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10.10 – 10.30 **Assoc. Prof. Salim ASADOV (online)**

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Production of “green” hydrogen by photoelectrochemical splitting of water using new semiconductor nanocatalysts-electrodes

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INTRODUCTION

We have investigated the electronic structure and photoelectrochemical properties of cells containing new materials. Within the framework of the model of generation of electron/hole pairs excited by a photon, photoelectrochemical water splitting is explained. In such water splitting, solar energy is converted into chemical energy.

The goal of the report is theoretical and experimental development of modified semiconductor (SC) electrode materials and the development of optimal water splitting design in photoelectrochemical (PEC) cells to improve photoelectrolysis efficiency. The issues at hand are to:

Task 1 – theoretically and experimentally formulate and develop a technological concept for effective photoelectrochemical water splitting.

Task 2 – develop effective methods for modifying the structure of semiconductor Si and TiO_2 (synthesis of SC nanomaterials, SC doping).

Task 3 – develop theoretical justifications and experimental conditions for the selected concept of photoelectrochemical water splitting using new SC materials and photoelectrode designs.

Task 4 – develop promising candidates for photosensitive SC materials based on Si and TiO_2 compounds (nanostructures and nanoparticles) for the production of solar hydrogen.

The photocatalytic activity of modified semiconductor materials is determined by the nanostructure, crystallinity, particle size, surface area of the material and the design of the electrodes in the electrochemical cell.

We have considered the mechanisms of photoelectrode reactions at the **electrode/electrolyte** interface in the electrochemical cell within the framework of both closed and open thermodynamic models.

Taking into account the experimental data, the main requirements for electrode materials have been formulated to ensure optimal operation of the photoelectrochemical cell.

Physicochemical data on alloyed electrode materials based on **silicon Si and titanium dioxide TiO_2** were obtained.

METHODOLOGY and SIMULATION METHODS

The scientific idea of the report is the creation of new light-sensitive **nanomaterials M (metal)-doped Si or M-TiO_2** for photoelectrodes and their use for water splitting.

In nanostructures, the sizes of a set of elements in one, two or three directions are commensurate with physical parameters that have the dimension of length.

The sizes of structural elements of nanostructures range from several nanometers to several tens of nanometers and do not exceed 100 nm.

If the size of a condensed substance or a physical parameter that has the dimension of length is commensurate with a specific physical phenomenon, then size effects on the properties are observed.

In nanostructures, due to the effects of size quantization, the electronic energy spectrum is split and goes from continuous to discrete.

Taking this into account, it is planned to **M-dope** these **semiconductors (Si or TiO_2) with lithium, silver and copper.**

This enables to control the parameters of the semiconductors (bandgap width, effective mass and mobility of charge carriers).

Thus, doping with **M(metal)-Si or M-TiO_2** has been studied to improve the properties of photoelectrode materials.

Efficient photoelectrodes will increase the yield of hydrogen and the efficiency of the photocell in water splitting using the photoelectrochemical method.

SIMULATION METHODS

To study the **a-Si** structure, a cubic diamond crystal was simulated using NPT MD calculation. The **c-Si** structures of different orientations were created by rotating the **Si(100)** structure taking into account the periodicity at the lattice boundary.

We focused on the doping process (in particular, lithiation).

That is, we did not take into account the possible effects of the electric current density, electrolyte materials and the cathode of the photoelectrochemical cell.

The size of the studied sample-electrode was taken large along the axial direction. This allowed to observe the development of lithiation of the Si semiconductor during the simulation.

The sample size was limited by the cutoff radius of the interatomic potential to 10 Å, which increases the efficiency of the calculations.

Thus, the size of the simulation region was 300 Å × 17 Å. Here, the lengths denote the axial and off-axial directions, respectively.

The axial direction was occupied by Si atoms up to 110 Å; the rest of the space contained Li atoms (Li:Si ratio = 11:7).

The systems consisted of 3777 and 6252 atoms, respectively.

The periodic boundary conditions were strengthened along both off-axis directions.

A virtual flat wall was built on the far axial boundary to create a perpendicular force.

This prevents the atoms from escaping the simulation box.

The MD calculations were performed at temperatures ranging from 600 to 1500 K, which reduces the simulation time by accelerating the chemical reactions.

The temperature was controlled by a Berendsen thermostat, which rescaled the atomic velocities at each step.

One MD time step was $\Delta t = 0.2$ fs. Charge transfer was performed using the charge equilibrium (Q_{Eq}) method at each step.

MATHEMATICAL PART OF MODELING

$$J_i = -c_t \sum_{j=1}^{n-1} D_{ij} \nabla x_j \tag{1}$$

$$J_1 = -c_t D_{11} \nabla x_1$$

$$J_2 = -c_t D_{22} \nabla x_2$$

(2,3)

Maxwell-Stefan (MS) approach

$$-\frac{1}{RT}\nabla\mu_i = \sum_{j=1,\, j\neq i}^{n} \frac{x_j(u_i - u_j)}{Đ_{ij}} \qquad \textbf{(4)}$$

Fick's law and the MS theory describe the same diffusion process

$$[D] = [B]^{-1}[\Gamma] \qquad (5)$$

[D] - matrix of Fick diffusion coefficients of size (n — 1) × (n — 1)

[B] - Elements of the matrix

[Γ] - thermodynamic factors

A model of pair interaction of non-polar molecules was used, describing the dependence of the interaction energy of two particles on the distance between them.

Coefficients for calculating MD

$$B_{ii} = \frac{x_i}{Đ_{in}} + \sum_{j=1, j \neq i}^{n} \frac{x_j}{Đ_{ij}}, \quad \text{with} \quad i = 1, \cdots, (n-1)$$

$$B_{ij} = -x_i \left(\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}} \right), \quad \text{with} \quad i, j = 1, \cdots, (n-1) \text{ and } i \neq j. \tag{6}$$

$$\Gamma_{ij} = \delta_{ij} + x_i \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right)_{T,p,\Sigma} \tag{7}$$

For binary systems, the relationship between the Fick diffusion coefficients and MS was used

$$D = \Gamma \times Đ_{12} \tag{8}$$

$$\Gamma = 1 + x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,p,\Sigma} = 1 + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,p,\Sigma} \tag{9}$$

Basic equation of MD modeling

$$a_i = \frac{F_i}{m_i} = \frac{\mathrm{d}^2 r_i}{\mathrm{d}\,t^2} \tag{10}$$

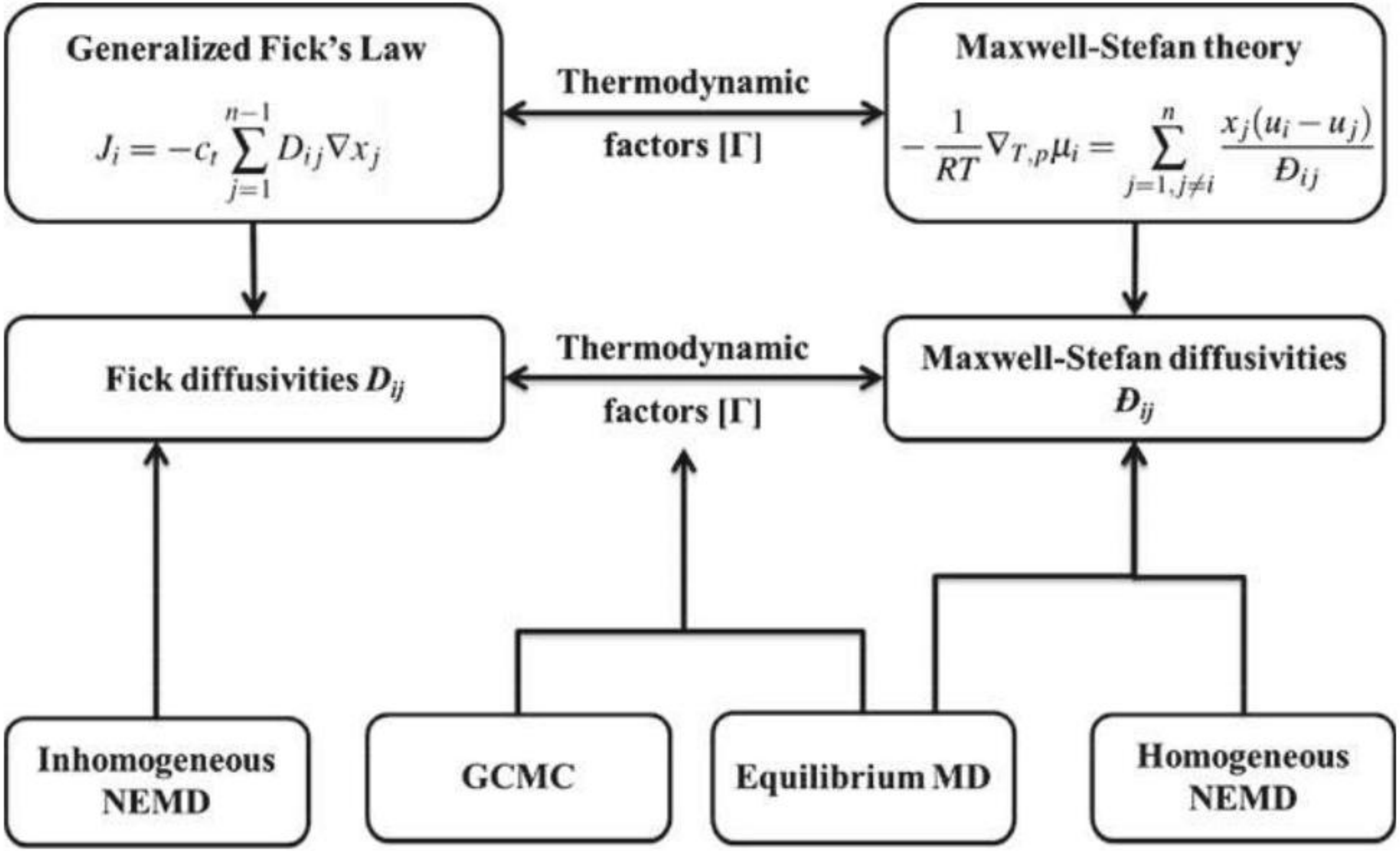
Equation of the time-reversible Verlet algorithm

$$r_i(t+\Delta t) = r_i(t) + v_i(t)\Delta t + \frac{F_i(t)}{2m_i}\Delta t^2,$$

$$v_i(t+\Delta t) = v_i(t) + \frac{F_i(t+\Delta t) + F_i(t)}{2m_i}\Delta t$$

(11, 12)

Algorithm for modeling the diffusion of nonequilibrium MD



Generalized Fick's Law

$$J_i = -c_t \sum_{j=1}^{n-1} D_{ij} \nabla x_j$$

Thermodynamic factors [Γ]

Maxwell-Stefan theory

$$-\frac{1}{RT} \nabla_{T,p} \mu_i = \sum_{j=1, j \neq i}^{n} \frac{x_j (u_i - u_j)}{Đ_{ij}}$$

Fick diffusivities D_{ij}

Thermodynamic factors [Γ]

Maxwell-Stefan diffusivities $Đ_{ij}$

Inhomogeneous NEMD

GCMC

Equilibrium MD

Homogeneous NEMD

Equations of non-stationary diffusion in a binary system

$$\frac{\partial c_i}{\partial t} = D\nabla^2 c_i$$

(13)

$$\nu = (D_1 - D_2)\frac{\partial N_1}{\partial x} = (D_2 - D_1)\frac{\partial N_2}{\partial x}.$$

(13a,b)

$$\tilde{D} = (N_1 D_2 + N_2 D_1)\frac{\partial \ln a_1}{\partial \ln N_1}.$$

Onsager Coefficients for Nonequilibrium Molecular Dynamics

$$\Lambda_{ij} = \frac{1}{6}\lim_{m\to\infty}\frac{1}{N}\frac{1}{m\cdot\Delta t}\times\left\langle\left(\sum_{l=1}^{N_i}(r_{l,i}(t+m\cdot\Delta t)-r_{l,i}(t))\right)\left(\sum_{k=1}^{N_j}(r_{k,j}(t+m\cdot\Delta t)-r_{k,j}(t))\right)\right\rangle \tag{14}$$

$$\Lambda_{ij} = \frac{1}{3N}\int_0^\infty \mathrm{d}t'\left\langle\sum_{l=1}^{N_i} v_{l,i}(t)\cdot\sum_{k=1}^{N_j} v_{k,j}(t+t')\right\rangle \tag{15}$$

In binary systems, the diffusion coefficient MS D_{12} is related to the Onsager coefficients

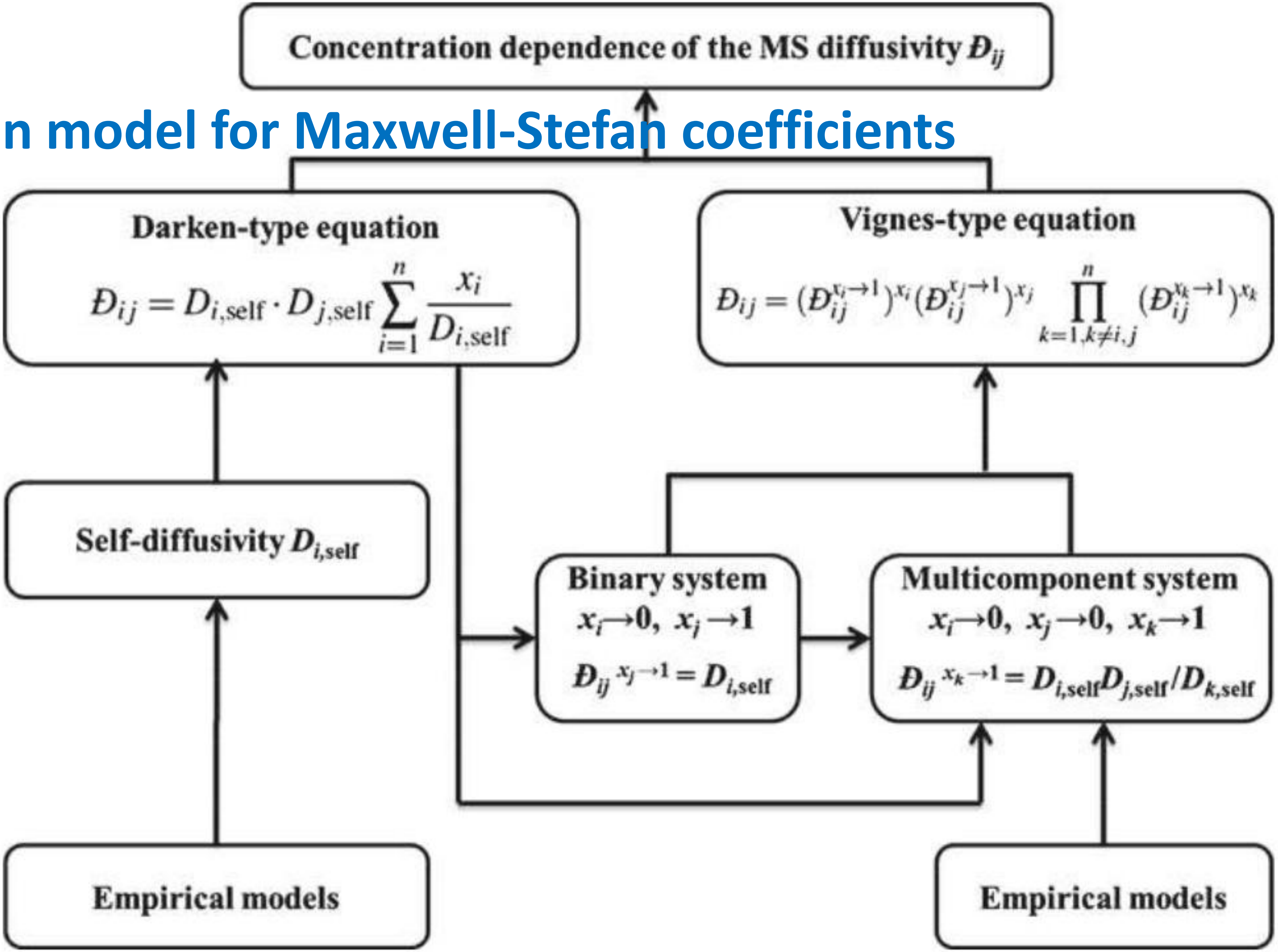
$$Đ_{12} = \frac{x_2}{x_1}\Lambda_{11} + \frac{x_1}{x_2}\Lambda_{22} - 2\Lambda_{12} \qquad \textbf{(16)}$$

The self-diffusion coefficient $D_{i,self}$ of ith component is related to the average molecular displacements in MD

$$D_{i,\mathrm{self}} = \frac{1}{6N_i} \lim_{m\to\infty} \frac{1}{m\cdot\Delta t} \left\langle \sum_{l=1}^{N_i} (r_{l,i}(t+m\cdot\Delta t) - r_{l,i}(t))^2 \right\rangle \tag{17}$$

$$= \frac{1}{3N_i} \int_0^\infty \mathrm{d}t' \left\langle \sum_{i=1}^{N_i} (v_{l,i}(t)\cdot v_{l,i}(t+t')) \right\rangle \tag{18}$$

Prediction model for Maxwell-Stefan coefficients



Concentration dependence of the MS diffusivity Đ_{ij}

Darken-type equation

$$\text{Đ}_{ij} = D_{i,\text{self}} \cdot D_{j,\text{self}} \sum_{i=1}^{n} \frac{x_i}{D_{i,\text{self}}}$$

Vignes-type equation

$$\text{Đ}_{ij} = (\text{Đ}_{ij}^{x_i \to 1})^{x_i} (\text{Đ}_{ij}^{x_j \to 1})^{x_j} \prod_{k=1, k \neq i,j}^{n} (\text{Đ}_{ij}^{x_k \to 1})^{x_k}$$

Self-diffusivity $D_{i,\text{self}}$

Binary system

$x_i \to 0,\ x_j \to 1$

$\text{Đ}_{ij}{}^{x_j \to 1} = D_{i,\text{self}}$

Multicomponent system

$x_i \to 0,\ x_j \to 0,\ x_k \to 1$

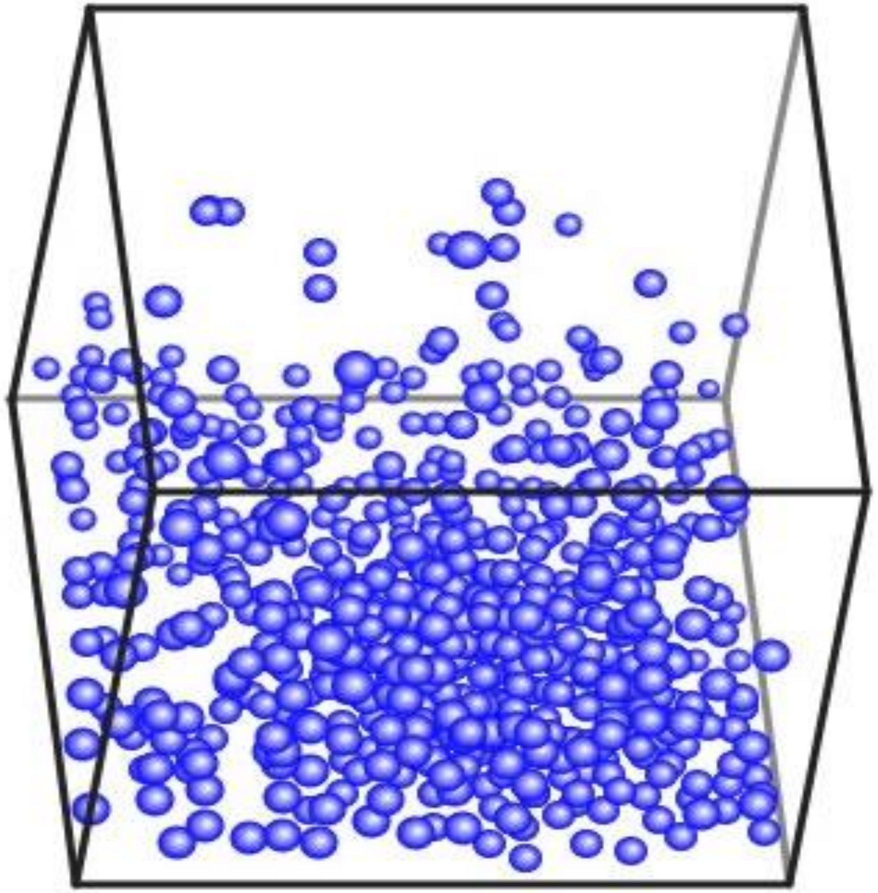
$\text{Đ}_{ij}{}^{x_k \to 1} = D_{i,\text{self}} D_{j,\text{self}} / D_{k,\text{self}}$

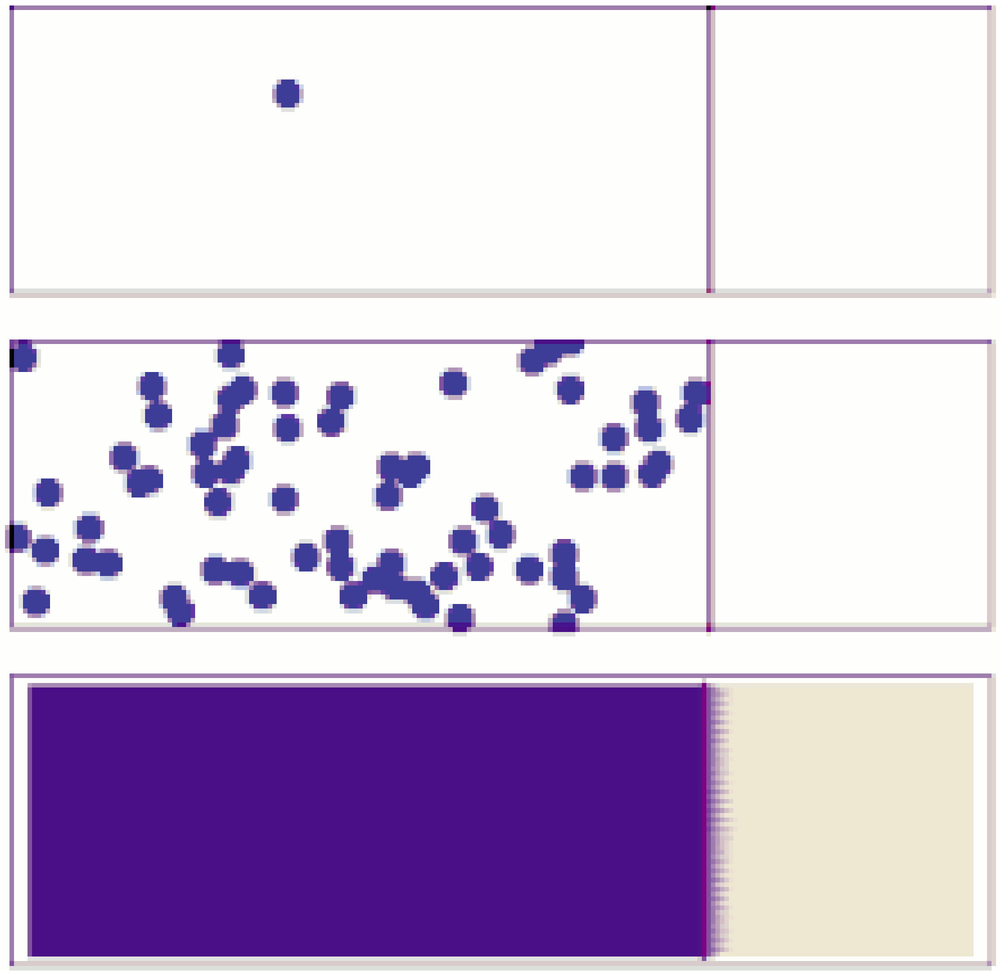
Empirical models

Empirical models

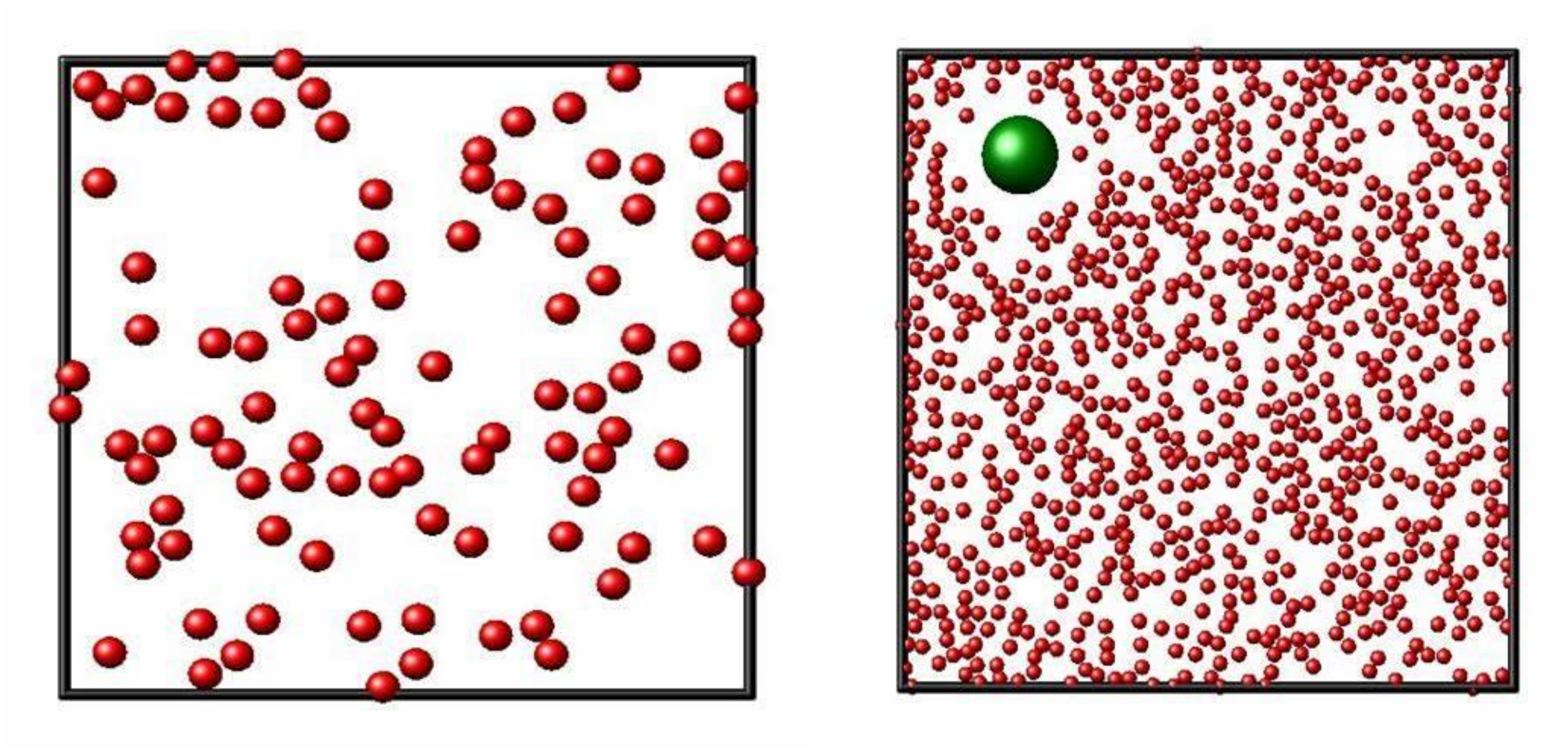
RESULTS AND DISCUSSION

LAMMPS



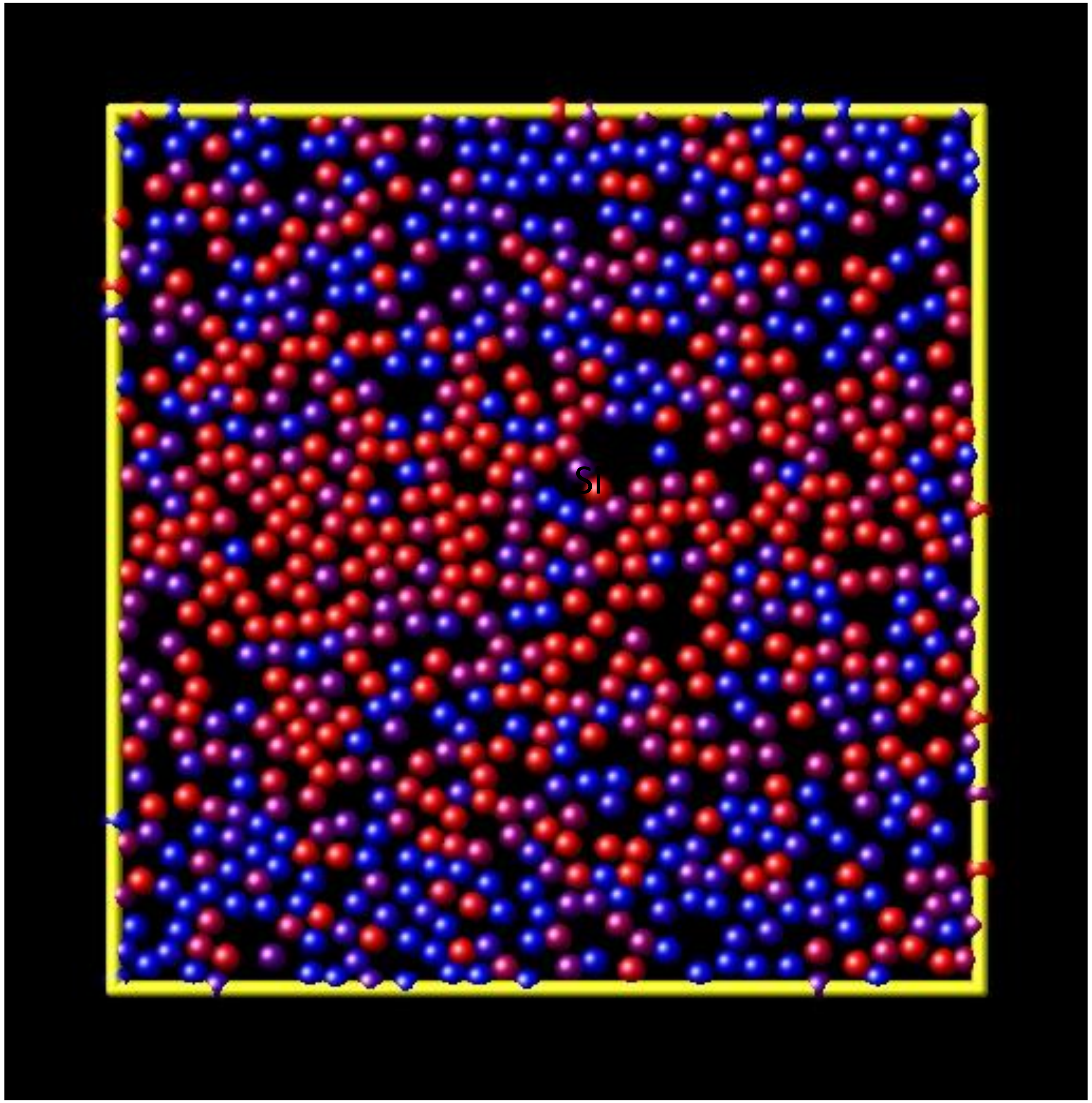


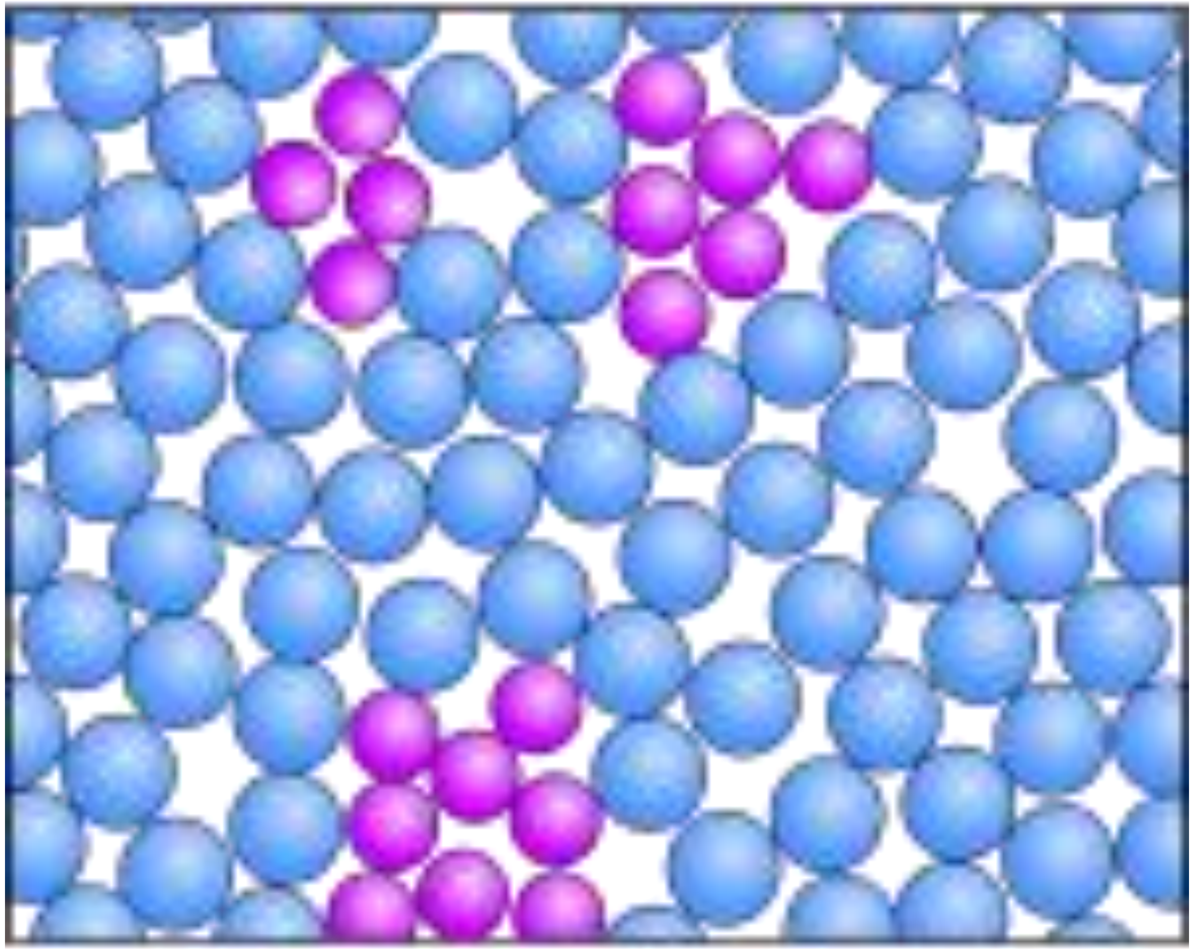
Modeling Results LAMMPS



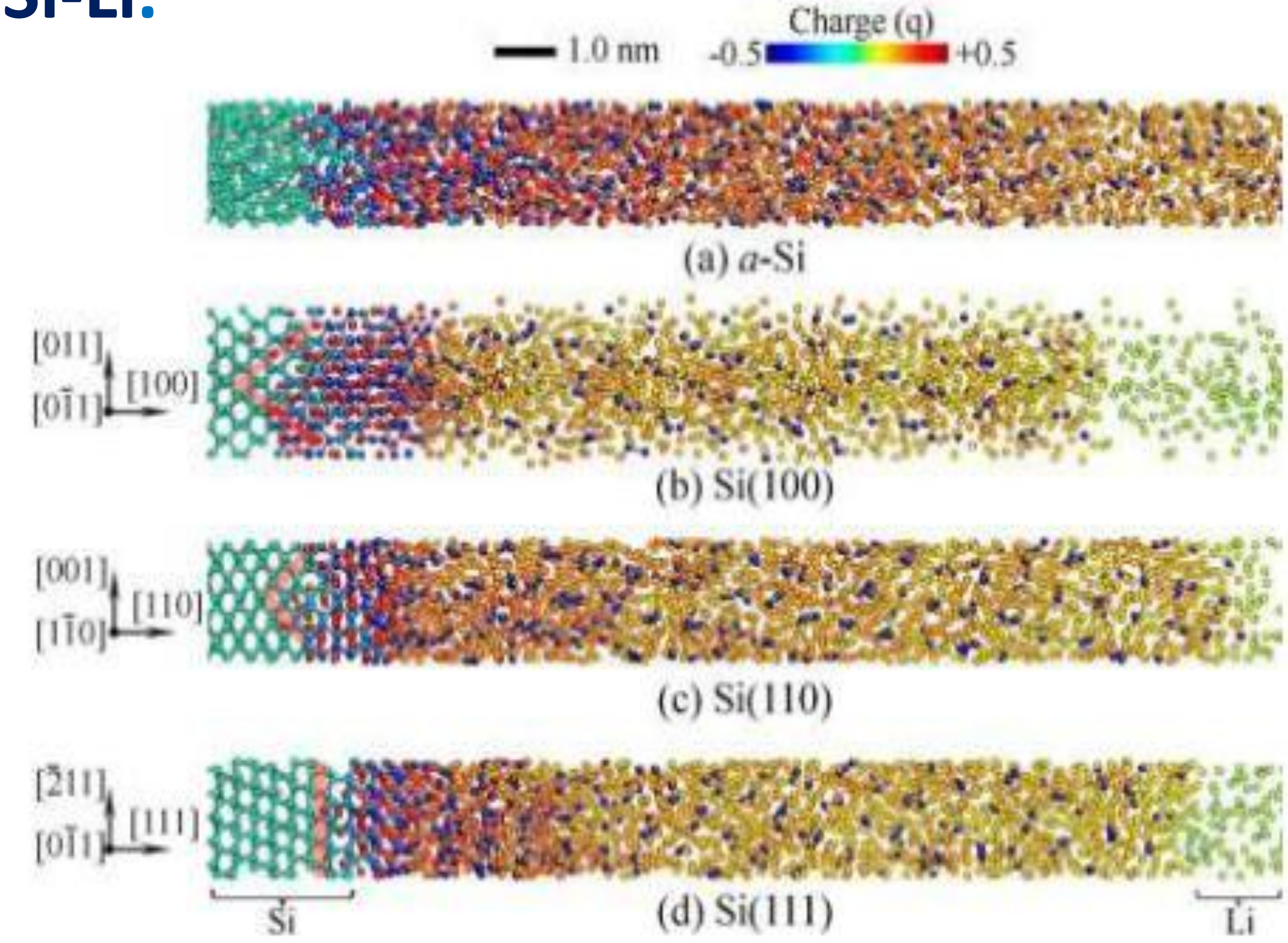
Modeling Results

LAMMPS





During the lithiation of Si, structural changes are observed in the lithiated region of various Si structures. The reaction is most active in **a-Si-Li**.



(a) *a*-Si

(b) Si(100)

(c) Si(110)

(d) Si(111)

Figure 1

Figure 1. Atom and charge configurations during initial lithiation of (a) a-Si and (b–d) c-Si.

[110] is the crystal direction, and (111) is the set of bonds connecting the two planes. Atom colors indicate the charge state.
Green color indicates neutral atoms, blue color indicates Si atoms with $q < -0.5e$, and red color indicates Li atoms with $q > +0.5e$.

Results after 200 ps Si+Li reaction time at 1200 K.

CONCLUSIONS

1. Molecular dynamics modeling of the electrode material doping process was performed for new semiconductor "nanocatalyst electrodes" taking into account atomistic mechanisms. A lithiated silicon-based material was used as an example of an electrode.

2. Obtained necessary data for controlling the electrode material in obtaining "green" hydrogen by photoelectrochemical water splitting using semiconductor materials.

3. The modified method for calculating diffusion coefficients enables to relate the Fick diffusion coefficients to the Maxwell-Stefan diffusion coefficient using MD modeling.
In other words, the gap between the experimental Fick diffusion coefficient and the MS diffusion coefficient can be reconciled using the MD modeling method.

4. In the chosen model, these diffusion coefficients were related to each other through a matrix of thermodynamic factors, which are uncertain.

5. Thermodynamic factors were calculated based on MD modeling using the small subsystems method.

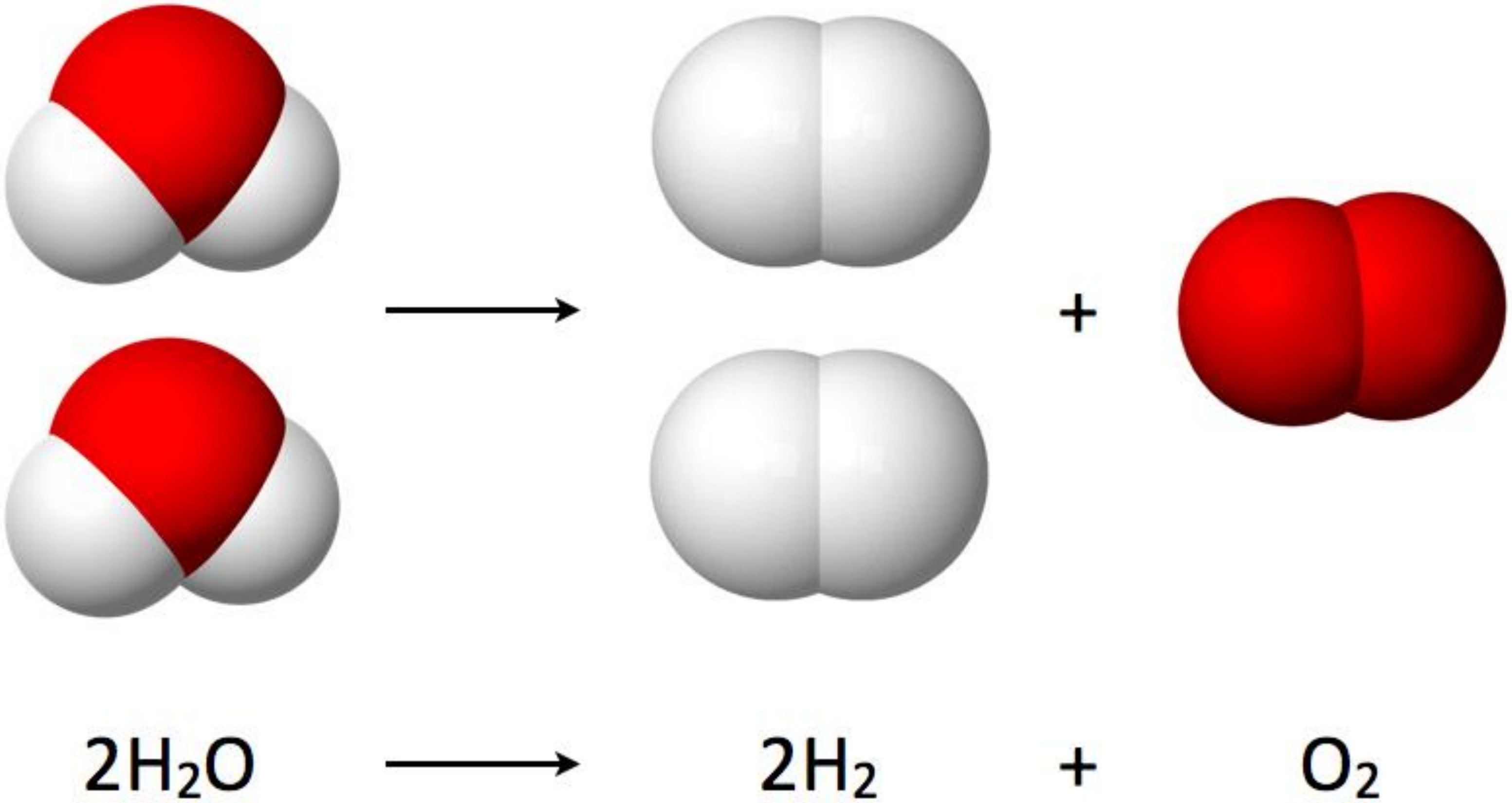
6.

a) These results are important for the prediction and production of new electrode photomaterials for "green chemistry" and "green energy".

b) The choice of an object based on M-Si (sunlight irradiation) and M-TiO_2 (UV light irradiation) is justified by the fact that semiconductor nanomaterials with strong absorption of visible light can be effective photocatalysts in electrochemical processes and new environmentally important technologies for producing H_2.

c) Such semiconductor systems allow to save energy consumption in photoelectrochemical processes for producing pure hydrogen.

Thank you for your attention!



$$2H_2O \longrightarrow 2H_2 + O_2$$