Recent Application of Machine Learning Force Field: Beyond Simple Molecular Dynamics Simulation

Presenter **Ji Woong Yu**

2024/11/21

Recent Application of Machine Learning **Force Field**: Beyond Simple **Molecular Dynamics** Simulation

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Given a system of particles described by a potential function, solve the equations of motion using

$$m_i \frac{d^2 R_i}{dt^2} = -\nabla V(R_1, R_2, \ldots, R_i, \ldots, R_N) \quad i = 1, \ldots, N$$

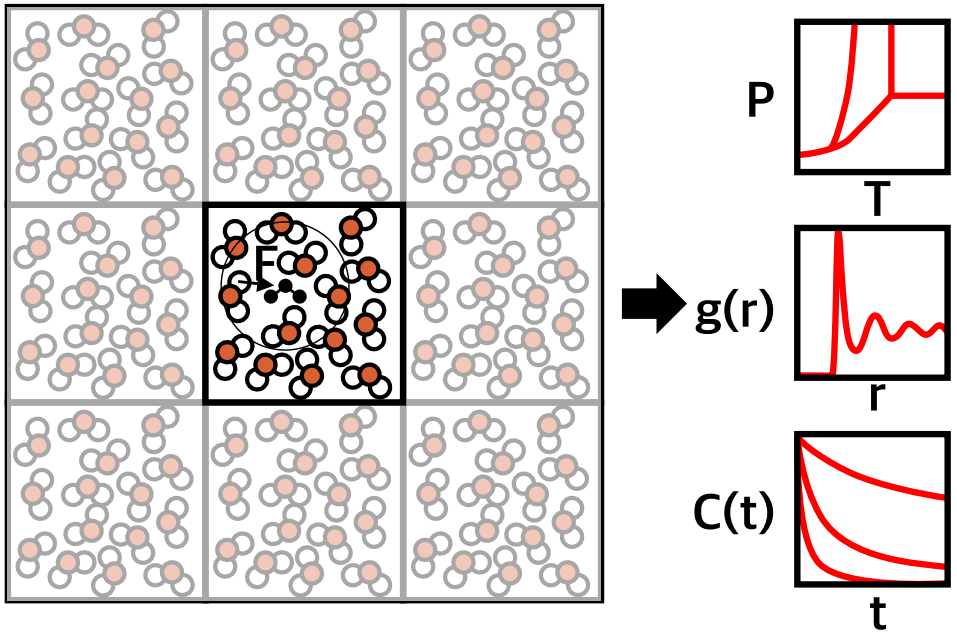
$$V(R_1, R_2, \ldots, R_N) \rightarrow E(r_1, r_2, \ldots)$$

Cartesian Internal

- Potential function
- Topology (Degrees of freedom)
- Initial and boundary conditions
- Algorithm for integration

Then measure properties from the simulation

- Phase transitions
- Structural properties
- Transport properties



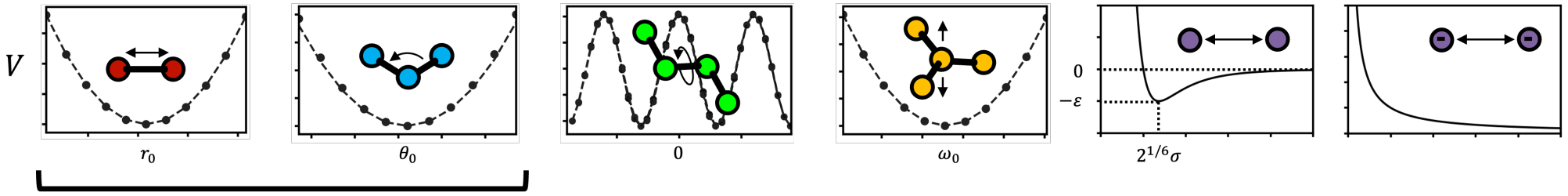
A force field is a set of functional forms and parameters that constitutes the potential energy function governing the interactions among atoms

$$V = \sum_{bonds} k_r(r - r_0)^2 + \sum_{angles} k_\theta(\theta - \theta_0)^2 + \sum_{dihedrals} \sum_{i=1}^{4} \frac{1}{2} V_i\left[1 + (-1)^{i+1}\cos(i\phi)\right]$$

bond stretching | angle bending | torsions

$$+ \sum_{impropers} k_\omega(\omega - \omega_0)^2 + \sum_{\substack{non-bonded \\ pairs}} \left\{ \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}} + 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]\right\}$$

impropers | vdW interactions+ electrostatic interactions

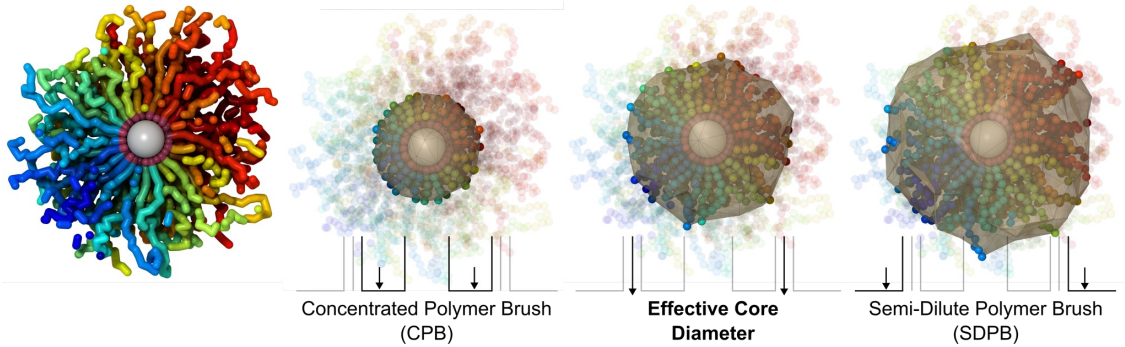


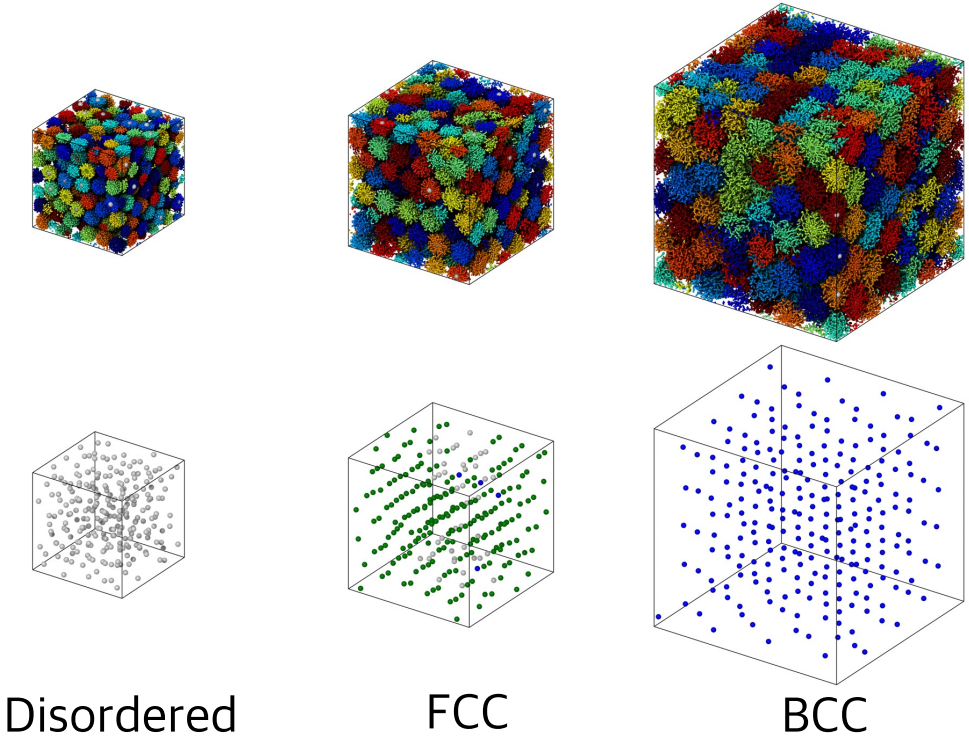
order of femto seconds (10^{-15} s): fastest motion of the system

$$\boldsymbol{F}_i = -\partial V/\partial \boldsymbol{r}_i \longrightarrow \boldsymbol{F}_i = m_i \boldsymbol{a}_i$$

Examples of Molecular Dynamics Simulation

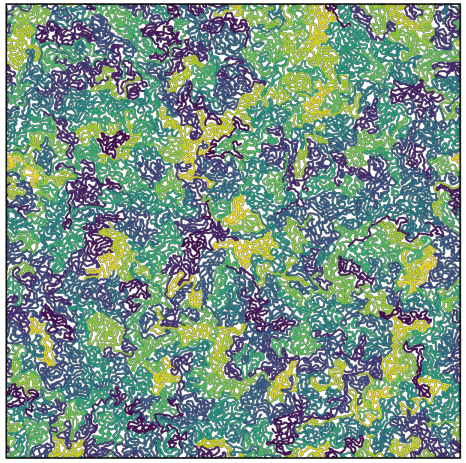
Self-assembly of polymer-grafted Nanoparticles



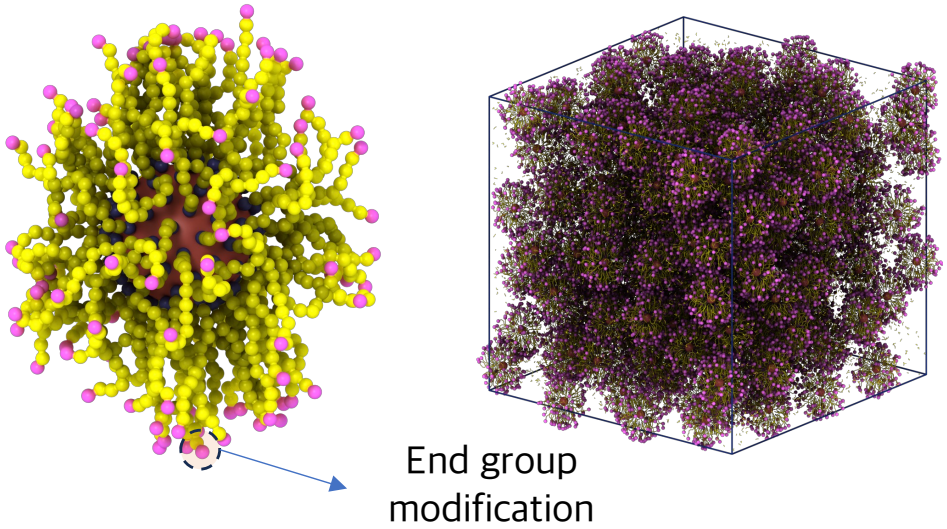


Yu et al., **Adv. Sci.** (2024)

Dynamics of two-dimensional polymers



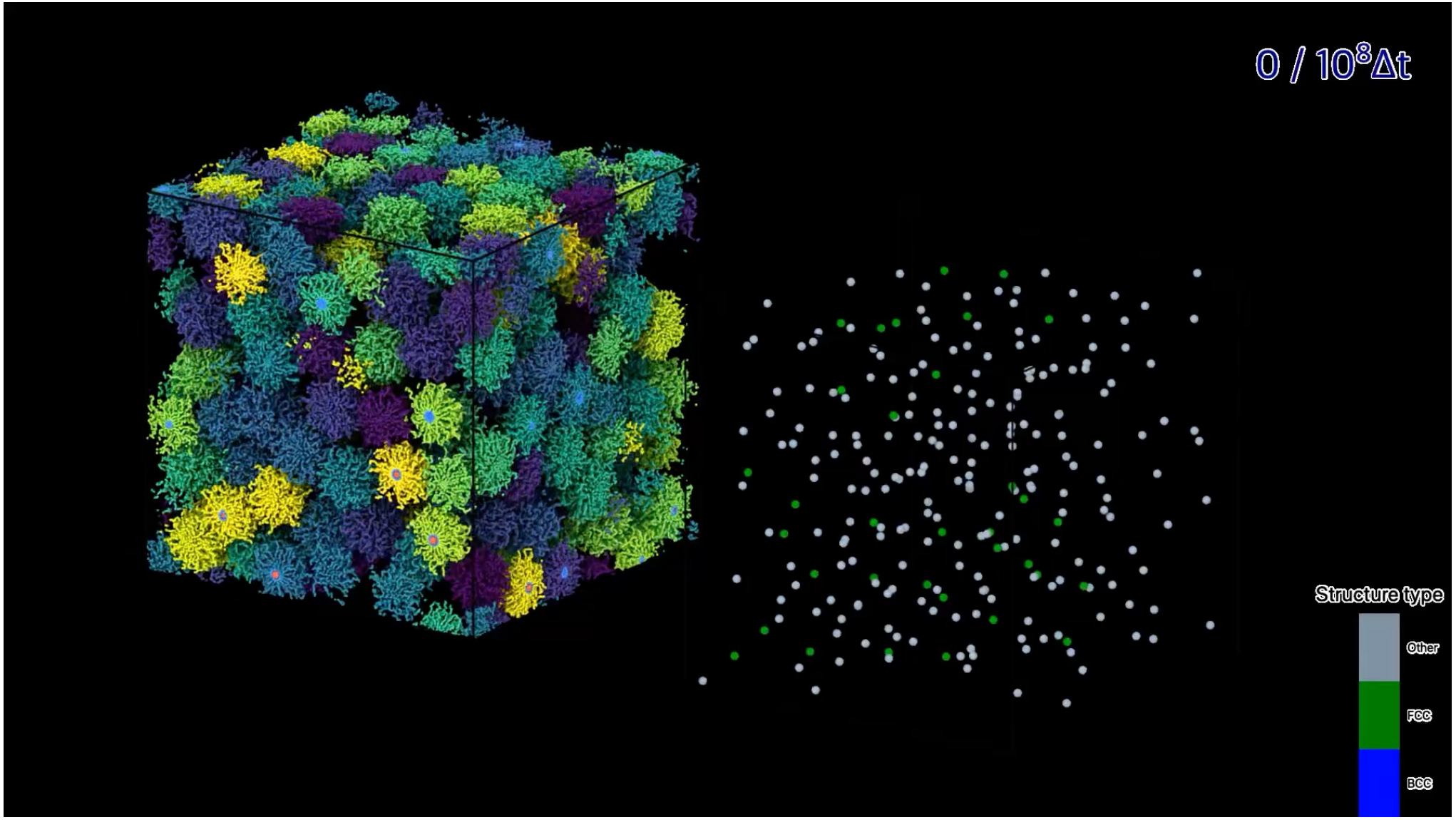
Effect of end-group modification on the symmetry of self-assembly



In preparation

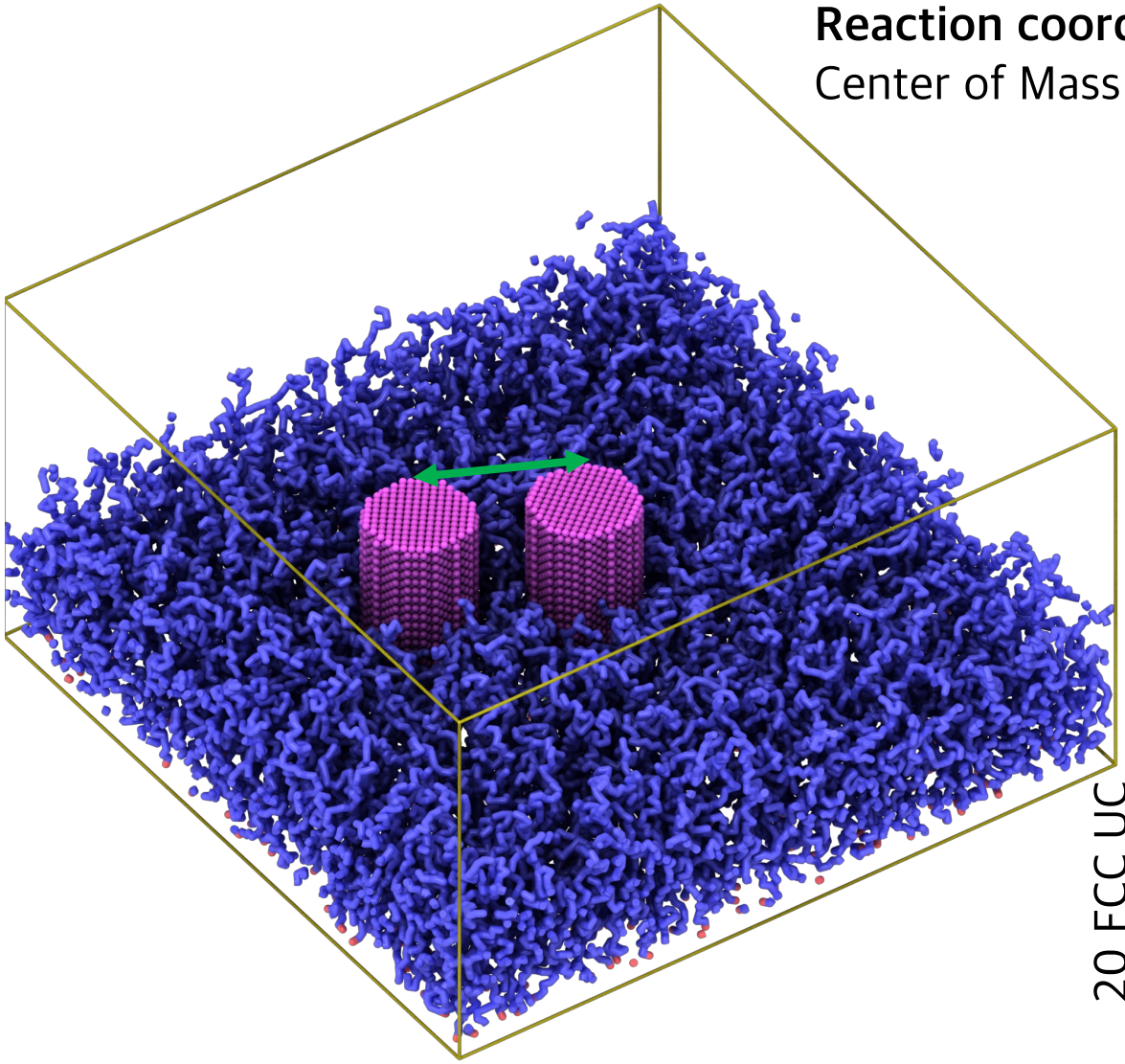
Examples of Molecular Dynamics Simulation

Self-assembly of polymer-grafted Nanoparticles



Yu et al., Advanced Science (2024)

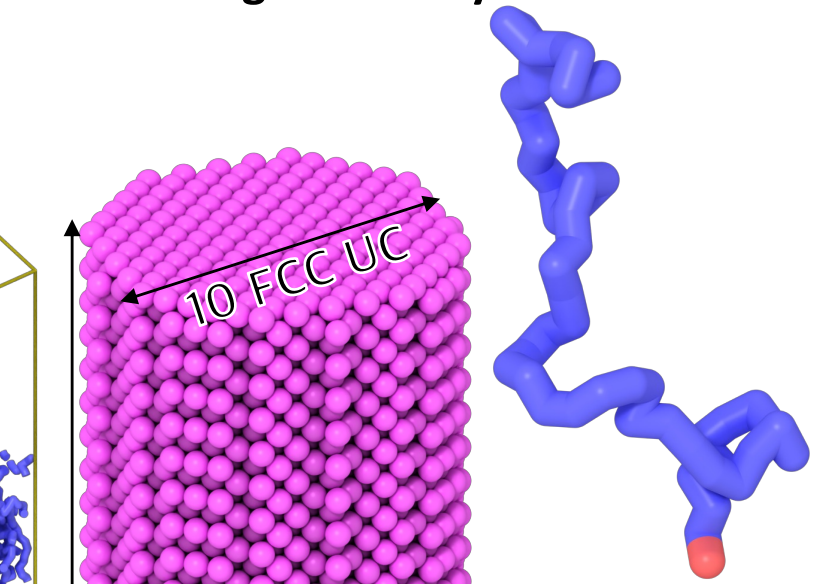
Depletion interaction between a pair of cylindrical objects



Reaction coordinates

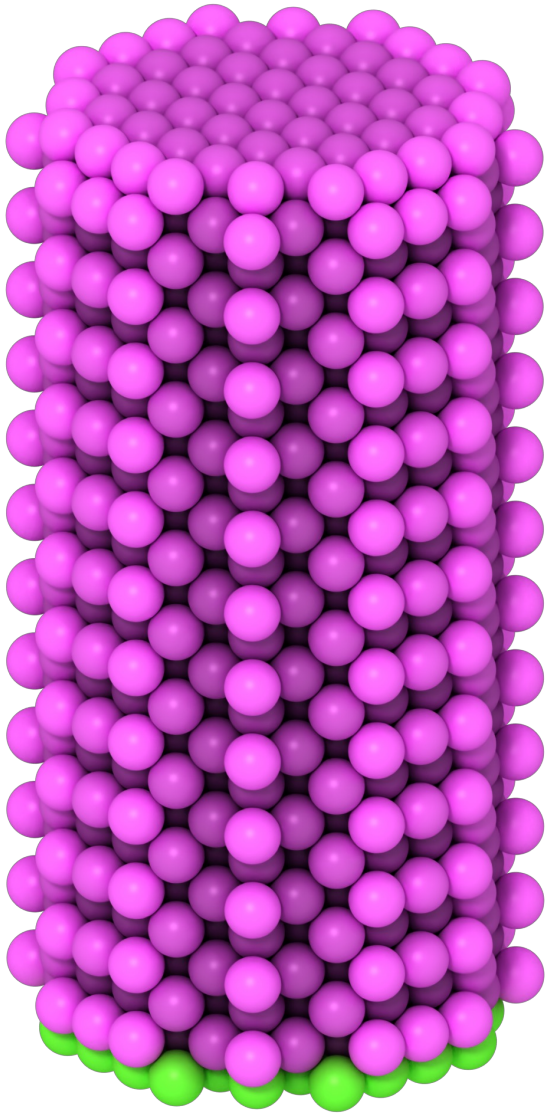
Center of Mass (CoM) separation between cylinders

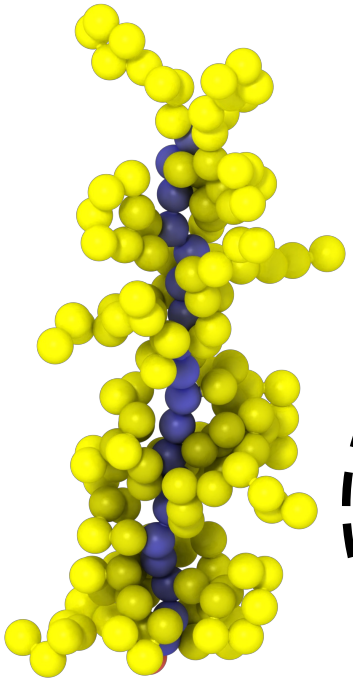
Degree of Polymerization = 50

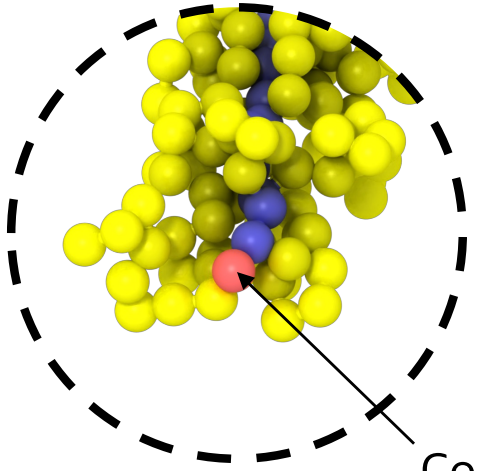


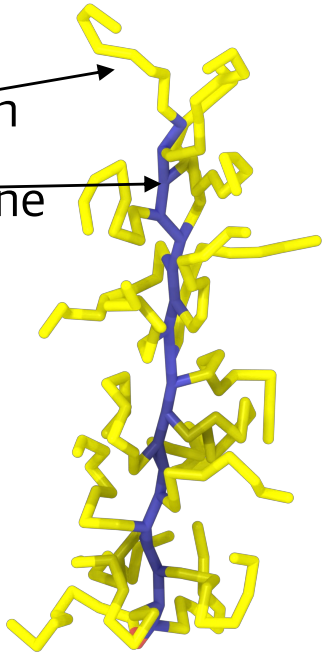
In preparation

Enhanced Clustering by changing polymer design



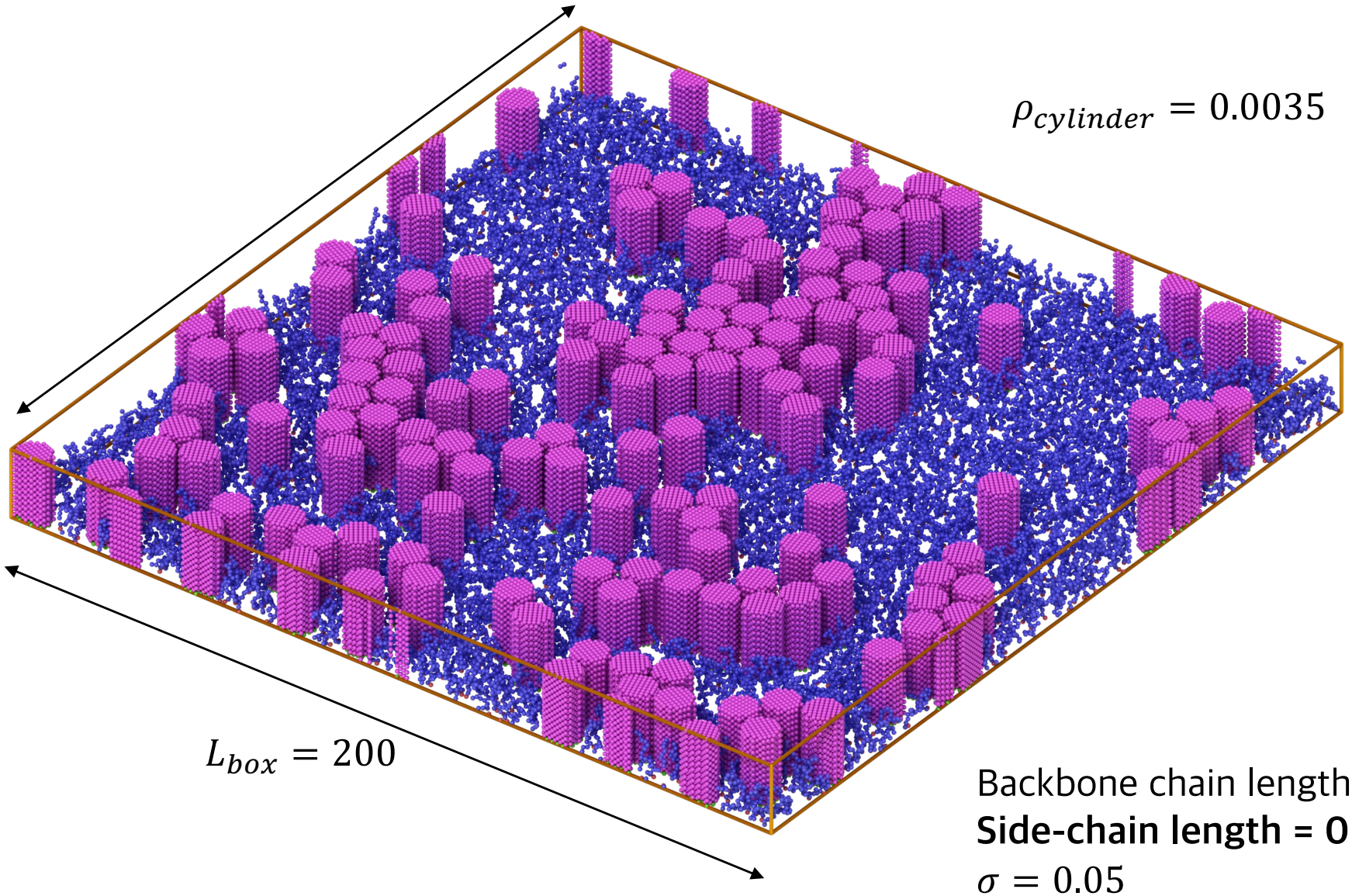






In preparation

Enhanced Clustering by changing polymer design



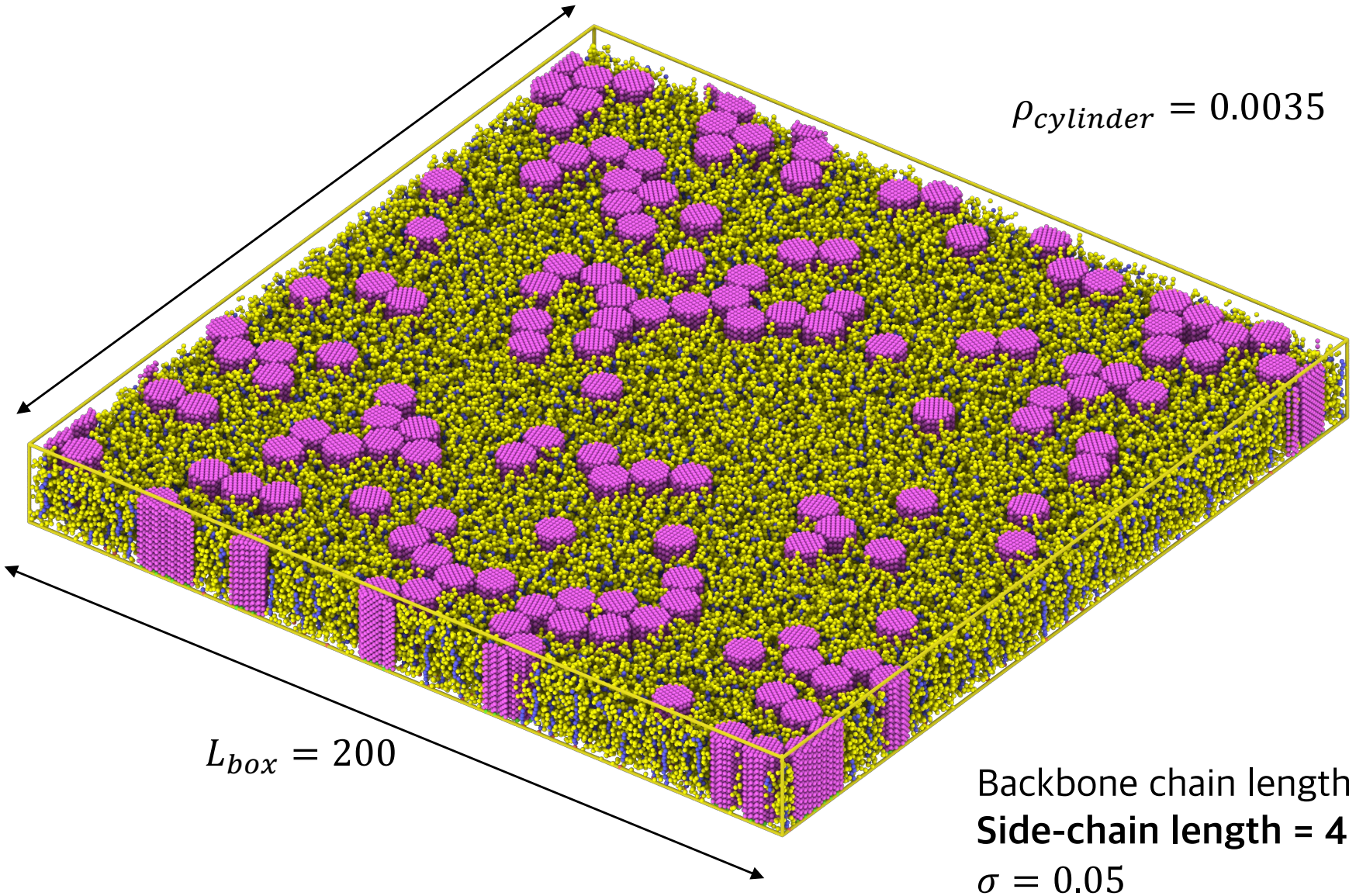
Backbone chain length = 20

Side-chain length = 0

$\sigma = 0.05$

In preparation

Enhanced Clustering by changing polymer design



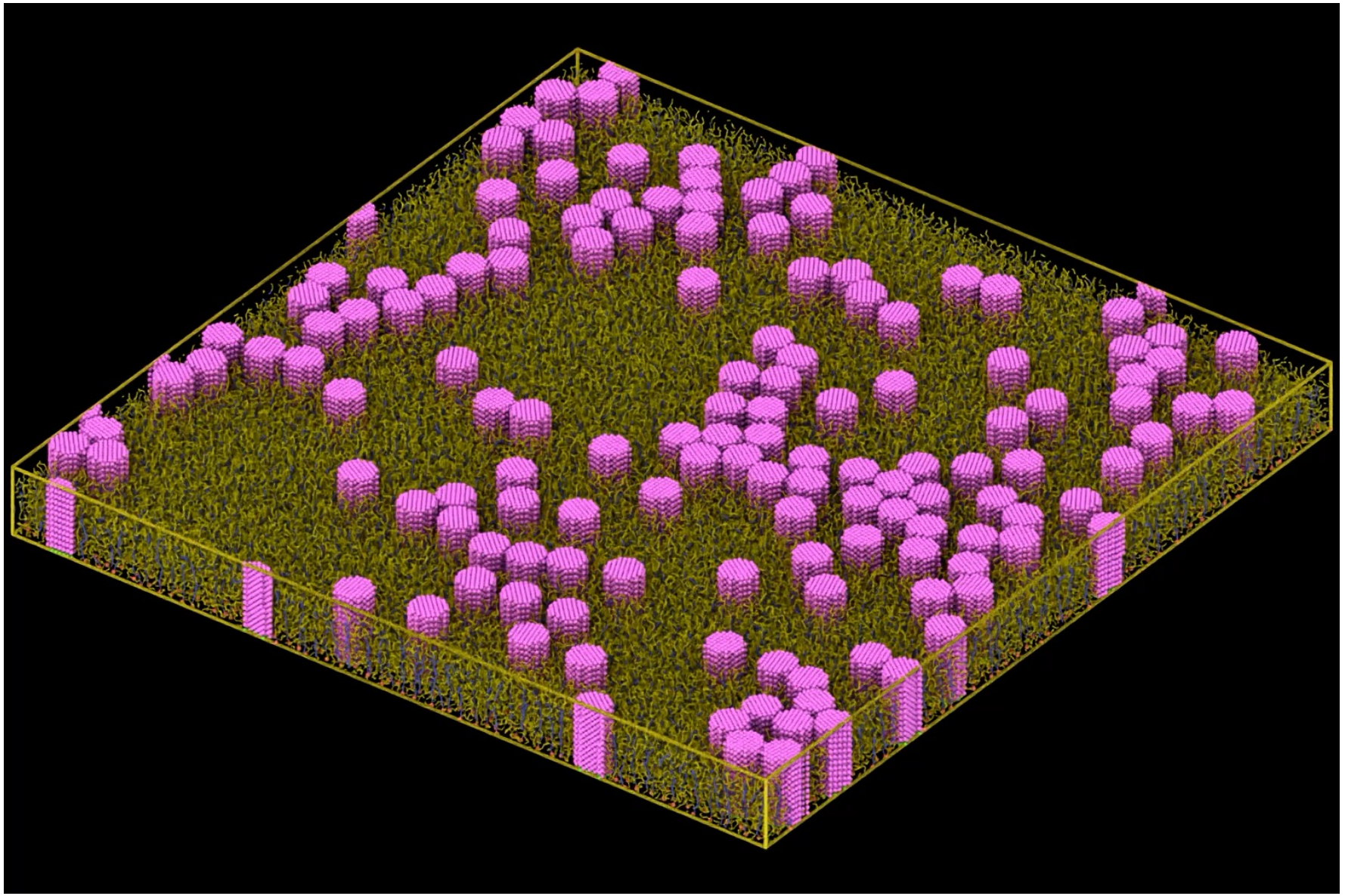
Backbone chain length = 20

Side-chain length = 4

$\sigma = 0.05$

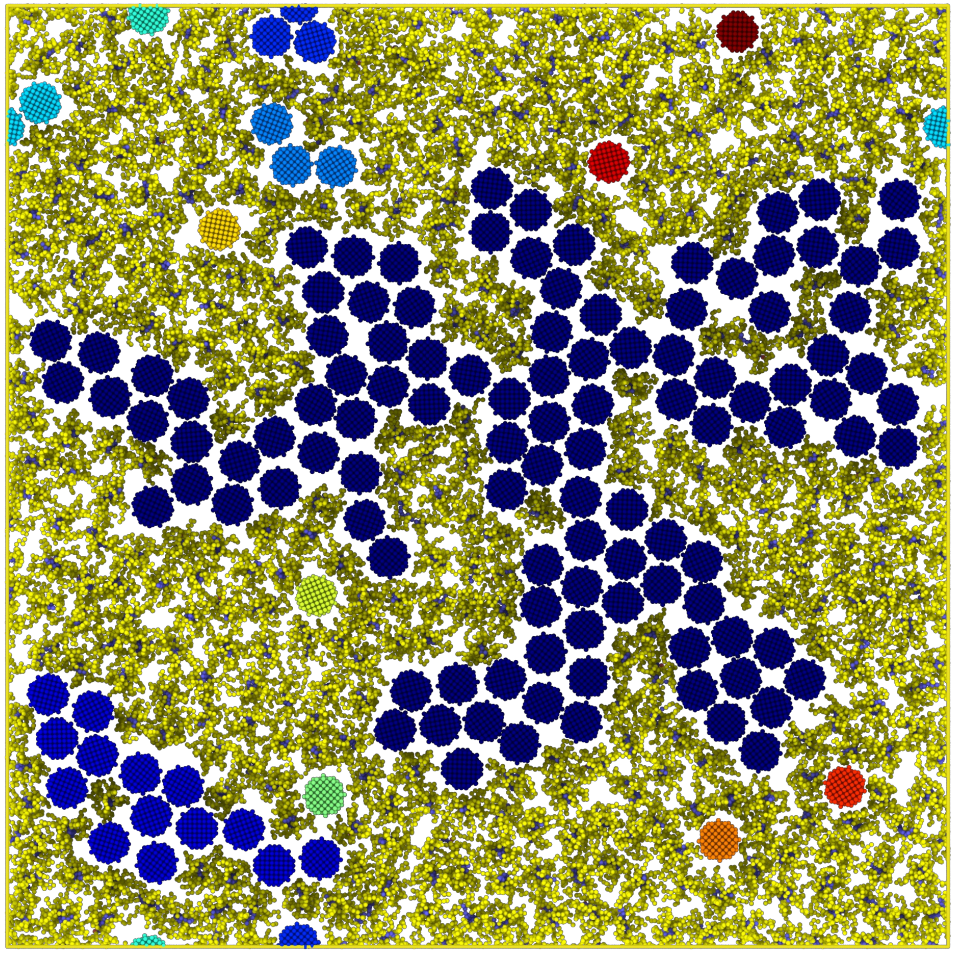
In preparation

Enhanced Clustering by changing polymer design

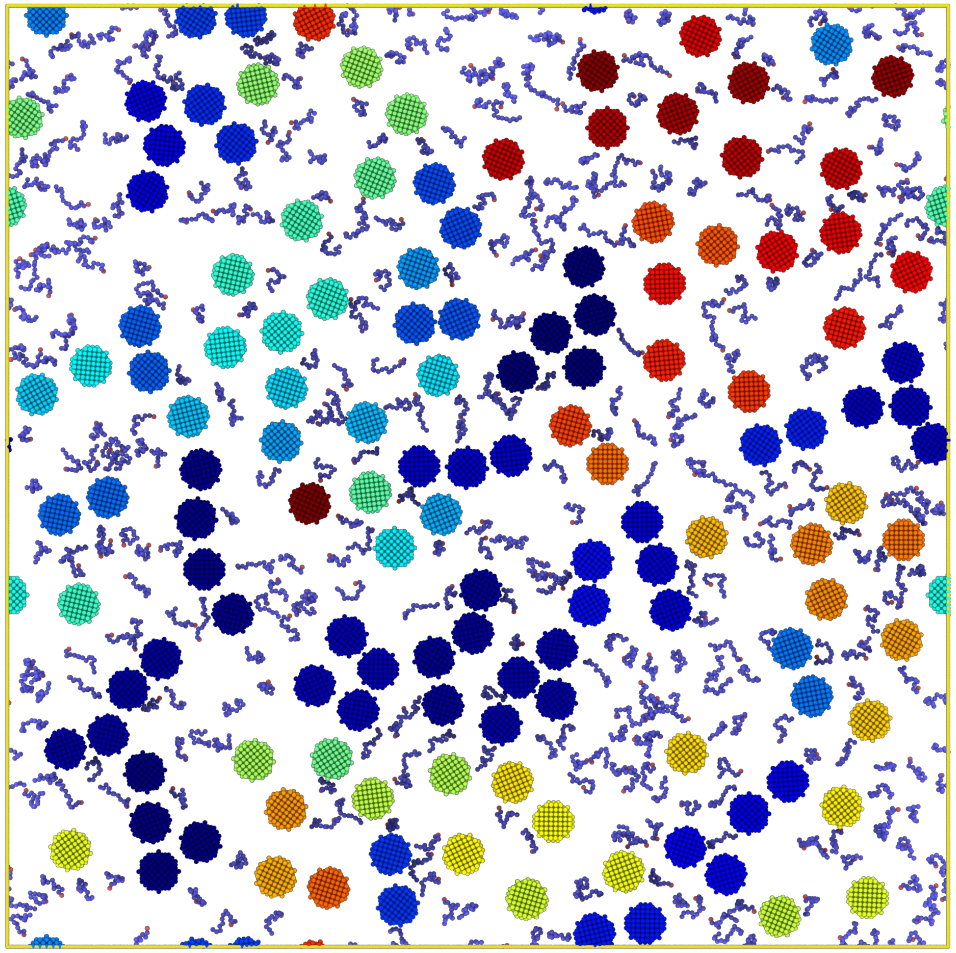


In preparation

Enhanced Clustering by changing polymer design



Backbone chain length = 15
Side-chain length = 4
$\sigma = 0.01$



Backbone chain length = 15
Side-chain length = 0
$\sigma = 0.01$

In preparation

What are the **problems** with the conventional force field?

- Fixed and limited functional forms

- Only handful of functional forms (LJ, Buckingham, etc.)

- Many-body effect

- Parameterization of 3B, 4B, ⋯, nB interaction is difficult

- Permanent topology

- Break or creation of bond is impossible

- Polarization effect

- Induced dipole

What are the **problems** with the conventional force field?

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$$U_{LJ}(r_{ij}) = \epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

$$U_{\text{Buck}}(r_{ij}) = A_{ij}\exp(-B_{ij}r_{ij}) - \frac{C_{ij}}{r^6}$$

Many-body effect

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Permanent topology

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$$V = \sum_i \sum_{i<j} V_{2B}(r_i, r_j) + \sum_i \sum_{i<j} \sum_{i<j<k} V_{3B}(r_i, r_j, r_k) + \cdots$$

Permanent topology

- Break or creation of bond is impossible

Polarization effect

- Induced dipole

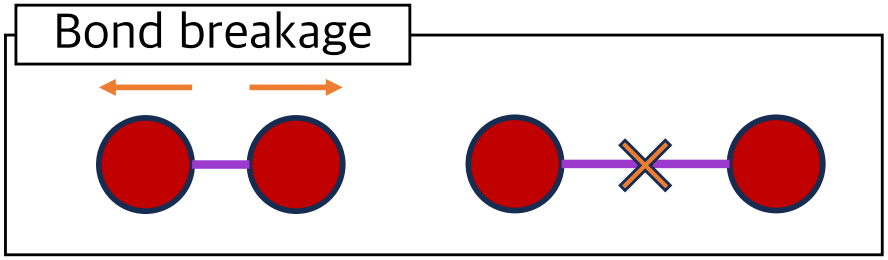
What are the **problems** with the conventional force field?

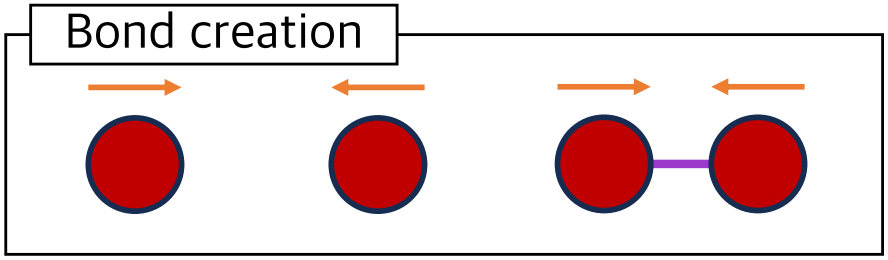
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Polarization effect
- Induced dipole

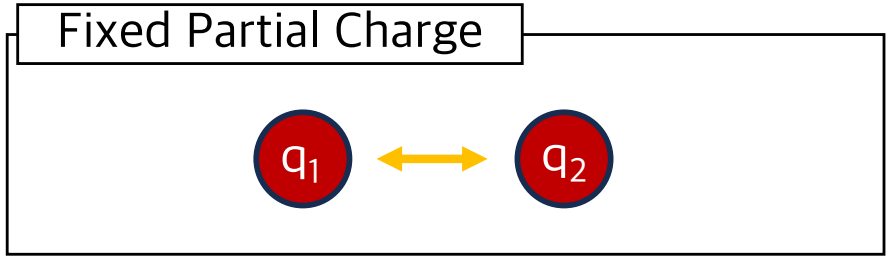
What are the **problems** with the conventional force field?

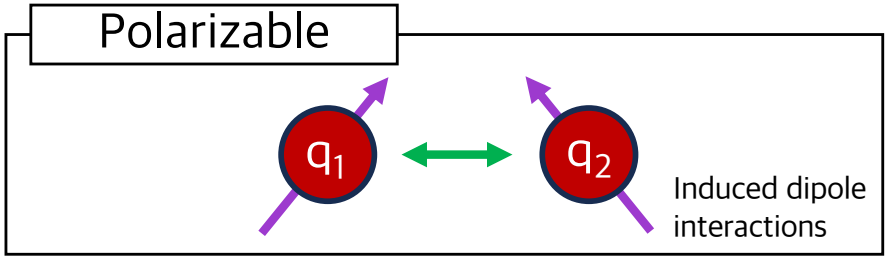
Fixed and limited functional forms
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Permanent topology
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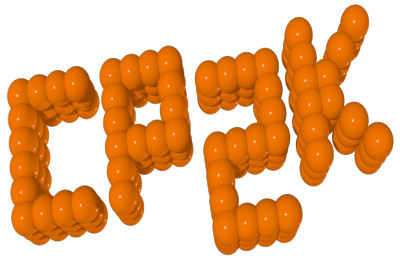
When **computational resources** are not a constraint,
we can measure the potential energy of the system with **very high precision.**

First-principle (or ab-initio) methods

- Hartree-Fock (HF) $\sim O(N^4)$
- Density Functional Theory (DFT) $\sim O(N^3)$
- Coupled Cluster Singles and Doubles with Perturbative Triples (CCSD(T)) $\sim O(N^7)$
- Second-order Møller-Plesset perturbation theory (MP2) $\sim O(N^5)$

where N is the system size





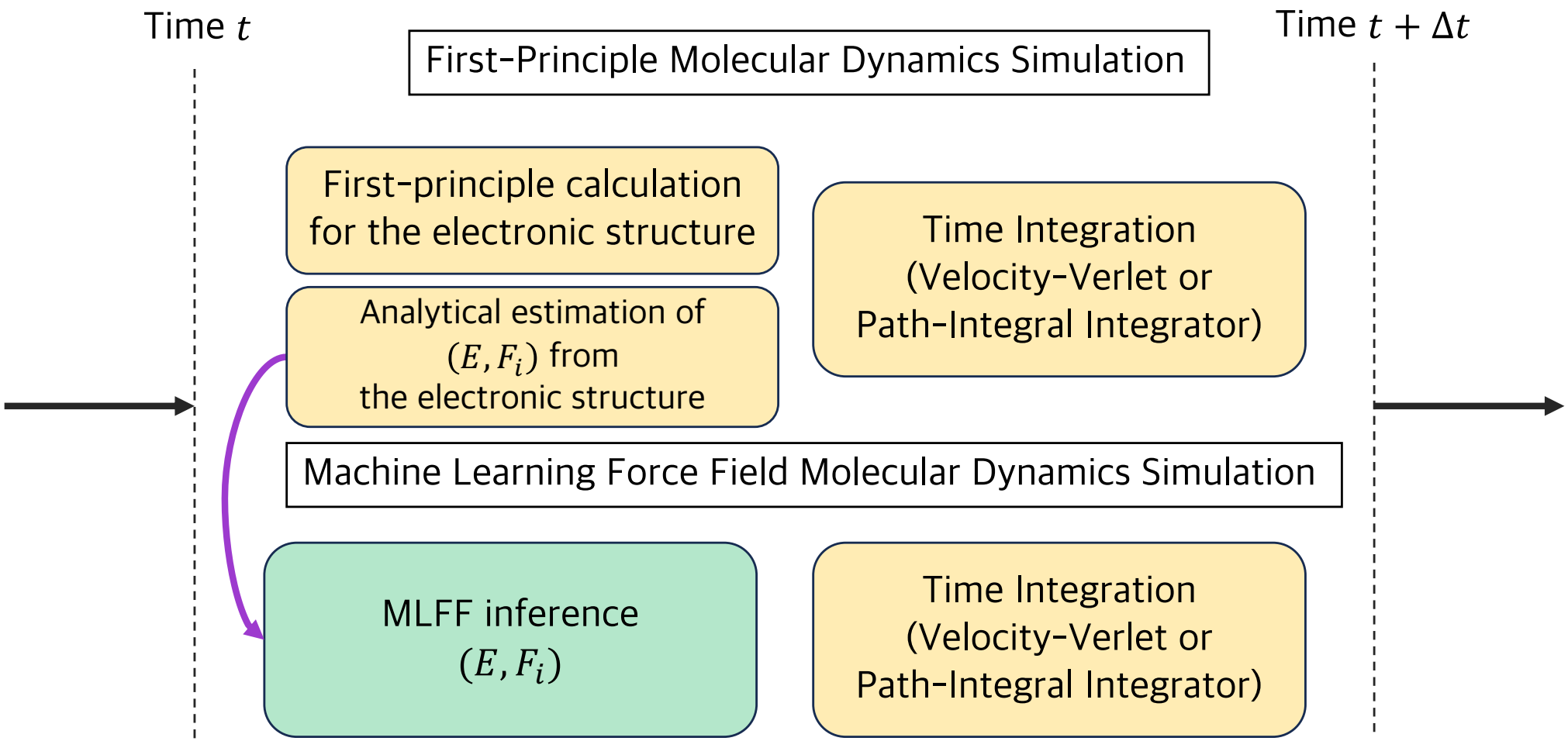








Machine Learning Force Field is a surrogate model for first-principle calculations



Early development of MLFF

Generalized neural-network representation of high-dimensional potential-energy surfaces

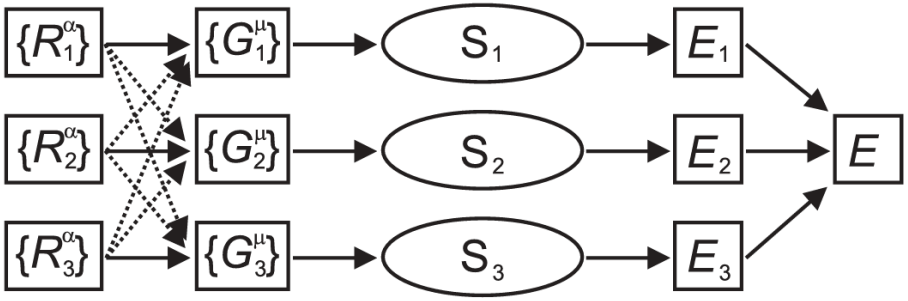
J **Behler**, M **Parrinello** - Physical review letters, 2007 - APS

The accurate description of chemical processes often requires the use of computationally demanding methods like density-functional theory (DFT), making long simulations of large …

☆ 저장 99 인용 4315회 인용 관련 학술자료 전체 9개의 버전

$$G_i^1 = \sum_{j \neq i}^{\text{all}} e^{-\eta(R_{ij}-R_s)^2} f_c(R_{ij}).$$

$$G_i^2 = 2^{1-\zeta} \sum_{j,k \neq i}^{\text{all}} (1 + \lambda \cos\theta_{ijk})^{\zeta} \times e^{-\eta(R_{ij}^2+R_{ik}^2+R_{jk}^2)} f_c(R_{ij}) f_c(R_{ik}) f_c(R_{jk}),$$



Now most popular ones become GNN-based models

[HTML] E (3)-equivariant graph neural networks for data-efficient and accurate interatomic potentials

S Batzner, A Musaelian, L Sun, M Geiger… - Nature …, 2022 - nature.com

… results using **NequIP** with those from published leading MLIP models. We find that **NequIP** … Importantly, we train and test separate **NequIP** models on both the original and the revised …

☆ 저장 99 인용 1100회 인용 관련 학술자료 전체 21개의 버전

MACE: Higher order equivariant message passing neural networks for fast and accurate force fields

I Batatia, DP Kovacs, G Simm… - Advances in Neural …, 2022 - proceedings.neurips.cc

Creating fast and accurate force fields is a long-standing challenge in computational chemistry and materials science. Recently, Equivariant Message Passing Neural Networks (MPNNs) have emerged as a powerful tool for building machine learning interatomic potentials, outperforming other approaches in terms of accuracy. However, they suffer from high computational cost and poor scalability. Moreover, most MPNNs only pass two-body messages leading to an intricate relationship between the number of layers and the …

☆ 저장 99 인용 415회 인용 관련 학술자료 전체 6개의 버전 »

Scalable Parallel Algorithm for Graph Neural Network Interatomic Potentials in Molecular Dynamics Simulations

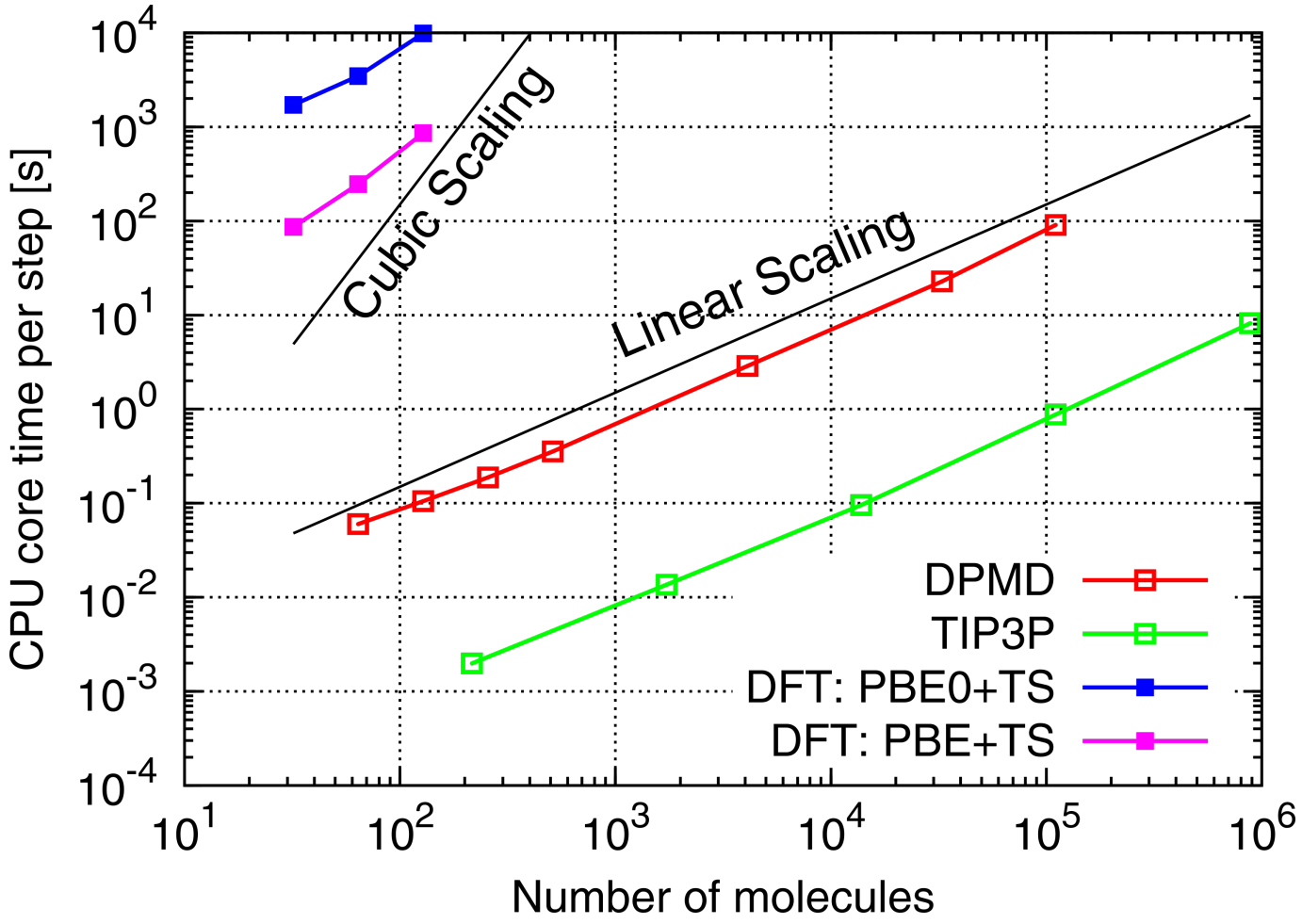
Y Park, J Kim, S Hwang, S Han

Journal of Chemical Theory and Computation, 2024 • ACS Publications

First-principle calculations
$O(N^3)$ scaling

Water MD simulation

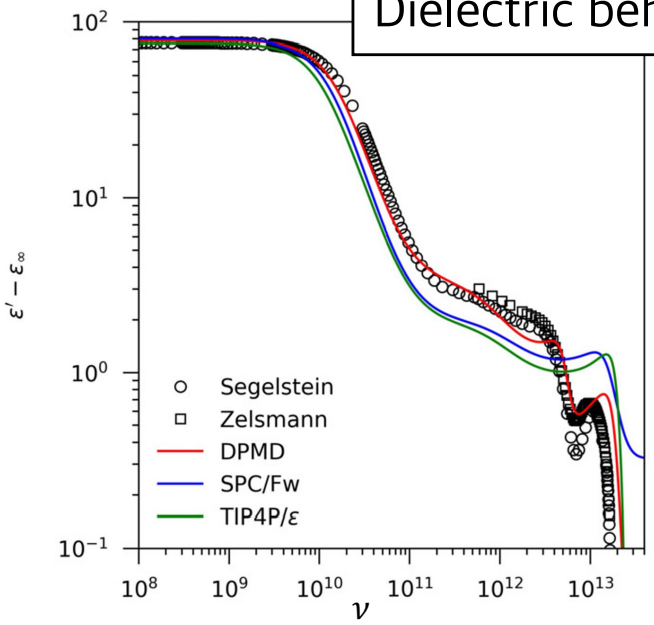
MLFF
O(N) scaling

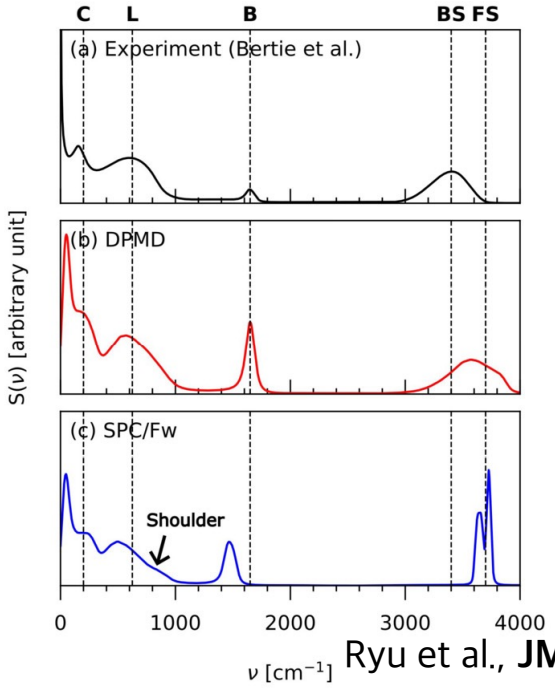


Linfeng Zhang et al., ***PRL***, 2018

Some of MLFF works

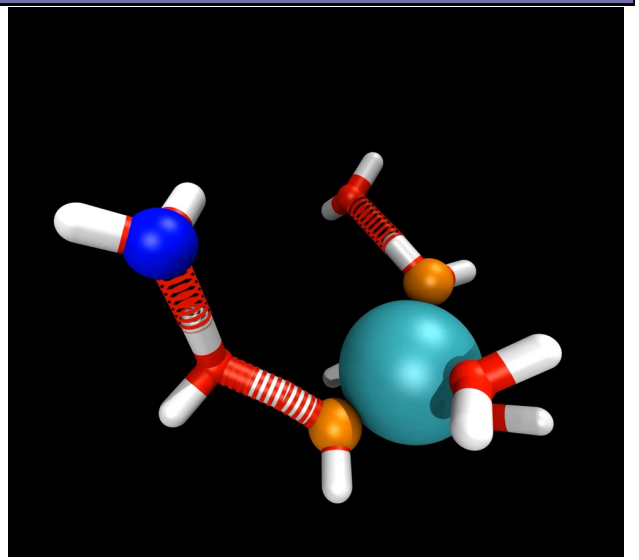
Dielectric behavior of liquid water



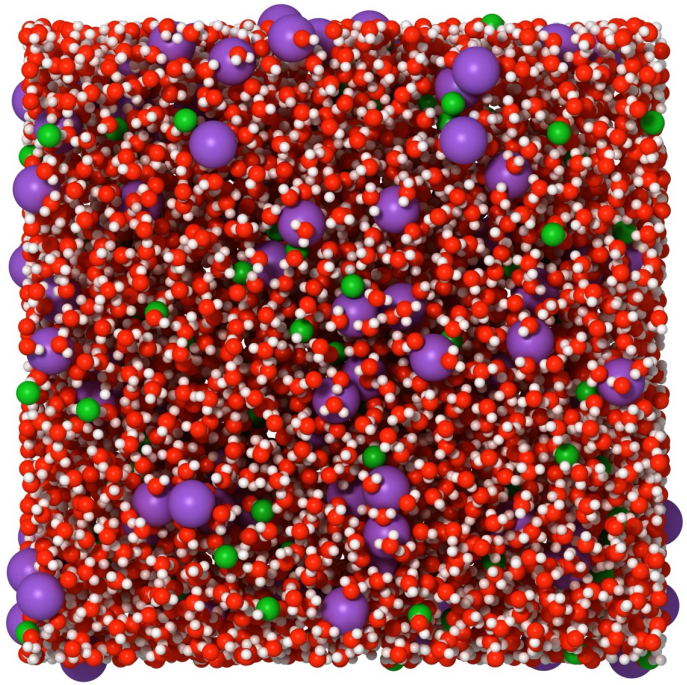


Ryu et al., **JML** (2024)

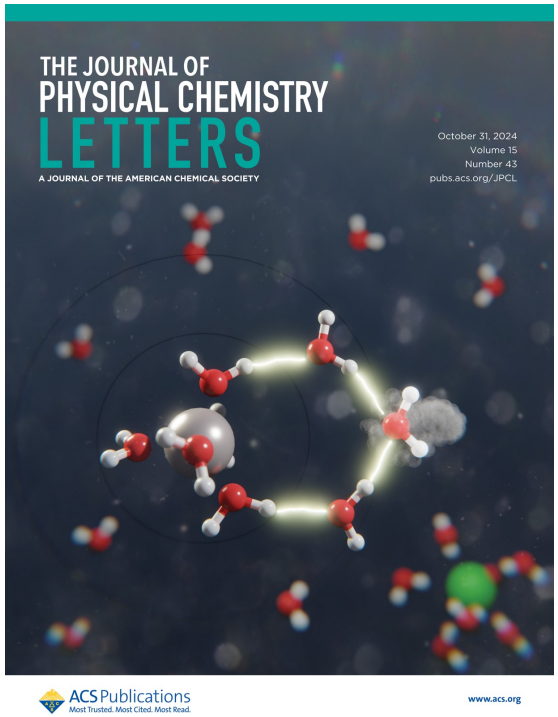
Aluminum ion dissolution mechanism



Water dynamics in salt solution



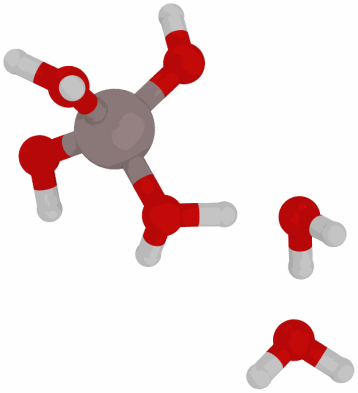
Yu et al., **Sci. Adv.** (Just Accepted)

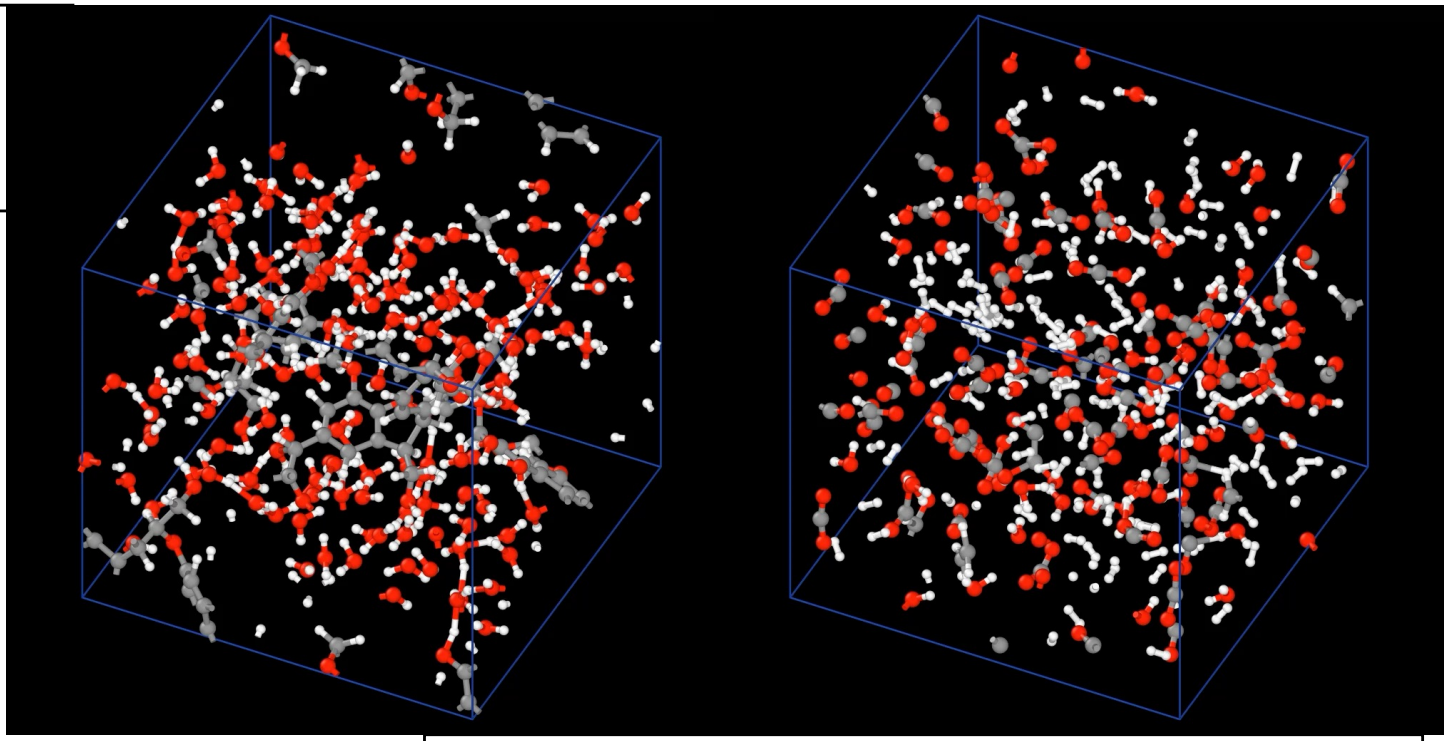


Kim et al., **JPCL** (Just Accepted)

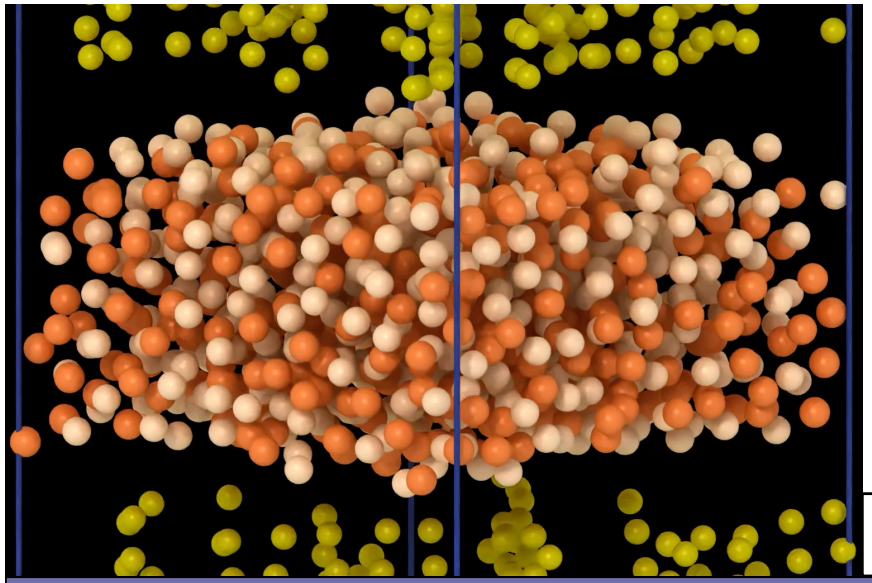
Chemical Reaction

Proton hopping due to hydrolysis (Grotthuss mechanism)





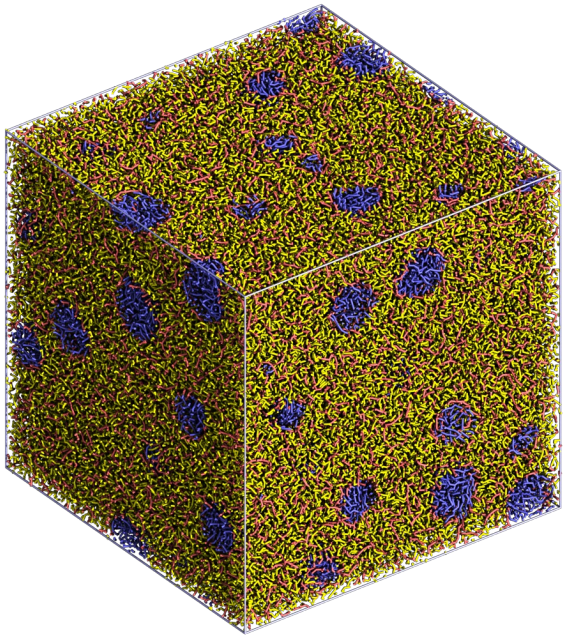
Lignin supercritical water oxidation reaction

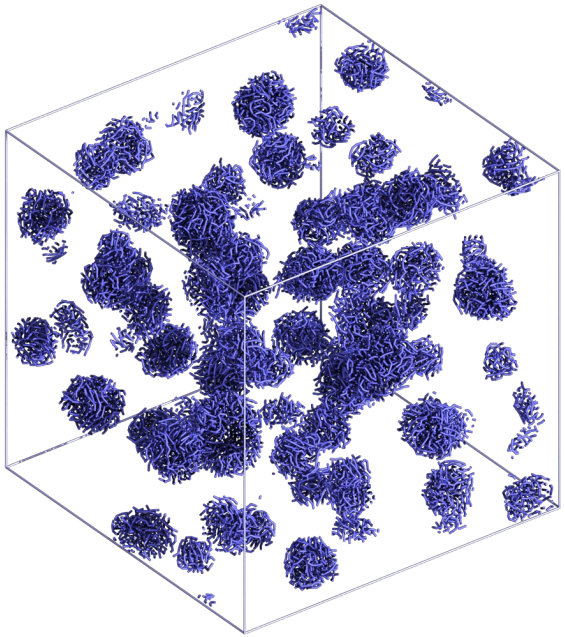


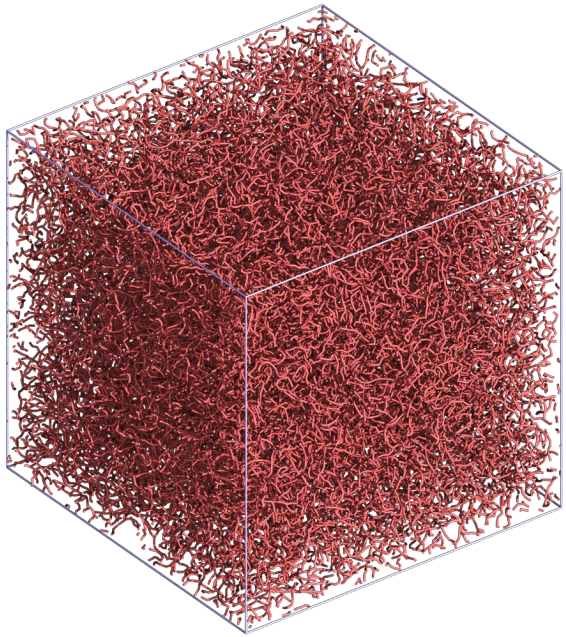
Sulfur reactive permeation into liquid Fe/Si metal

We can now naturally simulate chemical reaction in MD framework!

The current computational limit of MLFF







Still too slow for many soft matter systems!
It should handle $\sim O(10^2)$ns (corresponding to 1×10^8 iterations) with $\sim O(10^5)$ atoms

For rare-event or slow dynamics system,
If not the tracking of whole atoms is of interest,
We can use **advanced sampling**

Collective Variables (CVs)

$$\boldsymbol{S}(\boldsymbol{R}) = (S_1(\boldsymbol{R}), \cdots, S_d(\boldsymbol{R}))$$

where $\boldsymbol{R}$ is the atomic coordinates

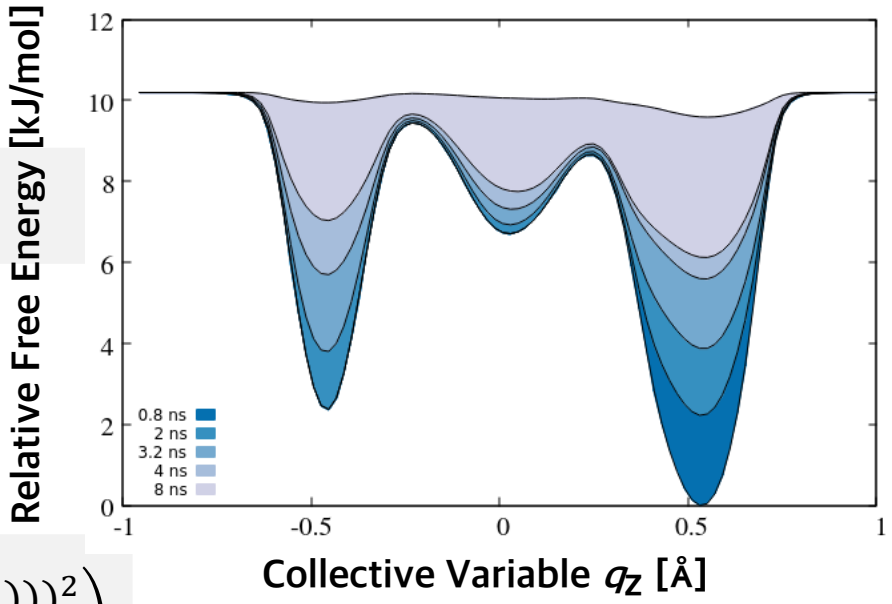
Algorithm

$$V_G(\boldsymbol{S}(\boldsymbol{R}), t) = w \sum_{t' = \tau_G, 2\tau_G, \ldots}^{t' < t} \exp\left(- \sum_{i=1}^{d} \frac{(S_i(\boldsymbol{R}) - s_i(\boldsymbol{R}(t')))^2}{2{\sigma_i}^2} \right)$$

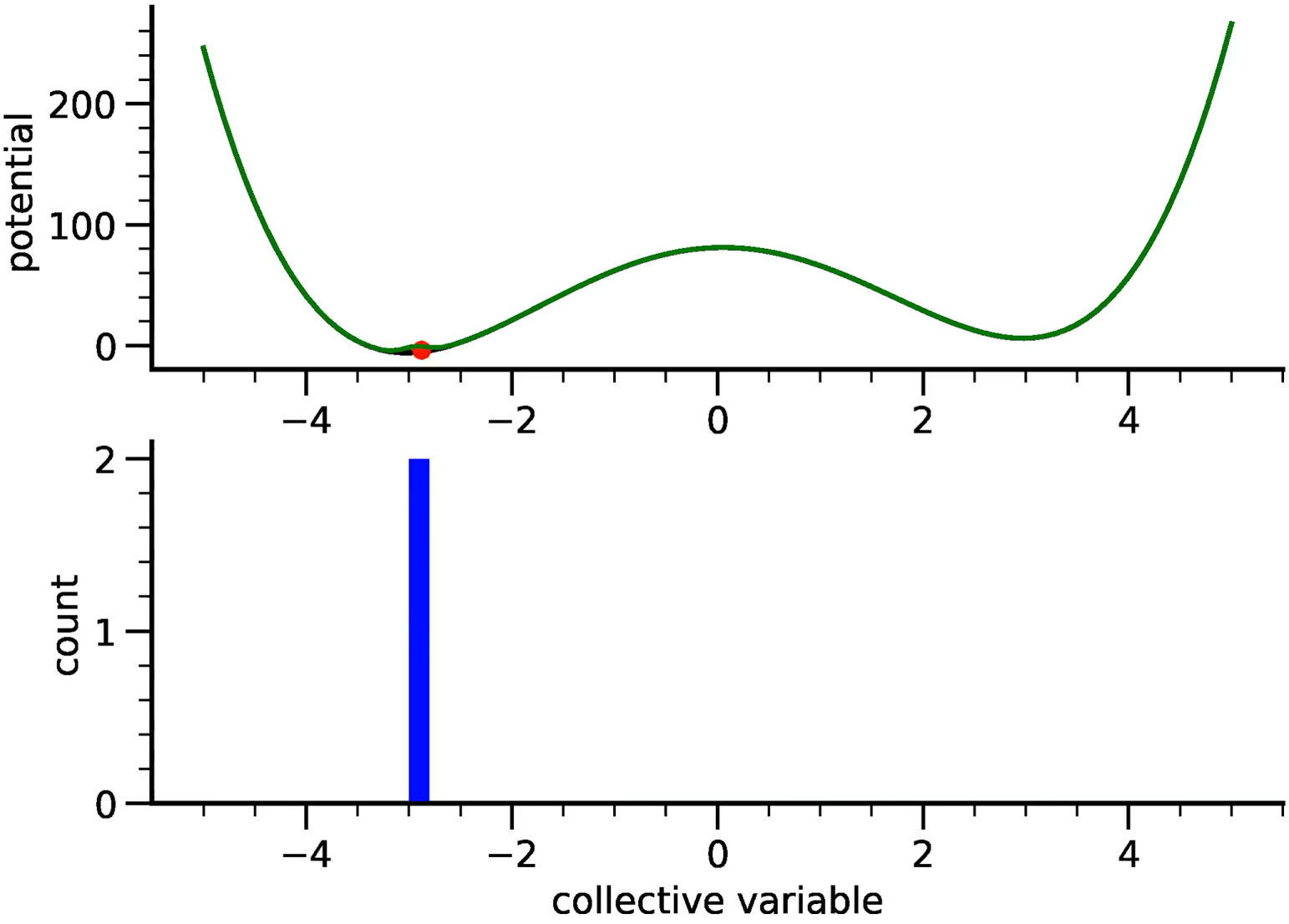
where $\boldsymbol{w}$: height, $\boldsymbol{\sigma_i}$: width, $\boldsymbol{\tau_G}$: frequency of added Gaussians.

Free Energy Surface (FES) Estimate

$$\lim_{t \to \infty} V_G(\boldsymbol{S}, t) \sim - F(\boldsymbol{S})$$

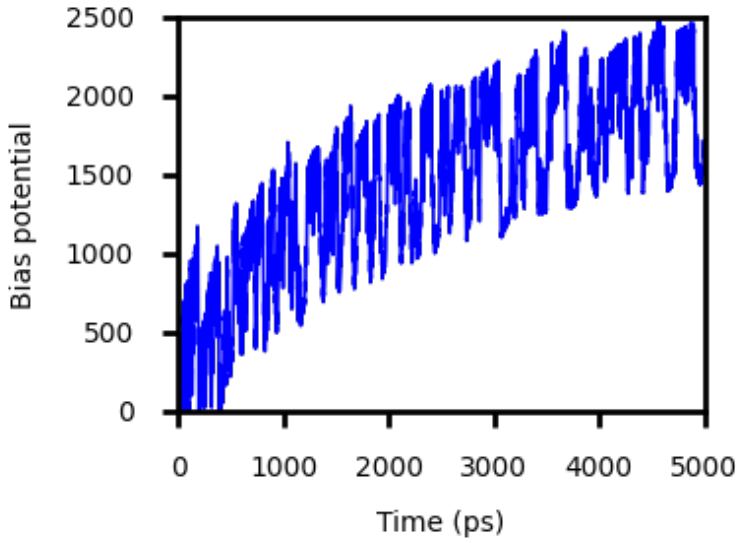


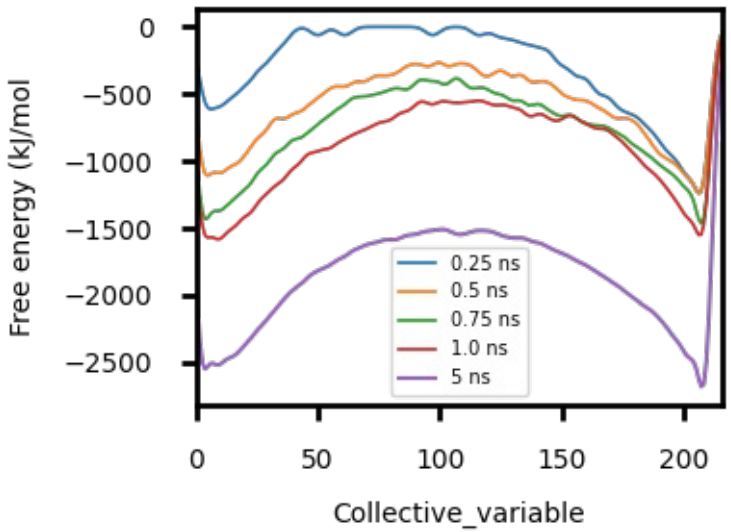
"*Ergodicity is not guaranteed within a single MD simulation trajectory for a rare event problem*"

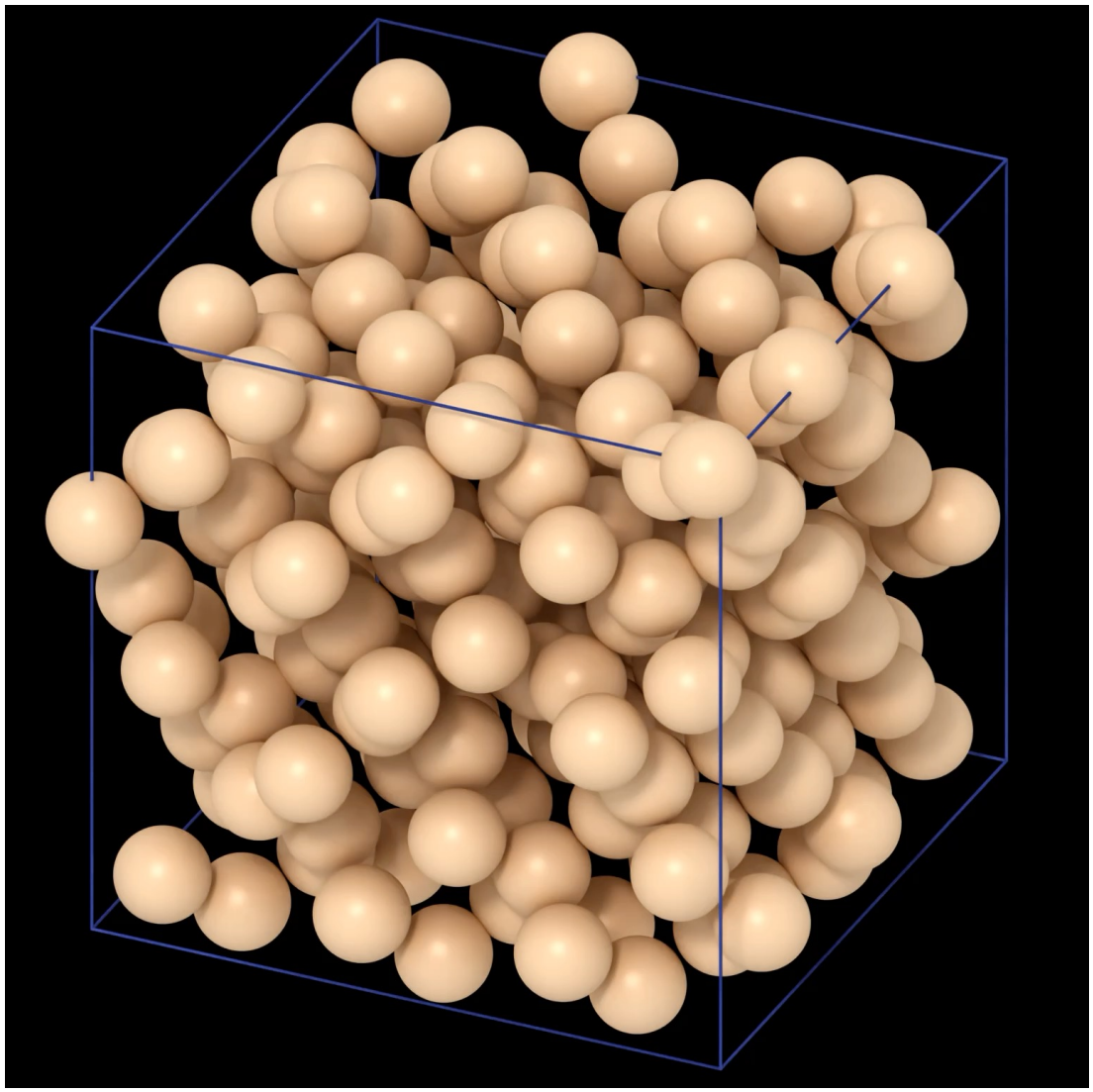


Metadynamics – wikipedia

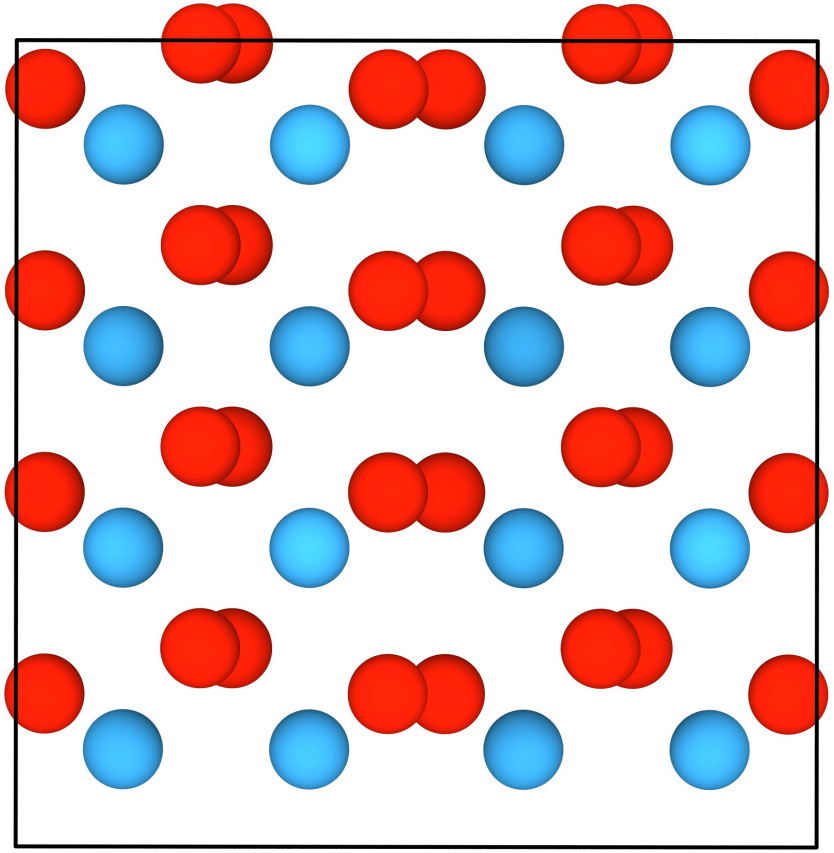
Silicon


Bias potential
2500
2000
1500
1000
500
0
0
1000
2000
3000
4000
5000
Time (ps)

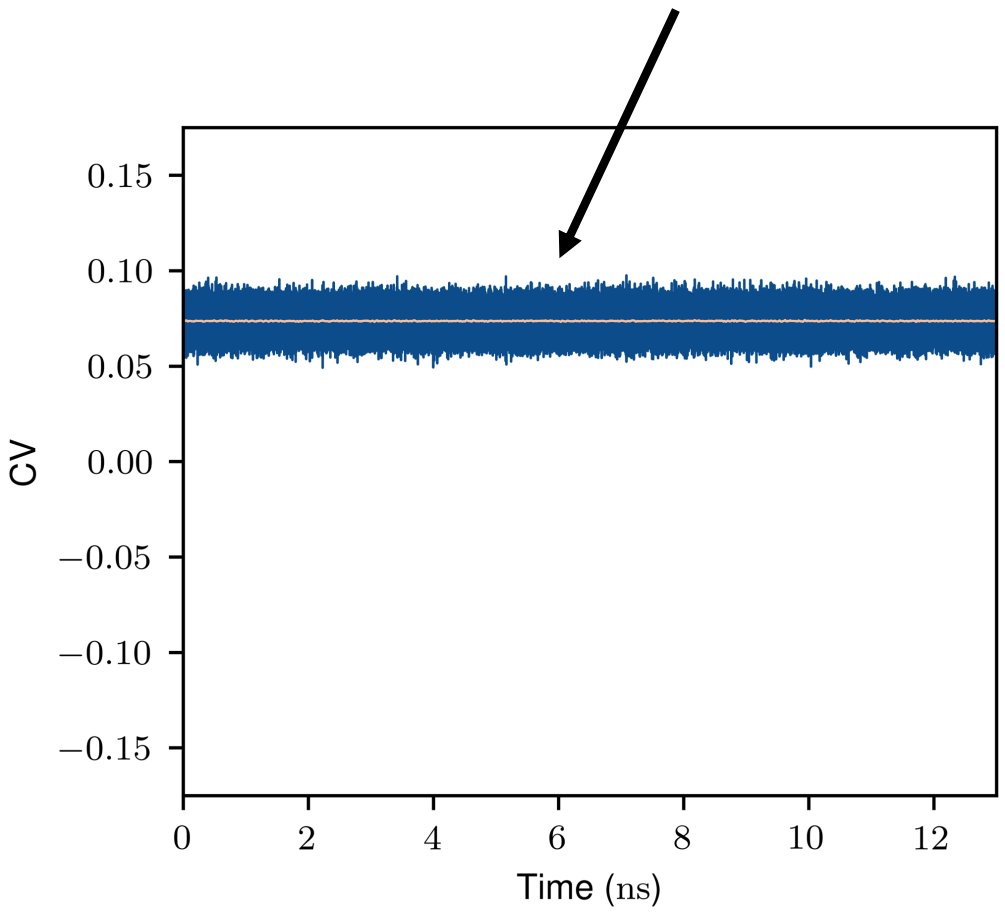

Free energy (kJ/mol
0
−500
−1000
−1500
−2000
−2500
0.25 ns
0.5 ns
0.75 ns
1.0 ns
5 ns
0
50
100
150
200
Collective_variable



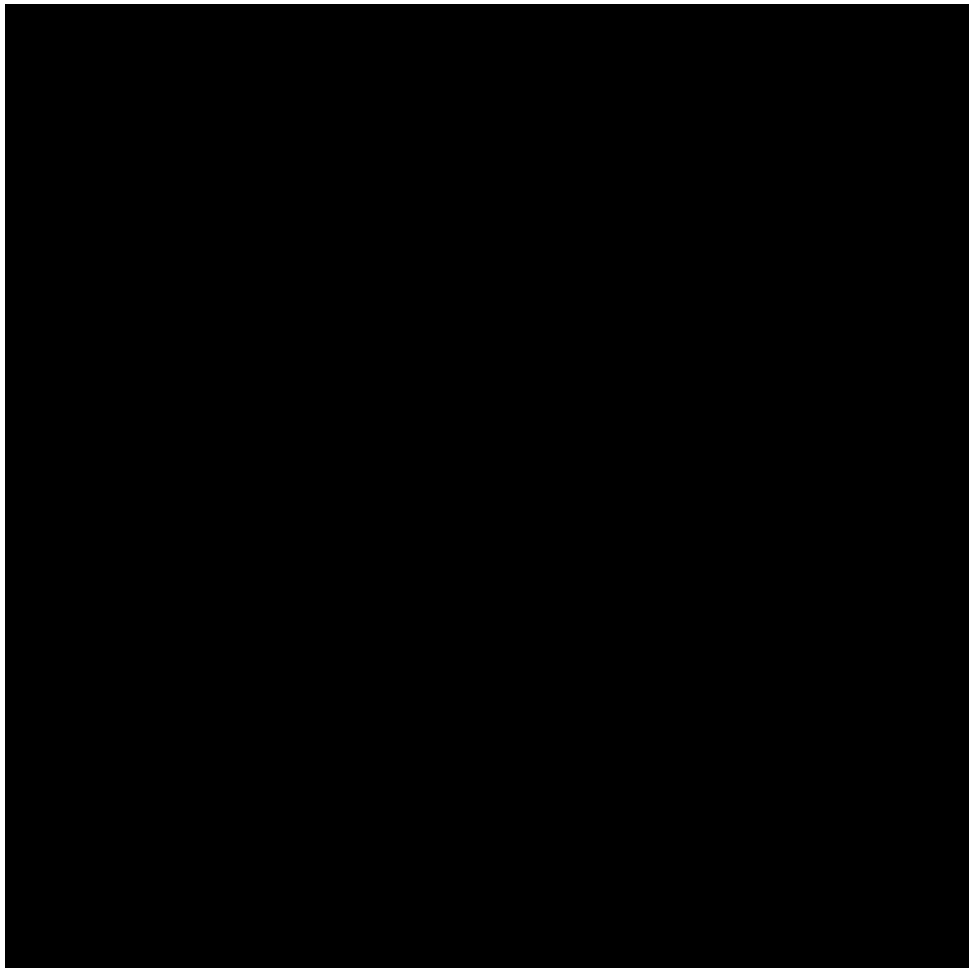
Thermal MD simulation

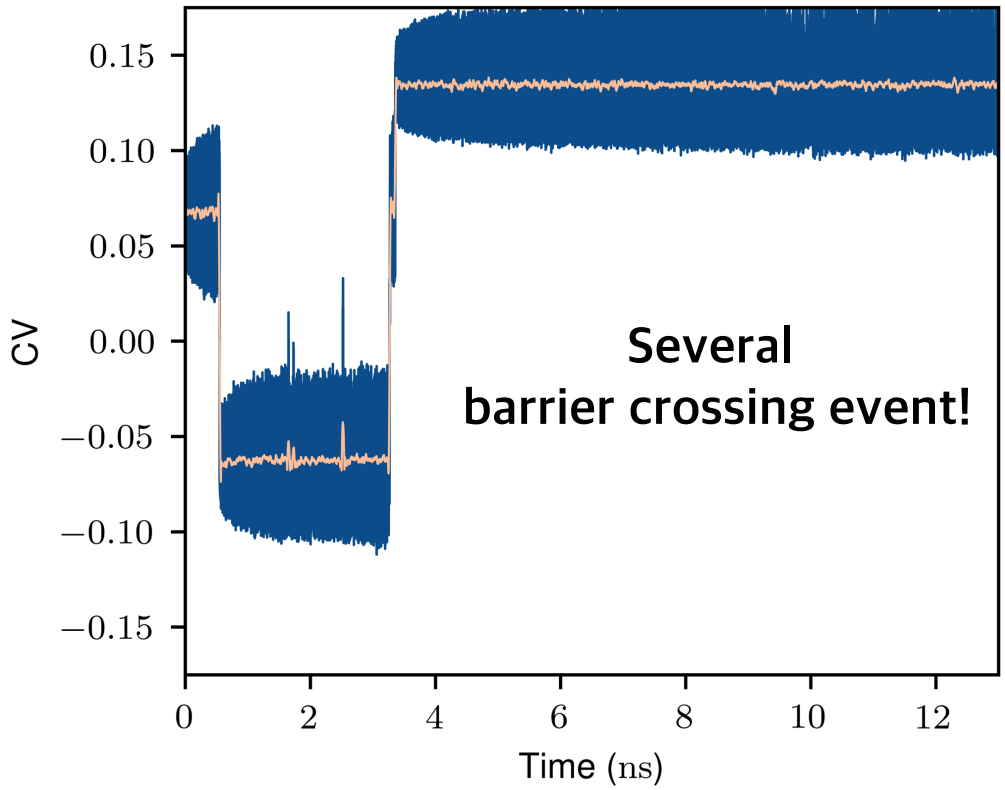


No change of ferroelectric phase!

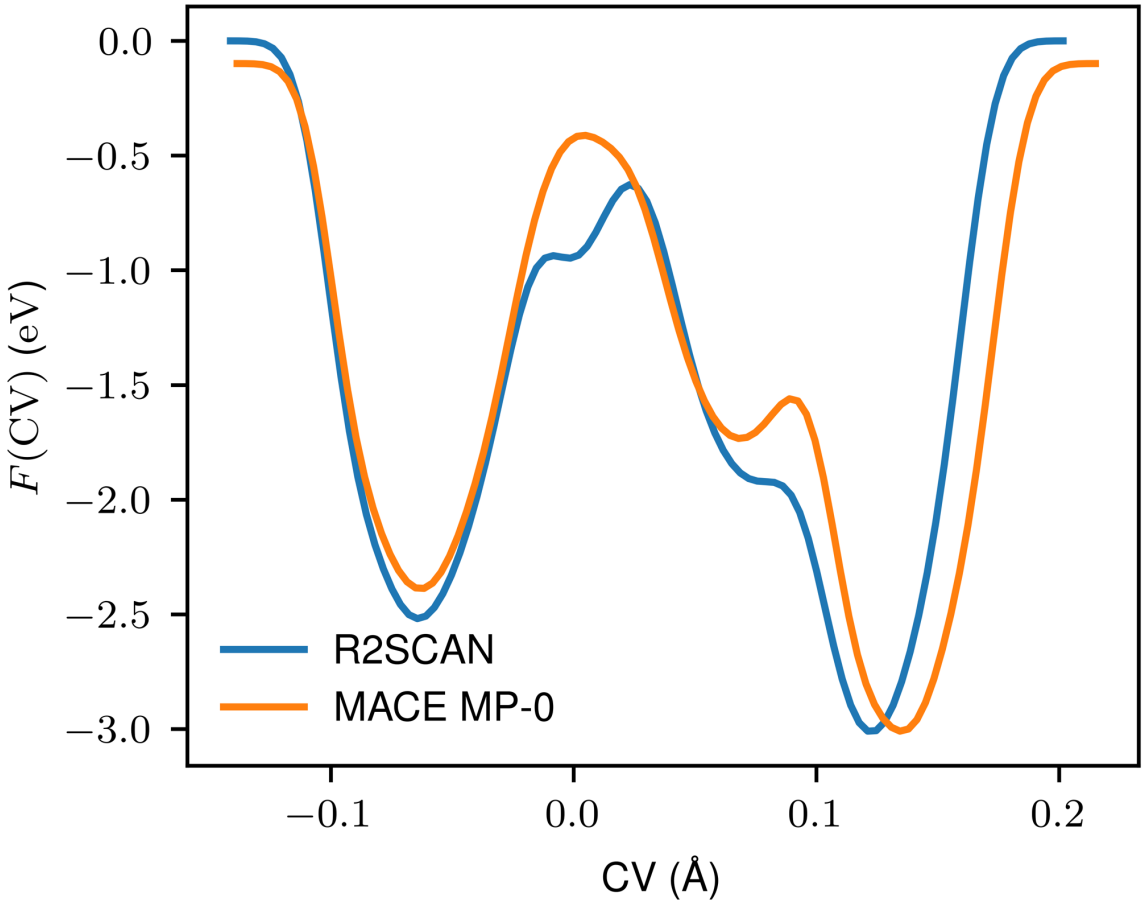


Metadynamics simulation





Resulting free energy landscape in CV space



Machine Learning Force Fields are driving a new era in physical chemistry

- **superior accuracy**
- **Qualitatively different from conventional force field (Reaction, Polarizability, Many-body effect)**

However

The performance of MLFF face significant limitations in **typical academic lab hardware**

Some of the problems can be circumvented by introducing advanced sampling such as metadynamics

Acknowledgement

Professors

Prof. Bumjoon Seo (SNUST)
Prof. Changbong Hyeon (KIAS)
Prof. Hongkee Yoon (KNU; co-affil. KIAS)
Prof. Tae Jun Yoon (SNU)
Prof. YongJoo Kim (KU)
Prof. Won Bo Lee (SNU)

Students

Jae Hyun Ryu (SNU)
Minwoo Kim (SNU)
Seungtae Kim (SNU)

Key References

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and classical pairwise potential"
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