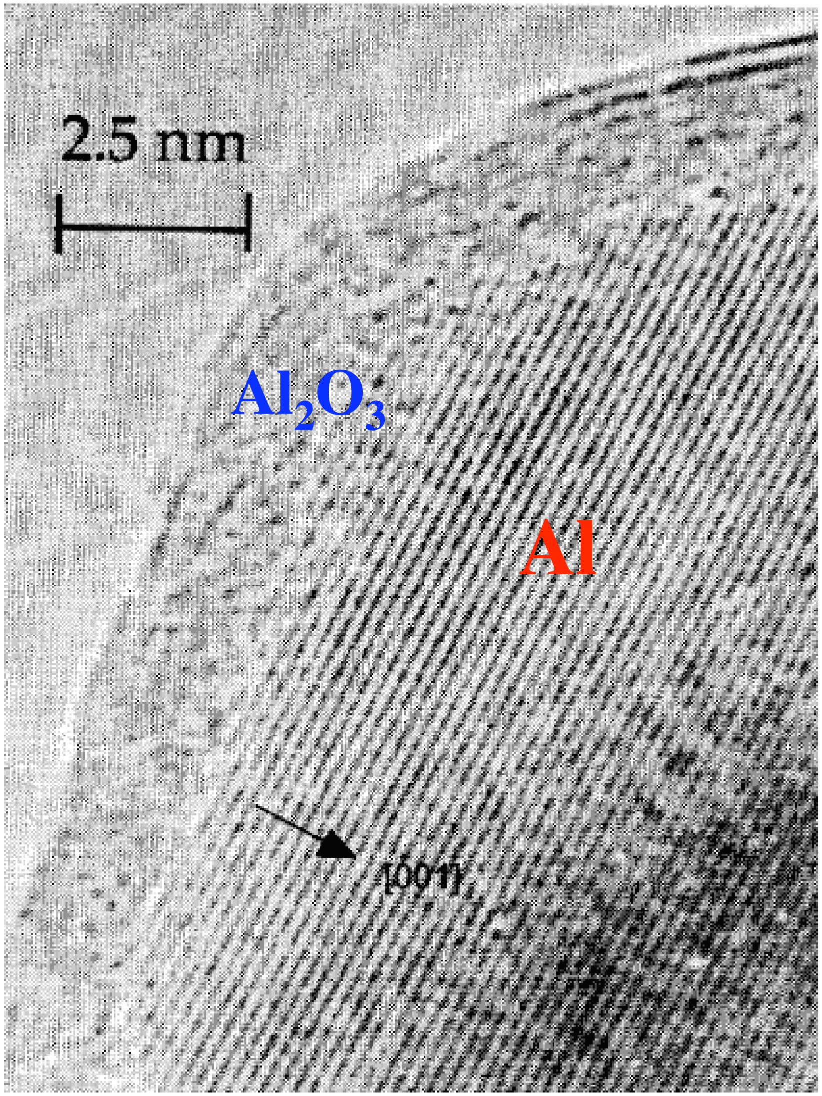
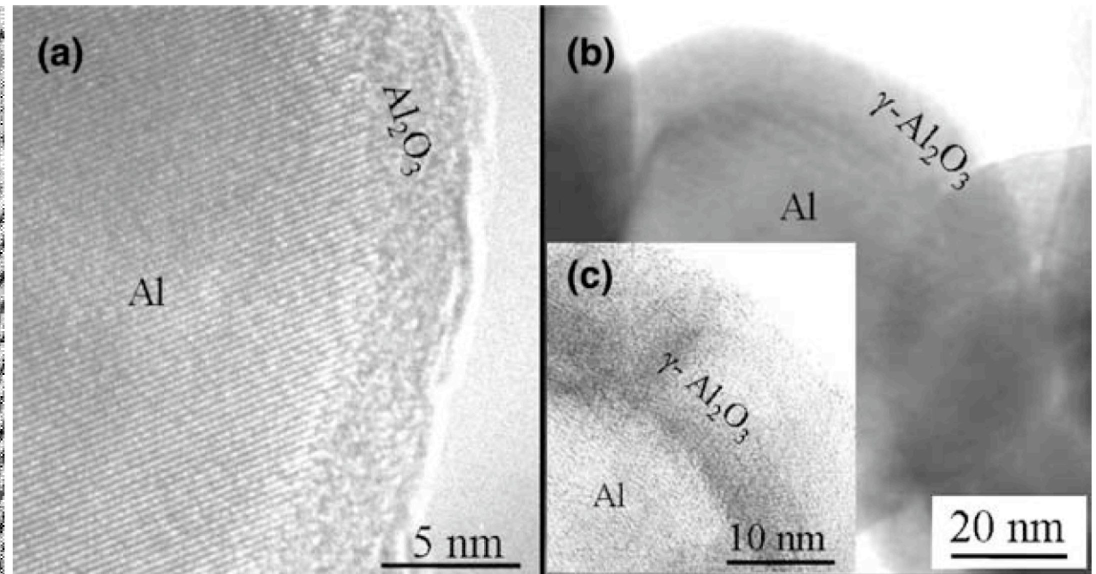
Simulations with Chemical Reactions

Experiments: Atomic Level Structure of Aluminum Nanoparticles





- **Left: High-resolution TEM of ANP**

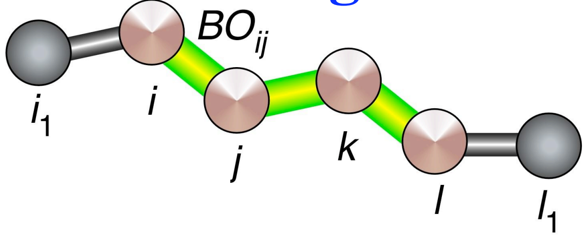
[A. L. Ramaswamy, et al., J. Ener. Mater. 23, 1-25 (2005)]

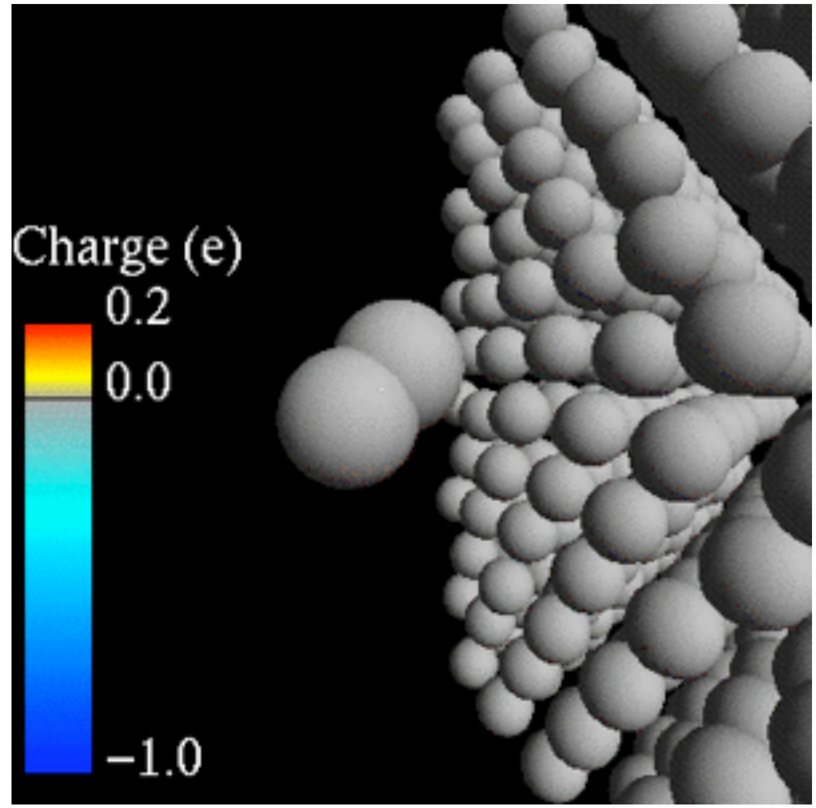
- **Top-Right: Crystallization of amorphous shell during heating of ANP**

[Mei, et al., Act. Mat. 53 (2005)]

Reactive Force-Field (ReaxFF) MD: Variable *N*-Charge Problem

- **Reactive bond order potential energy:** $E_{\mathrm{bond}}(\{r_{ij}\},\{r_{ijk}\},\{r_{ijkl}\},\{BO_{ij}\})$
  → Bond breakage & formation

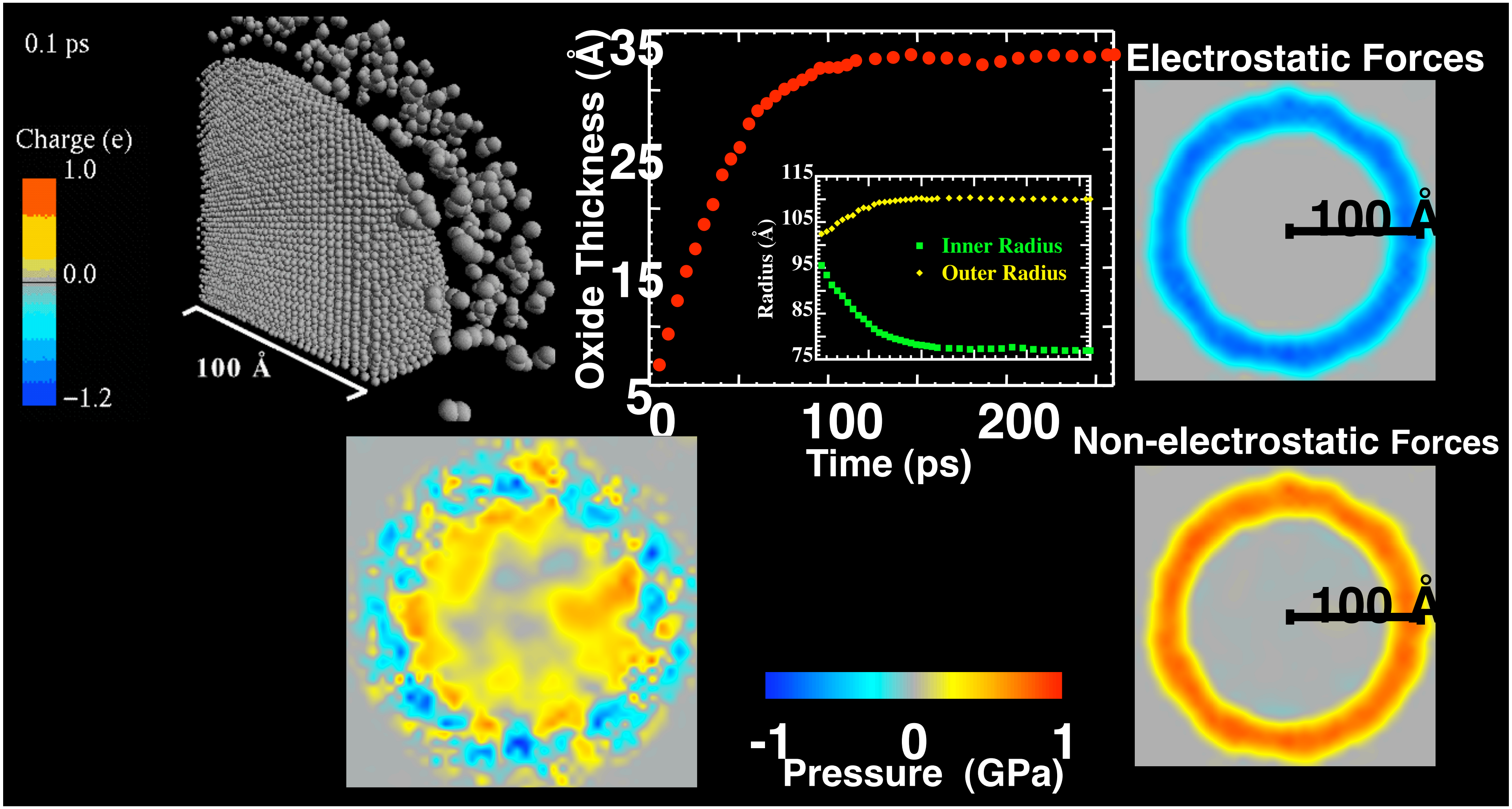




- **Charge-equilibration (QEq)**
  → Charge transfer
  Determine atomic charges $\{q_i \mid i = 1, ..., N\}$ every MD step to minimize $E_{\mathrm{ES}}(\mathbf{r}^N, q^N)$ with charge-neutrality constraint: $\Sigma_i\, q_i = 0$
  — Dense linear system: $M\,q = -\chi$
  ***O*(N^3)!**

$$E_{\mathrm{ES}}\left(\mathbf{r}^N, q^N\right) = \sum_i \left(\chi_i q_i + \frac{1}{2} J_i q_i^2\right) + \sum_{i<j} \int d\mathbf{x} \int d\mathbf{x}' \frac{\rho_i(q_i; \mathbf{x} - \mathbf{r}_i)\,\rho_j(q_j; \mathbf{x}' - \mathbf{r}_j)}{|\mathbf{x} - \mathbf{x}'|}$$

Oxidation of an Al Nanoparticle (n-Al)

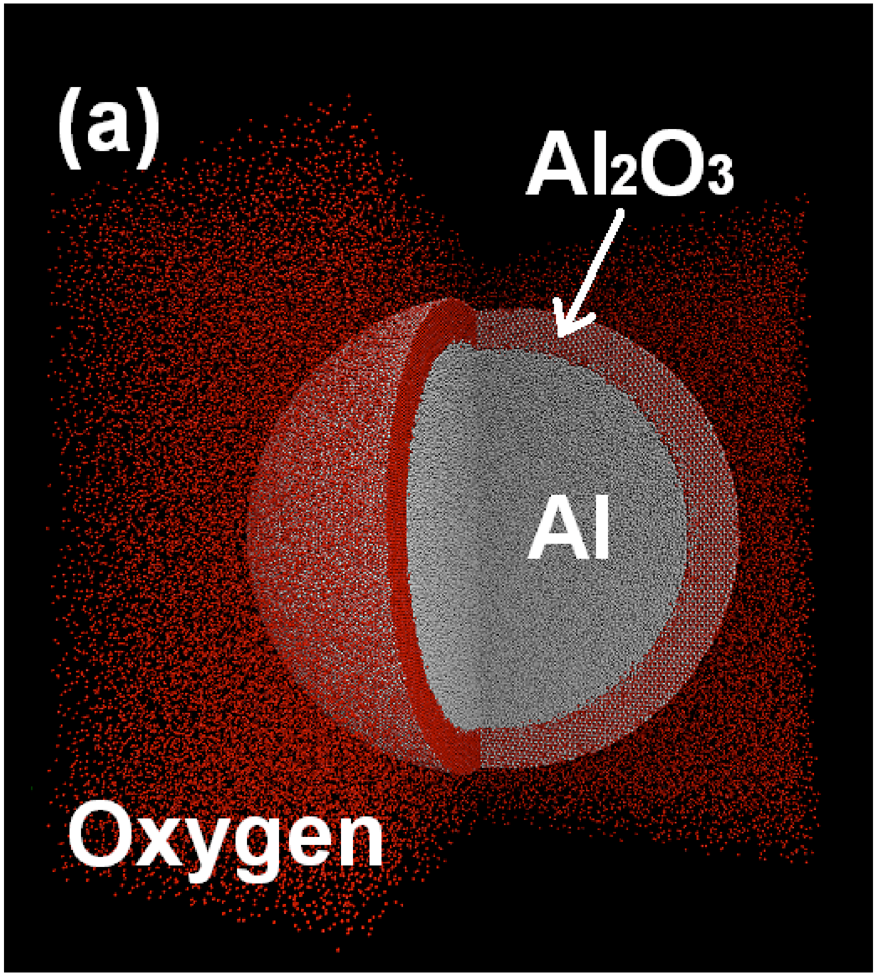


- Oxide thickness saturates at 40 Å after 0.5 ns, in agreement with experiments
- Oxide region/metal core is under negative/positive pressure
- Attractive Al-O Coulomb forces contribute large negative pressure in the oxide

Laser Flash Heating of

Core (Al)–Shell (Al_2O_3) Nanoparticle

Core-Shell Aluminum Nanoparticle



- Total Diameter of ANP = 48 nm
- Shell Thickness = 4 nm
- Shell Structures:
  - Crystalline (Al_2O_3)
  - Amorphous (a-Al_2O_3)
- Well thermalized three temperatures (T1, T2, T3)

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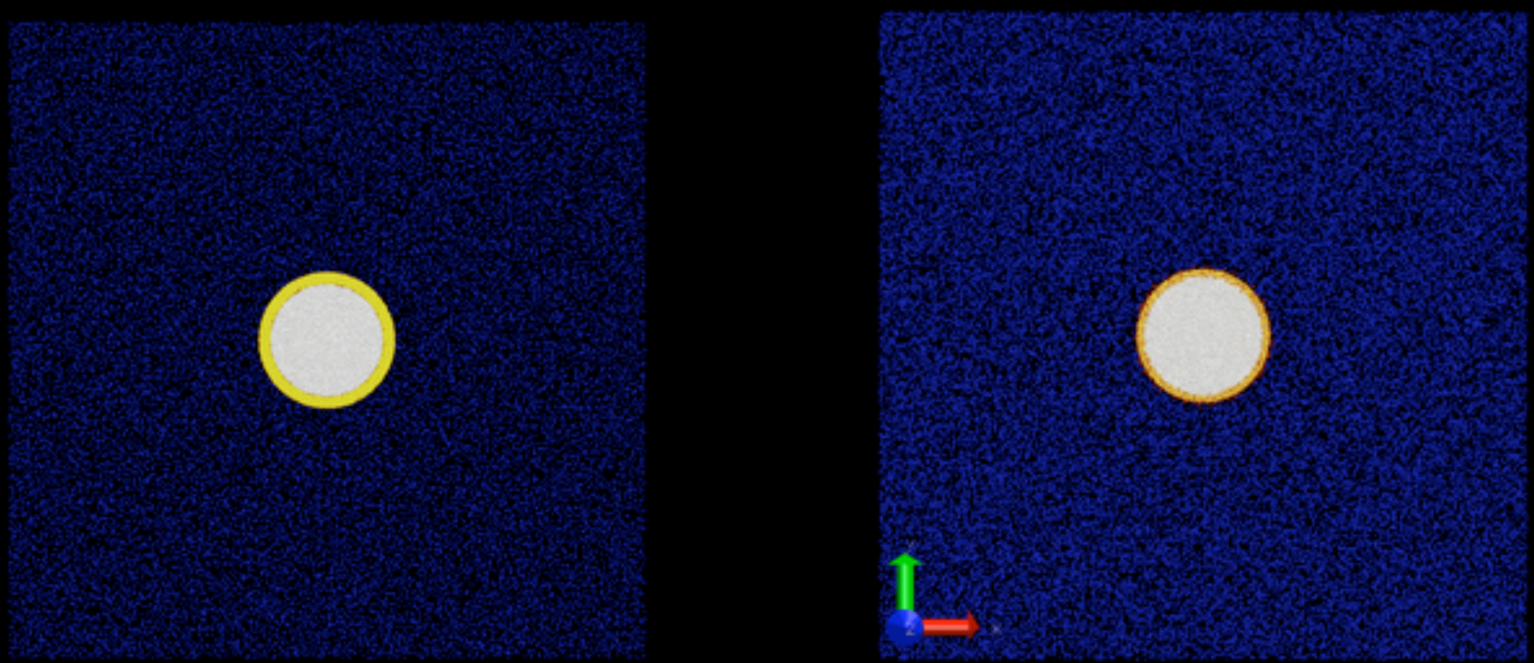
Crystalline and Amorphous Shells Nano-Explosion

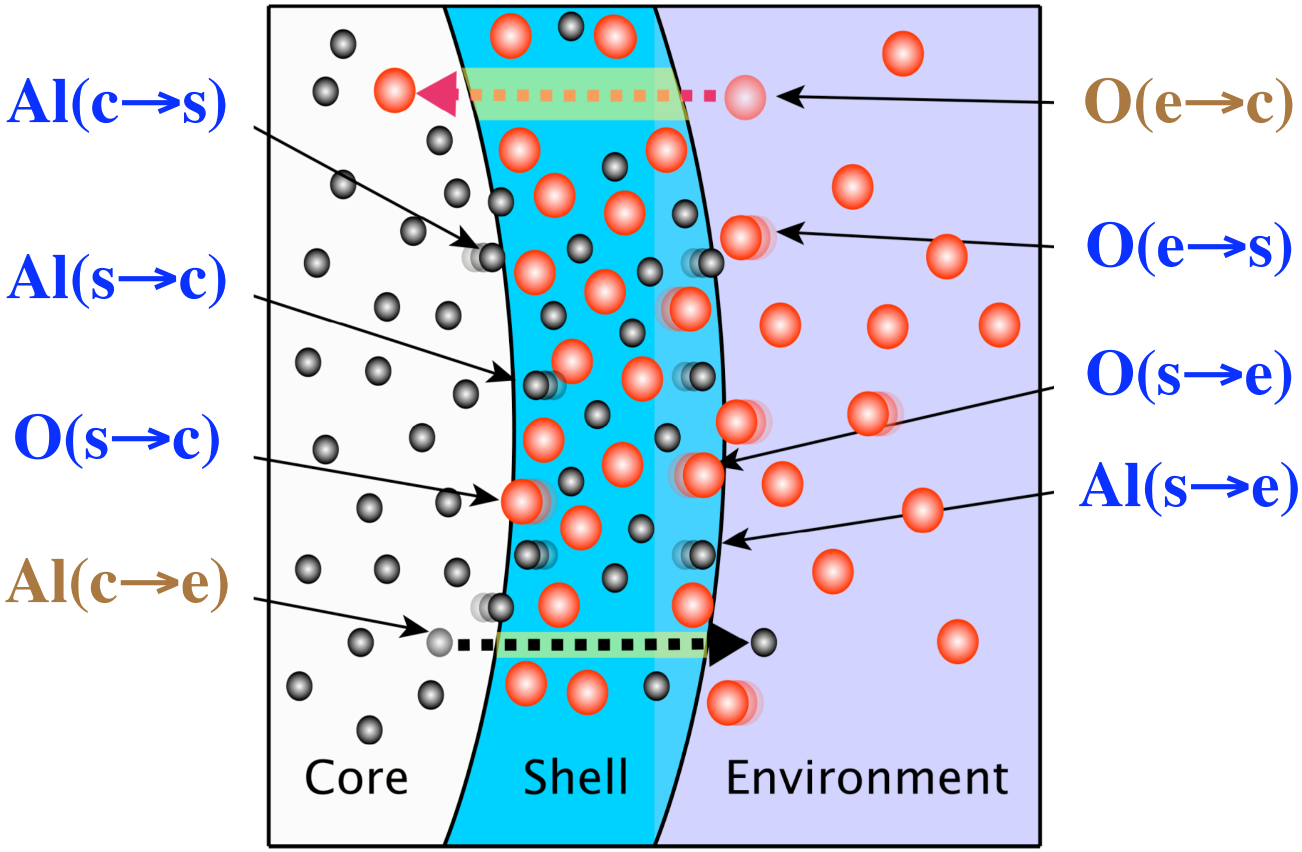


Crystalline: Expansion → Shell Broken → Oxidation Reaction

Amorphous: Expansion → Shell Shattered → Oxidation Reaction

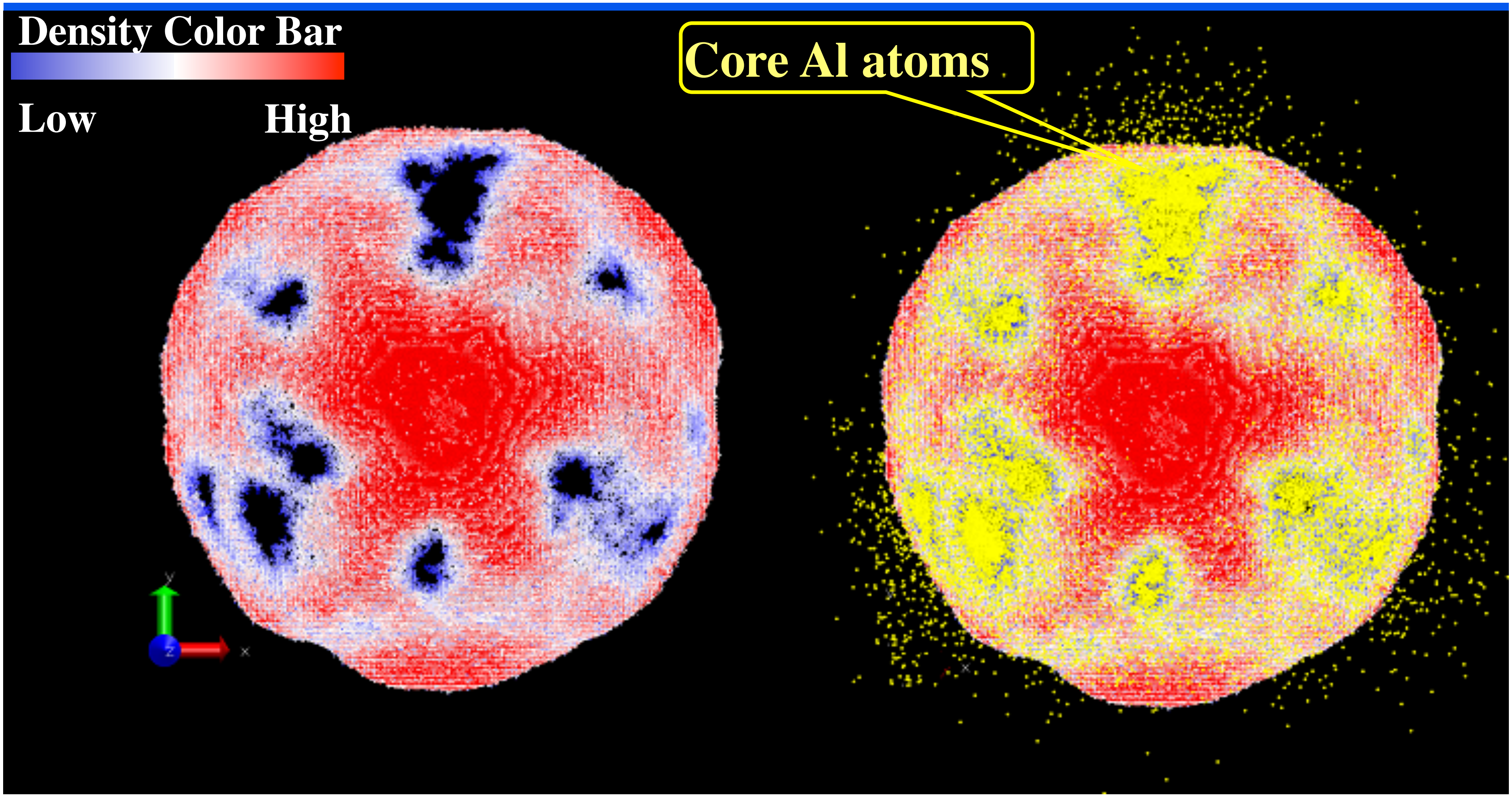
Migration of Atoms During Combustion

Core = c; Shell = s; Environment = e



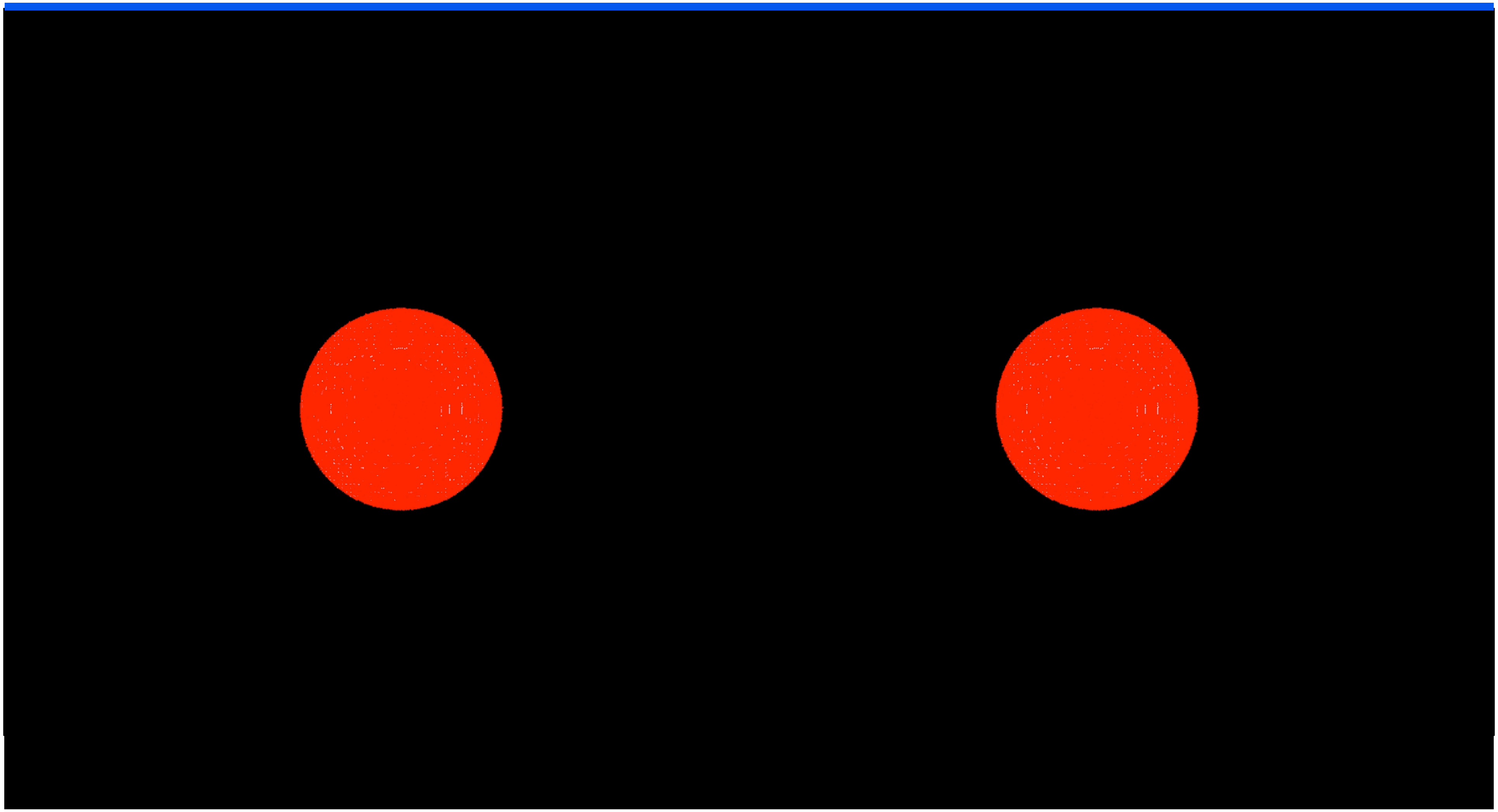
- **Migration of Atoms can be categorized into two types:**
  - **Events related to the shell - atoms into the shell or out of the shell**
  - **Direct transport of core Al and environmental Oxygen through the pores in the shell**

Jetting out of Al Core Atoms-Crystalline shell



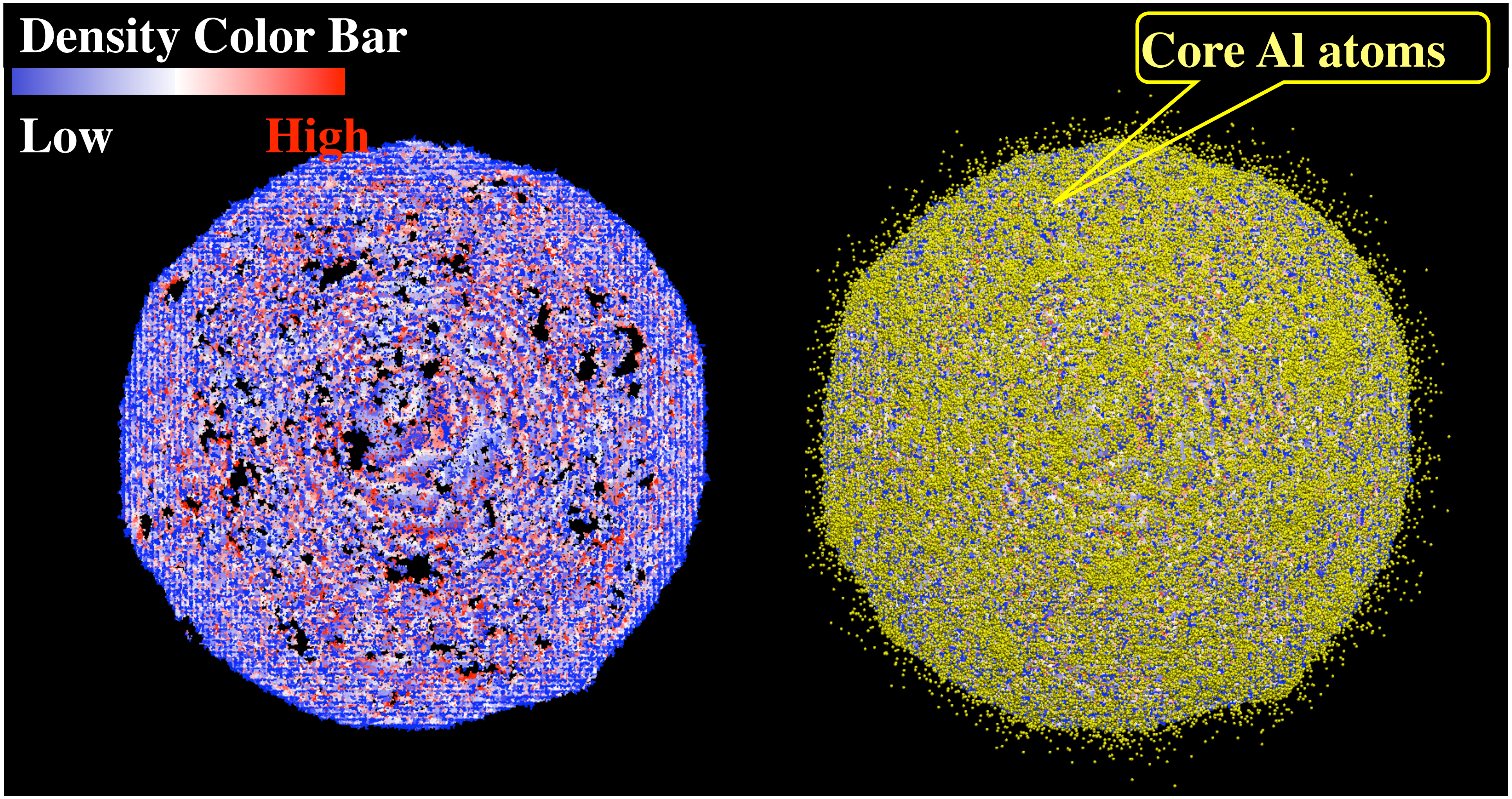
- More Al core atoms jet out from the weak areas of the shell

Jetting out of Al Core Atoms
40 nm Core, 4 nm Shell



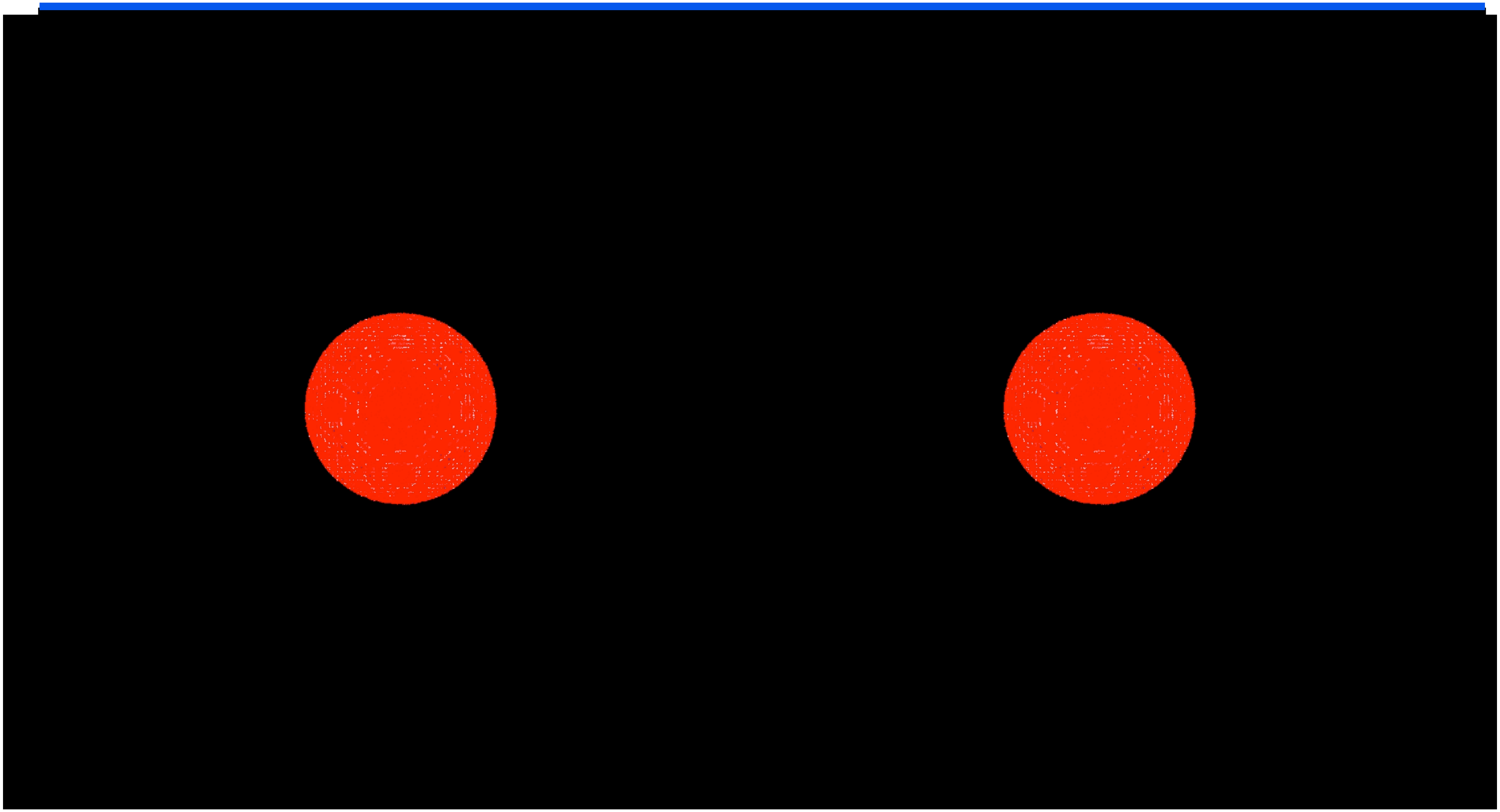
- More Al core atoms jet out from the weak areas of the shell

Jetting out of Al Core Atoms-Amorphous shell



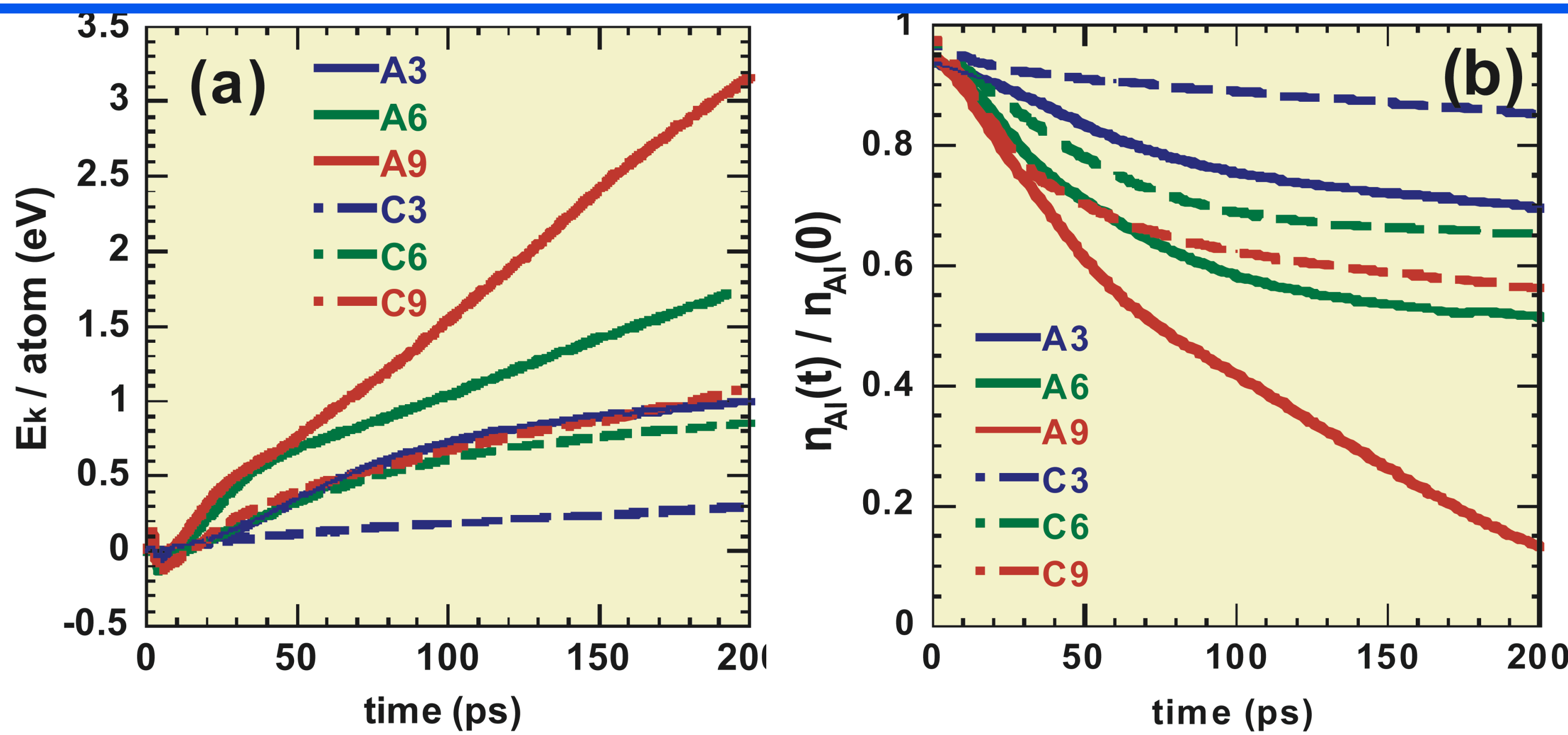
- Core Al jet out homogeneously from the shell

Jetting out of Al Core Atoms
Amorphous Shell



- Core Al jet out homogeneously from the shell

Energy Release Rate & Survival Fraction of Unoxodized Al atoms



- Effect of temperature on the energy release rate in ANPAS and ANPCS is similar
- Three mechanisms: diffusion-oxidation; ballistic transport followed by diffusion-oxidation; ballistic transport followed by coalescing of atoms into few-atom clusters-oxidation

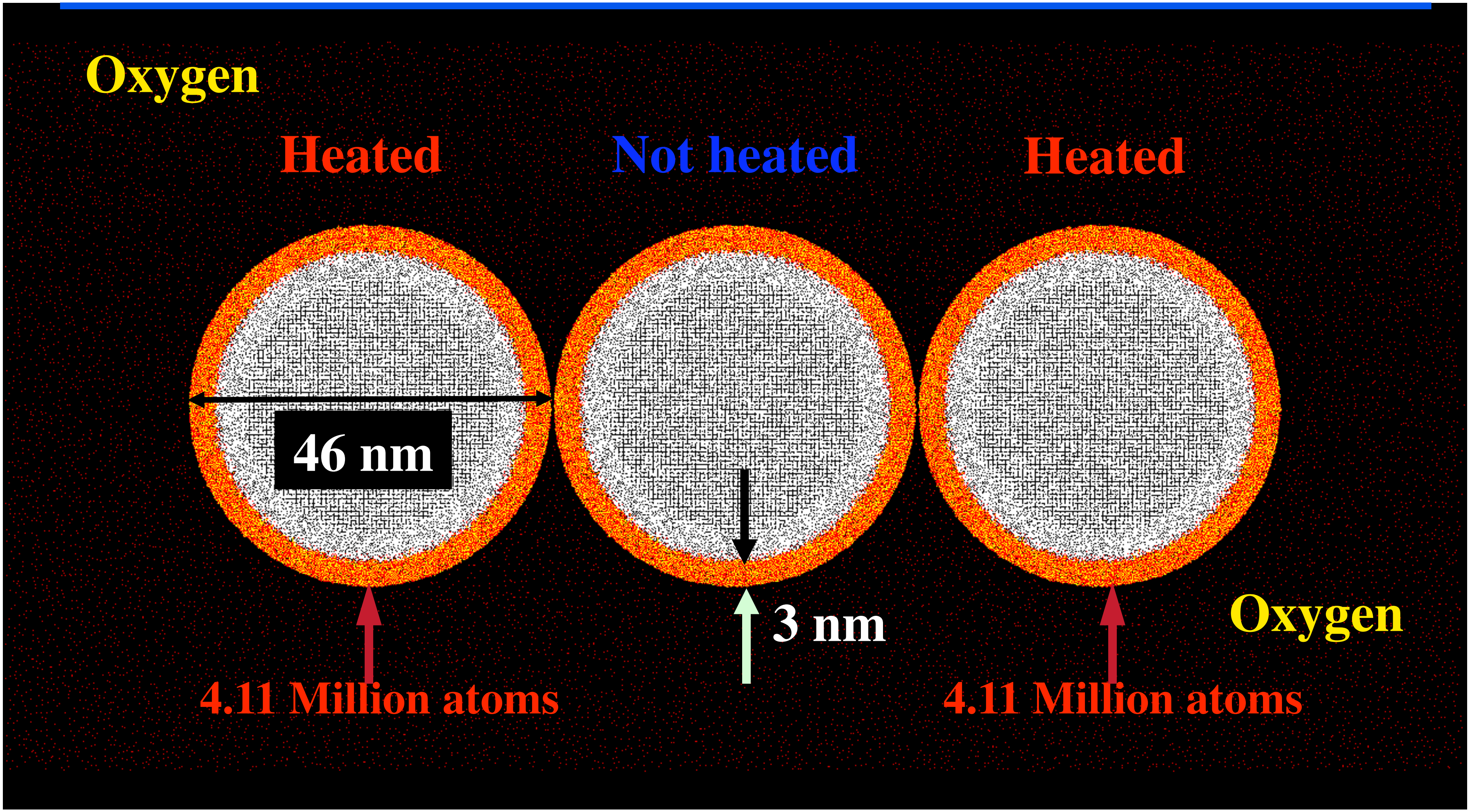
Isothermal Heating

Three Nanoparticles

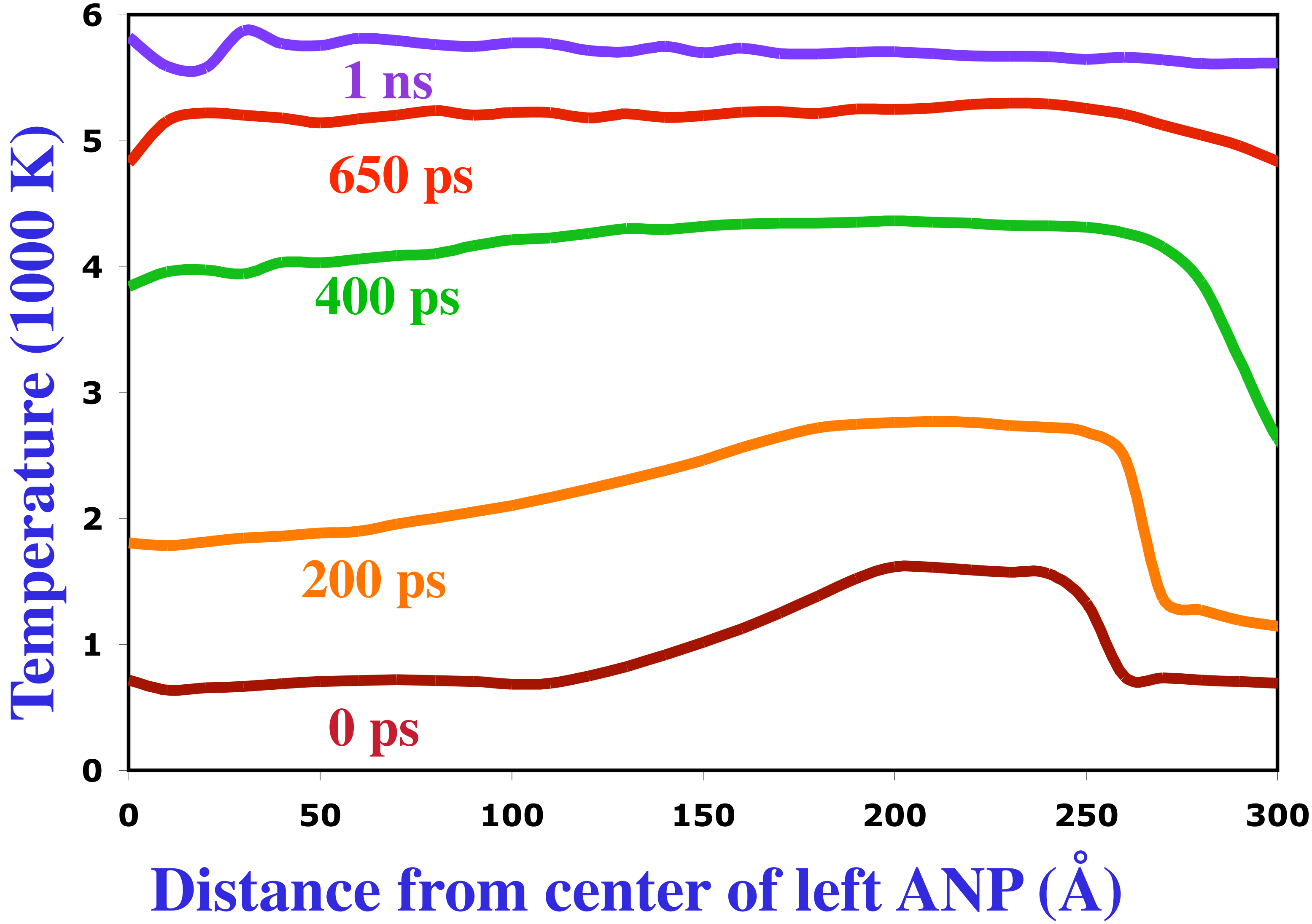
NP # 1 & # 3 heated (T = 1200K)

NP # 2 not heated

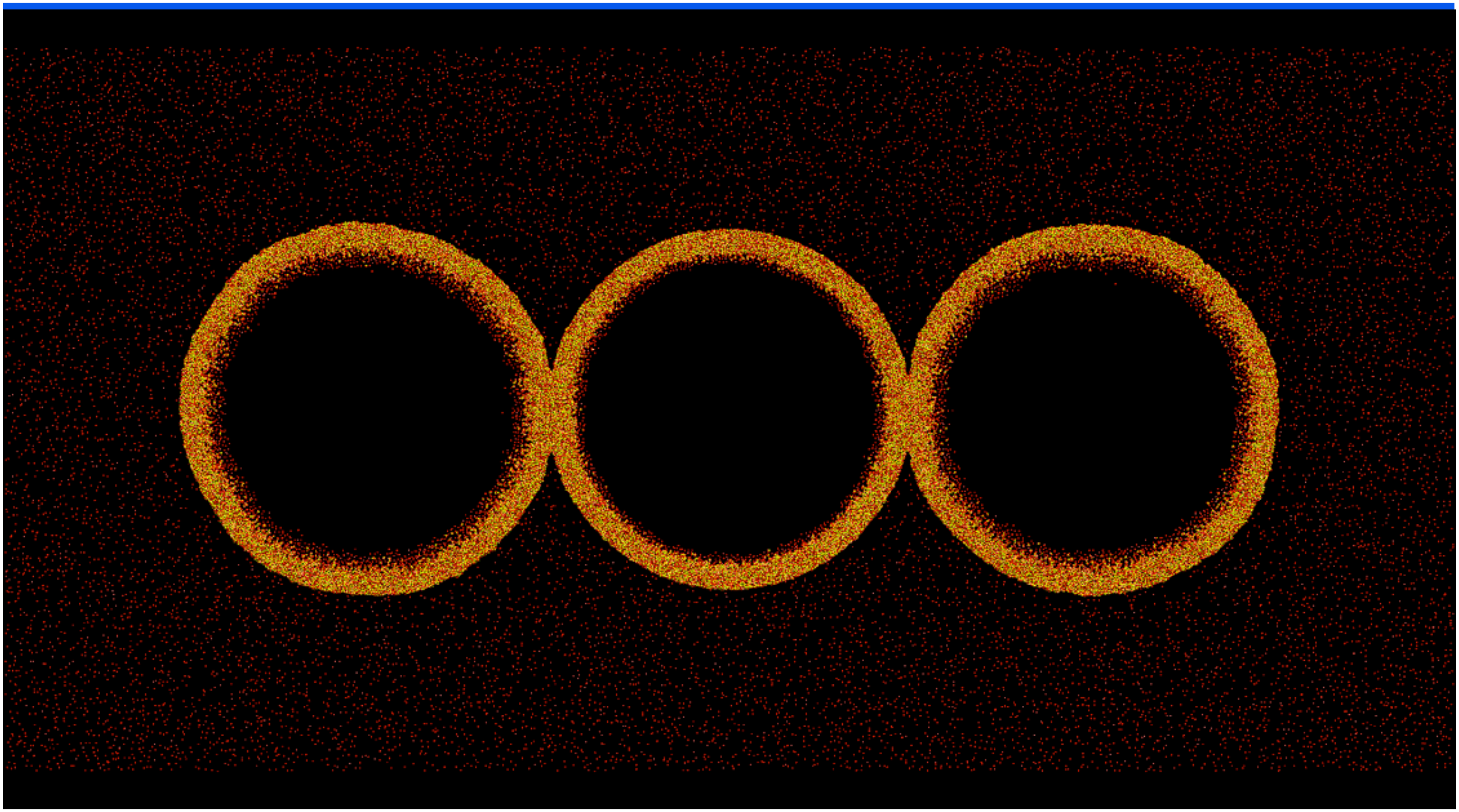
Three 46 nm Nanoparticles: Burning of the Center Nanoparticle



Radial Temperature Profile of the Left ANP

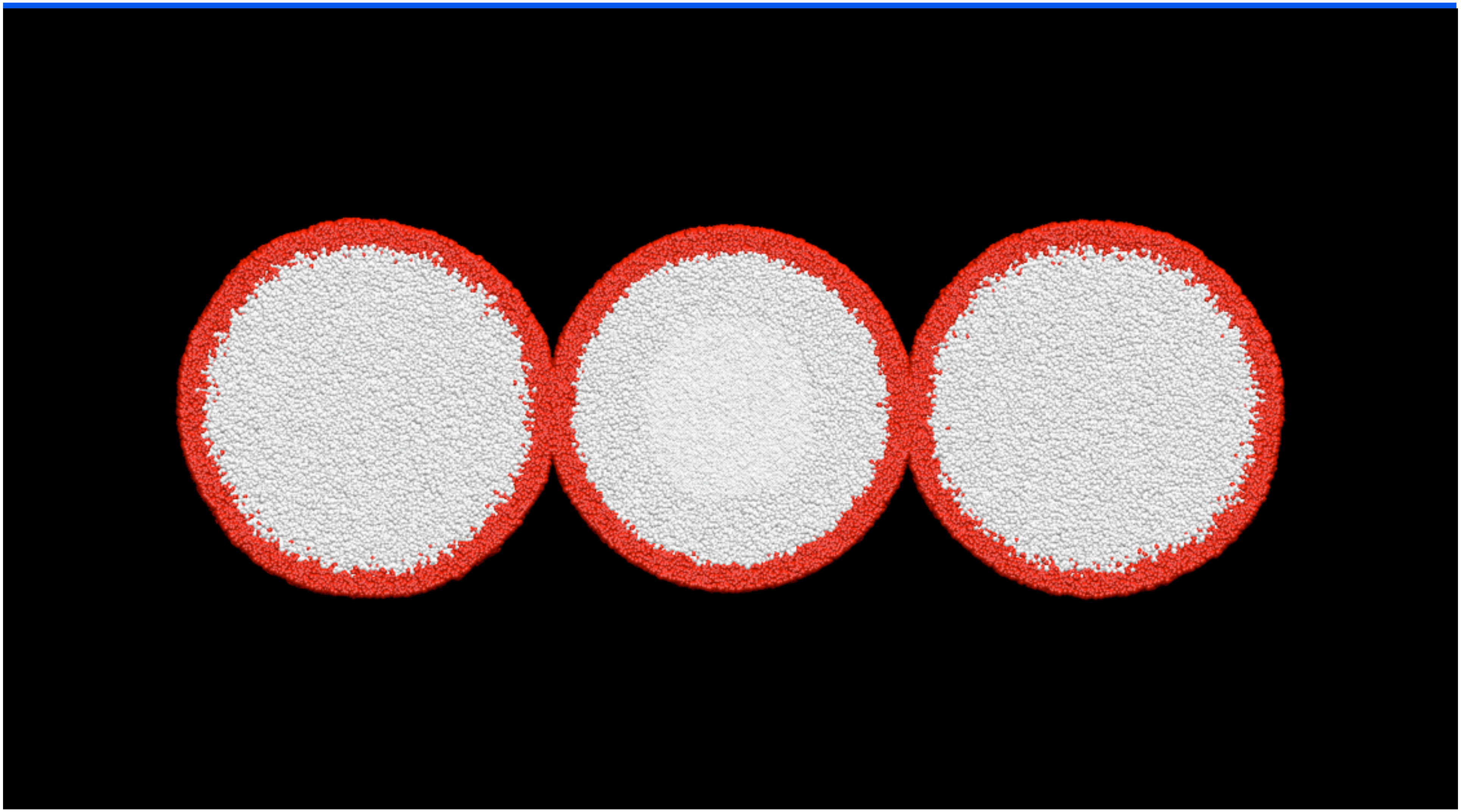


Burning of the Center Nanoparticle



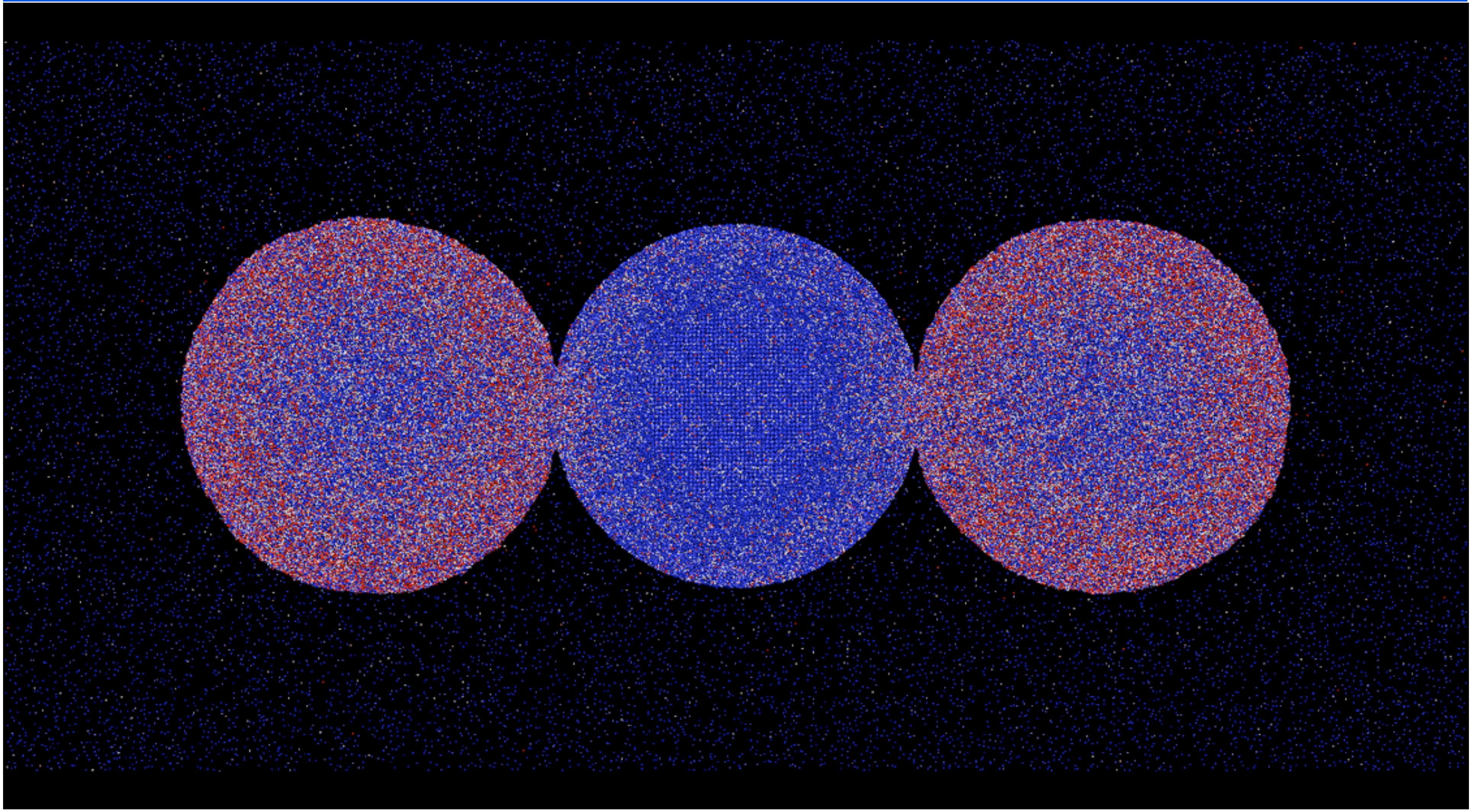
Oxidation reaction (Al core is not shown)

Burning of the Center Nanoparticle
Aluminum Ejections



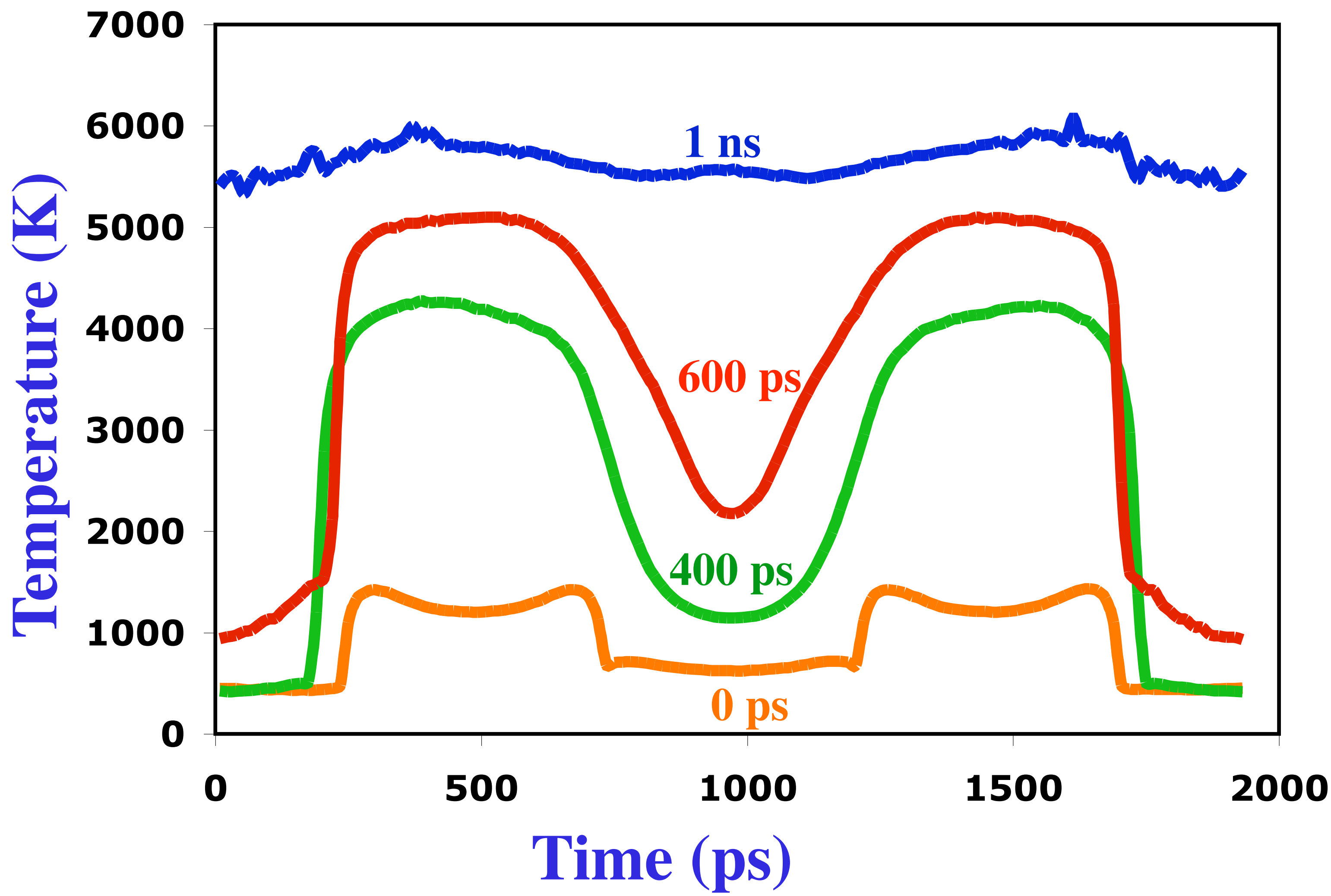
Aluminum ejections: core (white) and shell (red)

Temperature Profiles of Nanoparticles

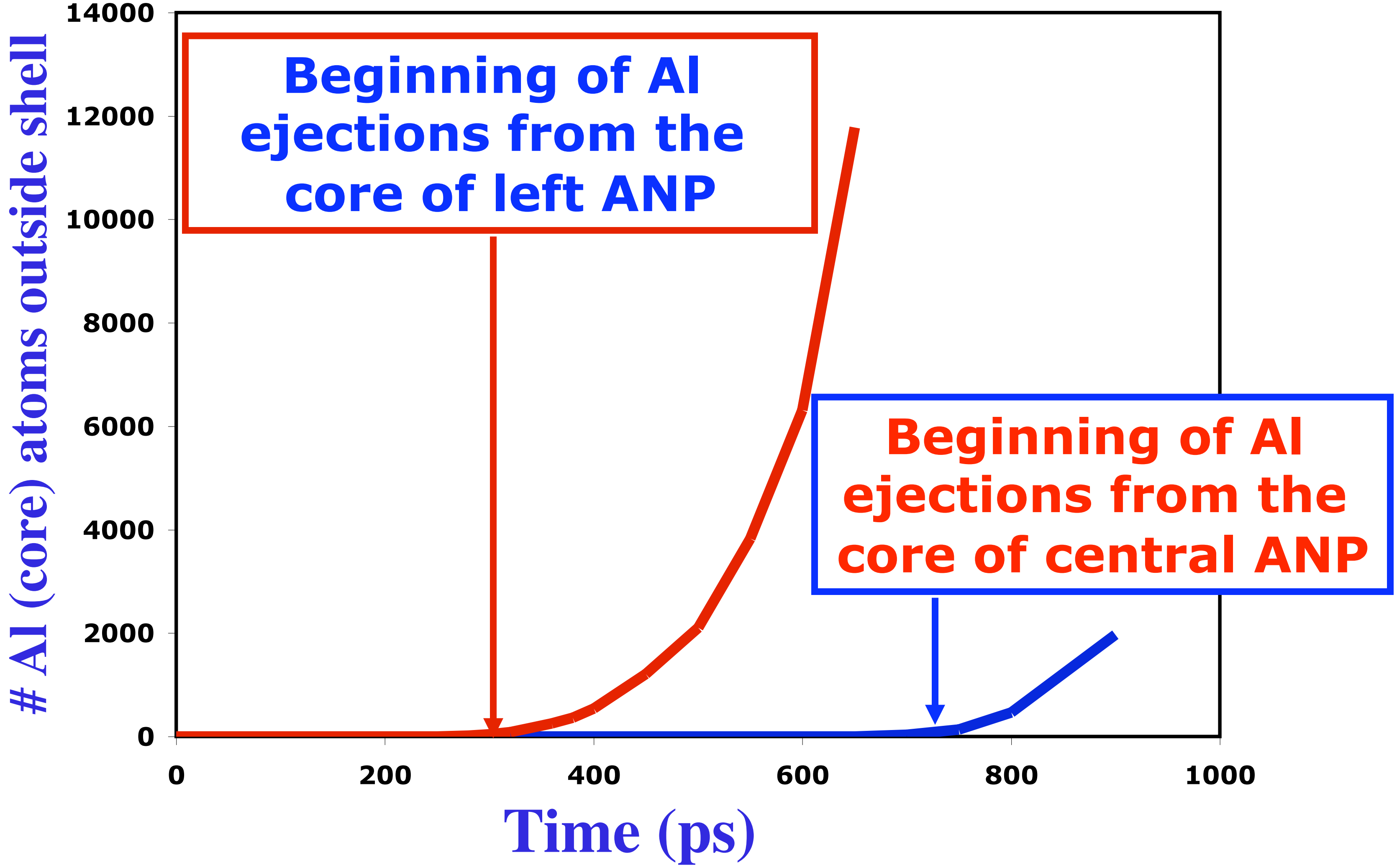


Cold (T<1000K) Hot (T>2500K)

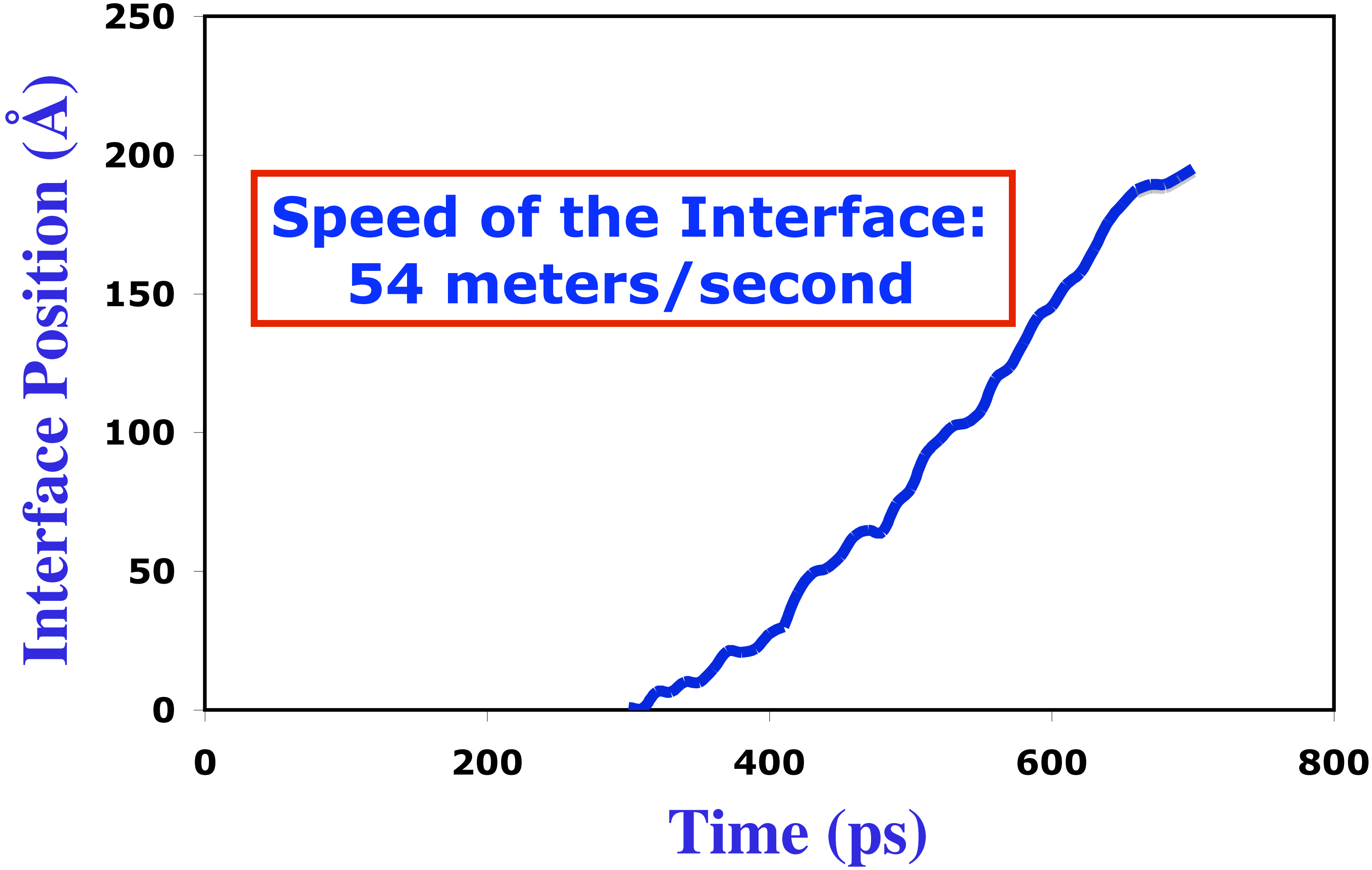
Temperature Profiles of three ANP



Al Ejections from the Cores of Three Nanoparticles



Speed of the Interface into Nanoparticle # 2



Research in Progress

Molecular dynamics with non-adiabatic transitions

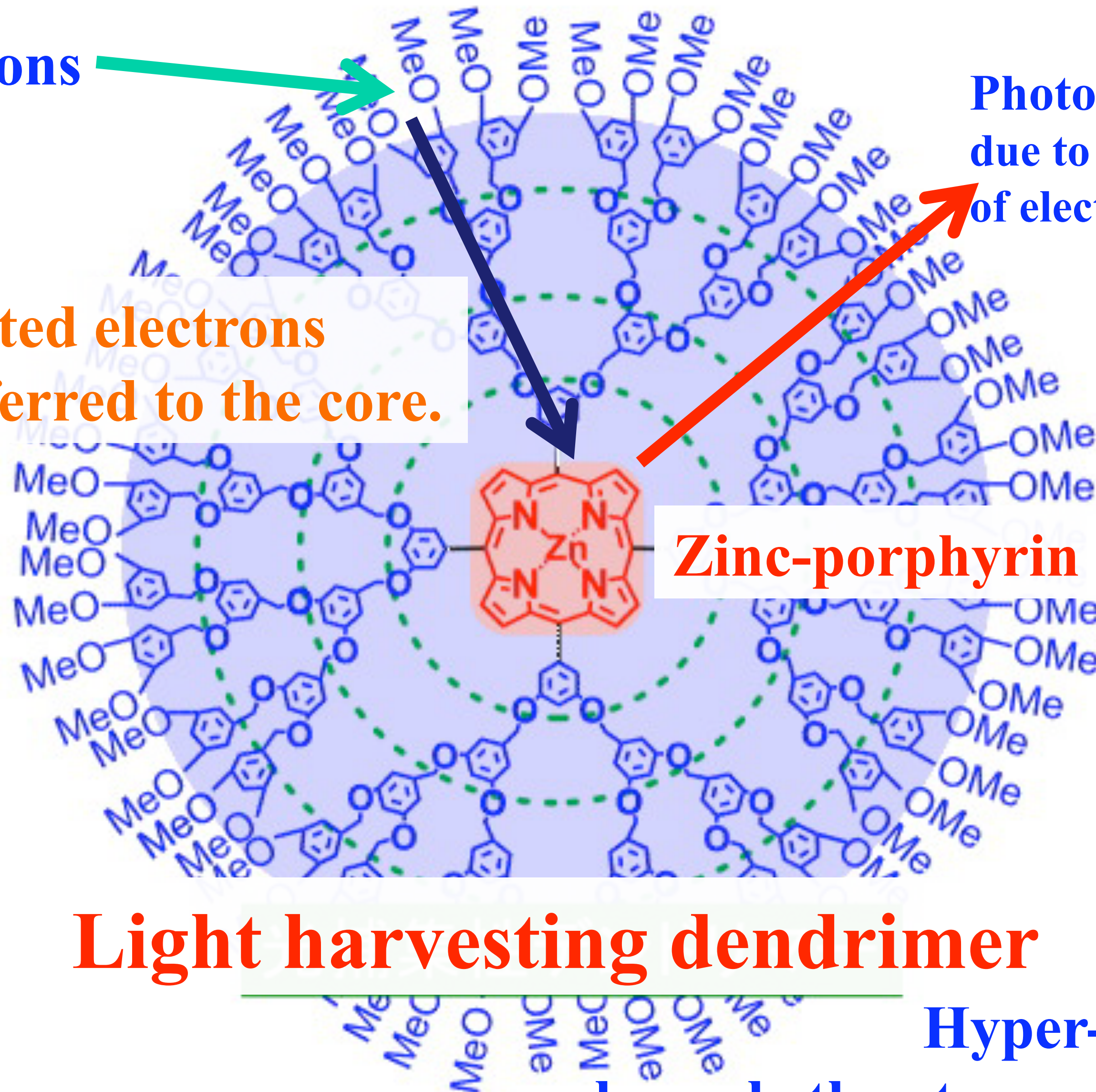
Energy Transfer in Dendrimer

http://pltop.shocomarec.kumamoto-u.ac.jp/index-j.html

Photons

Photoluminescence
due to the recombination
of electron-hole pairs

Photoexcited electrons
are transferred to the core.



Zinc-porphyrin core

Light harvesting dendrimer

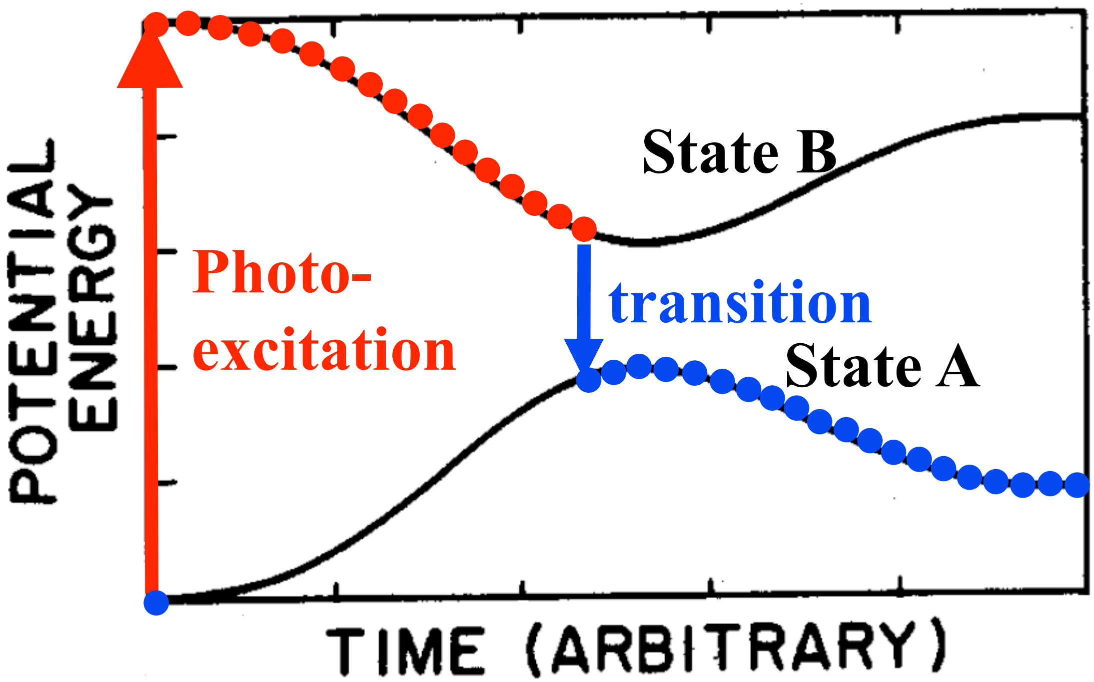
Hyper-branched
benzyl ether-type peripheries

MD Simulation with Electronic Transition

To account the nonadiabatic effects within the adiabatic MD simulations,

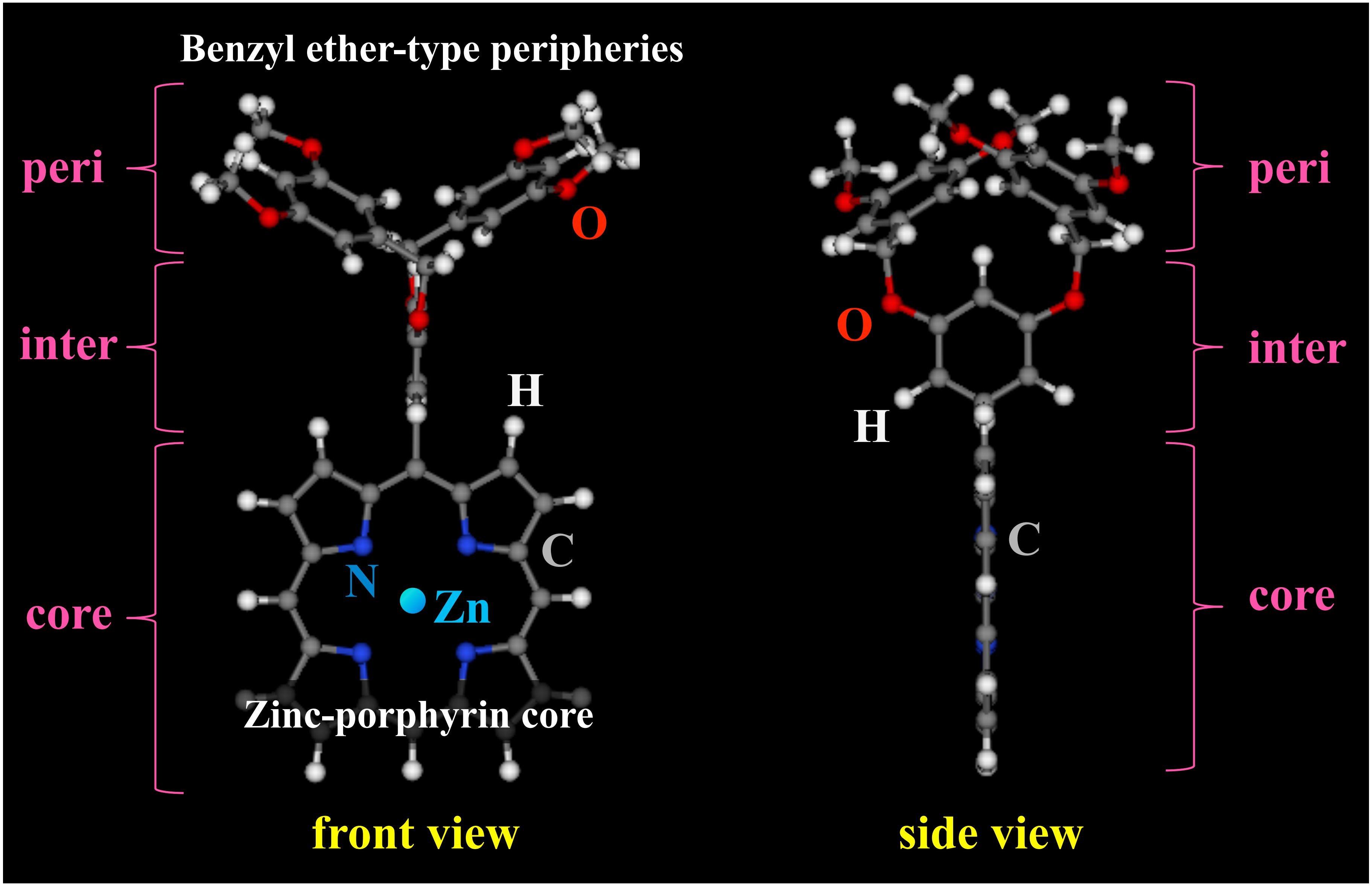
Time-Dependent Density-Functional Theory with Fewest-Switches Surface-Hopping method (TDDFT-FSSH)

Tully: J. Chem. Phys. 93, 1061 (1990)
Craig *et al.*: Phys. Rev. Lett. 95, 163001 (2005)



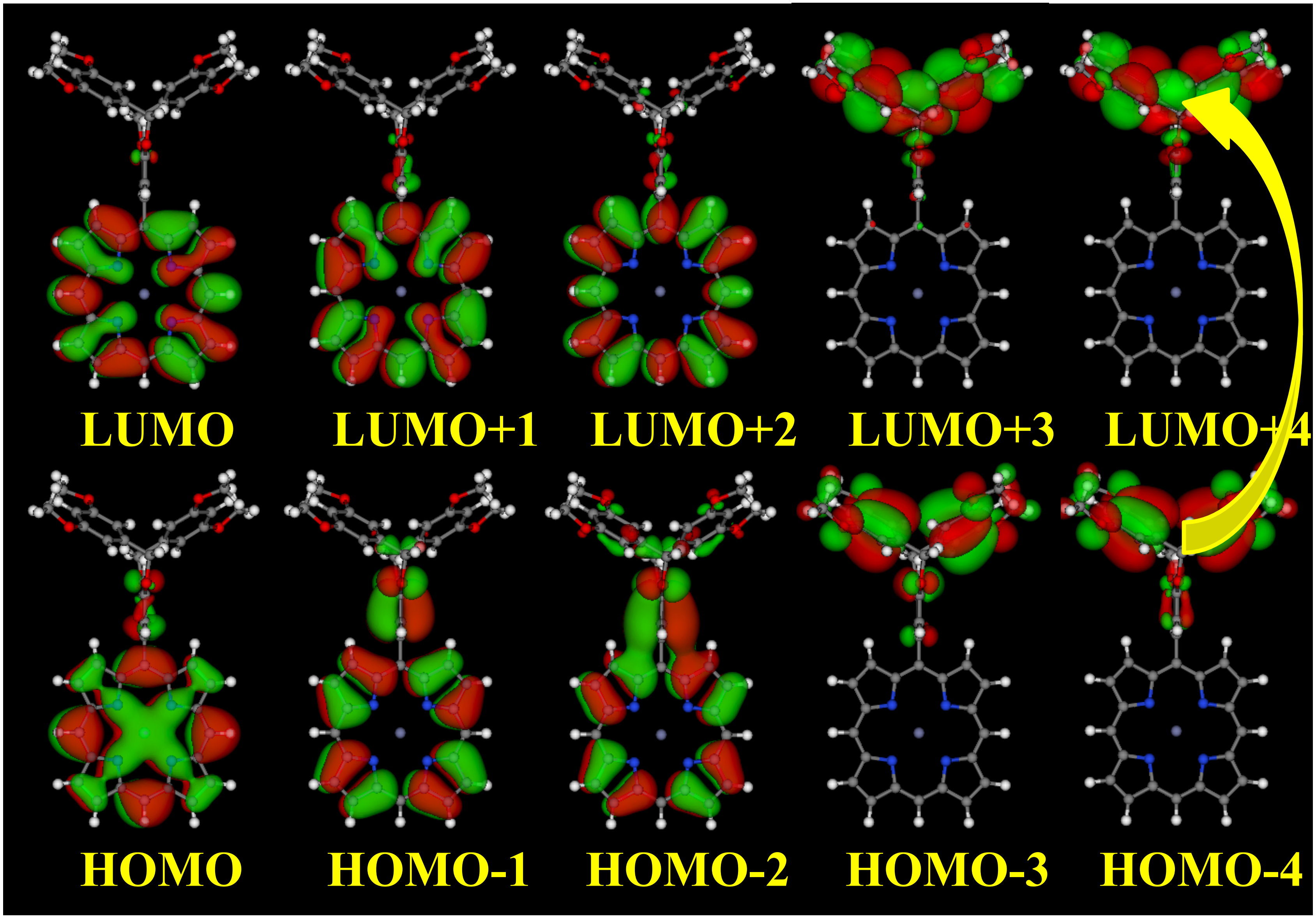
Electronic transitions from the current state to another state occur stochastically based on the switching probability obtained by solving the TD-KS equations.

The Model



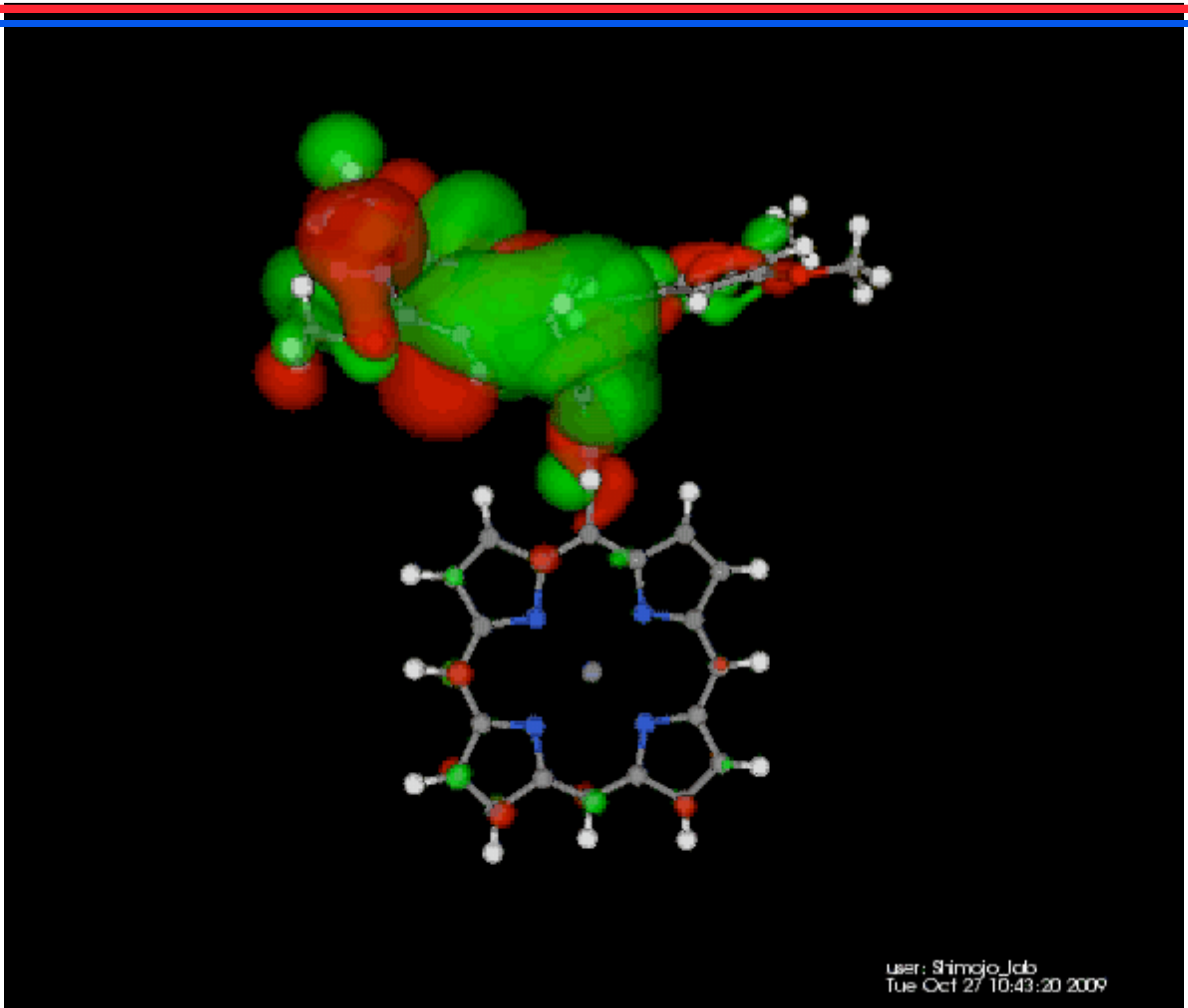
Benzyl ether-type peripheries
peri
inter
core
O
H
C
N
Zn
Zinc-porphyrin core
front view
peri
inter
core
O
H
C
side view

Simulation of Photoexcited State



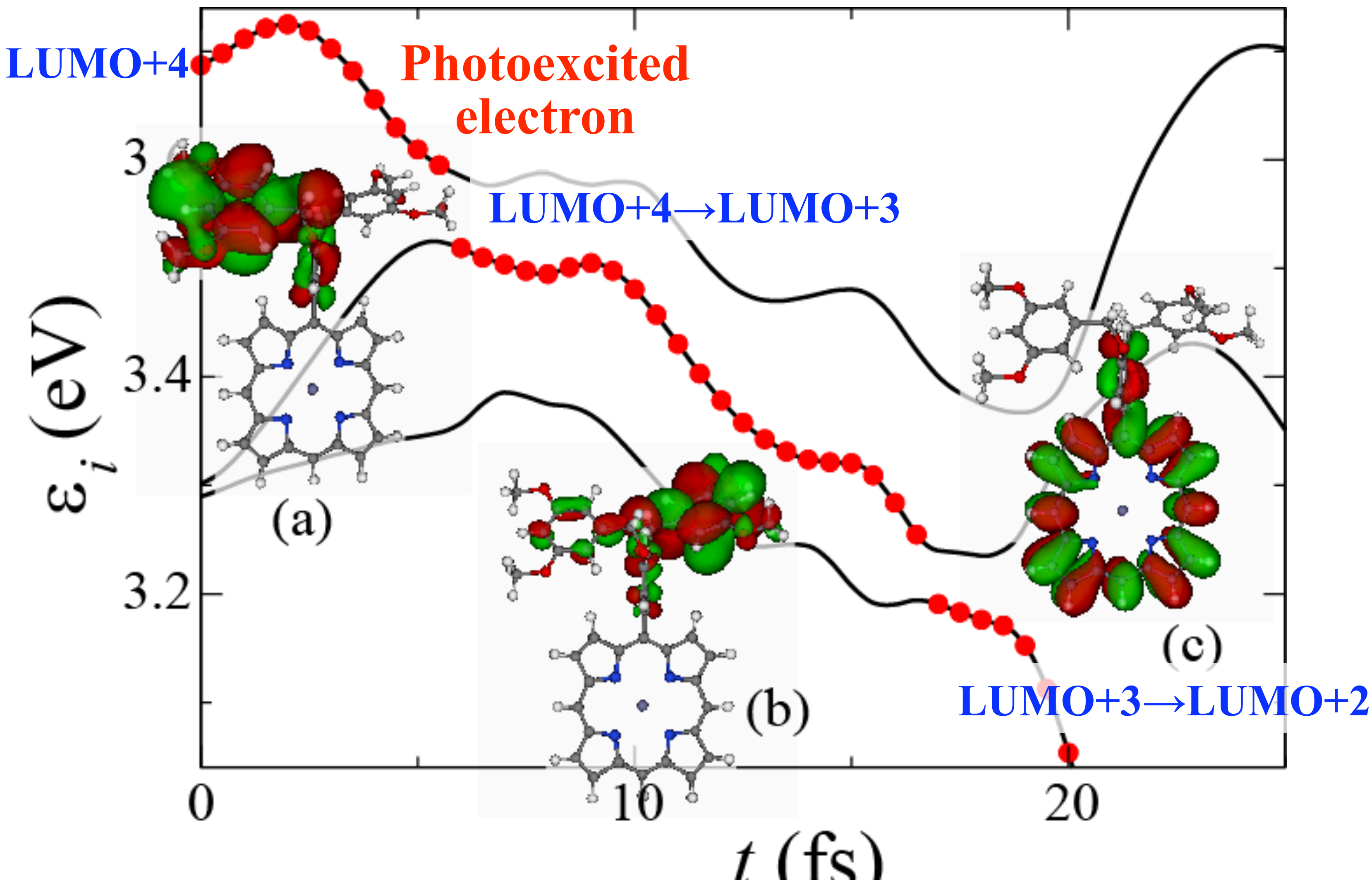
An electron in HOMO-4 is excited to LUMO+4.

Time Evolution of Spatial Distribution of Photoexcited Electron



Time Evolution of Eigenvalues

Excited State 300 K



The photoexcited electron is transferred to the core via overlapping orbitals.

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Thank you for your attention!