Thur. Jun. 28th

FY2018's 1st, CREST Workshop

Application of the latest Red Moon program to some polymerization systems catalyzed by organometallics towards the realization of chain shuttling polymerization *simulation*

Yuichi Suzuki

My research subjects

i. The development of RM program aiming a generalized simulation method for complex chemical reaction systems (collaborating with Dr. Takayanagi).
   - We are planning to make the program available for researchers at universities or companies (under license/copyright).

ii. The realization of chain shuttling polymerization (CSP) simulation using RM method (collaborating with Dr. Saha and Ms. Misawa).
   - This subject has to be completed by the next (/final) CREST report in the beginning of September.

iii. The establishment of a methodology to treat diffusion of molecules in addition to chemical reactions.
   - It is important to expand the RM methodology to be able to treat it occurring as a rare event.

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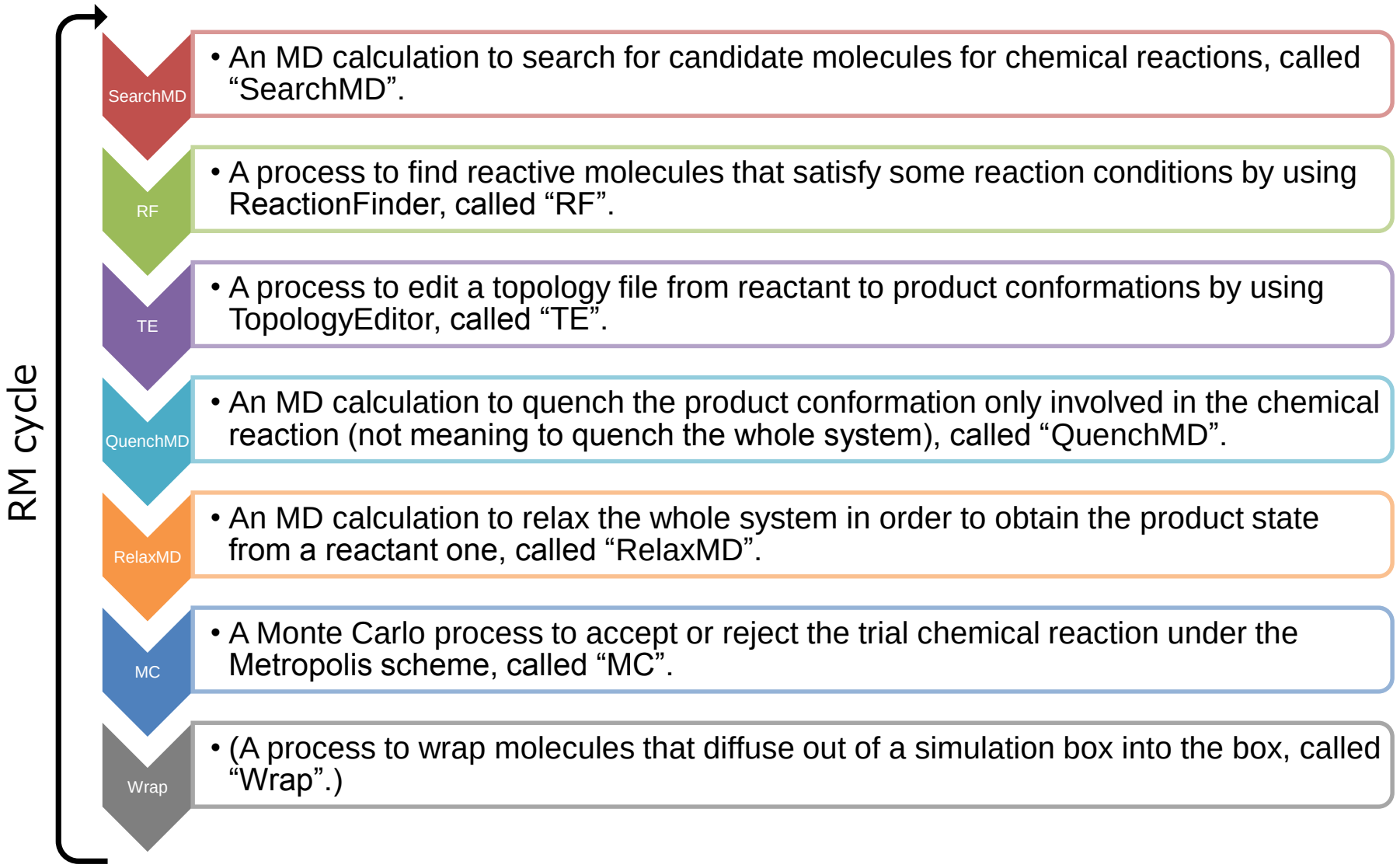
Basic computational processes in RM cycle



Modules constructing the present RM program

rm_main.py

The main script for all of the modules to perform RM simulation by successively calling the method “run” in each class of the modules.

rm_read_input.py

The script to read an input file “rm_input.dat” and return the parameter “proc_parms” that includes a set of the parameters for all the processes such as SearchMD, RF, TE, QuenchMD, RelaxMD, MC and Wrap.

amber_mdsolvers.py

The script to write an *mdin* file and execute any kinds of MD calculation such as SearchMD, QuenchMD and RelaxMD.

reaction_finder.py

The script to find molecules, satisfying some reaction conditions written in “rm_input.dat”, in the structures obtained by SearchMD.

topology_editor.py

The script to edit a topology file with TopologyEditor using the script file outputted from ReactionFinder.

rm_monte_carlo.py

The script to calculate energy difference between reactant and product states and then undo or redo the update of the whole structure under the Metropolis scheme.

wrap_into_box.py

The script to translate the whole structure under a specified condition and then wrap molecules into the simulation box by using the cpptraj program.

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Target system: Chain shuttling polymerization (CSP)

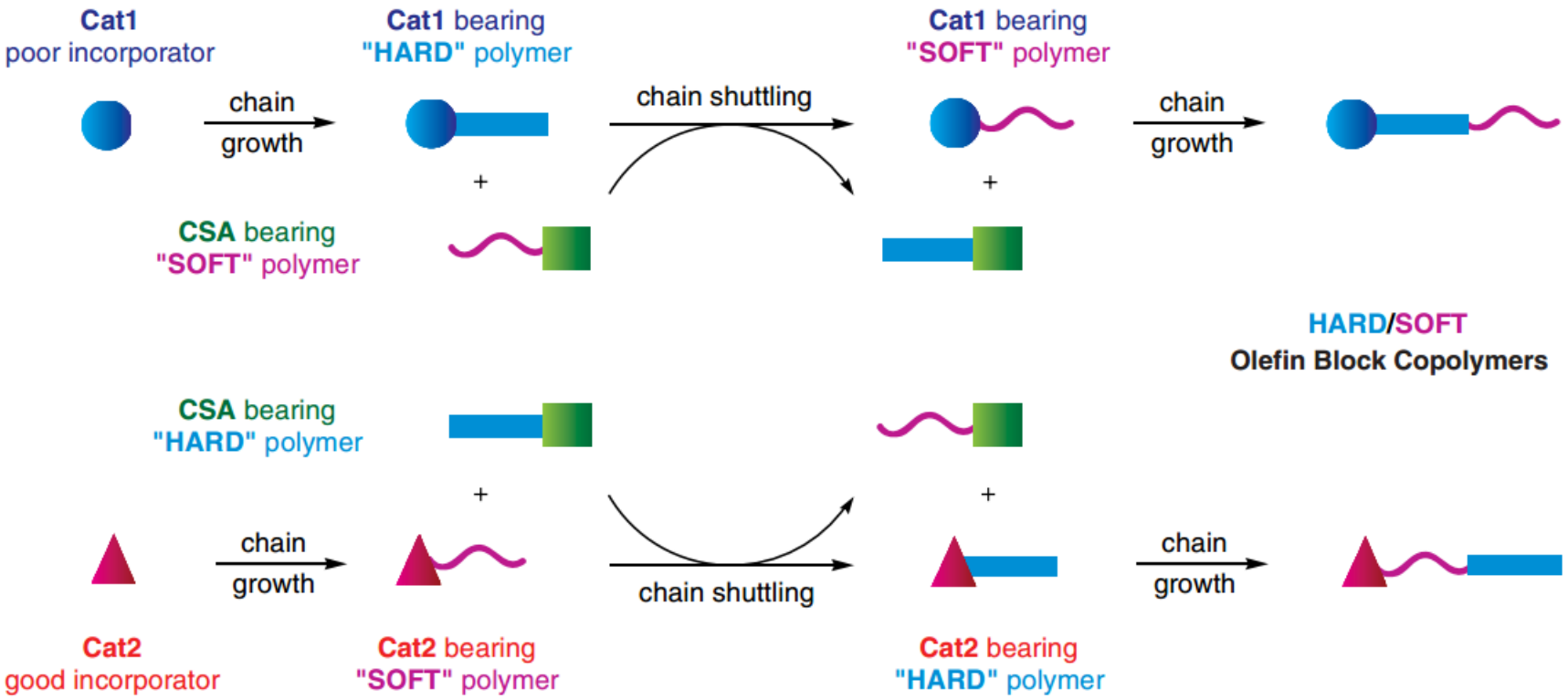

Fig. 1. Depiction of the likely chain shuttling mechanism in a single reactor, dual-catalyst approach. **Cat1** (solid circles) and **Cat2** (solid triangles) represent catalysts with high and low monomer selectivity, respectively, whereas the **CSA** (solid squares) facilitates the chain shuttling reaction. ⋯

Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714–719.

Procedure towards the realization of CSP simulation

Hf catalyst system

I. Ethylene IP simulation.

II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

} Complete!!

III. Ethylene and 1-octene IP simulation.

IV. CCTP simulation with ethylene and 1-octene as monomers, and with $ZnEt_2$ as CTA.

Zr catalyst system

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CSP system with Hf and Zr catalysts

I. CSP simulation in which the ethylene and 1-octene IP occurs on the Hf catalyst, and the ethylene IP occurs on the Zr catalyst, accompanying with chain transfer by $ZnEt_2$ as CSA.

IP: insertion polymerization
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RM simulations using the latest RM program

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(Hf-cat system II and Zr-cat system I)

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Addition of a new module

edit_top_LJ.py

The script to edit topology file in order to consider LJ interactions between specified atoms using TopologyEditor, which is impossible to treat such specified interactions using the modules in amber programs.

- This module executes not only TopolgyEditor but also “LJedit.py”, made by Dr. Matsumoto, to specify atoms necessary to consider LJ interactions.

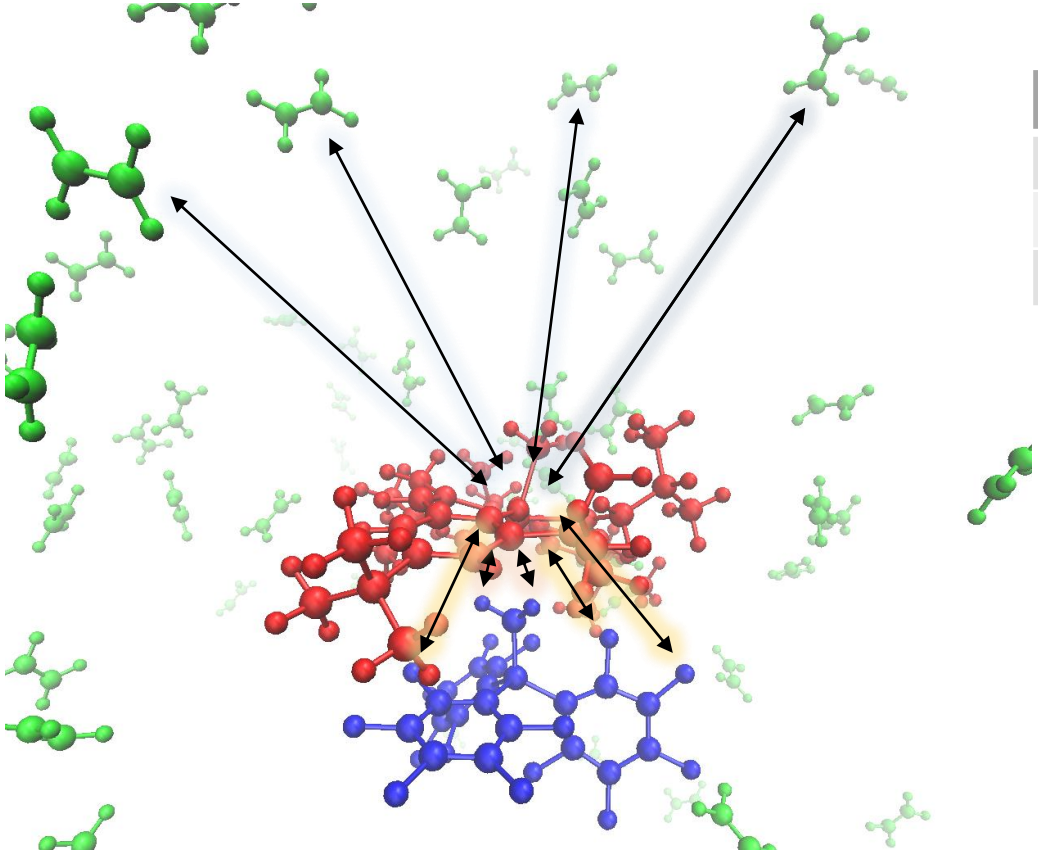

Table. the values of LJ parameters

	σ [Å]	ε [kcal/mol]
Zr-C(ethylene)	2.650	5.000
Zr-H(borate)	0.050	2.228
Zr-F(borate)	0.250	2.567

- The ethylene monomers are inserted between the Zr atom and the C atom in polymerization.
- The ethylene monomers become the parts of a polymer chain one by one during RM simulation.

Modification of the modules

rm_main.py

```
#--------------- Instances of Processes ---------------

# make all instances of processes
## the first argument: directory name
## the second argument: parameter set
SearchMD = AmberMD(**proc_parms["SearchMD"])
RF = ReactionFinder(**proc_parms["RF"])
TE = TopologyEditor(**proc_parms["TE"])
QuenchMD = AmberMD(**proc_parms["QuenchMD"])
RelaxMD = AmberMD(**proc_parms["RelaxMD"])
MC = MonteCarlo(**proc_parms["MC"])
Wrap = WrapIntoBox(**proc_parms["Wrap"])
TELJ1 = EditTopLJ(TEpath=proc_parms["TE"]["TEpath"], Process="TELJ1")
TELJ2 = EditTopLJ(TEpath=proc_parms["TE"]["TEpath"], Process="TELJ2")
#-------------------------------------------------------
#--------------- Run RM simulation ---------------
# start MC/MD cycle from 'init_cycle' to 'total_cycle'
```

Necessary conditions:

i. A topology file without LJ modification is kept at any RM cycles.
ii. LJ modification is executed just before MD processes.
iii. A topology file without LJ modification is updated for next RM cycle if a trial chemical reaction is accepted. If rejected, the topology file is kept without the update.
iv. If there is no candidate for chemical reactions, a topology file is kept without LJ modification for next RM cycle.

```
#--------------- Run RM simulation ---------------
# start MC/MD cycle from 'init_cycle' to 'total_cycle'
for cycle in range(init_cycle, total_cycle + 1):
…
    #----- modified for catpoly -----
    ## topology file without the LJ modification must be used as the input one
    TopWithoutLJ = main_parms["PathTop"]
    # run TELJ1
    main_parms.update(TELJ1.run(cycle, abspath_cycledir, **main_parms))
    #--------------------------------
    # run SearchMD
    main_parms.update(SearchMD.run(cycle, abspath_cycledir, **main_parms))
    # run RF
    main_parms.update(RF.run(cycle, abspath_cycledir, **main_parms))
    # whether one candiate is found at least or not
    if main_parms["RFisfound"]:

        TopWithoutLJ_BefTE = TopWithoutLJ  # modified for catpoly

        main_parms["PathTop"] = TopWithoutLJ  # modified for catpoly
        # run TE
        main_parms.update(TE.run(cycle, abspath_cycledir, **main_parms))
        #----- modified for catpoly -----
        TopWithoutLJ_AftTE = main_parms["PathTop"]
        # run TELJ2
        main_parms.update(TELJ2.run(cycle, abspath_cycledir, **main_parms))
        #--------------------------------
        # run QuenchMD
        main_parms.update(QuenchMD.run(cycle, abspath_cycledir, **main_parms))
        # run RelaxMD
        main_parms.update(RelaxMD.run(cycle, abspath_cycledir, **main_parms))
        # run MC
        main_parms.update(MC.run(cycle, abspath_cycledir, **main_parms))
        #----- modified for catpoly -----
        if main_parms["MCisrejected"]:
            main_parms["PathTop"] = TopWithoutLJ_BefTE
        else:
            main_parms["PathTop"] = TopWithoutLJ_AftTE
        #--------------------------------
    else:
        main_parms["PathTop"] = TopWithoutLJ  # modified for catpoly
    …
    # run Wrap
    main_parms.update(Wrap.run(cycle, abspath_cycledir, **main_parms))    …

quit()
#-------------------------------------------------
```

RM simulations using the latest RM program

Hf catalyst system

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IP: insertion polymerization
CCTP: coordinative chain transfer polymerization
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CSP: chain shuttling polymerization
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CCTP system with Hf-cat: rm_input.dat

rm_input.dat

```
# Red Moon main parameters
%RM
MainDir = ./Sample1,
InpTop = system_mod.top, InpCrd = prerun2.restrt,
InitCycle = 1, TotalCycle = 500,
Temp= 400, Ensemble = NVT,
RunMDCmd = pmemd.pbb.MPI,

# Search MD parameters
%SearchMD
MDstep = 25000, MDdt = 0.002,
MDntpr=1000, MDntwx=1000, MDntwr=1000,
MDnmropt=1, MDdisang=cctp_anion.RST,

# Relax MD parameters
%RelaxMD
MDstep = 5000, MDdt = 0.002,
MDntpr=1000, MDntwx=1000,
MDnmropt=1, MDdisang=cctp_anion.RST,

# Quenching MD parameters
%QuenchMD
MDntwr=500,
MDnmropt=1, MDdisang=cctp_anion.RST,

# Reaction Finder (RF) parameters
%RF
RFinpfile = ./rf_input.dat,
RFpath = /home/takayana/scripts/ReactionFinder/ReactionFinder,
RFcrdstep="1 25 1“

# Topology Editor (TE) parameters
%TE
TEpath = /home/takayana/scripts/TopologyEditor/TopologyEditor,
TEff = [/home/takayana/AMBER/amber14/dat/leap/parm/gaff.dat]
TEffmod = [./parms/hfc_all.frcmod, ./parms/znetme_all.frcmod,
           ./parms/frcmod.B, ./parms/frcmod.CB,
           ./parms/frcmod.PH2, ./parms/frcmod.PH3,
           ./parms/frcmod.Ph1, ./parms/frcmod.borate]

# Monte Carlo parameters
%MC
MCregion = whole,

# Wrap parameters
%Wrap
Centering = @Hf, Imaging = All,
PtrajBinary = cpptraj,
```

Some values of the above parameters are a little different from those specified by Dr. Matsumoto. This is because of the demonstration of the RM simulation using the present program.

CCTP system with Hf-cat: rf_input.dat

rf_input.dat

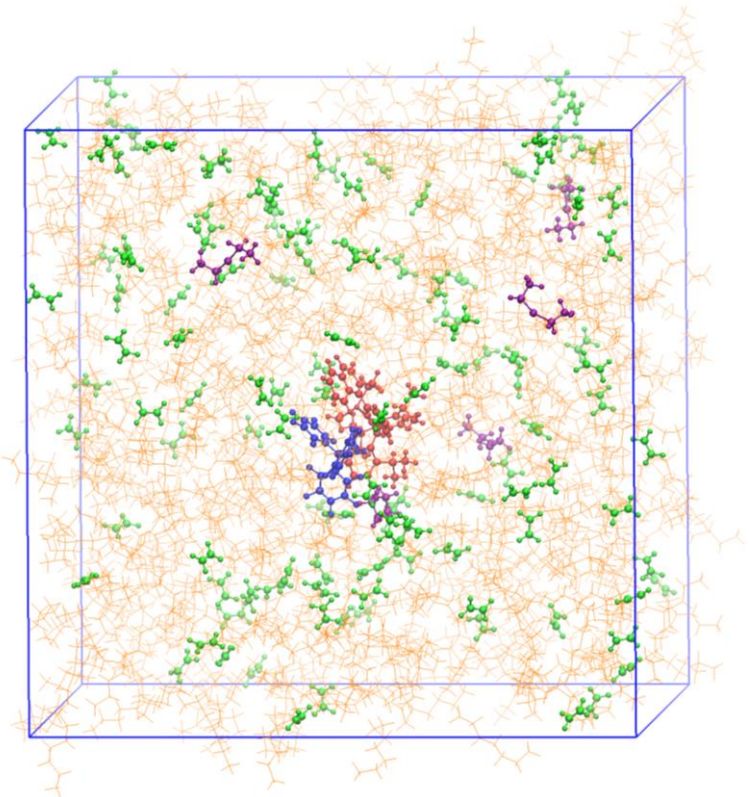
```
#-----------monomer insertion-----------
#Reaction 1 (HFB-MIC + EXX ---> HFB-ERC-MTX)
ReactID=1 Ea=0.0 dE=-17.3
"COND = distance(:HFB@Hf; :EXX@C1)<3.8
       && distance(:HFB@Hf; :EXX@C2)<3.8
       && dihedral(:MIC@C1; :HFB@Hf; :EXX@C1; :EXX@C2)
       =[-60.0,60.0]
       && angle(:HFB@N; :HFB@Hf; :EXX@C1)>100.0
       && distance(:HFB@Hf; :MIC@C1)<2.4"
"ACTION =
   createBond :HFB@Hf :EXX@C1;
   createBond :EXX@C2 :MIC@C1;
   deleteBond :HFB@Hf :MIC@C1;
   ModifyResByPrepin :EXX ./parms/erc.prepin;
   ModifyResByPrepin :MIC ./parms/mtx.prepin"
#Reaction 2 (HFB-EIC + EXX ---> HFB-ERC-ETX)
ReactID=2 Ea=0.0 dE=-17.3
"COND = distance(:HFB@Hf; :EXX@C1)<3.8
       && distance(:HFB@Hf; :EXX@C2)<3.8
       &&
dihedral(:EIC@C1; :HFB@Hf; :EXX@C1; :EXX@C2)=[-
60.0,60.0]
   createBond :EXX@C2 :EIC@C1;
   deleteBond :HFB@Hf :EIC@C1;
   ModifyResByPrepin :EXX ./parms/erc.prepin;
   ModifyResByPrepin :EIC ./parms/etx.prepin"
…
```

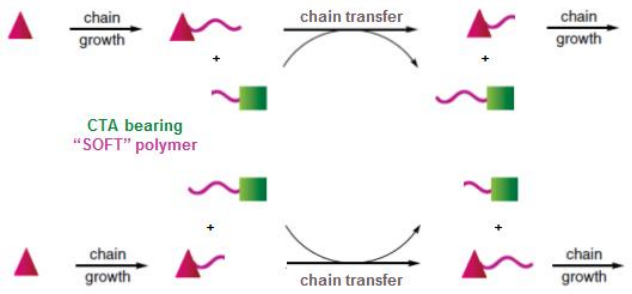
```
#-----------polymer exchange-----------
#Reaction 4 (HFB-MIC + ZN-EIZ ---> HFB-EIC + ZN-MIZ)
ReactID=4 Ea=0.01 dE=0.0
"COND = distance(:HFB@Hf; :EIZ@C1)<2.8
       && distance(:MIC@C1; :ZN@Zn)<2.8
       && distance(:HFB@Hf; :MIC@C1)<2.4
       && distance(:HFB@Hf; :HFB@N)<5.0
       && distance(:ZN@Zn; :EIZ@C1)<2.4"
"ACTION =
   createBond :HFB@Hf :EIZ@C1;
   createBond :ZN@Zn :MIC@C1;
   deleteBond :HFB@Hf :MIC@C1;
   deleteBond :ZN@Zn :EIZ@C1;
   ModifyResByPrepin :MIC ./parms/miz.prepin;
   ModifyResByPrepin :EIZ ./parms/eic.prepin"
…
#Reaction 9 (HFB-ERC-P1 + ZN-ERZ-P2 --->
                                HFB-ERC-P2 + ZN-ERZ-P1)
ReactID=9 Ea=0.01 dE=0.0
"COND = distance(:HFB@Hf; :ERZ@C1)<2.8
       && distance(:ERC@C1; :ZN@Zn)<2.8
       && distance(:HFB@Hf; :ERC@C1)<2.4
   createBond :ZN@Zn :ERC@C1;
   deleteBond :HFB@Hf :ERC@C1;
   deleteBond :ZN@Zn :ERZ@C1;
   ModifyResByPrepin :ERC ./parms/erz.prepin;
   ModifyResByPrepin :ERZ ./parms/erc.prepin"
```

There are the 9 patterns in the current format to treat all the chemical reactions that occur in this CCTP system.

CCTP system with Hf-cat: Computational details

- Molecules: 1 ion pair of Hf-cat^{+} and Borate^{-}, 120 ethylene and 480 heptane, and 5 $ZnEt_2$
- Force field : GAFF and some fitted parameters
- Atomic charge: RESP (QM)
- Calculation level of theory: M062X/LANL2DZ (for Hf atom), 6-31G(d,p) (for other atoms)
- Temperature: 400K
- Search NVT-MD: 50 ps
- Relax NVT-MD: 10 ps
- Total number of RM cycle: 500
- The number of sampling : 1
- Box size: 54.76 Å × 54.76 Å × 54.76 Å



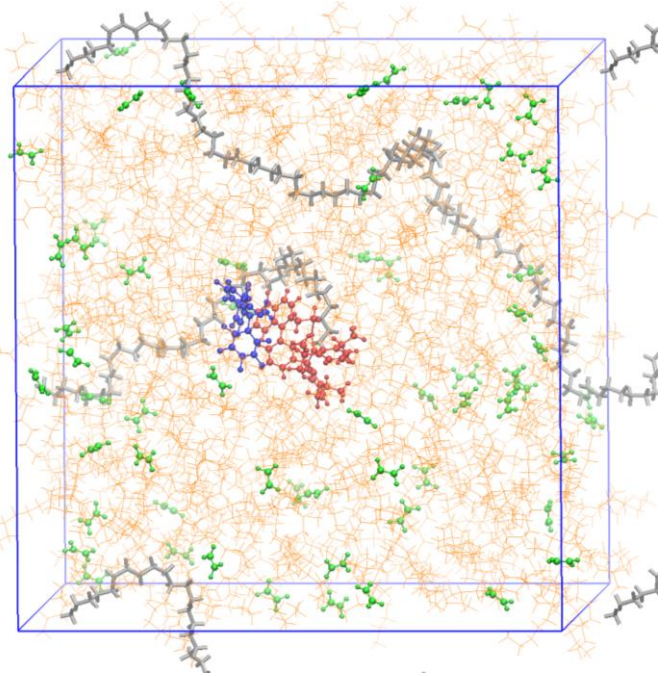


Schematic representation of CCTP mechanism.

CCTP system with Hf-cat: Simulation results

rm_mc_output.dat

```
Cycle      1 ReactID   1 Epro = 10865.9472 Erea = 11007.6866 dE =  -17.3000 dEmc =  -159.0394 Accepted
Cycle      7 ReactID   3 Epro = 10905.6990 Erea = 10986.6303 dE =  -17.3000 dEmc =   -98.2313 Accepted
Cycle     11 ReactID   3 Epro = 10894.5511 Erea = 10923.4577 dE =  -17.3000 dEmc =   -46.2066 Accepted
Cycle     14 ReactID   3 Epro = 10948.6890 Erea = 11035.2433 dE =  -17.3000 dEmc =  -103.8543 Accepted
Cycle     17 ReactID   3 Epro = 10820.9367 Erea = 10900.8651 dE =  -17.3000 dEmc =   -97.2284 Accepted
Cycle     20 ReactID   3 Epro = 10872.0101 Erea = 10936.4119 dE =  -17.3000 dEmc =   -81.7018 Accepted
Cycle     25 ReactID   3 Epro = 10837.6673 Erea = 10934.5597 dE =  -17.3000 dEmc =  -114.1924 Accepted
Cycle     34 ReactID   3 Epro = 10774.4072 Erea = 10894.5649 dE =  -17.3000 dEmc =  -137.4577 Accepted
Cycle     41 ReactID   3 Epro = 10923.9239 Erea = 11039.1382 dE =  -17.3000 dEmc =  -132.5143 Accepted
Cycle     46 ReactID   3 Epro = 10888.3781 Erea = 11007.7719 dE =  -17.3000 dEmc =  -136.6938 Accepted
Cycle     47 ReactID   3 Epro = 10919.2277 Erea = 10964.7201 dE =  -17.3000 dEmc =   -62.7924 Accepted
Cycle     50 ReactID   3 Epro = 10917.2662 Erea = 10928.2433 dE =  -17.3000 dEmc =   -28.2771 Accepted
...
Cycle    360 ReactID   3 Epro = 10718.8040 Erea = 10772.2091 dE =  -17.3000 dEmc =   -70.7051 Accepted
Cycle    367 ReactID   3 Epro = 10648.8613 Erea = 10878.8159 dE =  -17.3000 dEmc =  -247.2546 Accepted
Cycle    381 ReactID   3 Epro = 10772.4085 Erea = 10830.3295 dE =  -17.3000 dEmc =   -75.2210 Accepted
Cycle    383 ReactID   3 Epro = 10603.7701 Erea = 10811.0287 dE =  -17.3000 dEmc =  -224.5586 Accepted
Cycle    396 ReactID   3 Epro = 10751.4104 Erea = 10818.2428 dE =  -17.3000 dEmc =   -84.1324 Accepted
Cycle    412 ReactID   3 Epro = 10730.1118 Erea = 10766.5694 dE =  -17.3000 dEmc =   -53.7576 Accepted
Cycle    417 ReactID   3 Epro = 10798.5455 Erea = 10790.0089 dE =  -17.3000 dEmc =    -8.7634 Accepted
Cycle    419 ReactID   3 Epro = 10709.3319 Erea = 10755.7178 dE =  -17.3000 dEmc =   -63.6859 Accepted
Cycle    426 ReactID   7 Epro = 10714.0012 Erea = 10752.2005 dE =    0.0000 dEmc =   -38.1993 Accepted
Cycle    427 ReactID   8 Epro = 10708.3906 Erea = 10767.5850 dE =    0.0000 dEmc =   -59.1944 Accepted
```



- The ethylene insertion on the active site of the Hf-cat (ReacID 1 and 3) occurred 62 times at the RM cycles, which resulted in producing one polymer with 62 monomeric units.
- The bond exchange (ReacID 7) occurred at the 426th RM cycle to create two new chemical bonds between Hf-cat and $ZnEt_2$, and then that (ReacID 8) occurred again at the 427th RM cycle. As a result, it did not result in completing the chain transfer reaction.

➡ The present RM program could succeed in simulating the CCTP with the Hf-cat.

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CTA: chain transfer agent
CSP: chain shuttling polymerization
CSA: chain shuttling agent

IP system with Zr-cat: rm_input.dat

rm_input.dat

```
# Red Moon main parameters
%RM
MainDir = ./Sample1,
InpTop = ./top_crd/IP_Eth_Hep.prmtop,
InpCrd = ./top_crd/zrpoly_ip_inp.crd,
InitCycle = 1, TotalCycle = 500,
Temp= 400, Ensemble = NVT,
RunMDCmd = pmemd.pbb.MPI,

# Search MD parameters
%SearchMD
MDstep = 25000, MDdt = 0.002,
MDntpr=1000, MDntwx=1000, MDntwr=1000,
MDig = -1,

# Relax MD parameters
%RelaxMD
MDstep = 5000, MDdt = 0.002,
MDntpr=1000, MDntwx=1000,
MDig = -1,

# Quenching MD parameters
%QuenchMD
MDstep = 10000,
MDntwx=100,
MDig = -1,
```

```
# Reaction Finder (RF) parameters
%RF
RFinpfile = ./rf_input.dat,
RFpath = /home/takayana/scripts/ReactionFinder/ReactionFinder,
RFcrdstep="1 25 1“

# Topology Editor (TE) parameters
%TE
TEpath = /home/takayana/scripts/TopologyEditor/TopologyEditor.test,
TEff = [./parms/gaff.dat]
TEffmod = [./parms/all.frcmod]

# Monte Carlo parameters
%MC
MCregion = whole,

# Wrap parameters
%Wrap
Centering = @Zr, Imaging = All,
PtrajBinary = cpptraj,
```

The values of the above parameters are specified properly enough to demonstrate the IP simulation for the Zr-cat system.

IP system with Zr-cat: rf_input.dat

rf_input.dat

```
#-----------monomer insertion------------
#Reaction 1 (FIZ-MIC + ETH ---> FIZ-ERC-MTX)
ReactID=1 Ea=8.34 dE=-26.28
"COND = distance(:FIZ@Zr; :ETH@C1)<4.5
       && distance(:MIC@Ck4; :ETH@C4)<4.5"
"ACTION =
    createBond :FIZ@Zr :ETH@C1;
    createBond :MIC@Ck4 :ETH@C4;
    deleteBond :FIZ@Zr :MIC@Ck4;
    ModifyResByMol2 :MIC ./parms/MTX.mol2;
    ModifyResByMol2 :ETH ./parms/ERC.mol2"
#Reaction 2 (FIZ-ERC-MTX + ETH ---> FIZ-ERC-EMX-MTX)
ReactID=2 Ea=8.34 dE=-26.28
"COND = distance(:FIZ@Zr; :ETH@C1)<4.5
       && distance(:ERC@C1; :ETH@C4)<4.5"
"ACTION =
    createBond :FIZ@Zr :ETH@C1;
    createBond :ERC@C1 :ETH@C4;
    deleteBond :FIZ@Zr :ERC@C1;
    ModifyResByMol2 :ETH ./parms/ERC.mol2;
    ModifyResByMol2 :ERC ./parms/EMX.mol2"
```

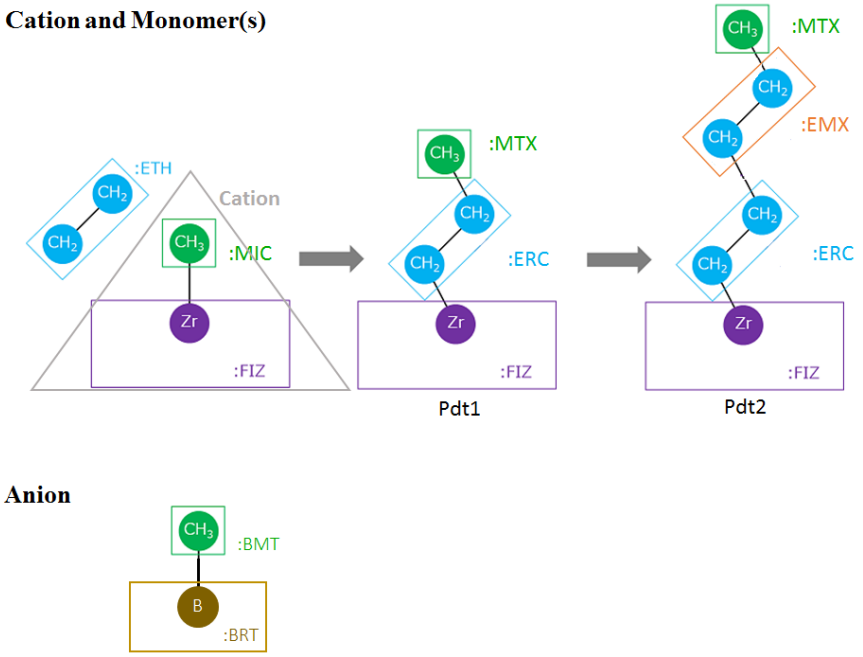
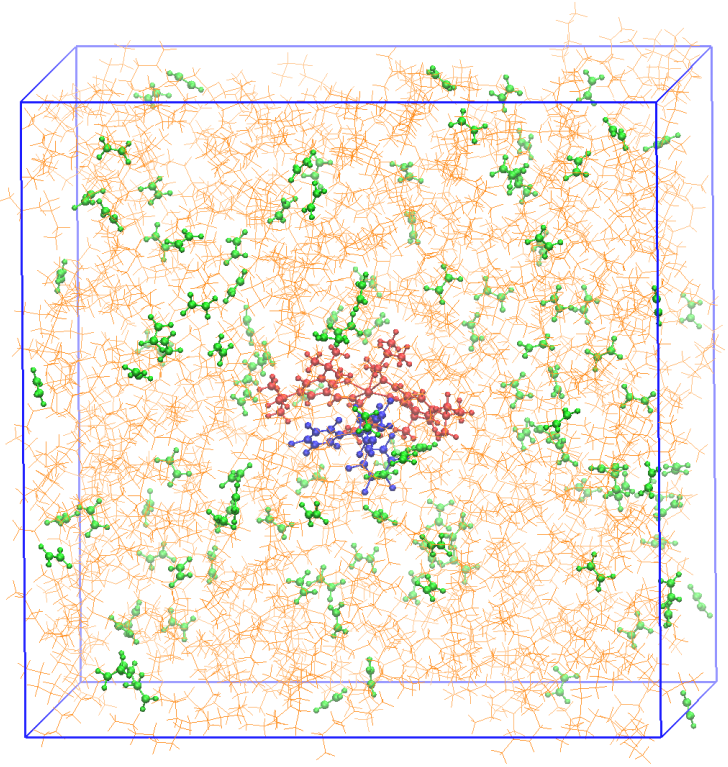


Figure. the technical approach to realize the IP reaction in the RM framework (made by Dr. Saha).

IP system with Zr-cat: Computational details

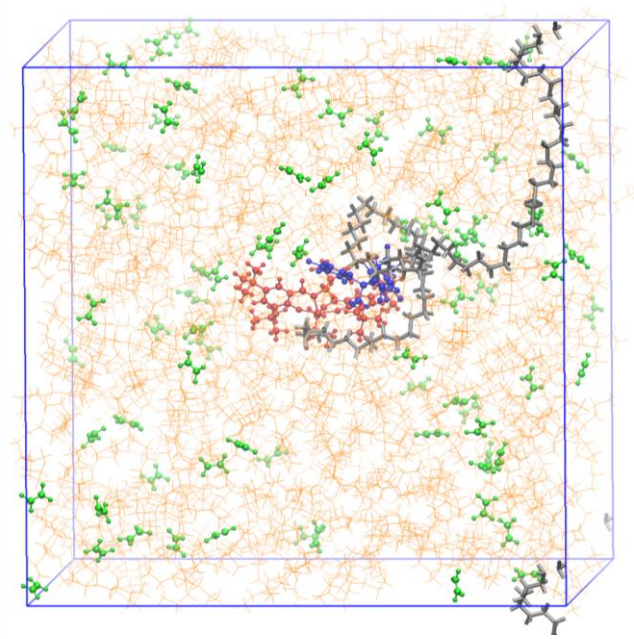
- Molecules: 1 ion pair of Zr-cat^{+} and Borate^{-}, 120 ethylene and 480 heptane
- Force field : GAFF and some fitted parameters
- Atomic charge: RESP (QM)
- Calculation level of theory: M06/LANL2DZ (for Zr atom), 6-31G(d,p) (for other atoms)
- Temperature: 400K
- Search NVT-MD: 50 ps
- Relax NVT-MD: 10 ps
- Total number of RM cycle: 500
- The number of sampling : 1
- Box size: 55.03 Å × 55.03 Å × 55.03 Å



IP system with Zr-cat: Simulation results

rm_mc_output.dat

```
Cycle     47 ReactID   1 Epro = 12894.5743 Erea = 12960.7373 dE =  -26.2800 dEmc =   -92.4430 Accepted
Cycle     64 ReactID   2 Epro = 12920.6637 Erea = 12999.6238 dE =  -26.2800 dEmc =  -105.2401 Accepted
Cycle     85 ReactID   2 Epro = 12869.0555 Erea = 12893.2644 dE =  -26.2800 dEmc =   -50.4889 Accepted
Cycle     88 ReactID   2 Epro = 12927.2813 Erea = 12900.7300 dE =  -26.2800 dEmc =     0.2713 Accepted
Cycle     90 ReactID   2 Epro = 12822.0206 Erea = 12965.1022 dE =  -26.2800 dEmc =  -169.3616 Accepted
Cycle    104 ReactID   2 Epro = 12864.1020 Erea = 12931.4927 dE =  -26.2800 dEmc =   -93.6707 Accepted
Cycle    141 ReactID   2 Epro = 12889.4911 Erea = 12868.5797 dE =  -26.2800 dEmc =    -5.3686 Accepted
Cycle    142 ReactID   2 Epro = 12729.1087 Erea = 12880.5267 dE =  -26.2800 dEmc =  -177.6980 Accepted
Cycle    145 ReactID   2 Epro = 12814.3207 Erea = 12862.2398 dE =  -26.2800 dEmc =   -74.1991 Accepted
Cycle    159 ReactID   2 Epro = 12808.0030 Erea = 12877.4100 dE =  -26.2800 dEmc =   -95.6870 Accepted
...
Cycle    313 ReactID   2 Epro = 12644.1561 Erea = 12645.2058 dE =  -26.2800 dEmc =   -27.3297 Accepted
Cycle    314 ReactID   2 Epro = 12555.3323 Erea = 12736.1453 dE =  -26.2800 dEmc =  -207.0930 Accepted
Cycle    315 ReactID   2 Epro = 12596.0255 Erea = 12697.5641 dE =  -26.2800 dEmc =  -127.8186 Accepted
Cycle    357 ReactID   2 Epro = 12691.6608 Erea = 12828.7741 dE =  -26.2800 dEmc =  -163.3933 Accepted
Cycle    361 ReactID   2 Epro = 12473.6483 Erea = 12828.7450 dE =  -26.2800 dEmc =  -381.3767 Accepted
Cycle    451 ReactID   2 Epro = 12594.1280 Erea = 12711.5105 dE =  -26.2800 dEmc =  -143.6625 Accepted
Cycle    464 ReactID   2 Epro = 12589.4505 Erea = 12569.8736 dE =  -26.2800 dEmc =    -6.7031 Accepted
Cycle    488 ReactID   2 Epro = 12571.4269 Erea = 12676.9771 dE =  -26.2800 dEmc =  -131.8302 Accepted
Cycle    497 ReactID   2 Epro = 12598.6380 Erea = 12662.1221 dE =  -26.2800 dEmc =   -89.7641 Accepted
Cycle    499 ReactID   2 Epro = 12523.3997 Erea = 12543.0116 dE =  -26.2800 dEmc =   -45.8919 Accepted
Cycle    500 ReactID   2 Epro = 12542.4327 Erea = 12575.2373 dE =  -26.2800 dEmc =   -59.0846 Accepted
```



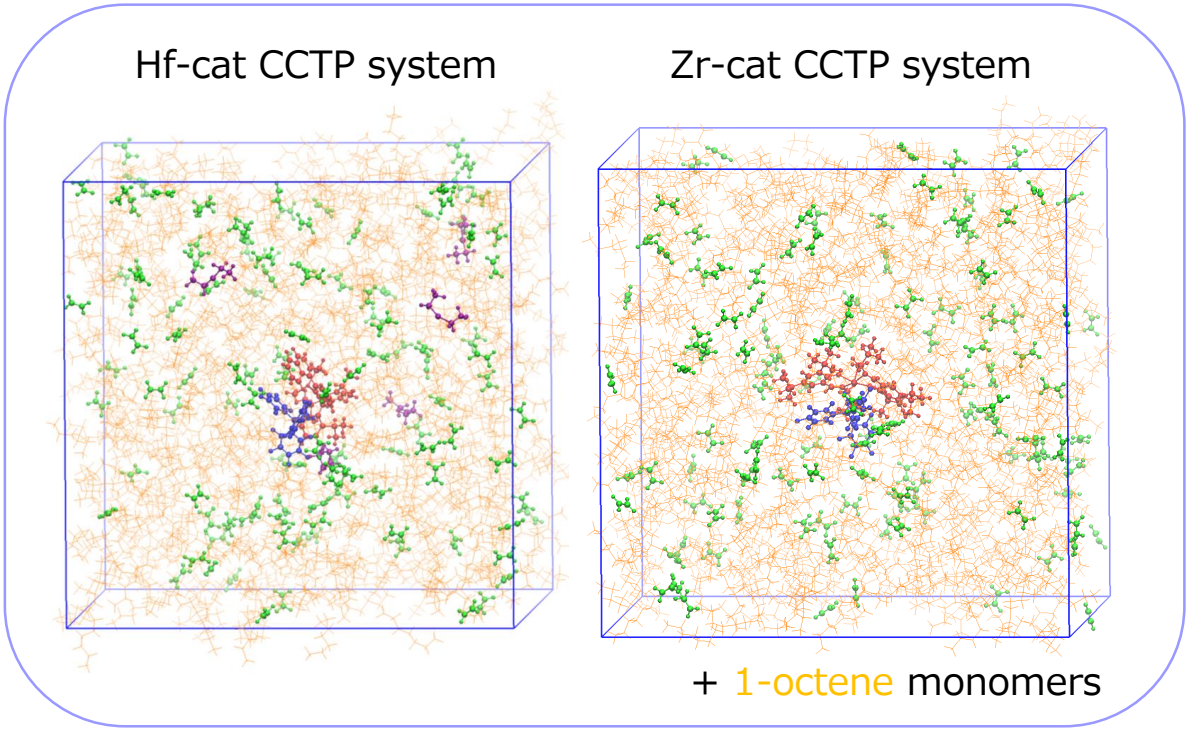
- The ethylene insertion on the active site of the Zr-cat (ReacID 1 and 2) occurred 38 times, which resulted in producing one polymer with 38 monomeric units.
- In the case of the IP system WIHOUT the anion, the candidate for the first insertion were found under the reaction condition of distance (<4.0). However, in the present case, they were rarely found, even using a bit longer distance (<4.5). This might be because of the steric hindrance of the cation associated with the presence of the anion.

➡ The present RM program could succeed in simulating the IP with the Zr-cat as well as the CCTP with the Hf-cat.

Strategy for the realization of CSP simulation 1/3

- Combine the Hf-cat CCTP system with the Zr-cat CCTP system adding 1-octene monomers, as a CSP whole system.
- All values such as activation energies, formation energies, those of force fields parameters that should be investigated by QM approach will be temporary specified by the values obtained in the previous studies.

One simulation box/CSP whole system



Strategy for the realization of CSP simulation 2/3

Hf catalyst system

I. Ethylene IP simulation.

II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

III. Ethylene and 1-octene IP simulation.

IV. CCTP simulation with ethylene and 1-octene as monomers, and with $ZnEt_2$ as CTA.

Zr catalyst system

I. Ethylene IP simulation.

II. CCTP simulation with ethylene as monomer and $ZnEt_2$ as CTA.

The next target simulations using the whole model system of CSP (but assuming chemical reactions only involved in the target system).

CSP system with Hf and Zr catalysts

I. CSP simulation in which the ethylene and 1-octene IP occurs on the Hf catalyst, and the ethylene IP occurs on the Zr catalyst, accompanying with chain transfer by $ZnEt_2$ as CSA.

IP: insertion polymerization
CCTP: coordinative chain transfer polymerization
CTA: chain transfer agent
CSP: chain shuttling polymerization
CSA: chain shuttling agent

Strategy for the realization of CSP simulation 3/3

- The number of the reaction pattern becomes over 70 (estimated by Ms. Misawa) in the current format of input file to RF, which is almost impossible to execute RF because of the highly computational cost.
  (200 [snapshots] × 3 [distance, bond angle and dihedral angle]
  × 70 [patterns] = 42000 [number of calculations] per one RF execution)
- There are not some necessary functions in RF, e.g., "||" (or) statement for reaction conditions, and calculation of distances, bond angles and dihedral angles of atoms inbetween molecules with the same name.

➢ It is necessary to make a new format to write reaction conditions and a program similar to RF.

My research subjects

i. The development of RM program aiming a generalized simulation method for complex chemical reaction systems (collaborating with Dr. Takayanagi).

My research subjects

i. The development of RM program aiming a generalized simulation method for complex chemical reaction systems (collaborating with Dr. Takayanagi).
   - We are planning to make the program available for researchers at universities or companies (under license/copyright).

ii. The realization of chain shuttling polymerization (CSP) simulation using RM method (collaborating with Dr. Saha and Ms. Misawa).
   - This subject has to be completed by the next (/final) CREST report in the beginning of September.

iii. The establishment of a methodology to treat diffusion of molecules in addition to chemical reactions.
   - It is important to expand the RM methodology to be able to treat it occurring as a rare event.

Necessity of a methodology to treat diffusion

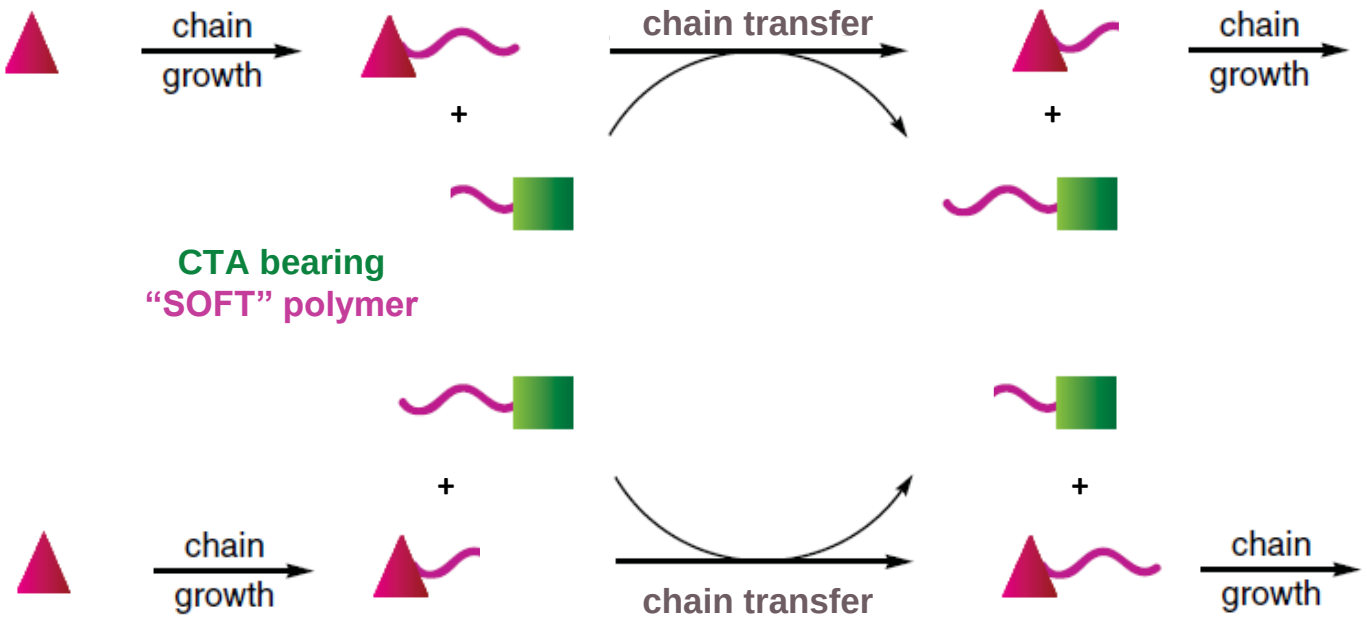
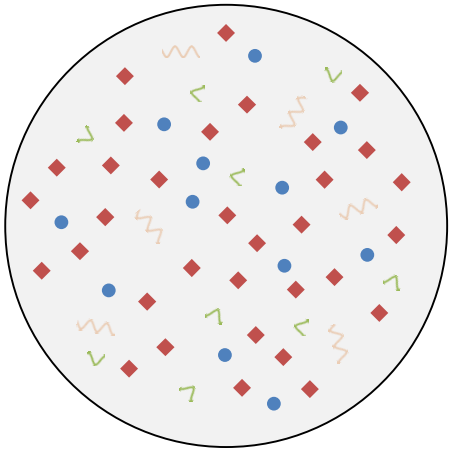


Figure. Schematic representation of CCTP mechanism.

- In the present model system of the CCTP with the Hf-cat, there is only one Hf-cat in the simulation box, which does not result in the polymer exchanges between the different Hf-cats.
- It is impossible to treat the model system including the two catalysts because of the highly computational cost, considering its concentration in the experiments.

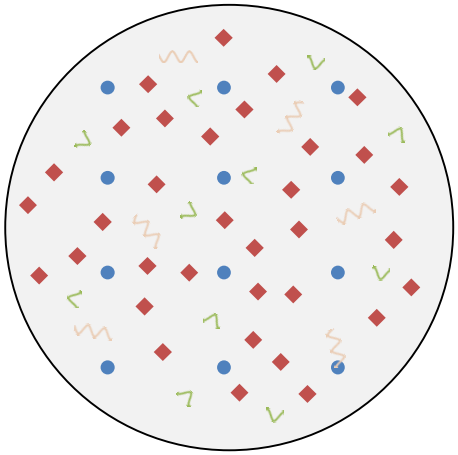
➡ It is necessary to establish a methodology to overcome this issue (that is to treat diffusion of molecules).

A methodology to treat diffusion of molecules 1/4



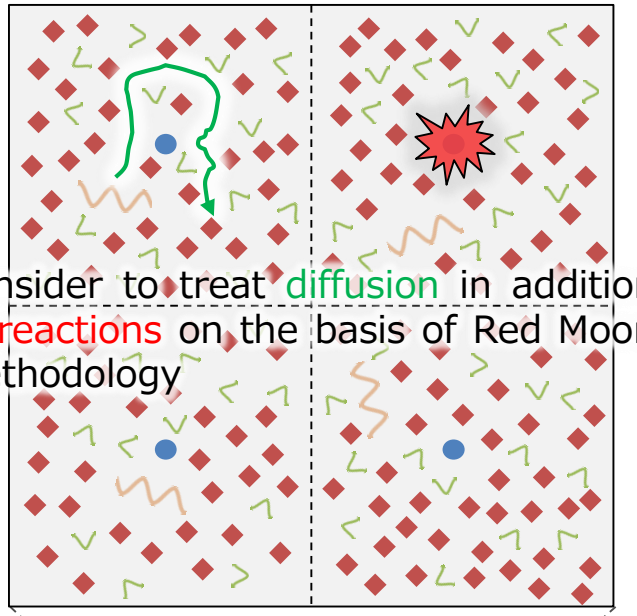
Catalyst
Organic solvent
Monomer
Polymer

■Catalyzed polymerization system from “macroscopic” point of view

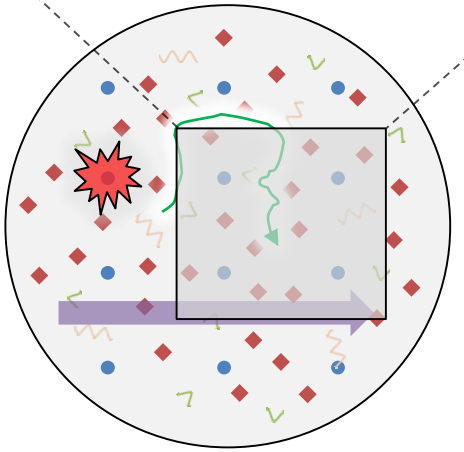


■A state of the system from average (/approximate) point of view (i.e., to regard catalysts distributed homogenously)

Consider to treat diffusion in addition to reactions on the basis of Red Moon methodology

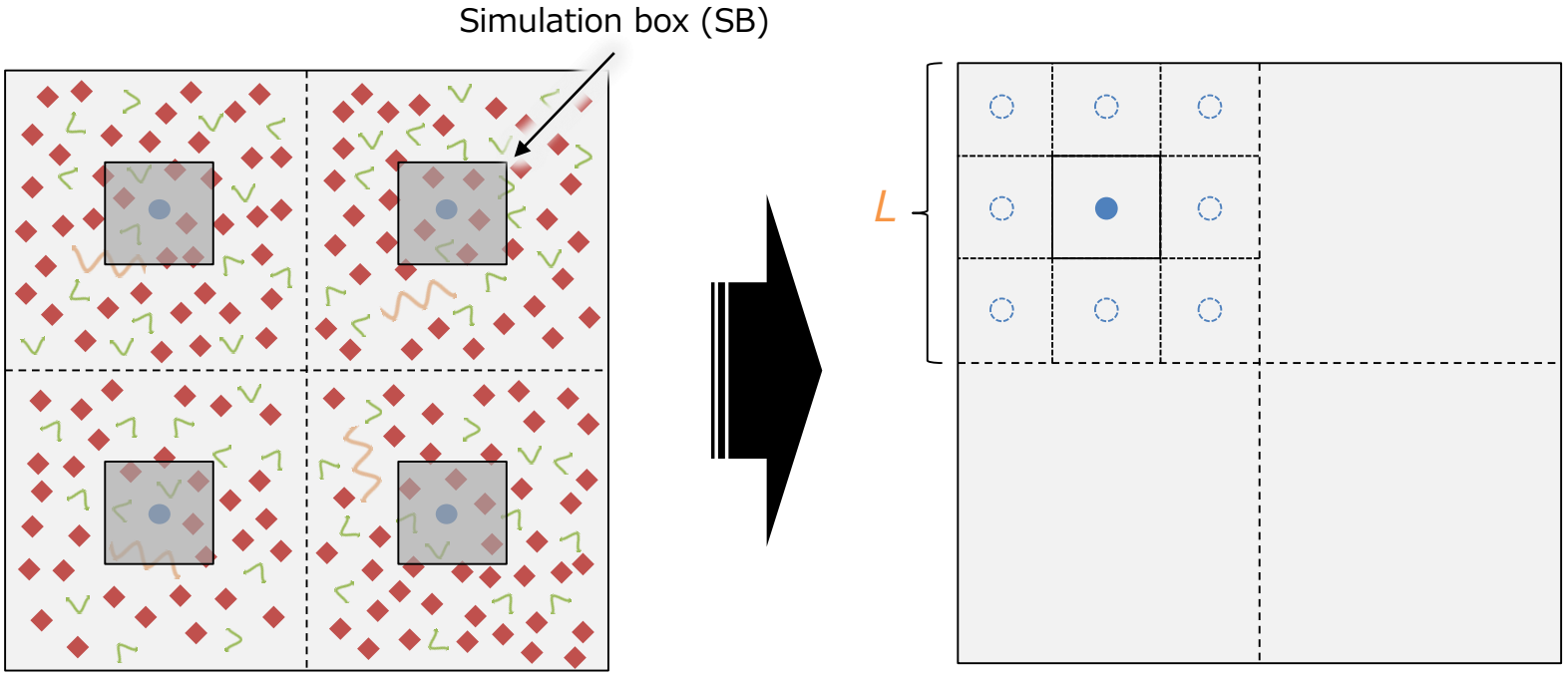


■Focus on a further specific “microscopic” region



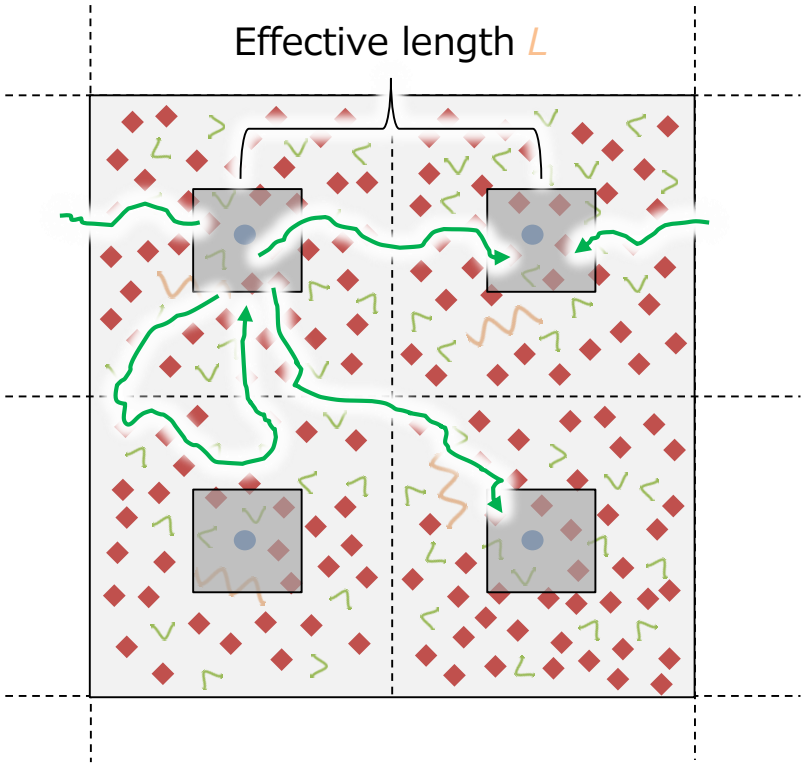
■Occurrences of reactions, diffusion and convection currents

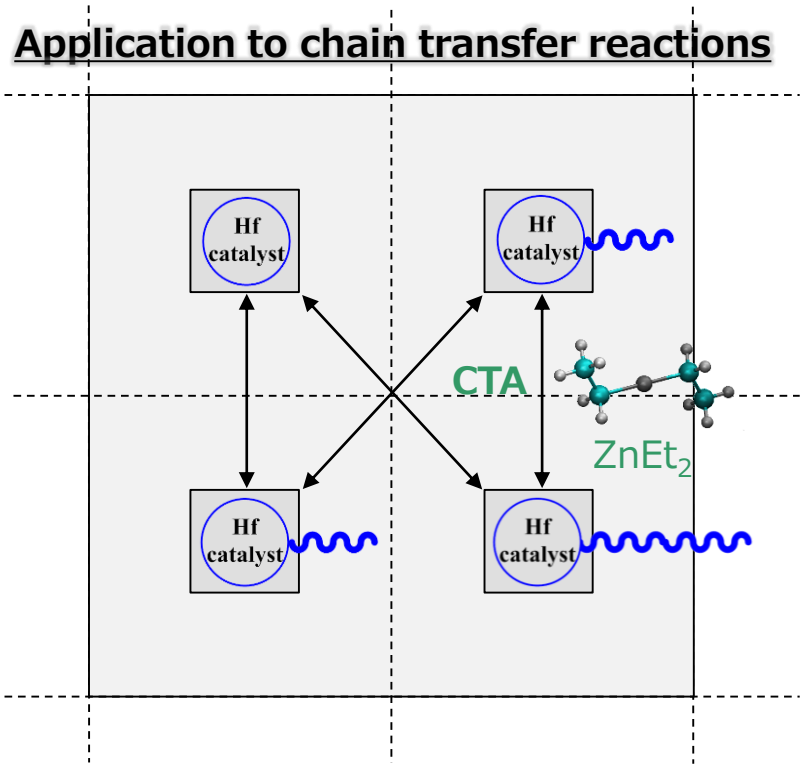
A methodology to treat diffusion of molecules 2/4



- It is difficult to computationally treat the same concentrations with the experimental ones.
  - Model a region centering around the catalyst with a simulation box (SB) so that the size of SB would be enough to treat reactions and diffusion of molecules in the target system.
- In the surroundings of the region, the diffusion just occurs without any reactions, and assume that the surroundings can be artificially described by the replicas of the SB.
  - Assume that the size including the replicas (*L* each side) is the effectively corresp-onding size of the model system with the experimental one.

A methodology to treat diffusion of molecules 3/4





- Using the multiple SBs, move a *heavy* polymer produced in a SB to the other SB (diffusion), and then the polymer continues to grow there.
  - ➢ Suggestion of a new RM methodology that can treat diffusion in addition to reaction in one simulation.

- Exchange **CTA** with **polymer** between SBs.
  - ➢ The polymer produced on a catalyst moves with CTA to the other catalyst in the other SB.
  - ➢ Possible to realize a more realistic CCTP.

It does not (/is not necessary to) exchange the other molecules such as catalysts, solvents and monomers. This can be realized by defining a SB region enough large to properly treat their diffusion.

A methodology to treat diffusion of molecules 4/4

Reaction:

- Search for atom pairs that satisfy reaction conditions and then select one among them by using the following weight.

$$w^{\mathrm{Reac}_i} = N_{\mathrm{cand}}^{\mathrm{Reac}_i} \exp\left(-\beta \Delta E_{\mathrm{a}}^{\mathrm{Reac}_i}\right)$$

$N_{\mathrm{cand}}^{\mathrm{React}_i}$: number of candidates for chemical reaction *i*
$\Delta E_{\mathrm{a}}^{\mathrm{Reac}_i}$: activation energy of chemical reaction *i*

Diffusion:

- Select one among the possible diffusing species by using the following weight.

$$w^{\mathrm{Diff_X}} = 4\pi d D_{\mathrm{X}} / \mathrm{N_A} V$$

D_{X}: diffusion coefficient of component X
d: moving distance
N_{X}: number of the component X

When the number of diffusion satisfies the equation $N_{\mathrm{diff}} \times w^{\mathrm{Diff_X}} \approx w^{\mathrm{React}_i}$, the diffusion occurs with equal probability with the reaction.

- The potential energy differences before and after reaction and diffusion are calculated as follows.

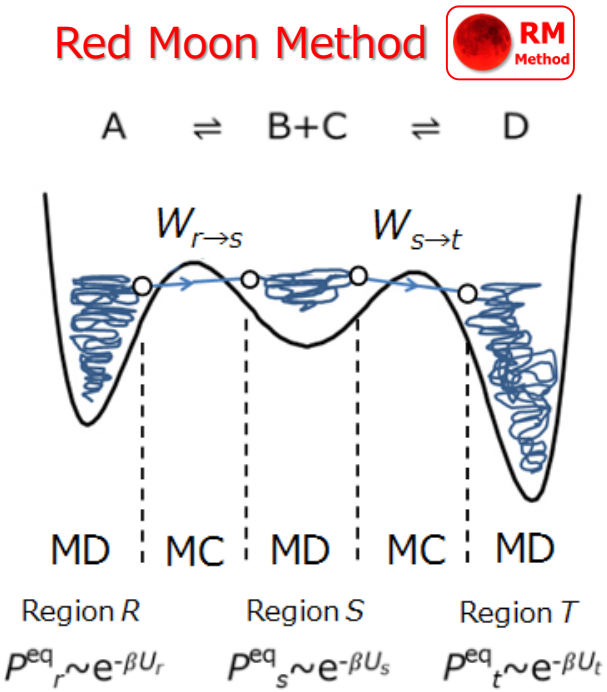
$$\Delta E_{rs}^{\mathrm{Reac}} = \left(U_{\mathrm{aft\_reac}}^{\mathrm{SB}_k} - U_{\mathrm{bef\_reac}}^{\mathrm{SB}_k}\right) + \Delta E_{rs}^{\mathrm{Reac}_i} = \Delta U_{\mathrm{rs}}^{\mathrm{SB}_k} + \Delta E_{rs}^{\mathrm{Reac}_i},$$

$$\Delta E_{rs}^{\mathrm{diff}} = \left(U_{\mathrm{aft\_diff}}^{\mathrm{SB}_i} + U_{\mathrm{aft\_diff}}^{\mathrm{SB}_j}\right) - \left(U_{\mathrm{bef\_diff}}^{\mathrm{SB}_i} + U_{\mathrm{bef\_diff}}^{\mathrm{SB}_j}\right) = \Delta U_{rs}^{\mathrm{SB}_i} + \Delta U_{rs}^{\mathrm{SB}_j}$$

- The trial state change is accepted or rejected according to the following transition probability in the Metropolis scheme.

$$W_{r\to s} = \min\left\{1, \exp\left[-\beta \Delta E_{rs}\right]\right\}$$

Red Moon Method



RM simulation in each SB is executed by one computer, thus the computational cost will be the same with that of the usual RM simulation! !

Future research plan

Towards the realization of CSP simulation

- Make a new format for reaction conditions and a program similar to RF.
  - Develop a new format for reaction conditions to decrease the reaction patterns possible to calculate.
  - Make a program similar to RF in order to read the new format and to write an output file used for an input file to TE.
  - Make the program possible to calculate distances, bond angles and dihedral angles with a parallel computing (e.g., OpenMPI).
- Reconsider all of the force field files so as to make a consistency among all the atom types of the model molecules in order to construct the CSP model system.
- Try to execute RM simulations for Hf-cat system III and IV, and Zr-cat system II, using the new format and the new RF-like program.

Thank you for your attention.