

CHEM4001

Intro #1

Paolo Raiteri - February 2023

Why computer simulations ?

- Reproduce experiments - sometimes...
- Replace experiments
- Interpret experiments
- Test theories
- Make predictions
- Guide future experiments
- It's fun
- It's easy
- It's cheap

Computational science 70M\$ (each)



@Pawsey Centre (Perth)

Architecture: Cray XE

Computing Power: circa 50 PetaFLOPS

1,600 CPU nodes, 750 GPU nodes

Memory: 548 Terabytes

Interconnect: Slingshot

Local storage: 3 Petabytes

exa	E	10^{18}
peta	P	10^{15}
tera	T	10^{12}
giga	G	10^9
mega	M	10^6
kilo	k	10^3
hecto	h	10^2
deca	da	10^1

@NCI (Canberra)

Architecture: Intel Xeon Platinum

Computing Power: 2 PetaFLOPS, from 3000 nodes

Memory: 576 TBytes (192 Gigabytes per node)

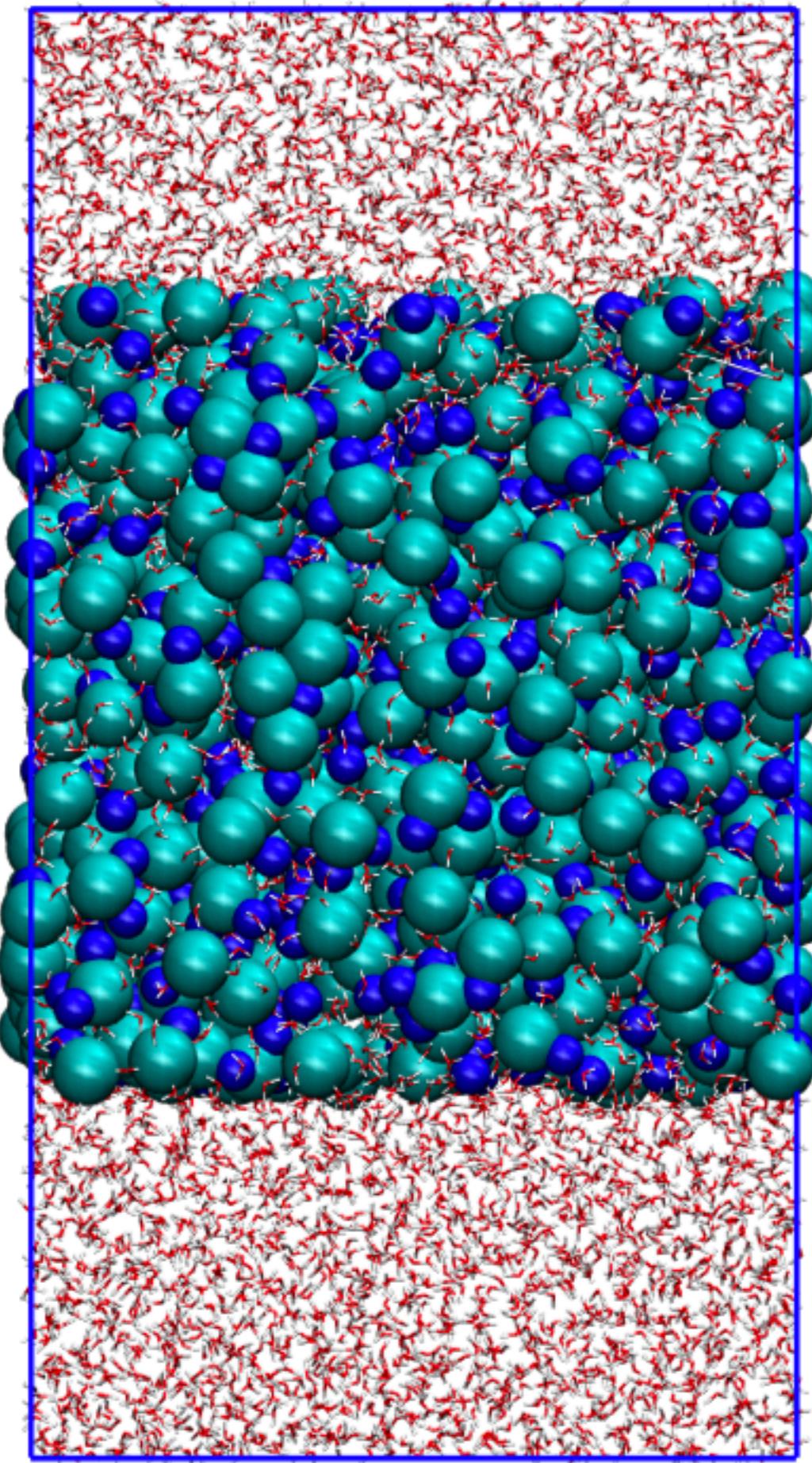
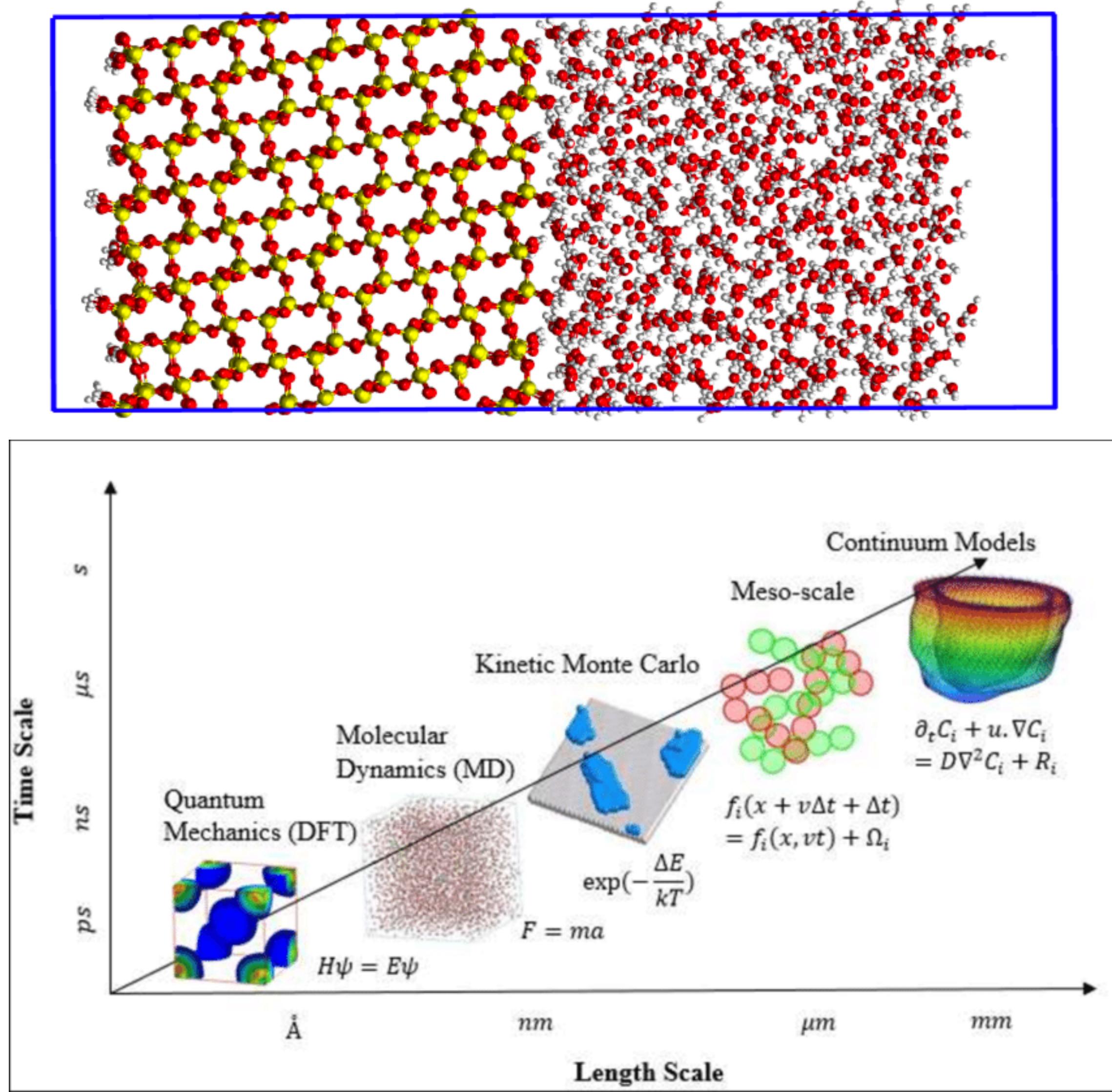
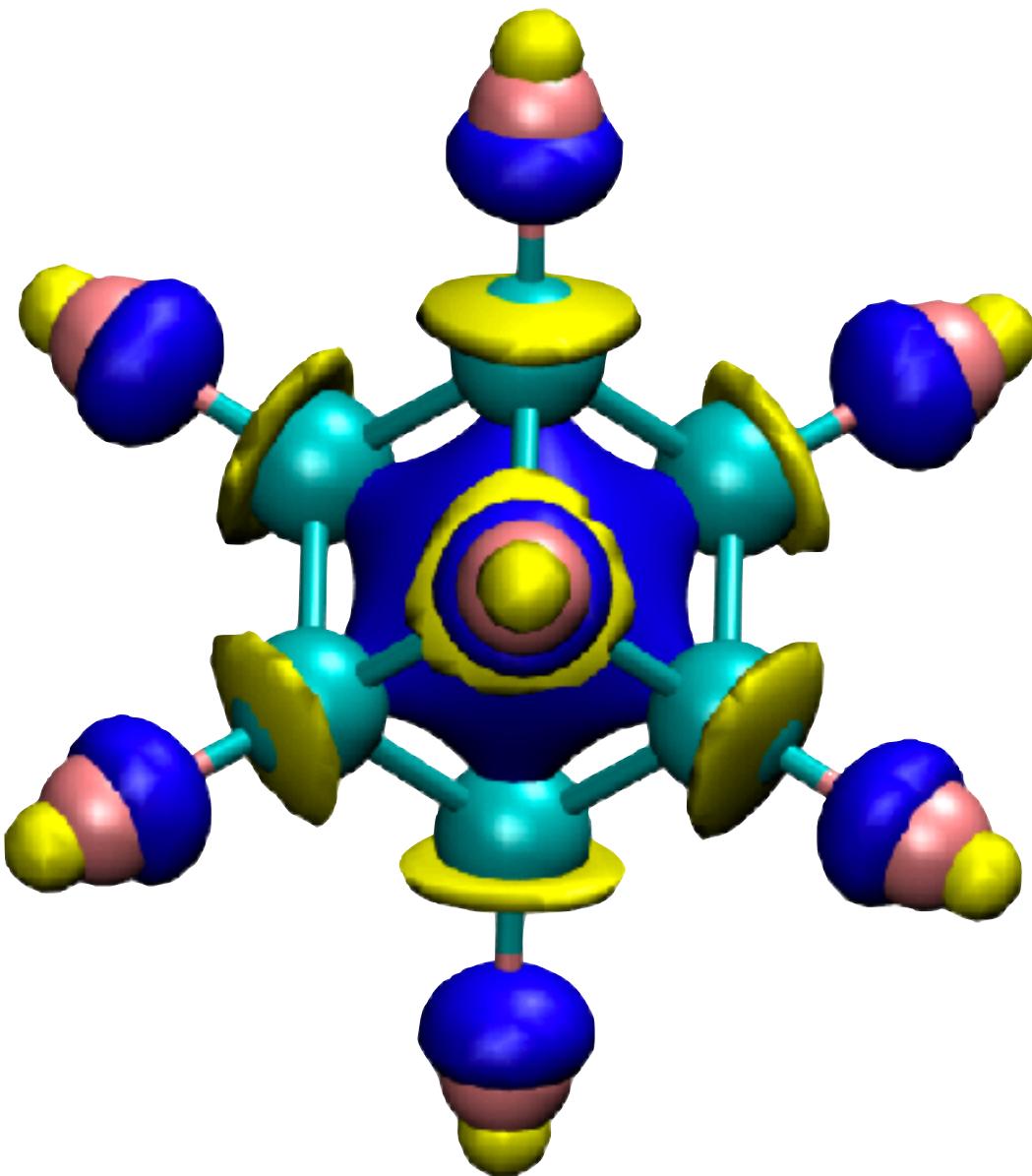
Interconnect: Infiniband FDR

Local storage: 10 Petabytes

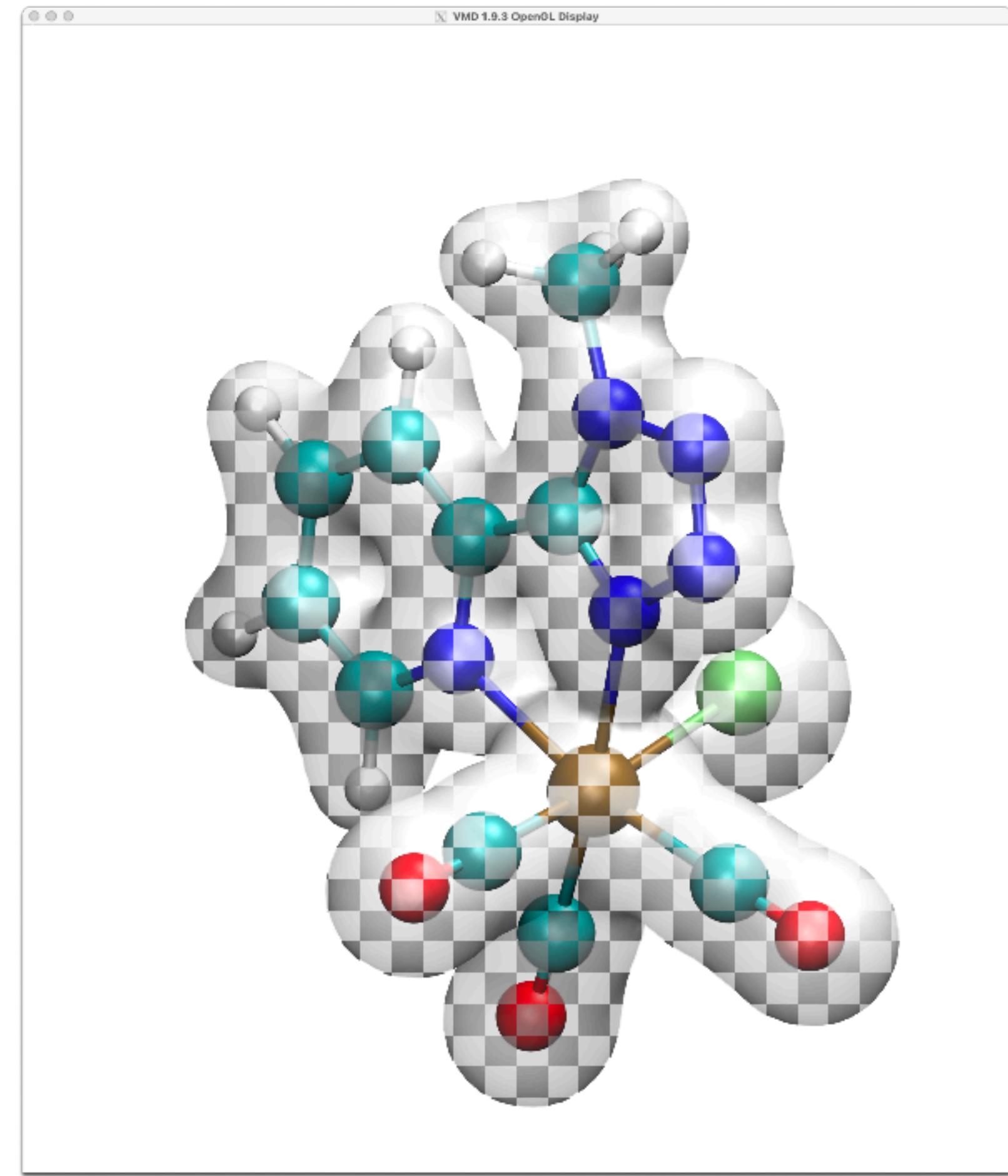
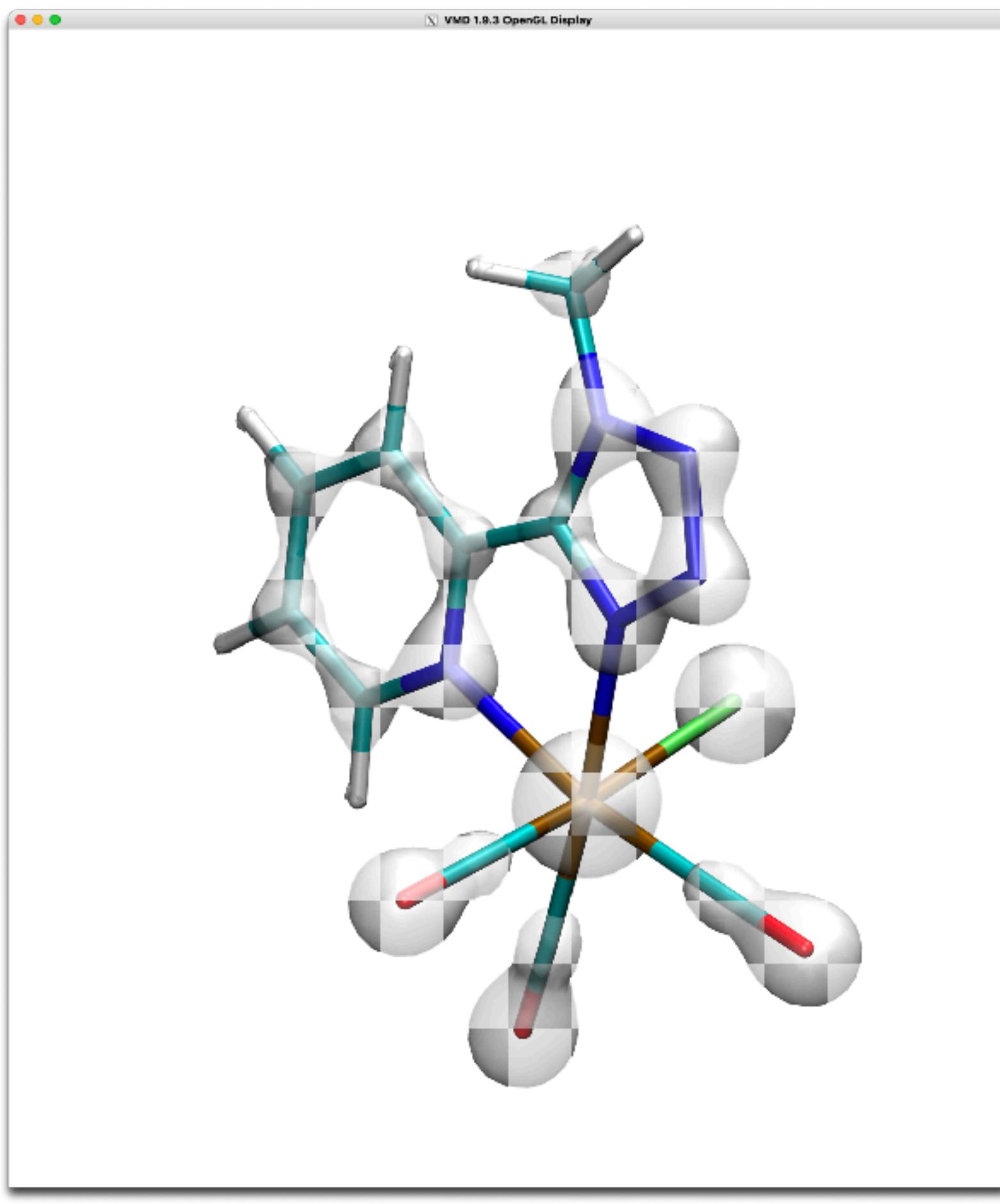
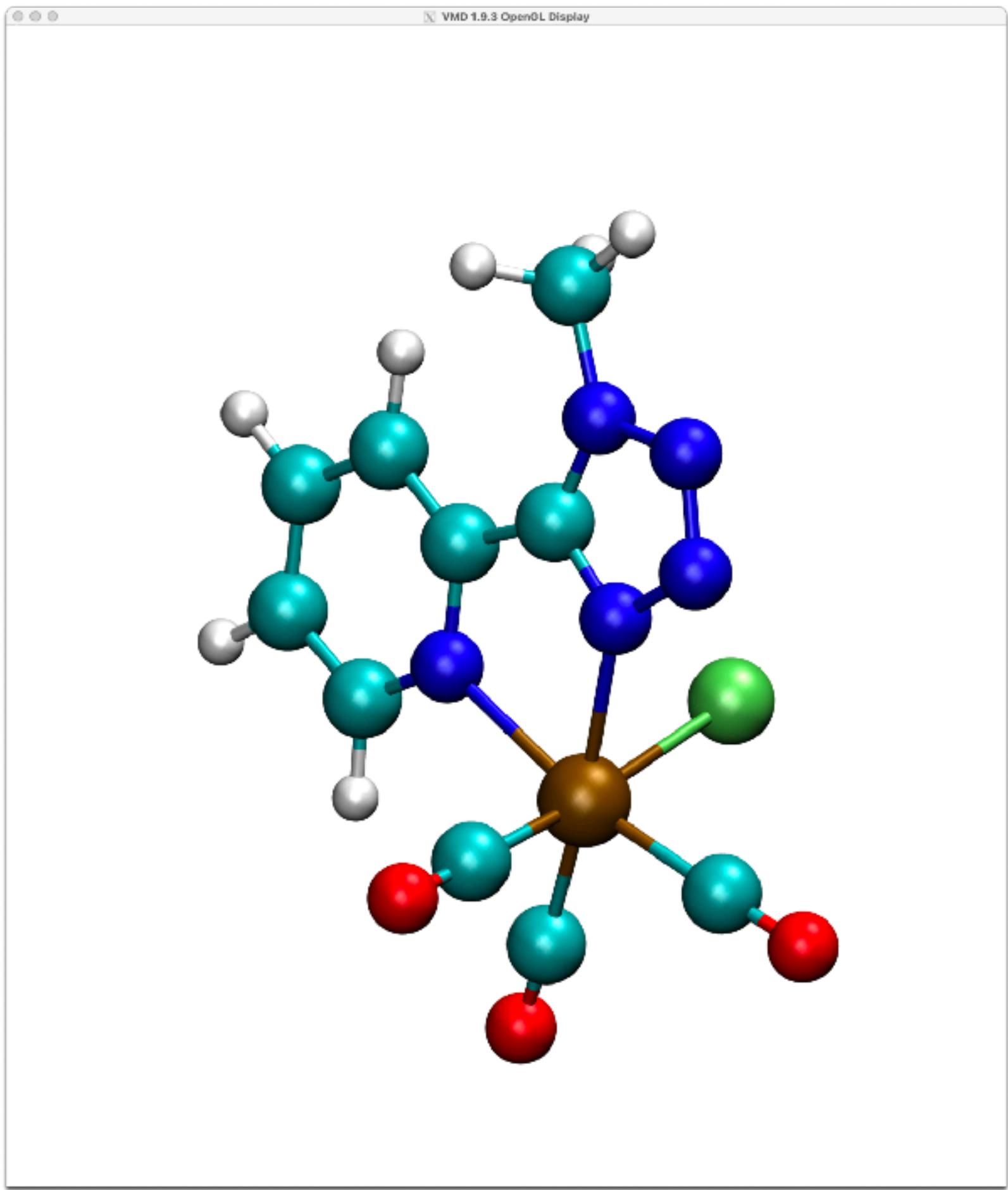


1 PetaFLOP: circa 10,000 times more computing power than a desktop computer

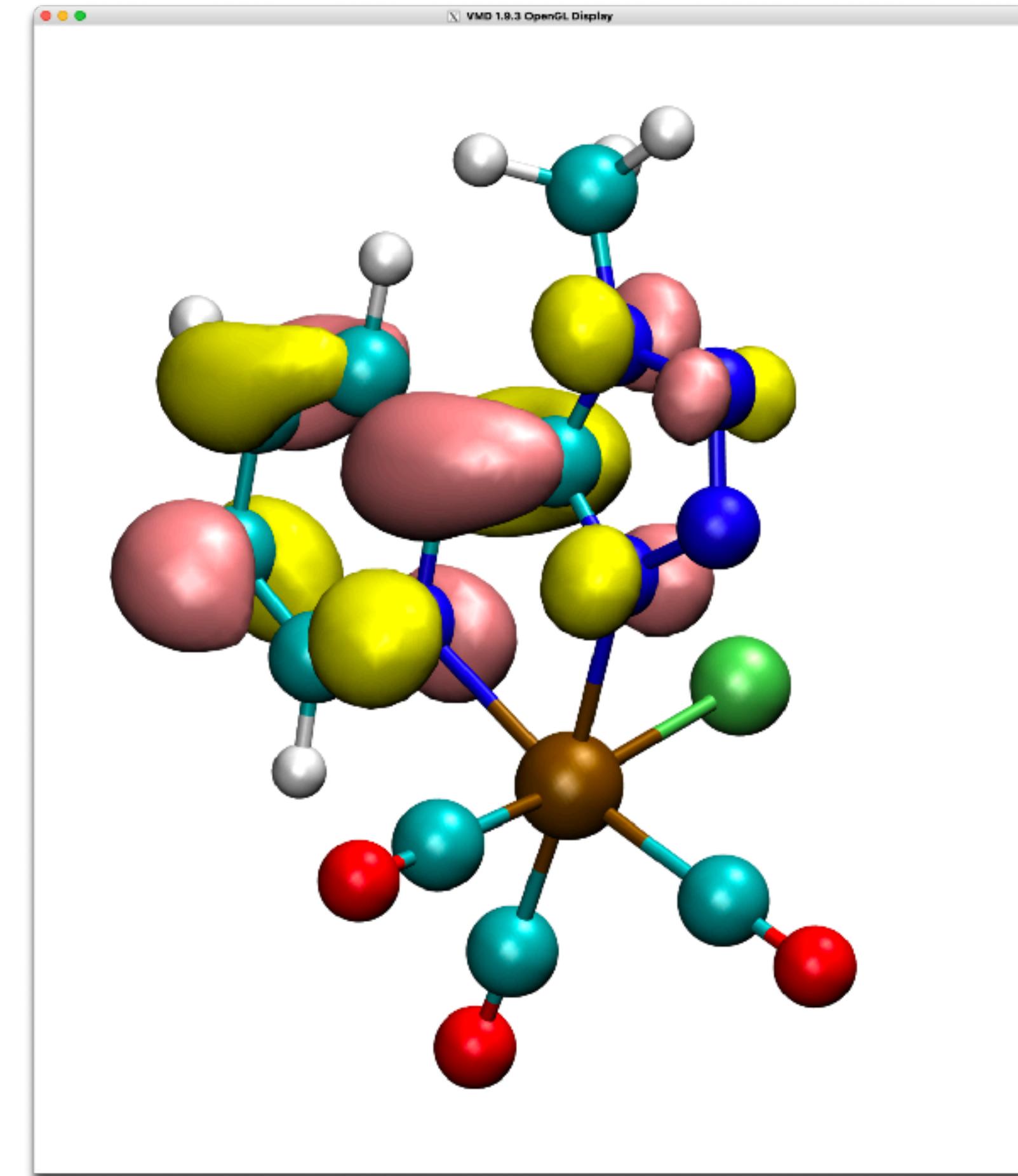
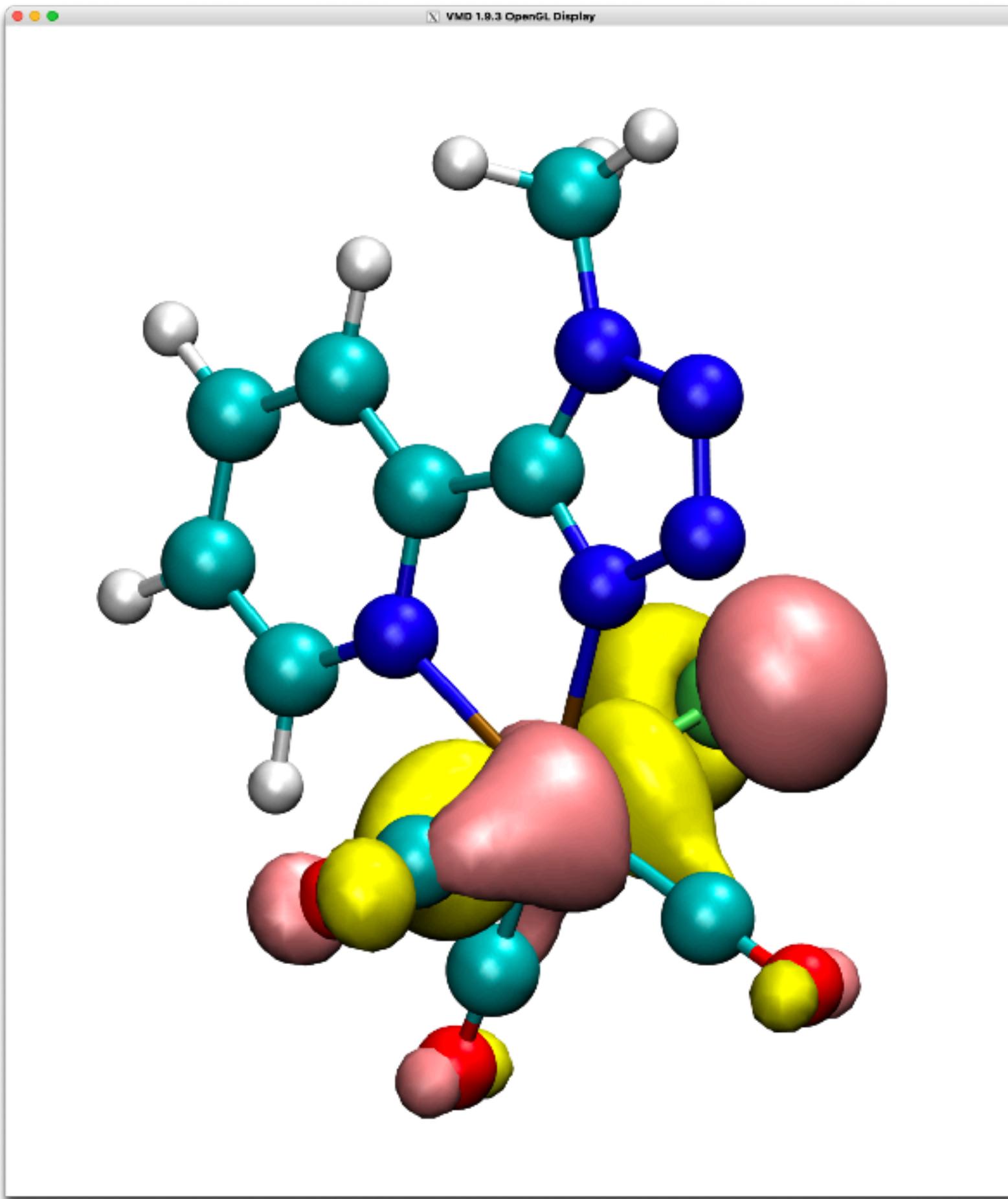
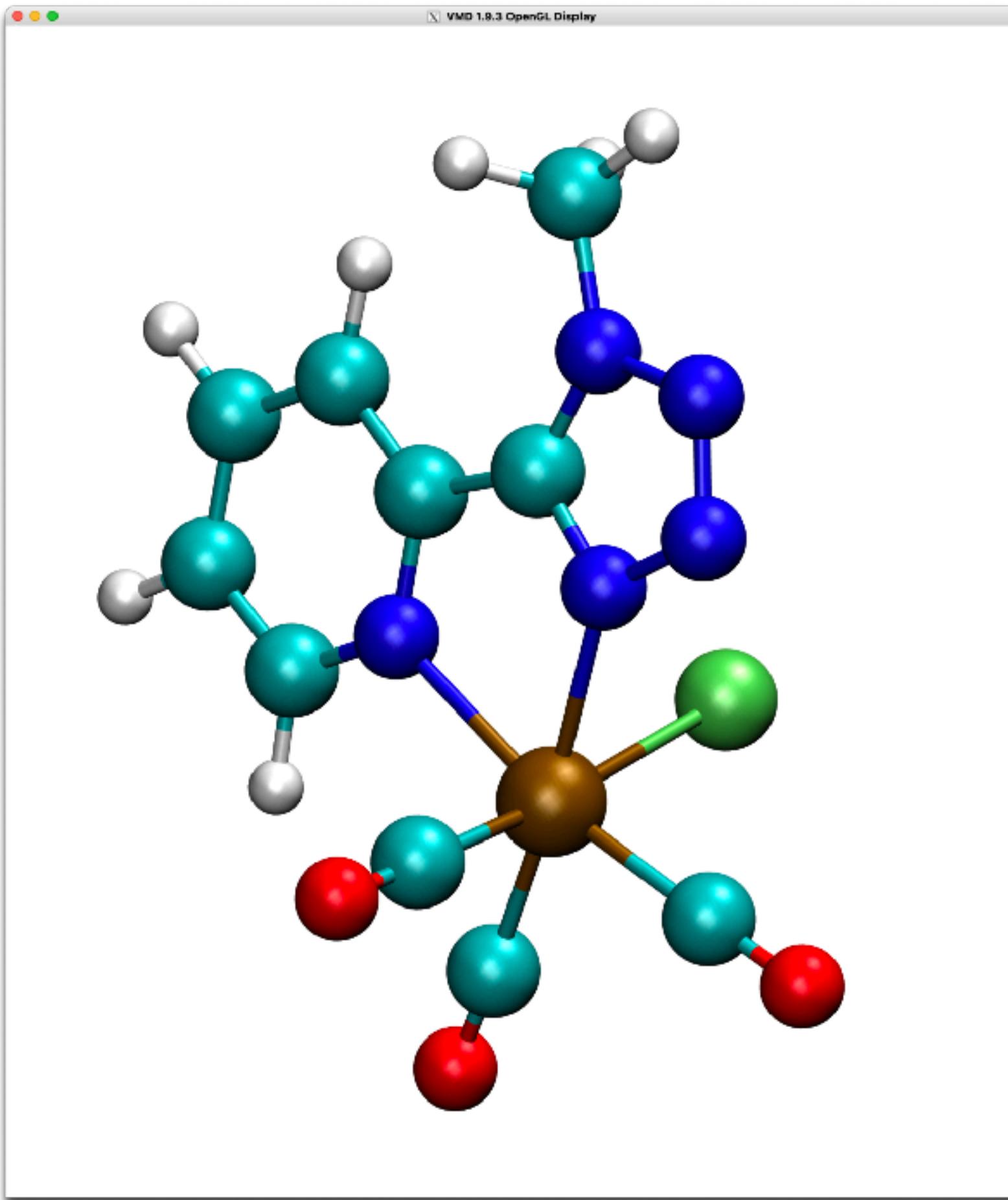
Computational methods



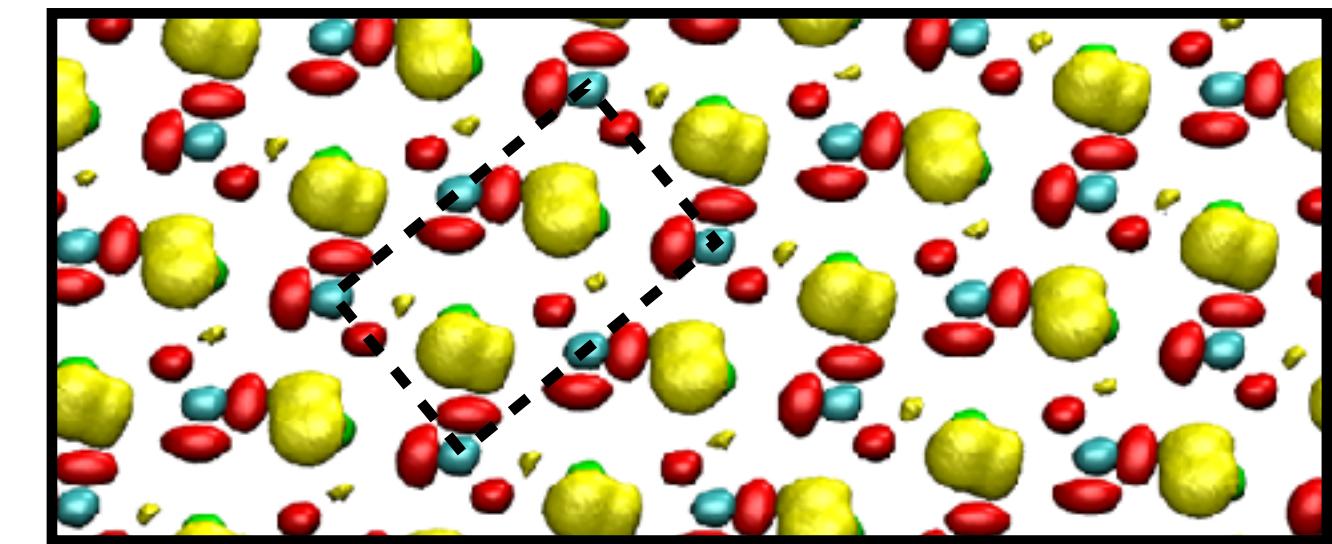
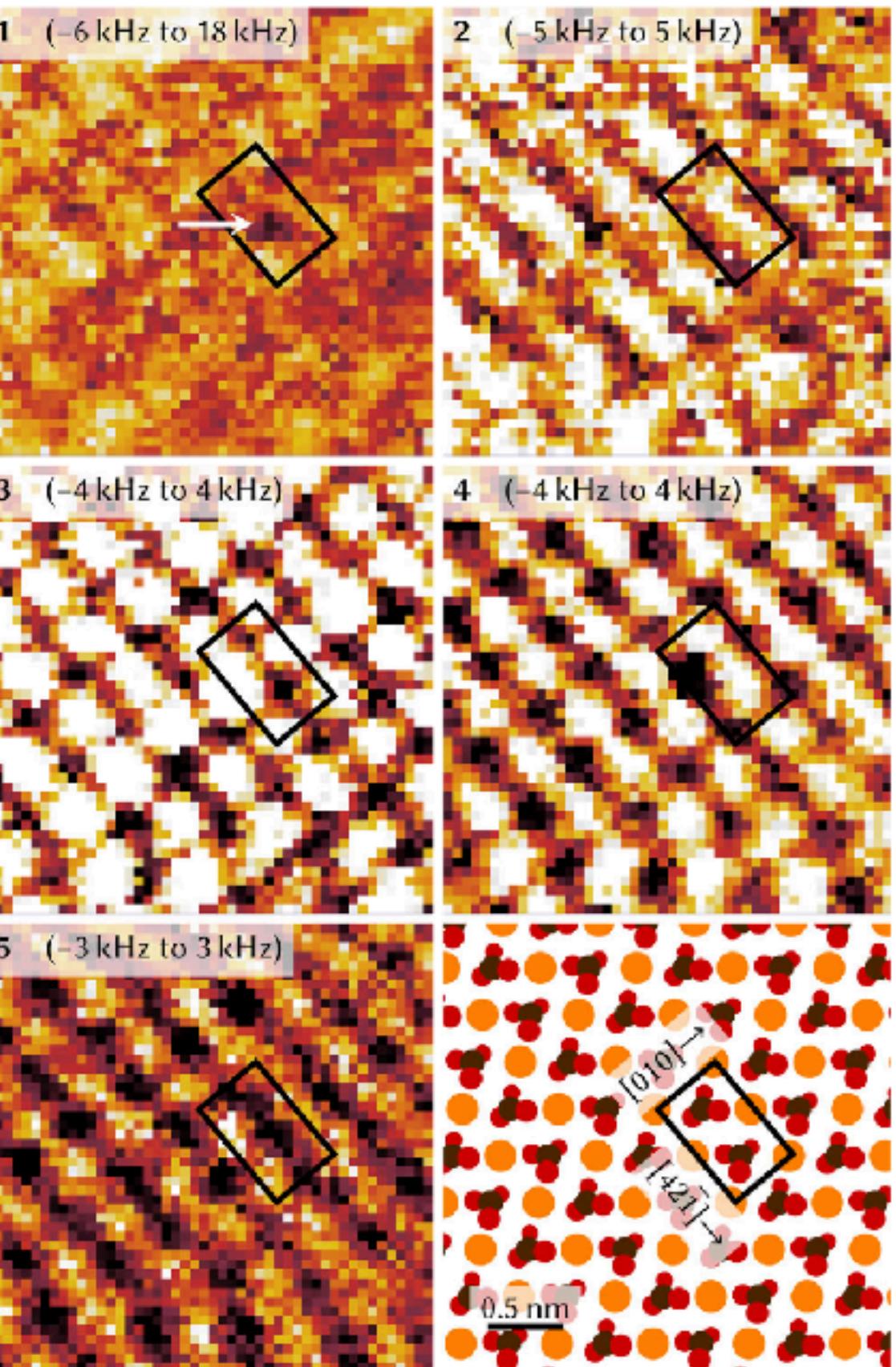
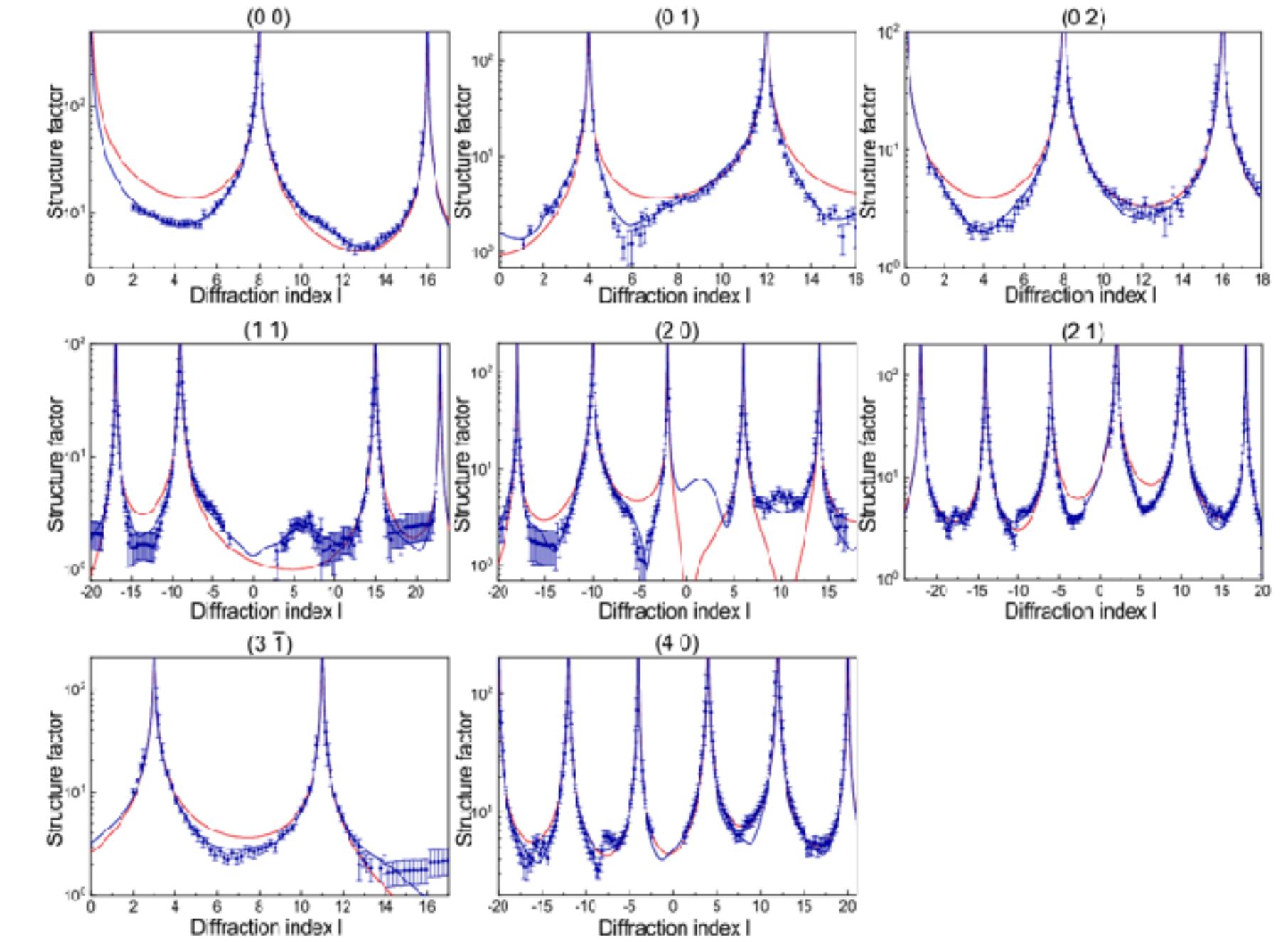
Electron density



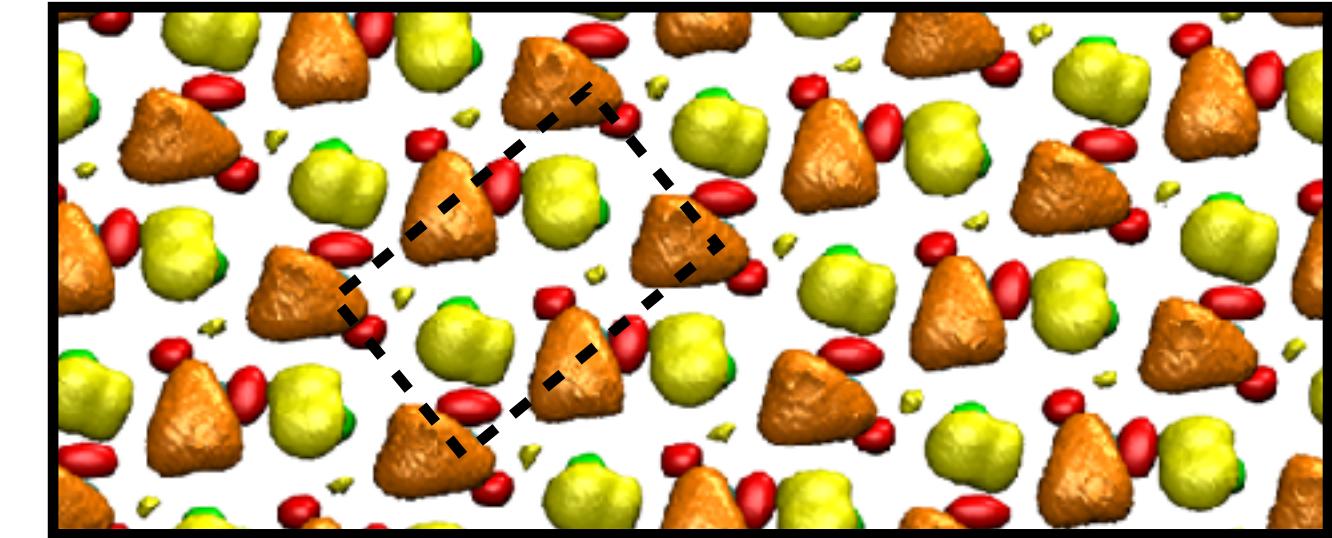
HOMO - LUMO



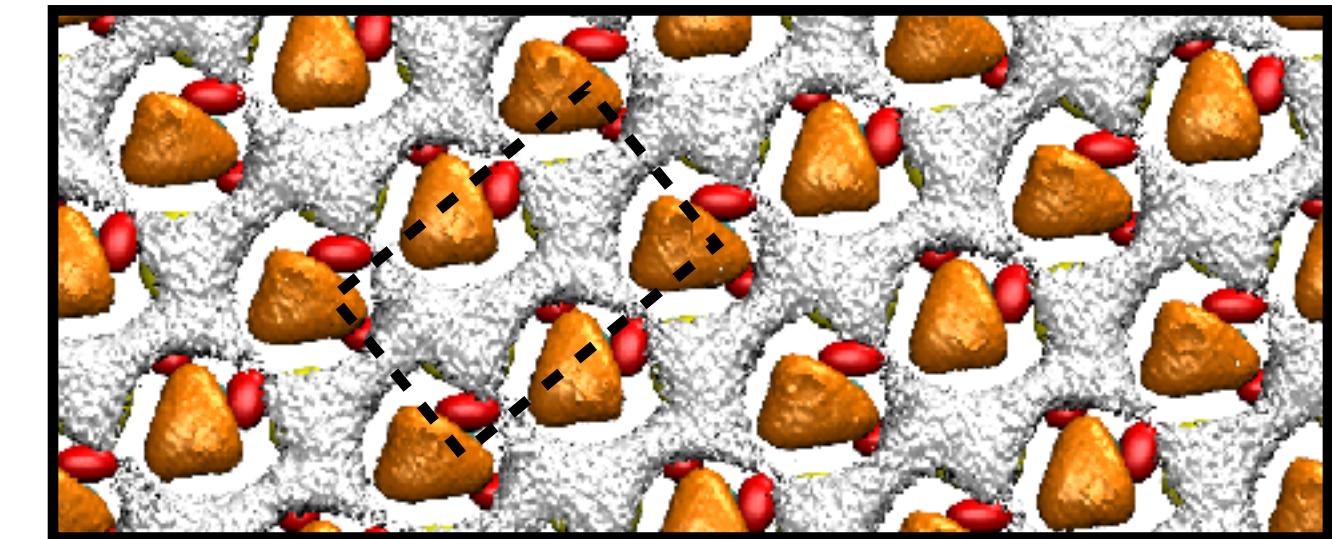
Calcite water interface



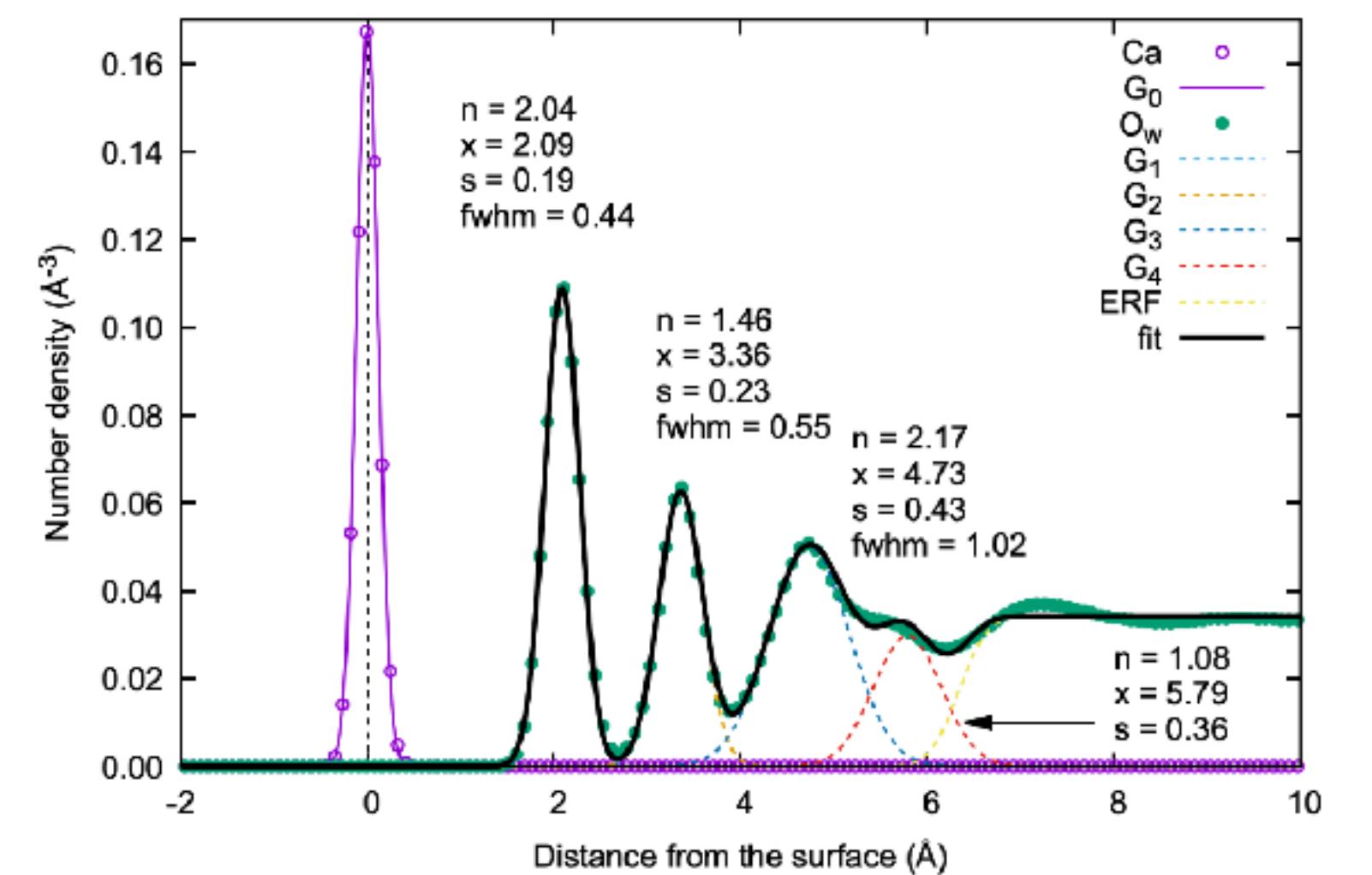
1st layer



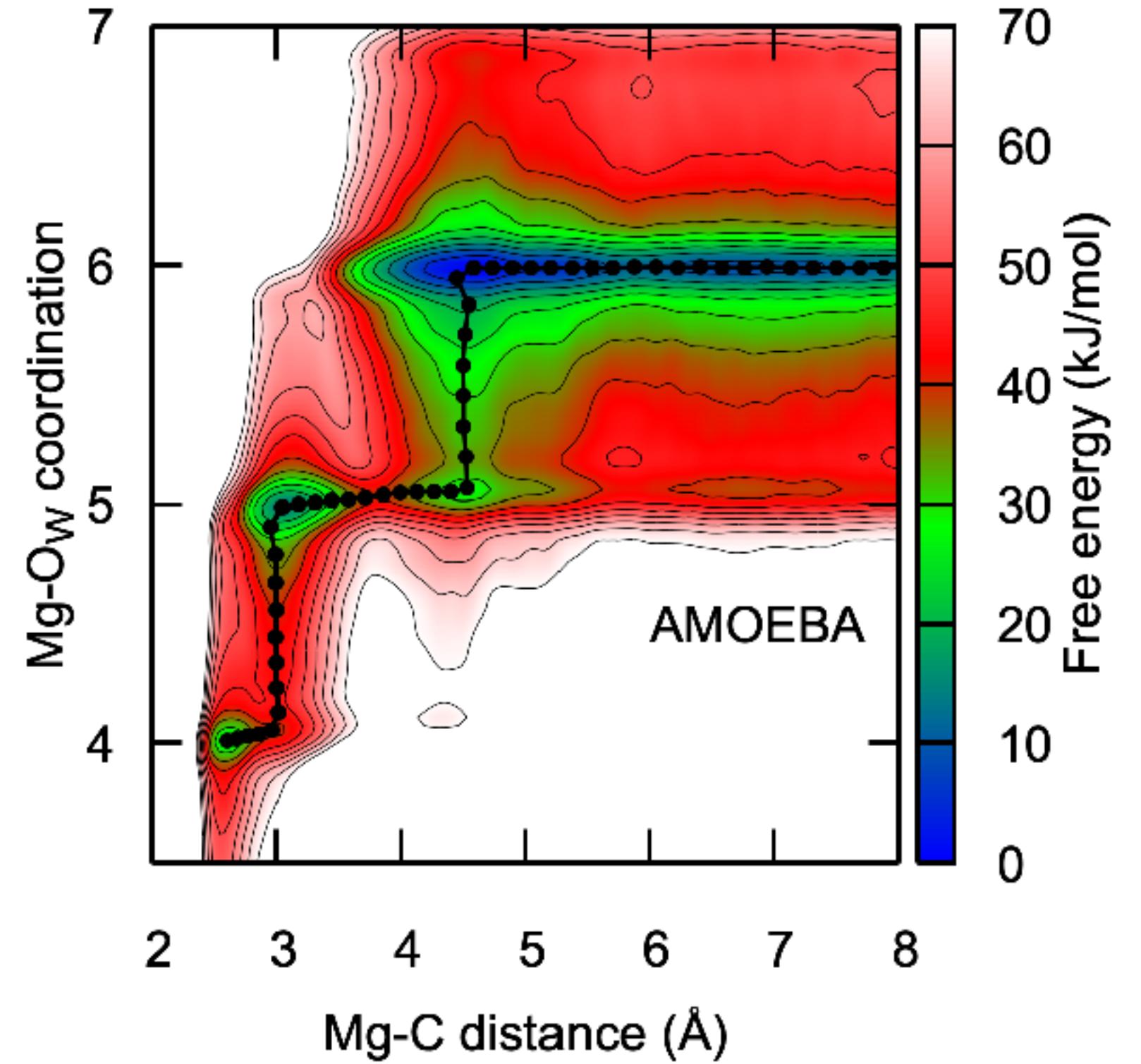
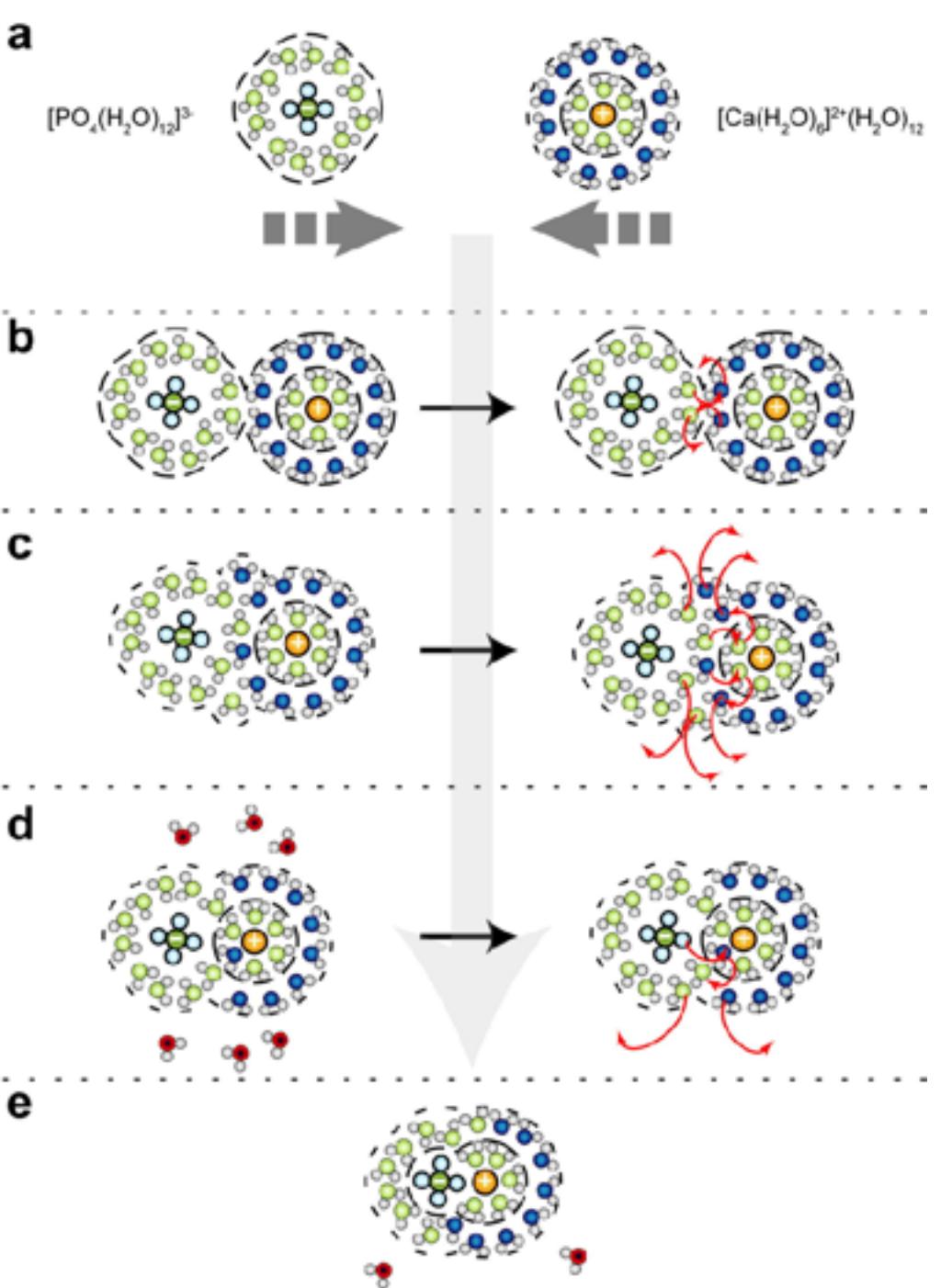
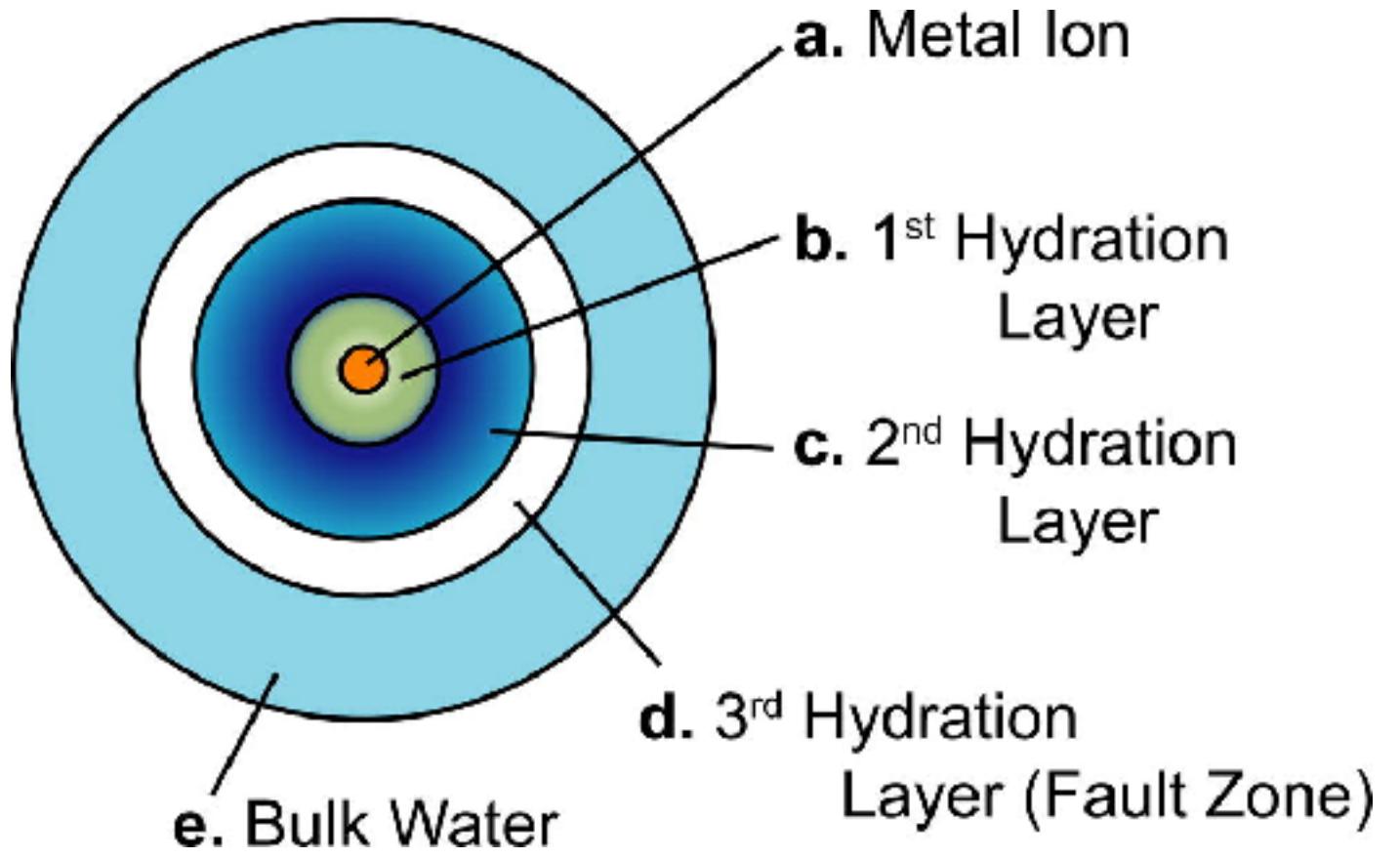
2nd layer



3rd layer



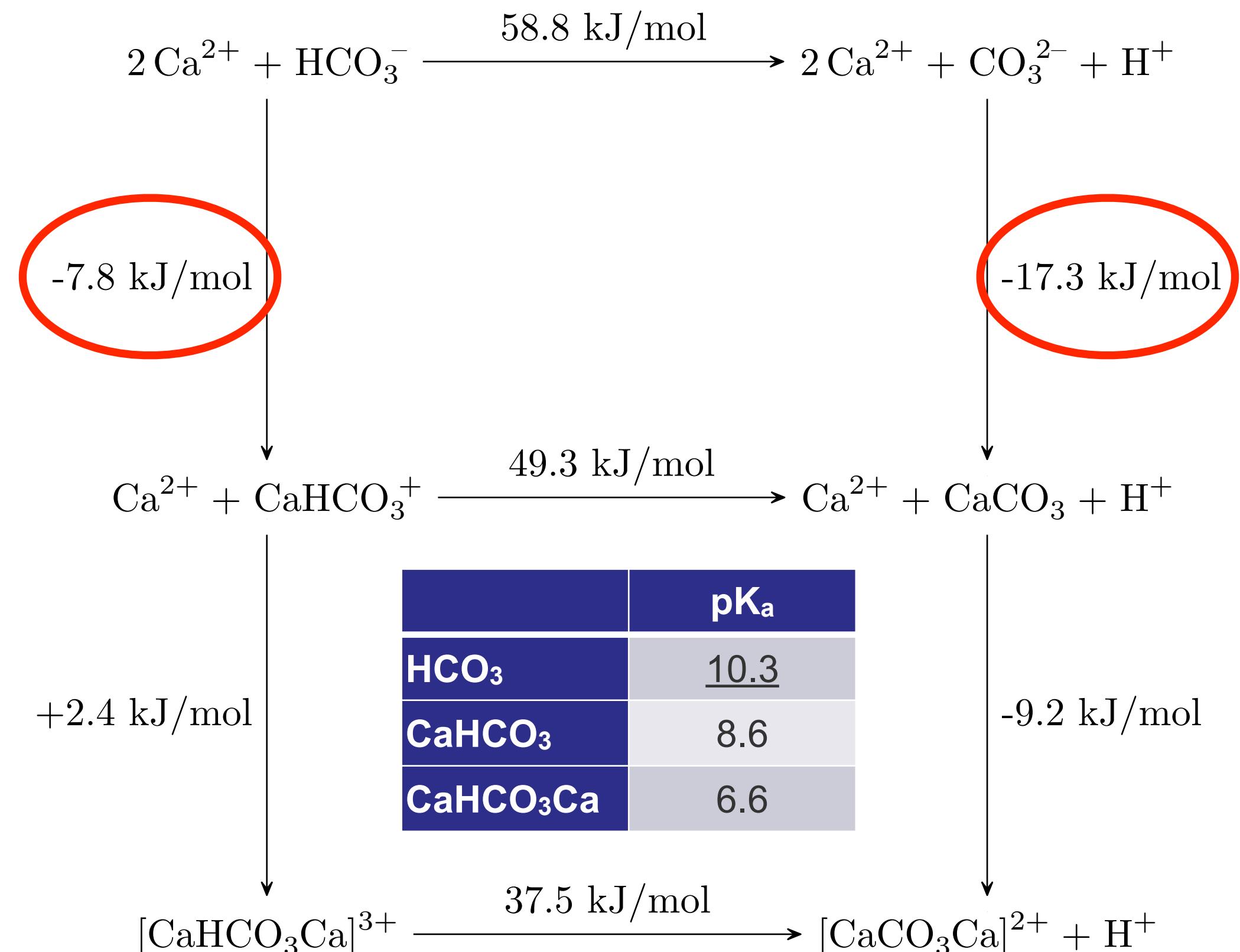
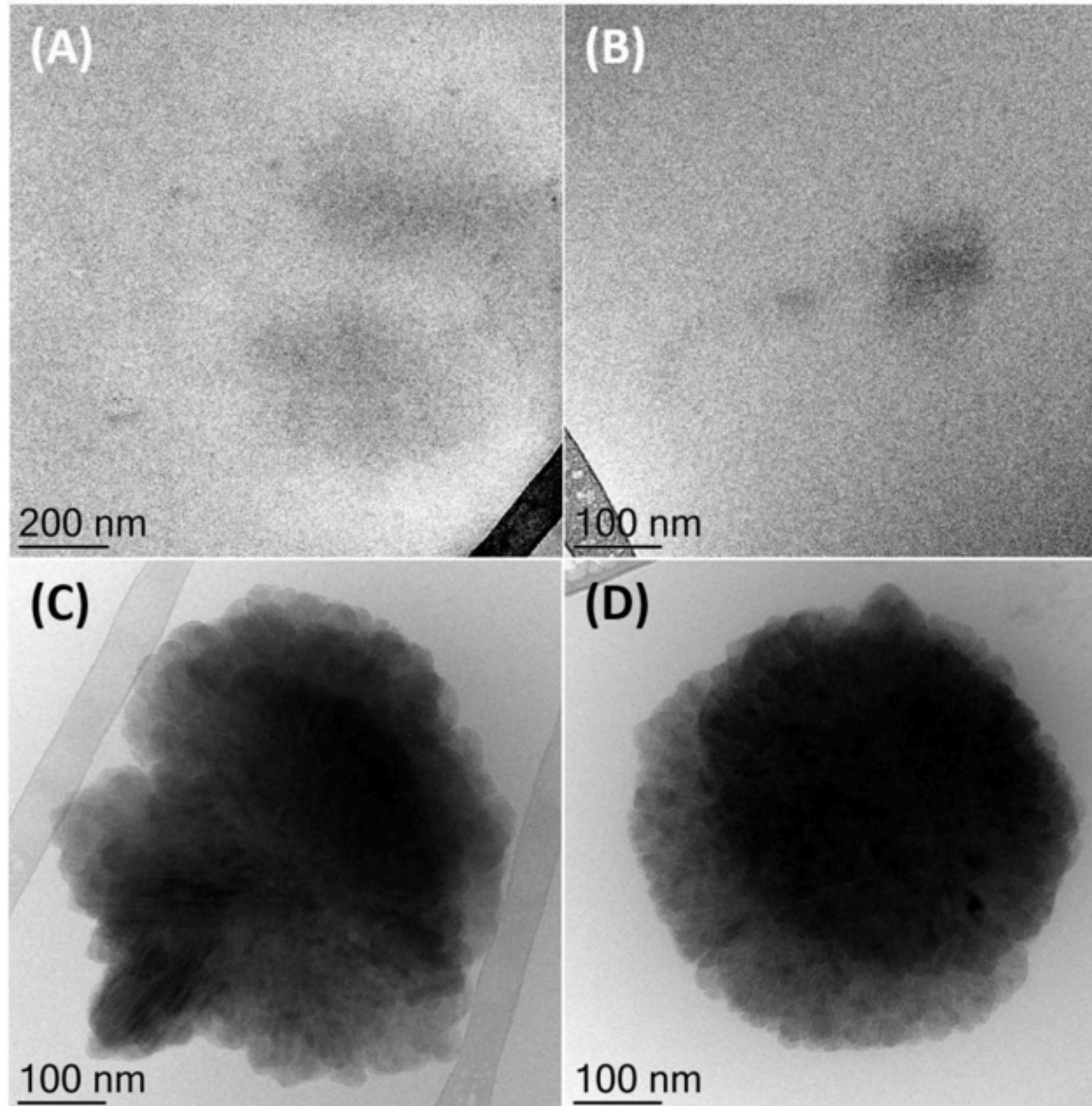
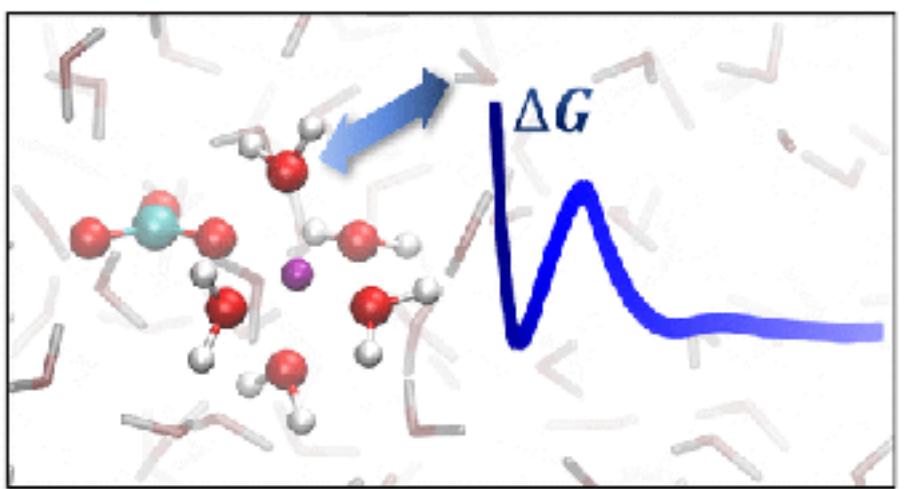
Ion-pair formation



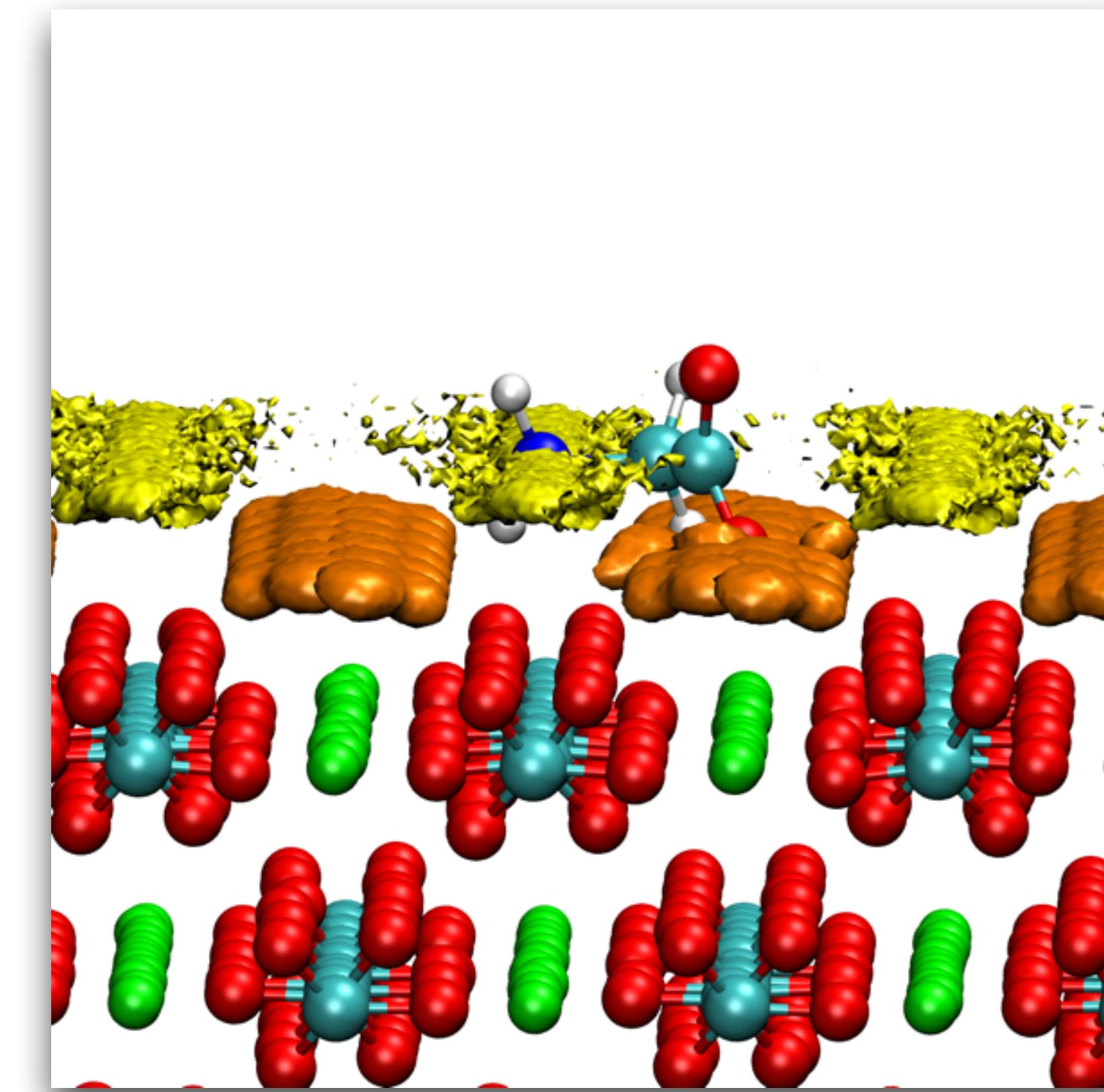
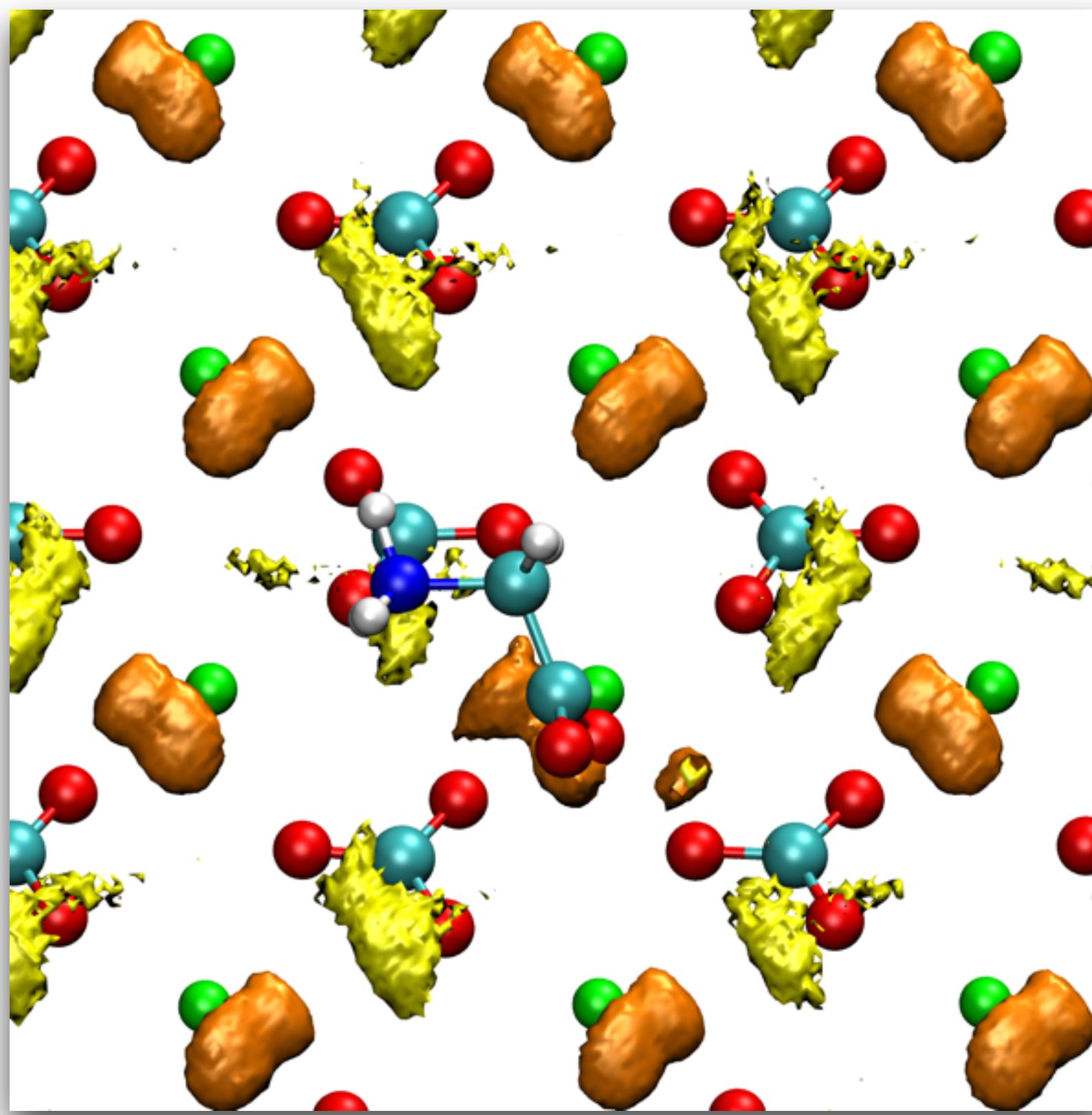
$$K_a = c_{MD} \int_{R_0}^{R_1} \exp \left[-w(r)/k_B T \right] 4\pi r^2 \, dr$$

$$w(r) = \Delta G_{meta}(r) + k_B T \ln(4\pi r^2)$$

Bicarbonate acidity



Adsorption of Glycine (AMOEBA)

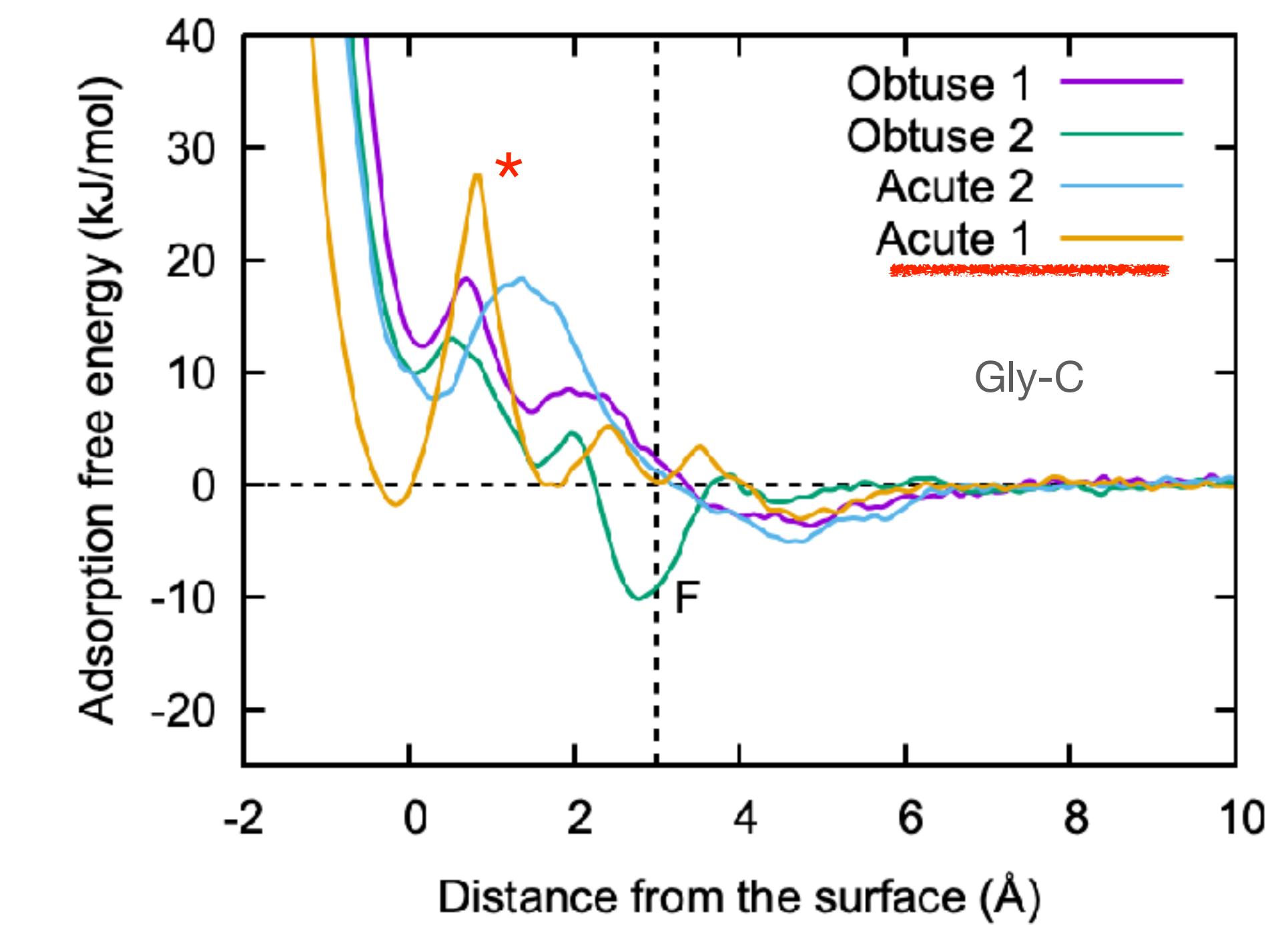
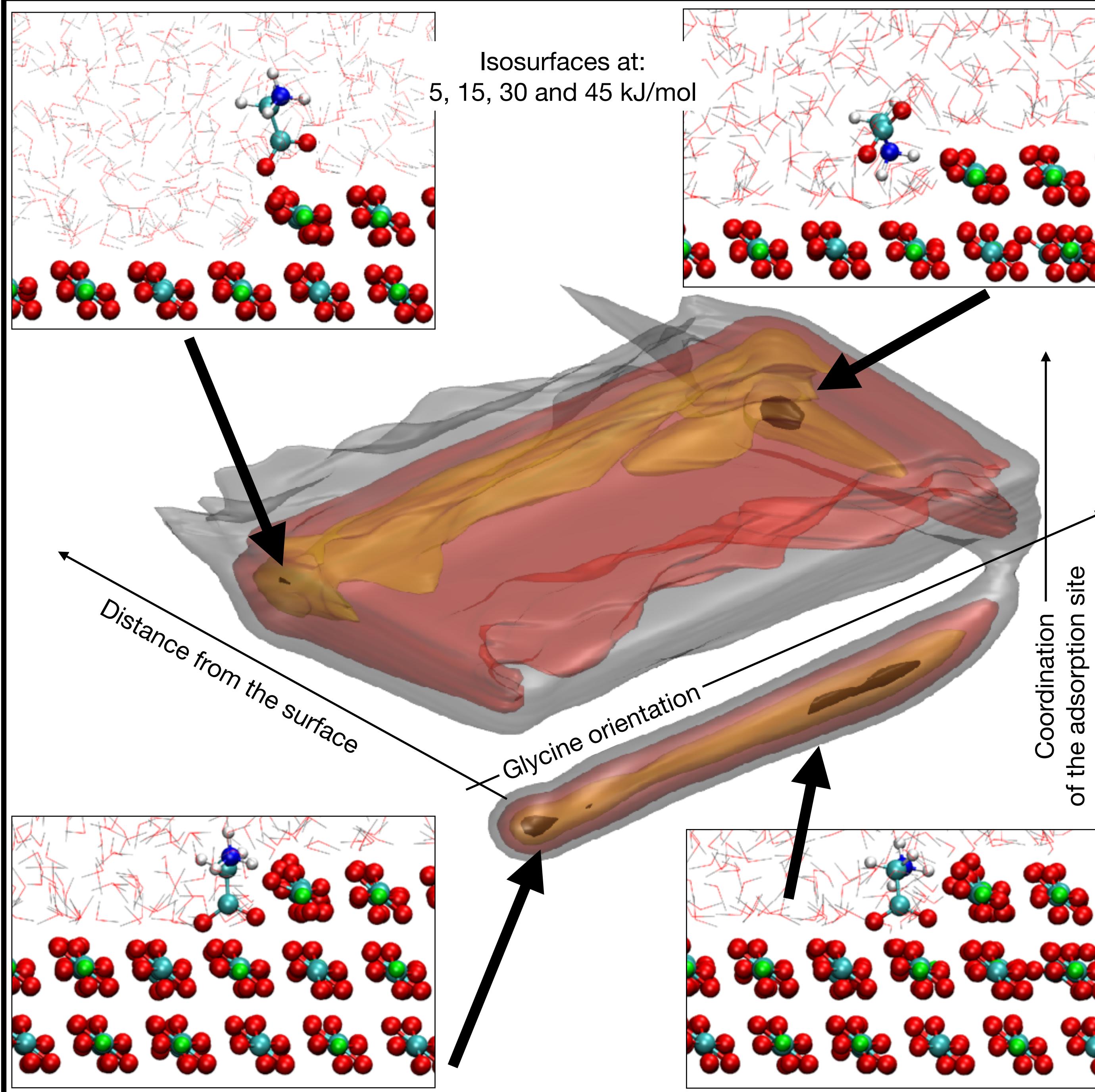


The presence of two tightly bound ordered water layers hinders the adsorption of molecules in direct contact with the surface



Curtin University

Glycine- CO_2

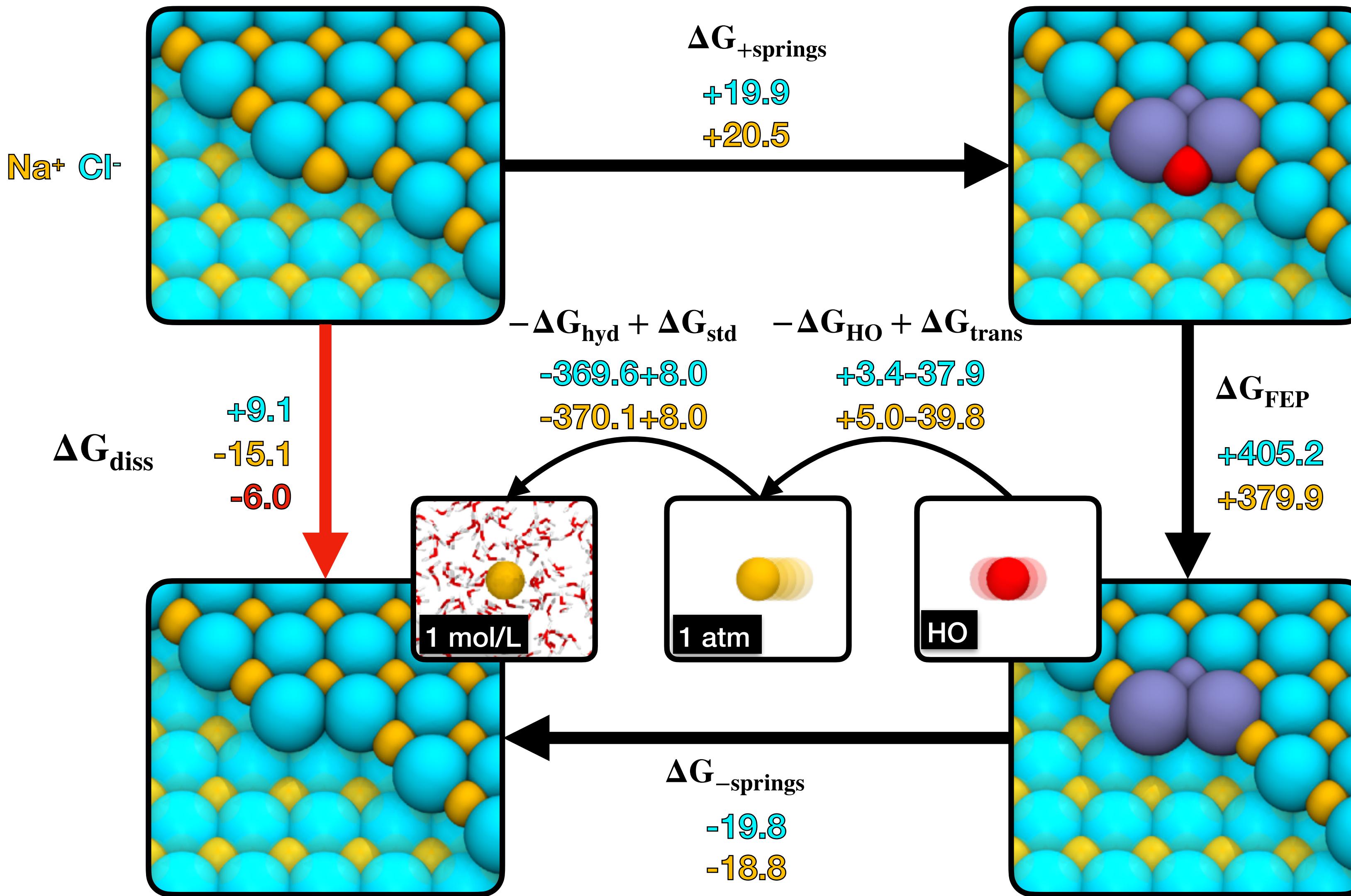


<https://doi.org/10.1021/acs.cgd.1c01414>



Curtin University

Dissolution free energy of halide



Joung, I. S. & Cheatham, T. E.
Journal of Physical Chemistry B **113**, 13279–13290 (2009).

Aragones, J. L., Sanz, E. & Vega, C.
J Chem Phys **136**, 244508 (2012).

Mester, Z. & Panagiotopoulos, A. Z.
J Chem Phys **142**, 044507 (2015).

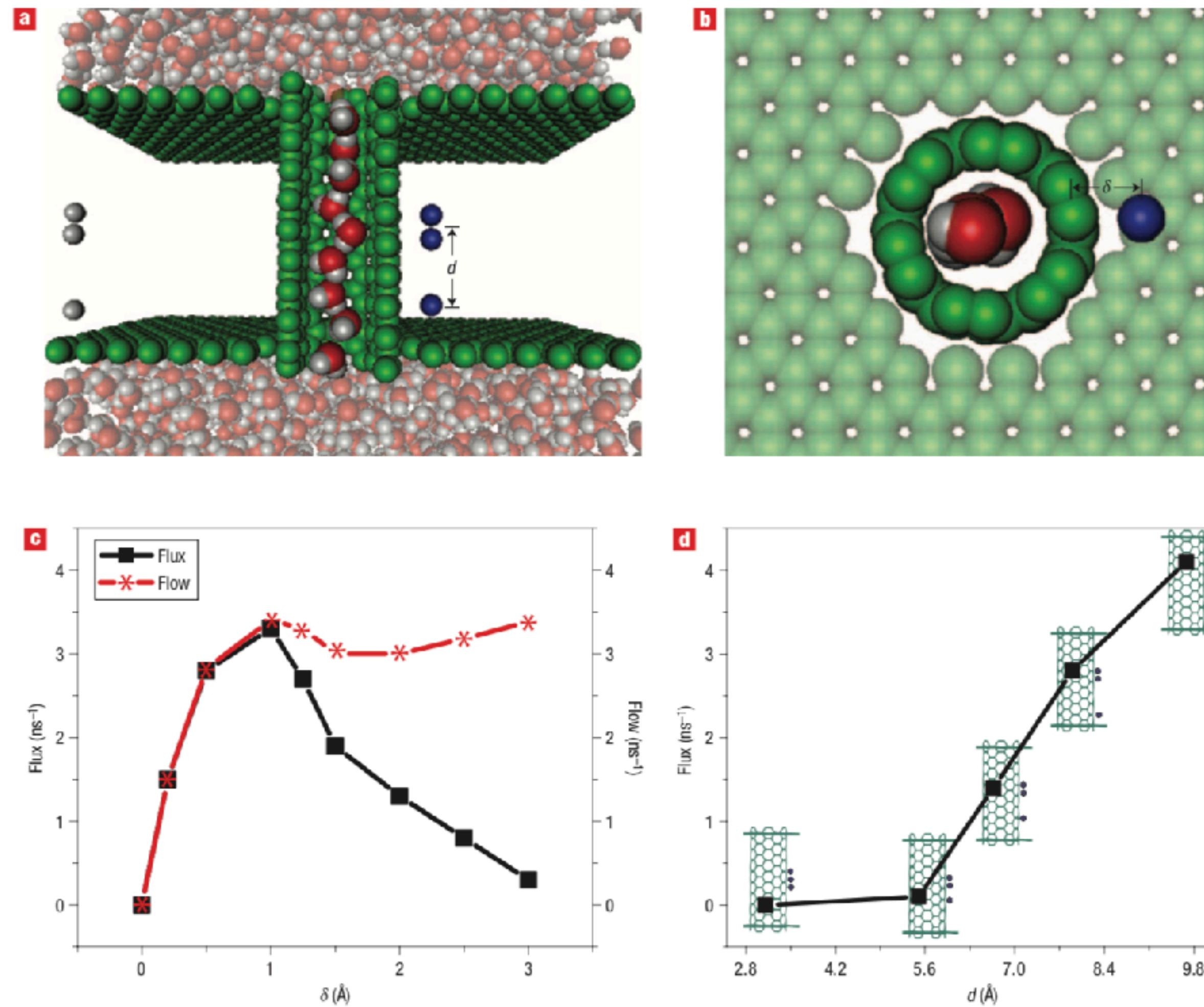
	$\Delta G_{\text{diss}}^\ominus$
Exp	-8
Aragones	-7
Mester	-7
This work	-6



How to read the methods section of a paper?

- Do you know any of the authors ?
- Gauge the results rather than the method !
- Any obvious red flags ?
- Often trends are more reliable than absolute numbers
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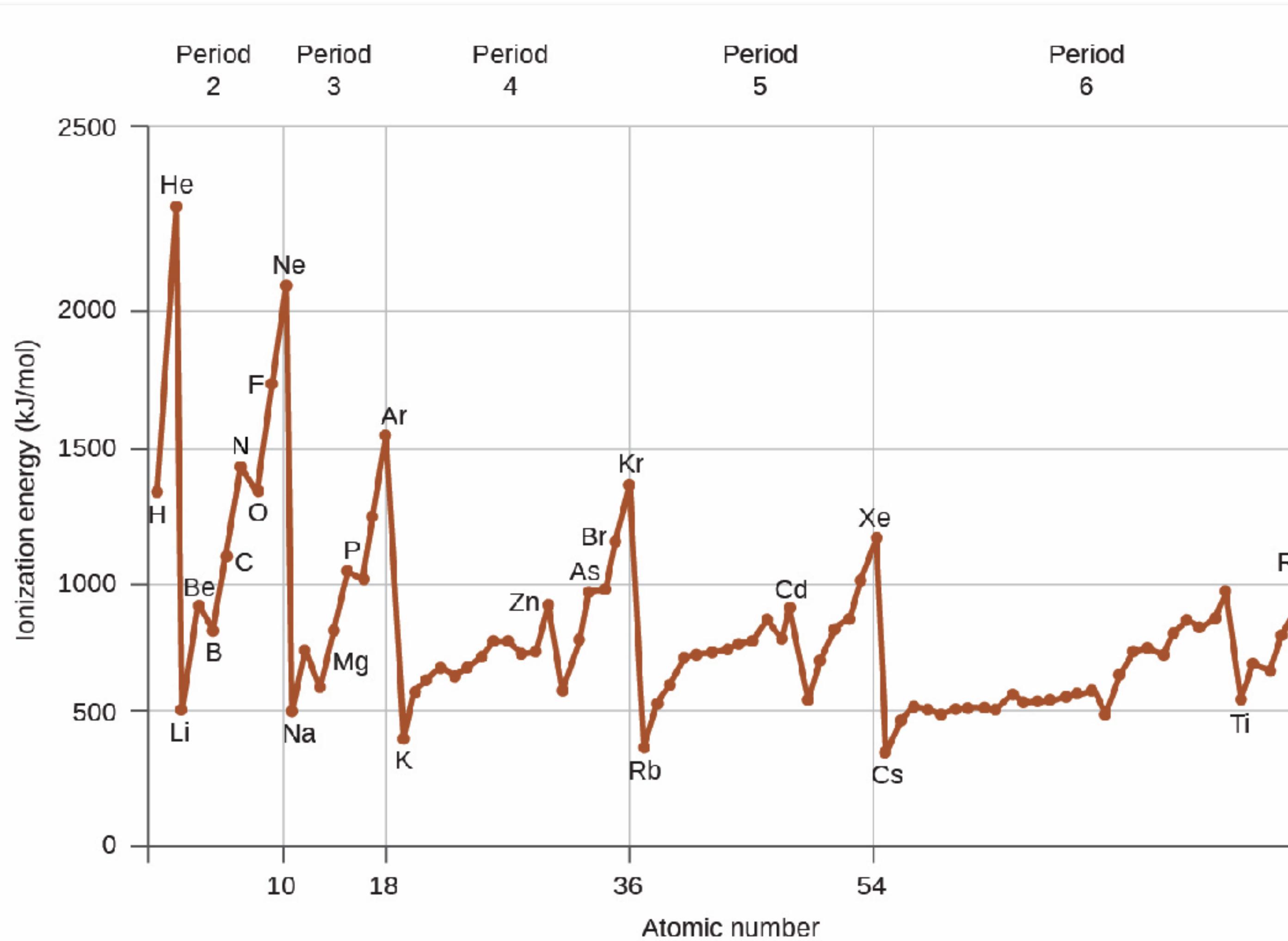
Thermodynamics cannot be violated !!



Put the numbers into context



Table 1. Summary of Binding Residues and Interaction Energies^a between SCA-1 and the Calcite (104) Surface for All Systems



E_{ele} kJ/mol	E_{vdW} kJ/mol	E_{tot} kJ/mol
-385.95	-3.45	-389.40
-377.32	5.69	-371.63
-798.95	-5.62	-804.57
-329.59	-7.53	-337.12
-582.08	-33.77	-615.85
-354.18	-27.92	-382.11
-337.78	10.78	-327.00

63 nm (the position of the end of the second water ring the last 15 ns. ^cAny atom of the residue located at or near the calcite surface for a period of time (~5 ns)

No comparison with readily available experiments [water g(r)]

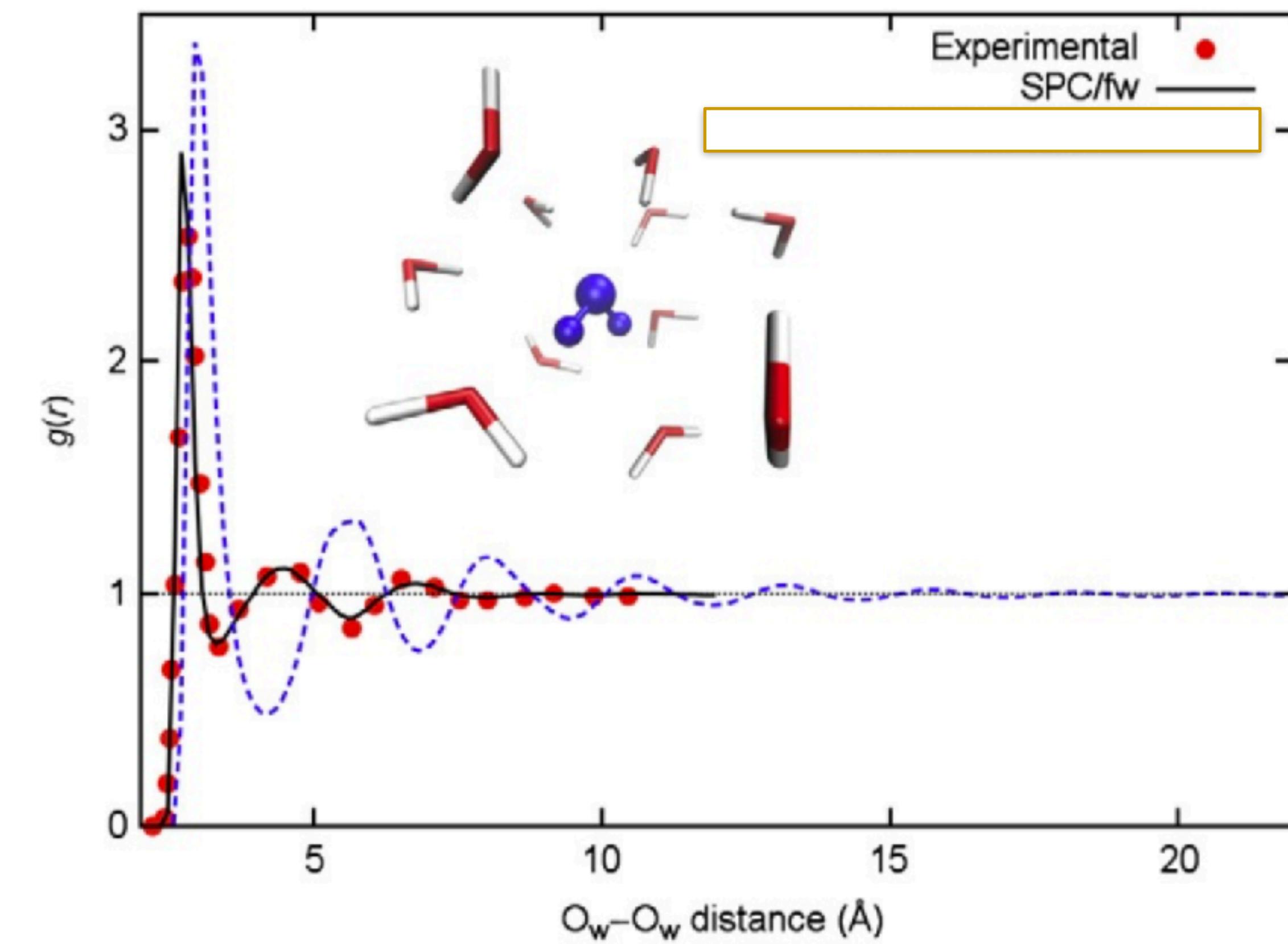
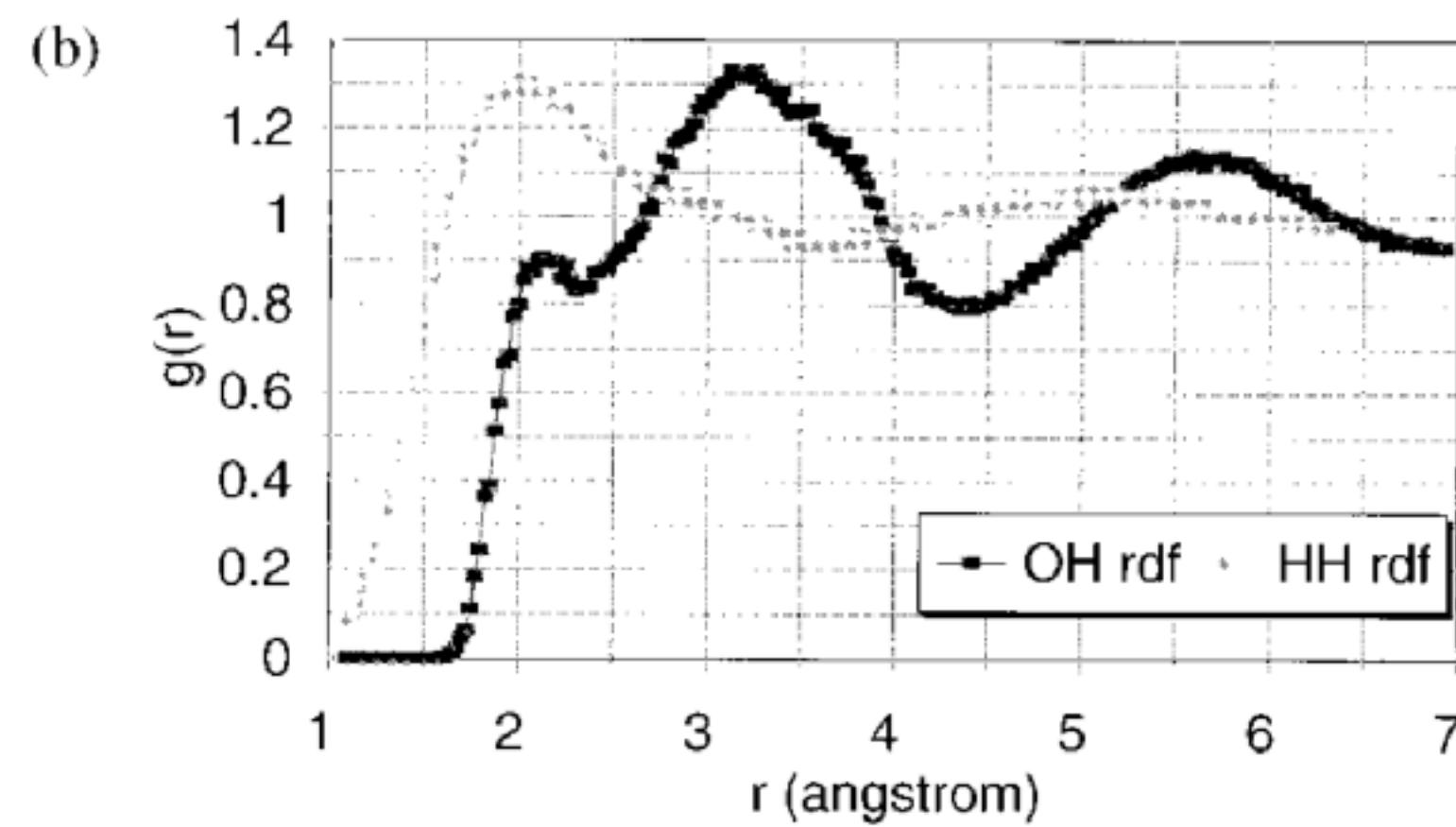
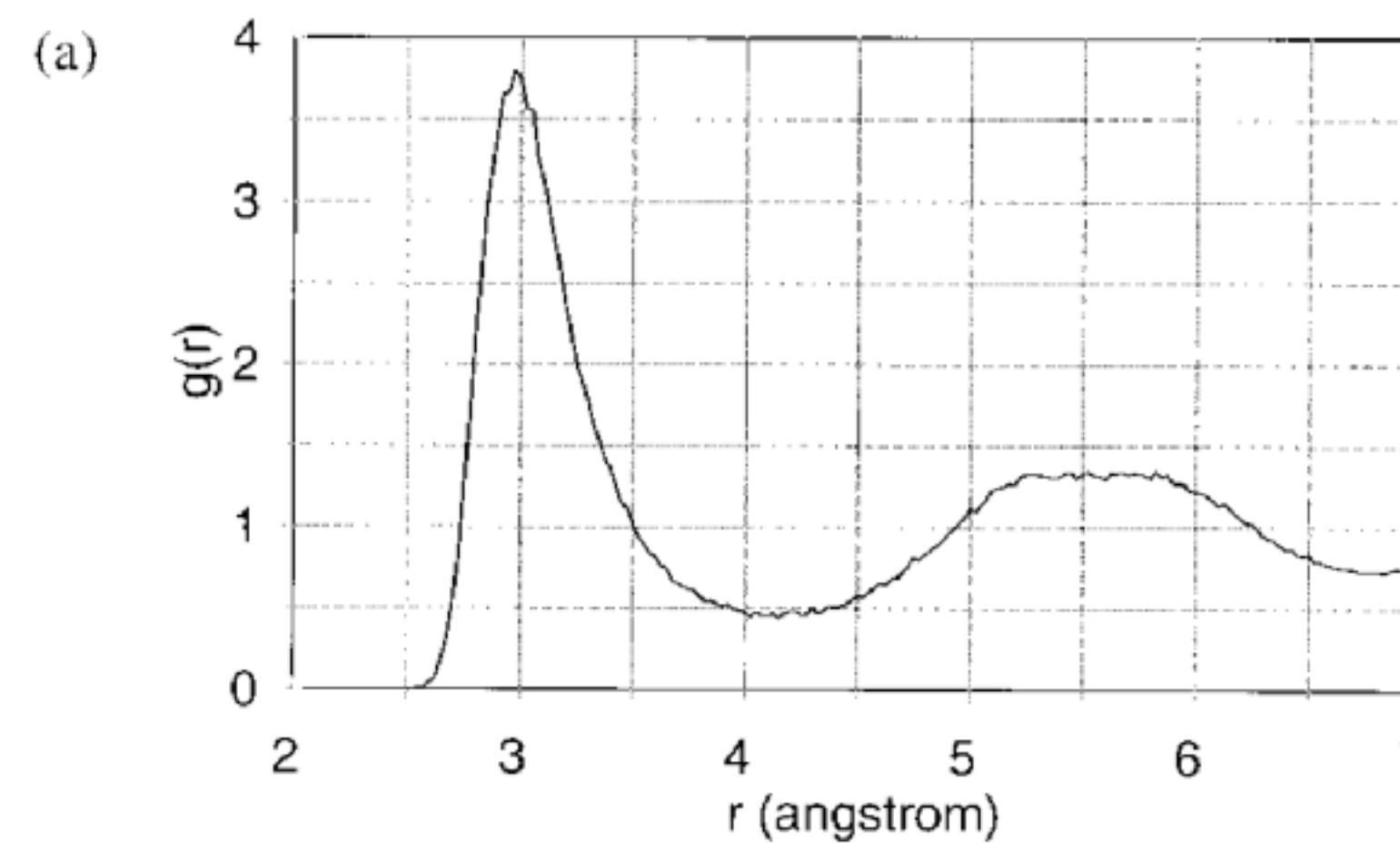


FIG. 3. (a) O-O and (b) O-H and H-H radial distribution functions, omitting intramolecular OH and HH interactions.

Simplistic model

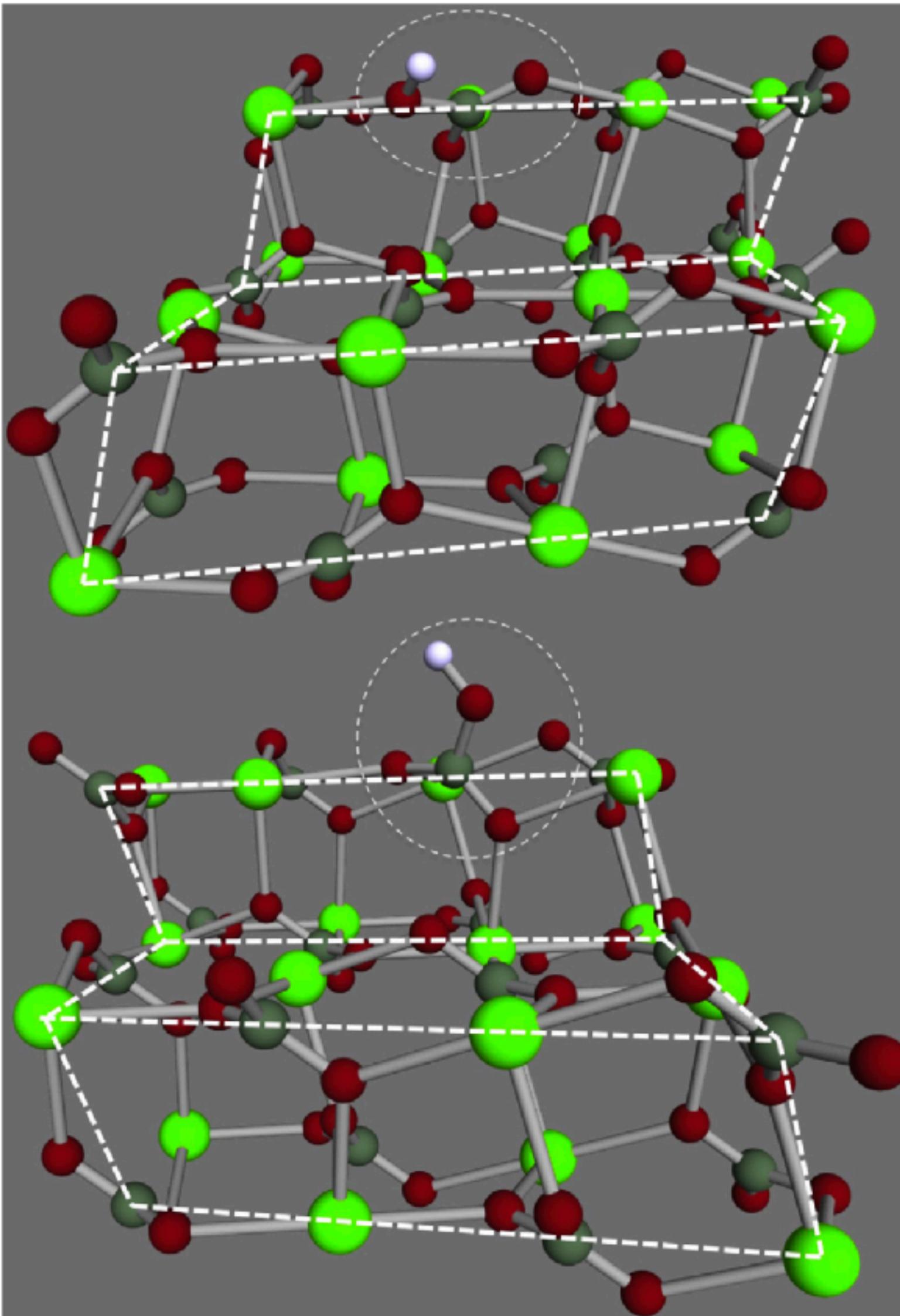


Table 1

Predicted pK_a for the bicarbonate deprotonation reaction to carbonate, $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$, at various surface sites of calcite. For the step and kink sites, there are two different orientations of the carbonate group and both pK_a values are presented. The values are calculated for the case where there is no surface potential.

Site	pK_a
Free in solution	10.35
Adsorbed on {10.4} (outer shell)	7.4
Adsorbed on {10.4} (inner shell)	7.5
{10.4} terrace	-6.0
Acute step	-5.6, -3.7
Obtuse step	-5.0, -4.4
Kink site acute step, long $\text{CO}_3^- \text{CO}_3$	-2.6, -1.7
Kink site acute step, short $\text{CO}_3^- \text{CO}_3$	-4.0, 2.4
Kink site obtuse step, long $\text{CO}_3^- \text{CO}_3$	-2.4, -1.8
Kink site obtuse step, short $\text{CO}_3^- \text{CO}_3$	-0.1, 0.0

Table 2

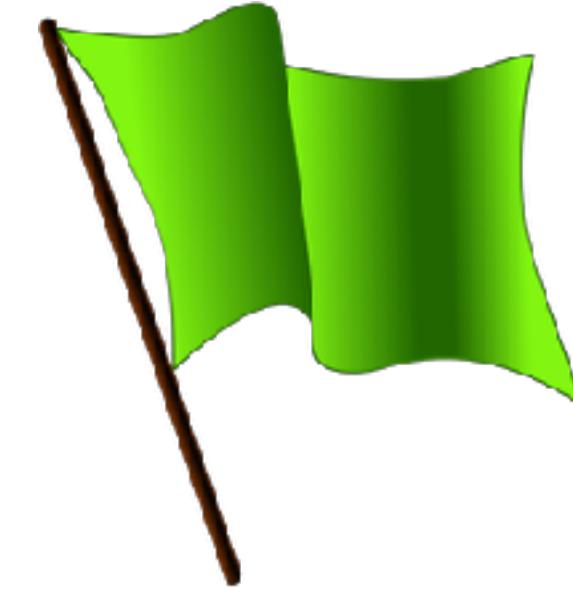
Adsorption energy of carbonate from aqueous solution onto calcite {10.4}, modelled by an 80 atom calcite cluster in inner and outer sphere geometry.

Adsorption geometry	ΔG_{ads} (kJ/mol)
CO_3^{2-} on calcite {10.4}, outer shell	-50
HCO_3^- on calcite {10.4}, outer shell	-18
CO_3^{2-} on calcite {10.4}, inner shell	4
HCO_3^- on calcite {10.4}, inner shell	34



Trends probably
reasonable

Computational chemistry works!



Potential high- T_c superconducting lanthanum and yttrium hydrides at high pressure

Hanyu Liu^a, Ivan I. Naumov^a, Roald Hoffmann^b, N. W. Ashcroft^c, and Russell J. Hemley^{d,e,1}

^aGeophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015; ^bDepartment of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853; ^cLaboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853; ^dDepartment of Civil and Environmental Engineering, The George Washington University, Washington, DC 20052; and ^eSchool of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853

Contributed by Russell J. Hemley, May 5, 2017 (sent for review March 20, 2017; reviewed by Panchapakesan Ganesh, Jeffrey C. Grossman, and Dimitrios Papaconstantopoulos)

PHYSICAL REVIEW LETTERS 122, 027001 (2019)

Editors' Suggestion

Featured in Physics

PNAS

We predict that YH_{10} is the energetically stable phase from 250 to 300 GPa, and is dynamically stable down to 220 GPa.

The predicted T_c for YH_{10} is very high (Fig. 7) using similar EPC calculations. At 250 GPa, the λ is 2.56 and gives a T_c of 305–326 K with $\mu^* = 0.1\text{--}0.13$ based on numerically solving the Eliashberg equations. The T_c of YH_{10} increased by ~30 K relative to YH_6 (30) despite the fact that λ decreases (from 2.93 to 2.56). But, this change is offset by the higher average ω_{\log} calculated for YH_{10} compared with YH_6 (1,282 K versus 1,124 K), as a result of the higher hydrogen content in the former.

Evidence for Superconductivity above 260 K in Lanthanum Superhydride at Megabar Pressures

Maddury Somayazulu,^{1,*} Muhtar Ahart,¹ Ajay K. Mishra,^{2,†} Zachary M. Geballe,² Maria Baldini,² Yue Meng,³ Viktor V. Struzhkin,² and Russell J. Hemley^{1,‡}

¹Institute for Materials Science and Department of Civil and Environmental Engineering, The George Washington University, Washington, DC 20052, USA

²Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA

³HPCAT, X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

In summary, we report four-probe, ac resistance measurements on LaH_{10+x} synthesized at pressures of 180–200 GPa by a modulated, pulsed laser heating technique that preserves the integrity of multiprobe electrical contacts on the sample after synthesis. Our multiple measurements reveal the signature of superconductivity at temperatures above 260 K at pressures of 180–200 GPa. The transition temperature is close to that predicted for the superconducting T_c based on BCS-type calculations for LaH_{10} at comparable pressures.

How to read the methods section of a paper?

- Do you know any of the authors ?
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-
- Identify the level of theory (*ab initio*, forcefield...)
 - System size and simulation length appropriateness
 - Molecular dynamics, Monte Carlo, lattice dynamics...
-
- Any “special” techniques used (Metadynamics) ?

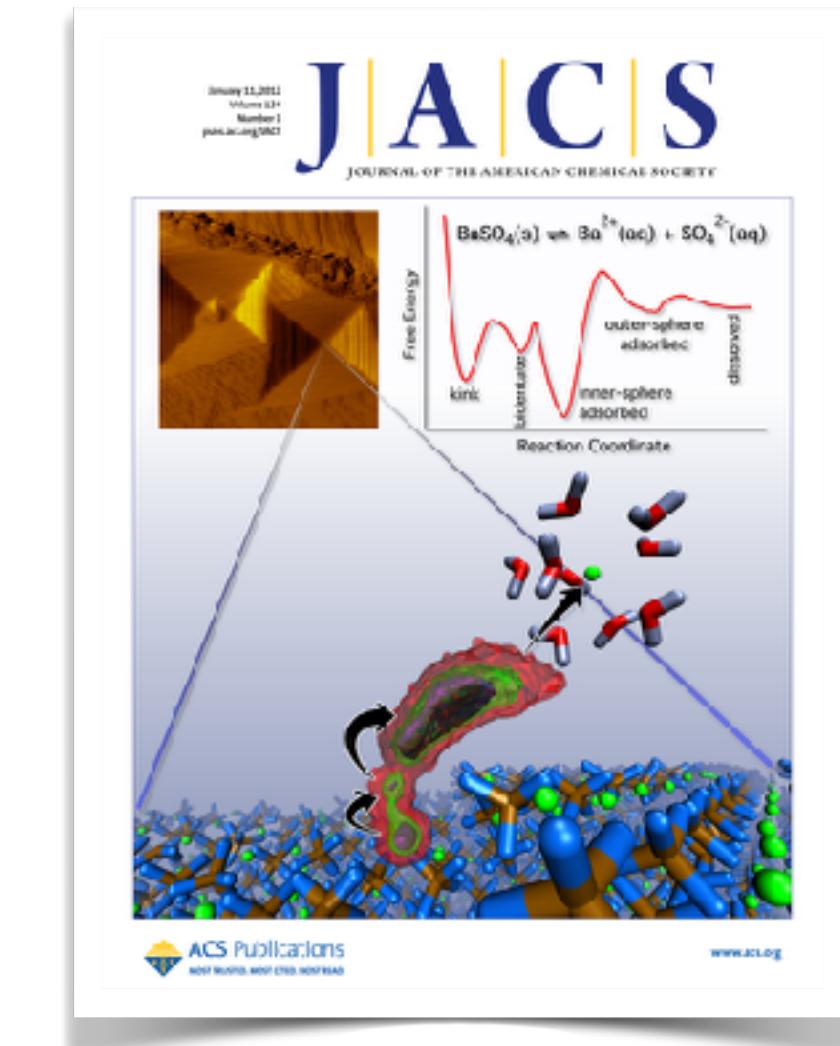
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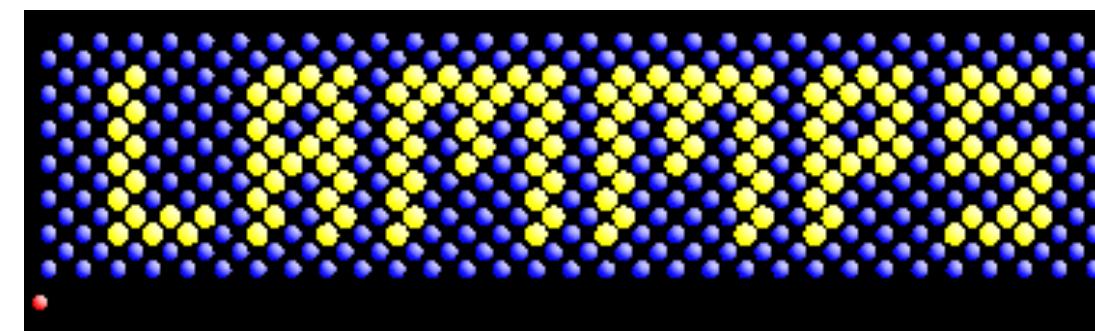
Computer simulations (of minerals)

- **Objectives:**
 - Atomistic picture
 - Thermodynamics
 - Connect with experiments
- **Challenges:**
 - Timescale ($> \mu\text{s}$)
 - Concentration ($< 1 \text{ mM}$)
 - Reactivity
 - Accuracy of the methods
- **Approaches:**
 - *Ab initio* methods
 - Forcefields methods
 - Monte Carlo
 - Lattice dynamics
 - Molecular dynamics
- **Extras:**
 - Free energy methods

GULP



PLUMED



CP2K



Ab initio methods

$$\vec{F}_i = -\frac{\partial \varepsilon}{\partial \vec{x}_i} = m_i \vec{a}_i$$

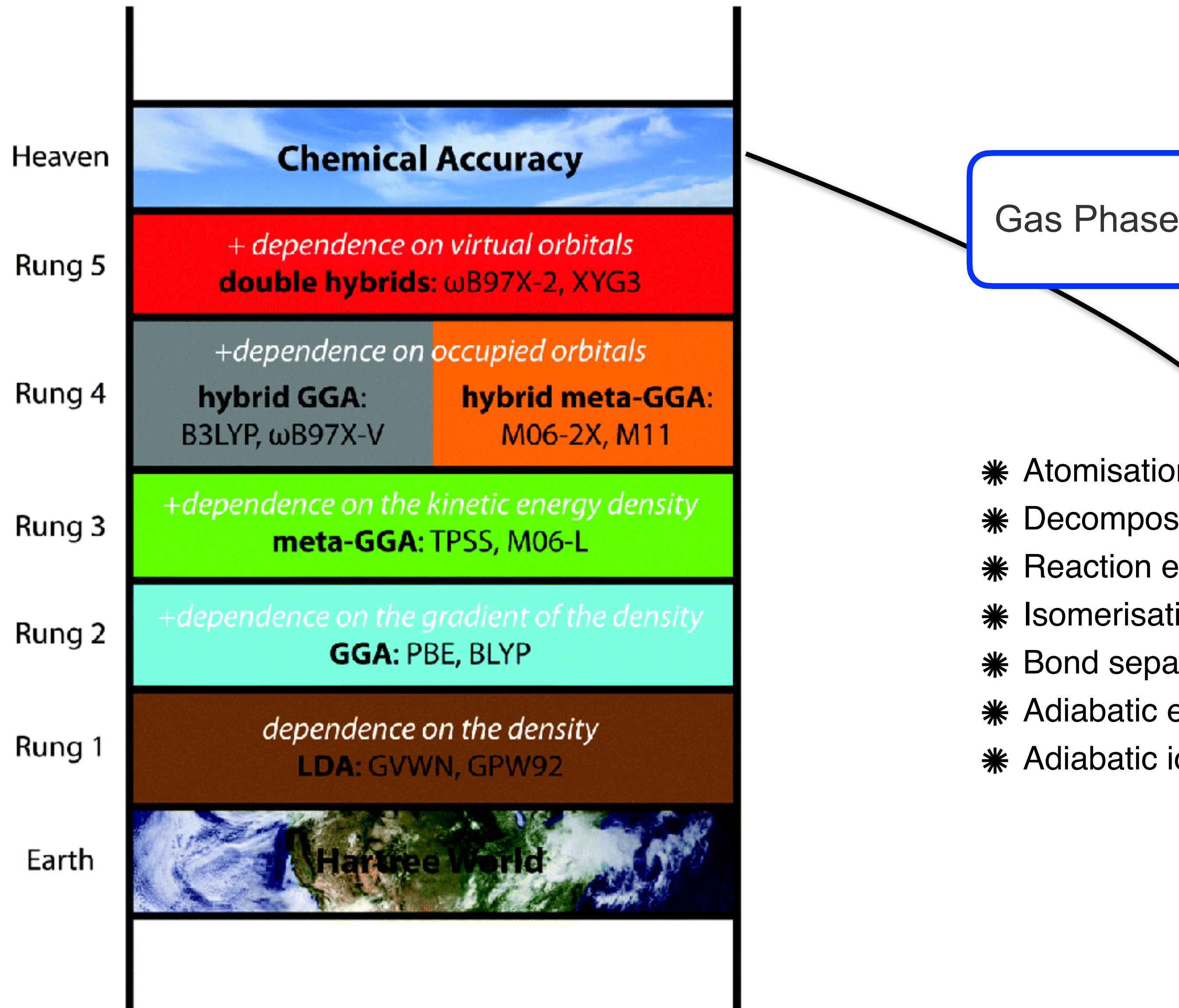
- Schrödinger equation

$$\hat{H}\Psi = \left[\sum_i^N \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right) + \sum_i^N V(\vec{r}_i) + \sum_{i < j}^N U(\vec{r}_i, \vec{r}_j) \right] \Psi = \varepsilon \Psi$$

- Born–Oppenheimer approximation
- Density Functional Theory
- Basis set
- Exchange and Correlation
- Huge zoo of methods (B3LYP, PBE0...)
- Poor treatment of the vdw interactions

$$\rho = \int \dots \int d\mathbf{x}^{3N} \Psi^* \Psi$$

Jacob's ladder of DFT



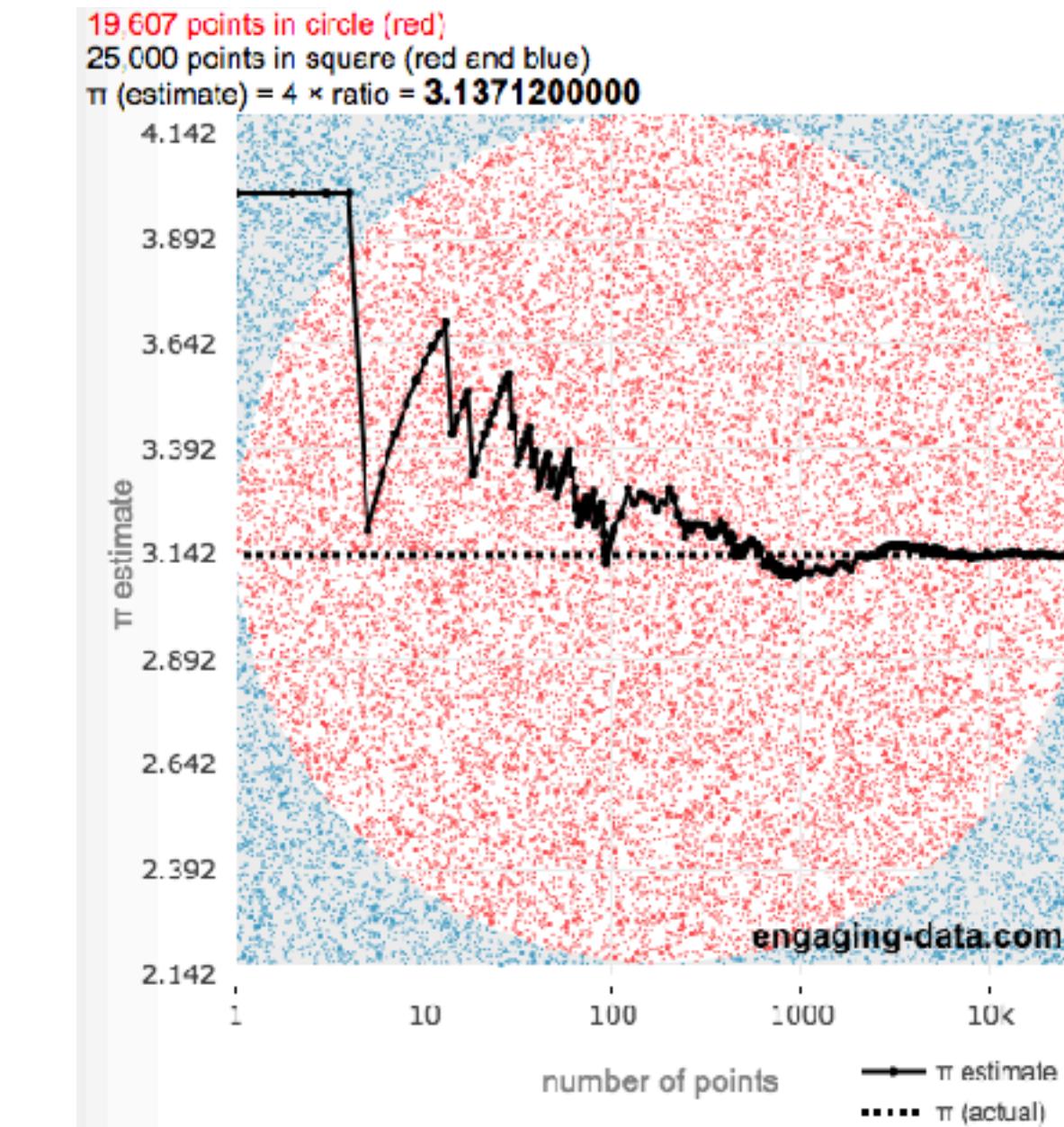
Monte Carlo simulations

- Many useful applications in science
- Not widely used in atomistic simulations
- Stochastic method

$$\langle A \rangle \approx \frac{1}{M} \sum_{i=1}^M A(\mathbf{x}_i^N)$$

- No dynamics or kinetics
- “Random” movements - importance sampling

$$acc(\mathbf{x}^N \rightarrow \mathbf{y}^N) = \min \left(1, \exp\{-\beta[U(\mathbf{y}^N) - U(\mathbf{x}^N)]\} \right)$$



Lattice Dynamics

- Based on statistical thermodynamics
- Useful to describe crystals below the Debye temperature (and isolated molecules)
- Free energies can be computed using quasi-harmonic approximations from the phonons/vibrations
- Limited applications to liquids and amorphous materials

- We use it routinely to develop forcefields that accurately reproduce the solid phases and their solubilities

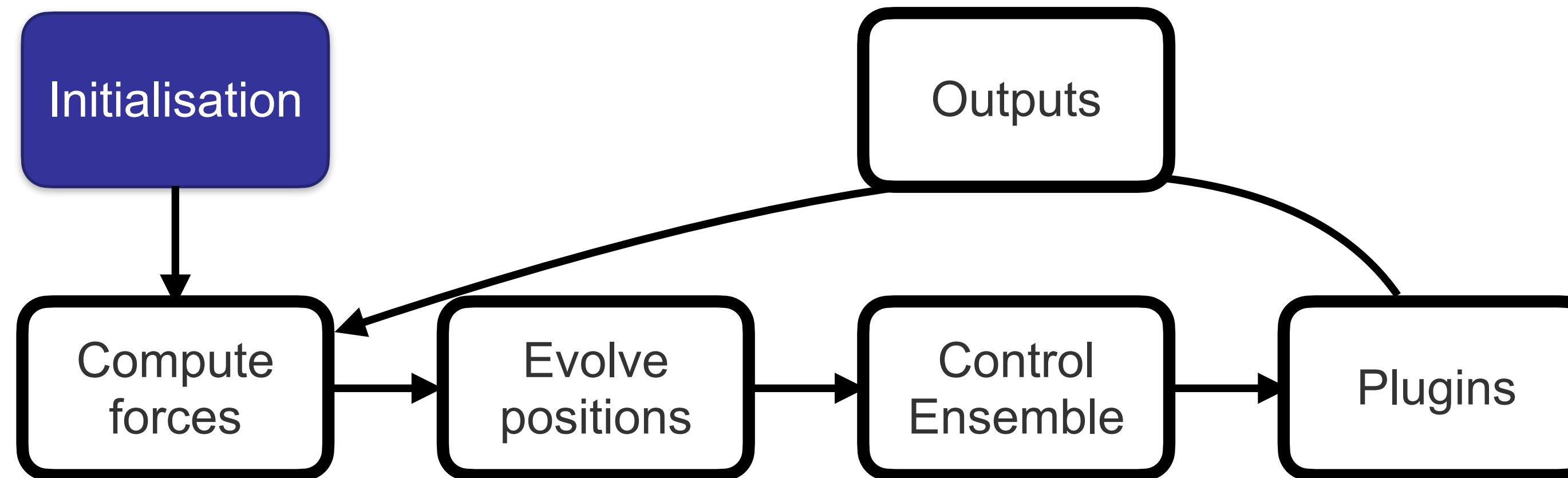
Molecular Dynamics

- Most widely used computational tool for atomistic simulations
- Based on Newtonian dynamics
- Statistical mechanics can be used to compute properties
- Atomic trajectories can give access to kinetics

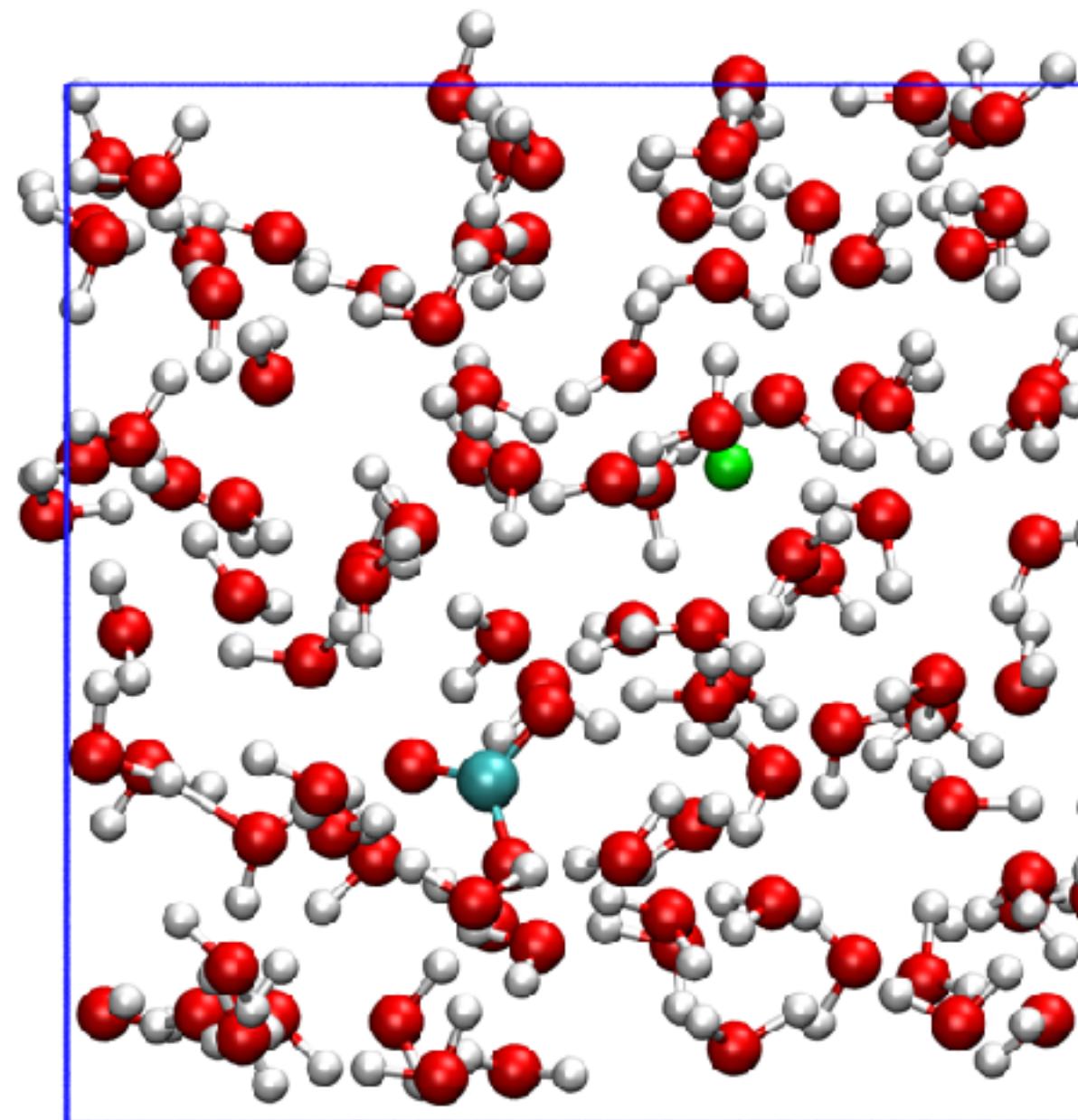
- Only difference is how the energy and forces are computed

Molecular Dynamics

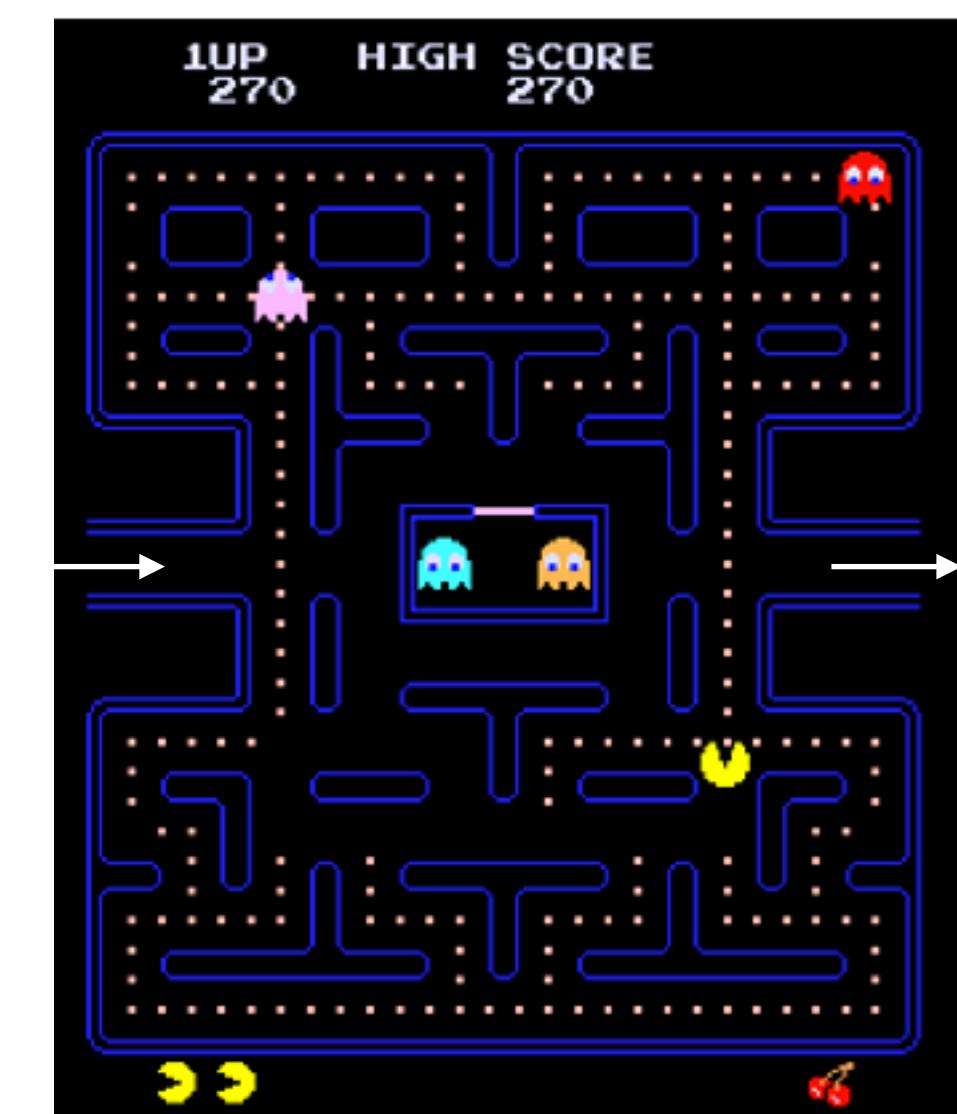
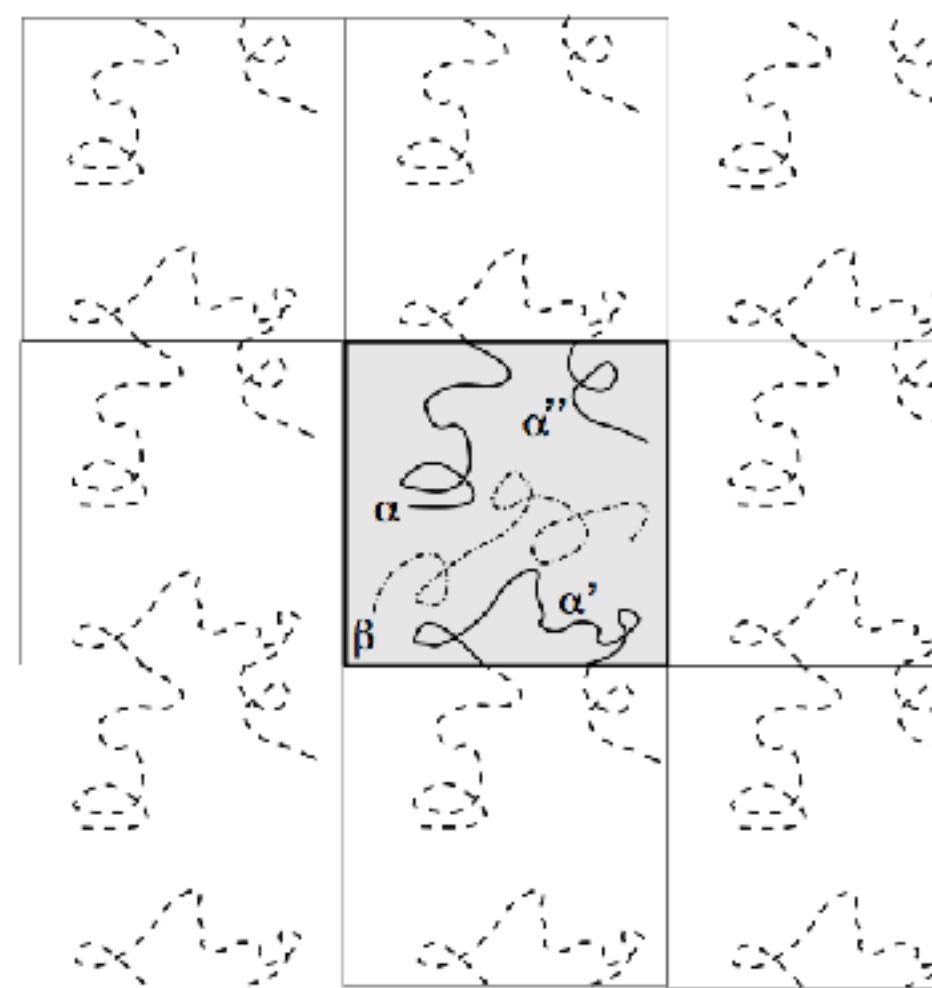
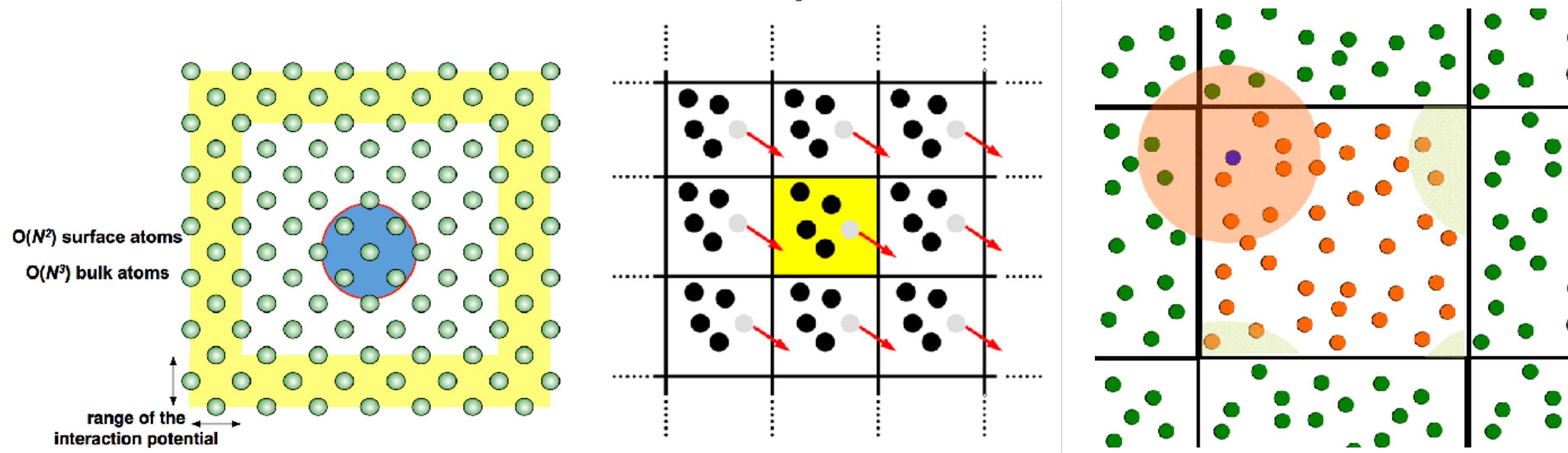
Each cycle propagates the system forward in time



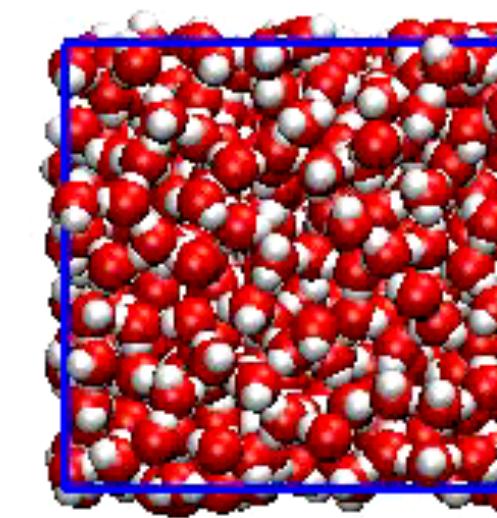
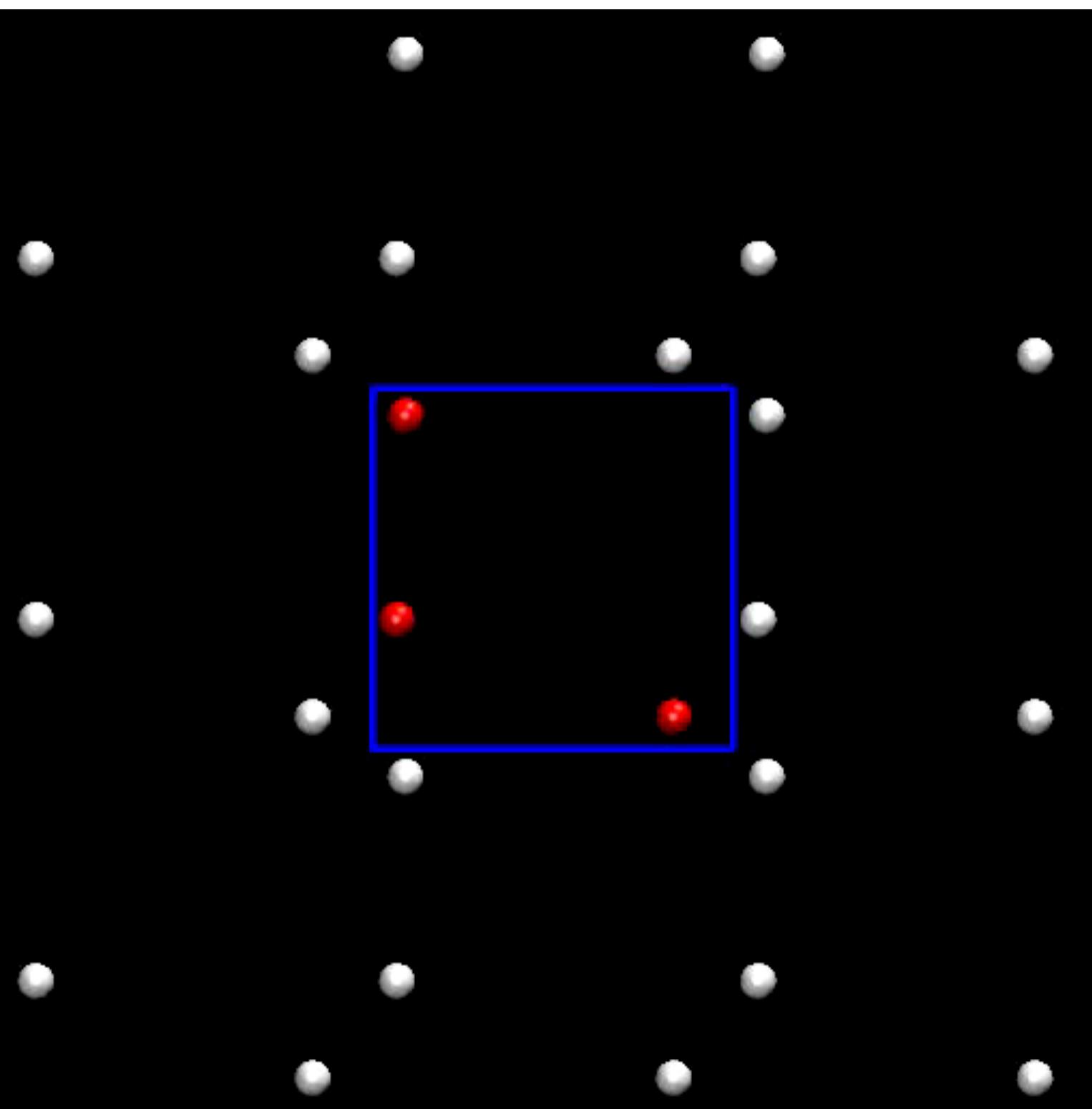
- Box size
- Positions
- Temperature
 - Velocities
- Simulation parameters



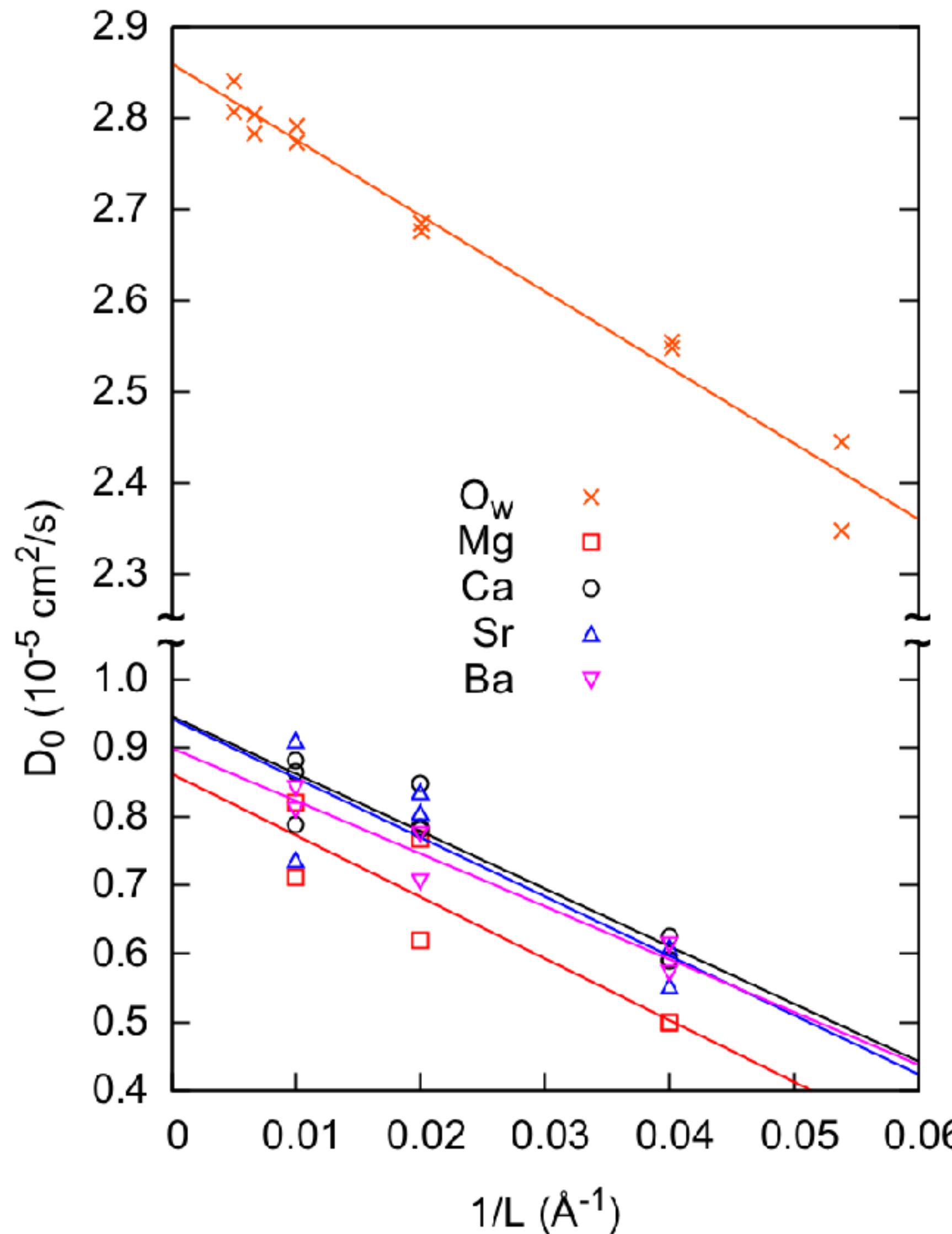
Finite size and boundary conditions



Finite size and boundary conditions



Finite size - Diffusion



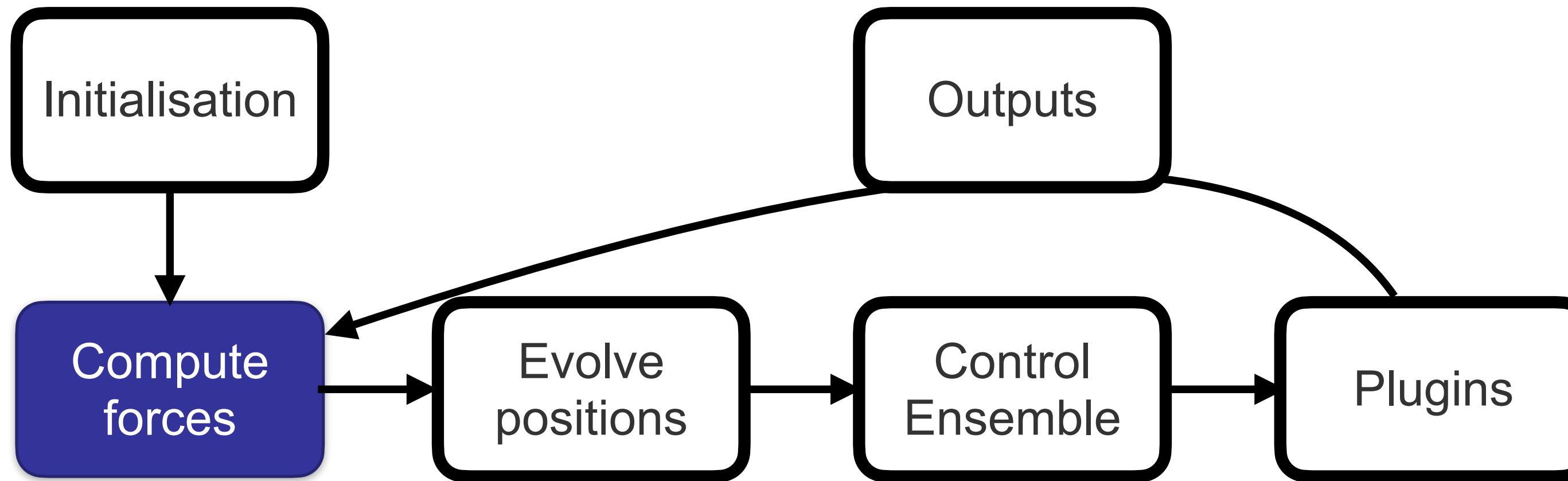
J. Phys. Chem. B (2004), **108**, 15873–15879.

$$D_{PBC} = D^\infty - \frac{k_B T \xi}{6\pi \eta L}$$

[1] Atkinson *et al.*; *J. Phys. Chem.* (1974), **78**, 1913–1917.

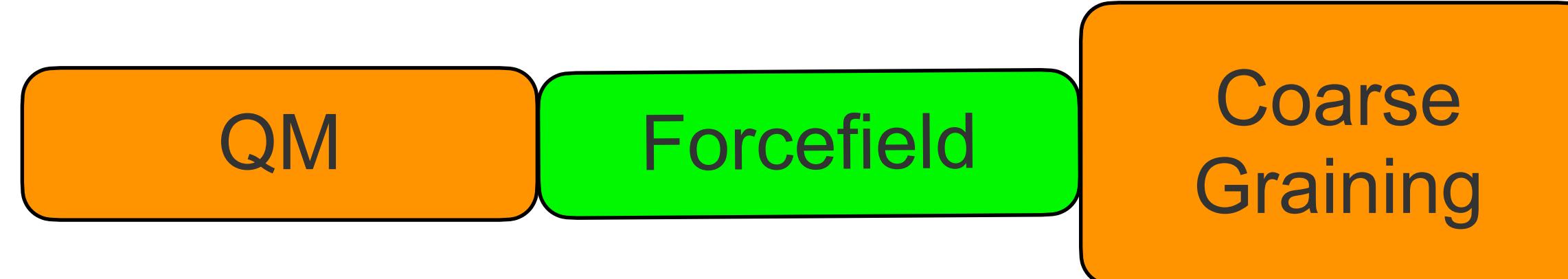
D_0 ($10^{-5} \text{ cm}^2/\text{s}$)	Exp [1]	Theory
Mg	0.71	0.86
Ca	0.79	0.95
Sr	0.79	0.94
Ba	0.84	0.90
H_2O	2.30	2.86

Molecular Dynamics

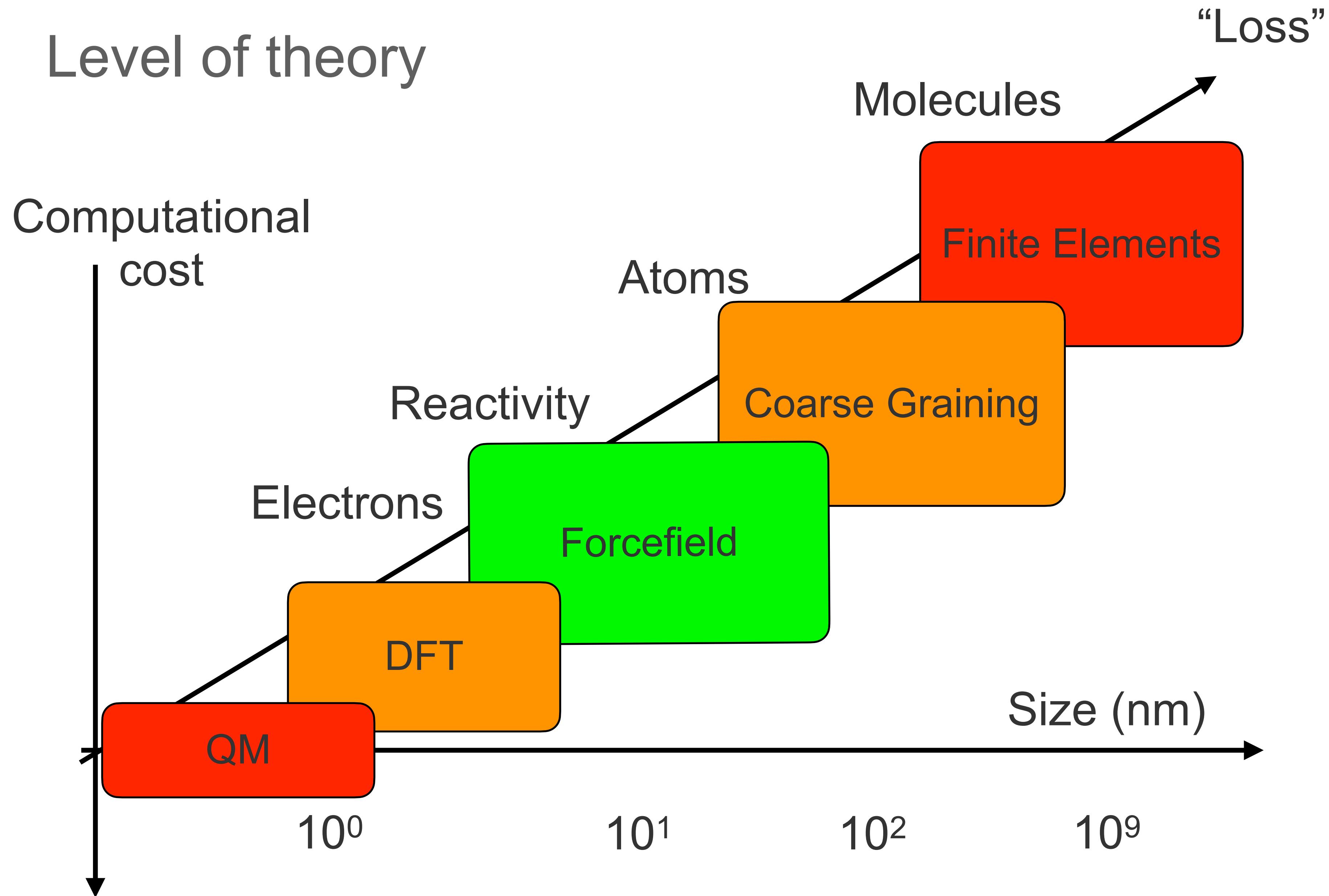


Newton's second law

$$\vec{F}_i = -\frac{\partial U}{\partial \vec{x}_i} + q_i \vec{E} = m_i \vec{a}_i$$

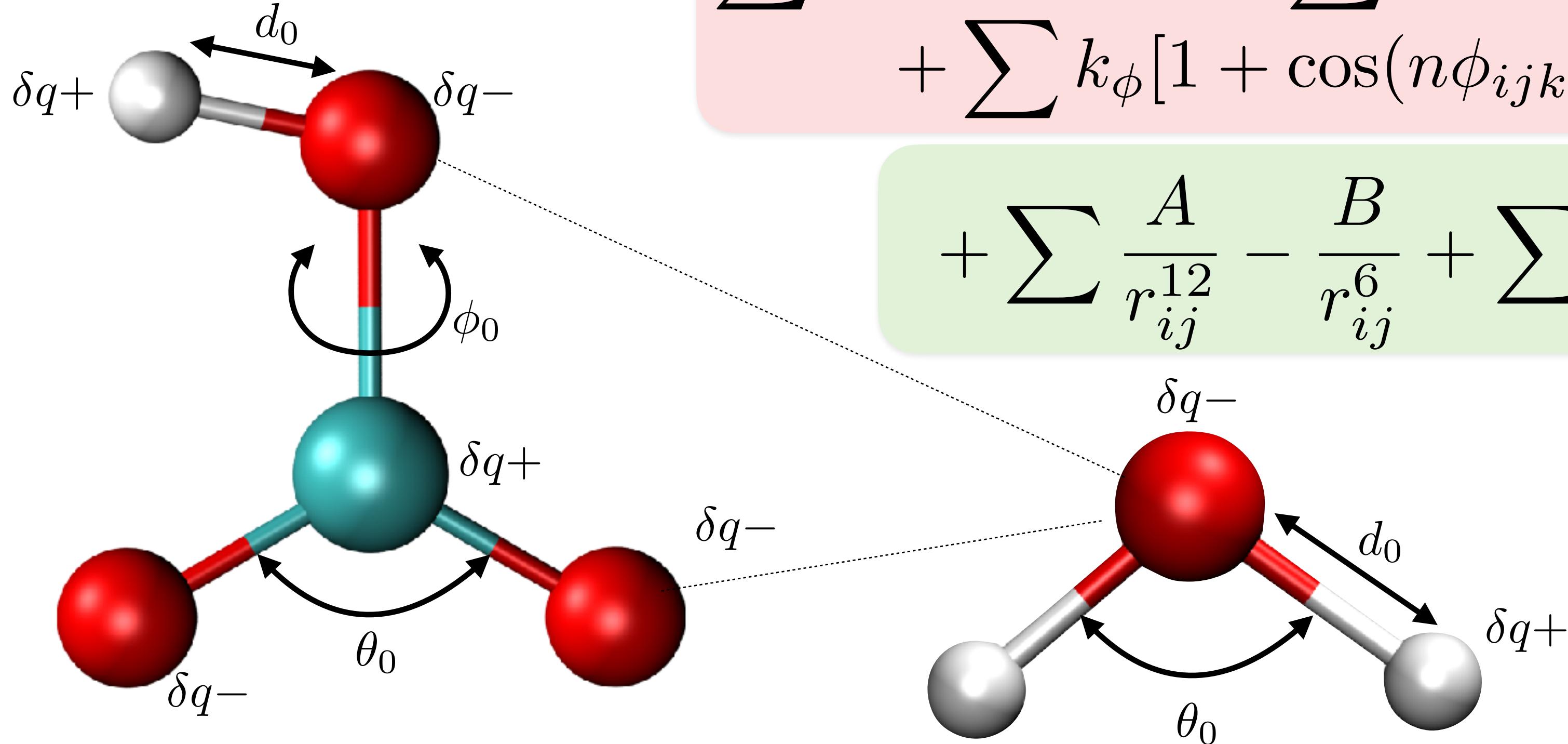


Level of theory



Force field

$$\vec{F}_i = -\frac{\partial U}{\partial \vec{r}_i} + q_i \vec{E} = m_i \vec{a}_i$$

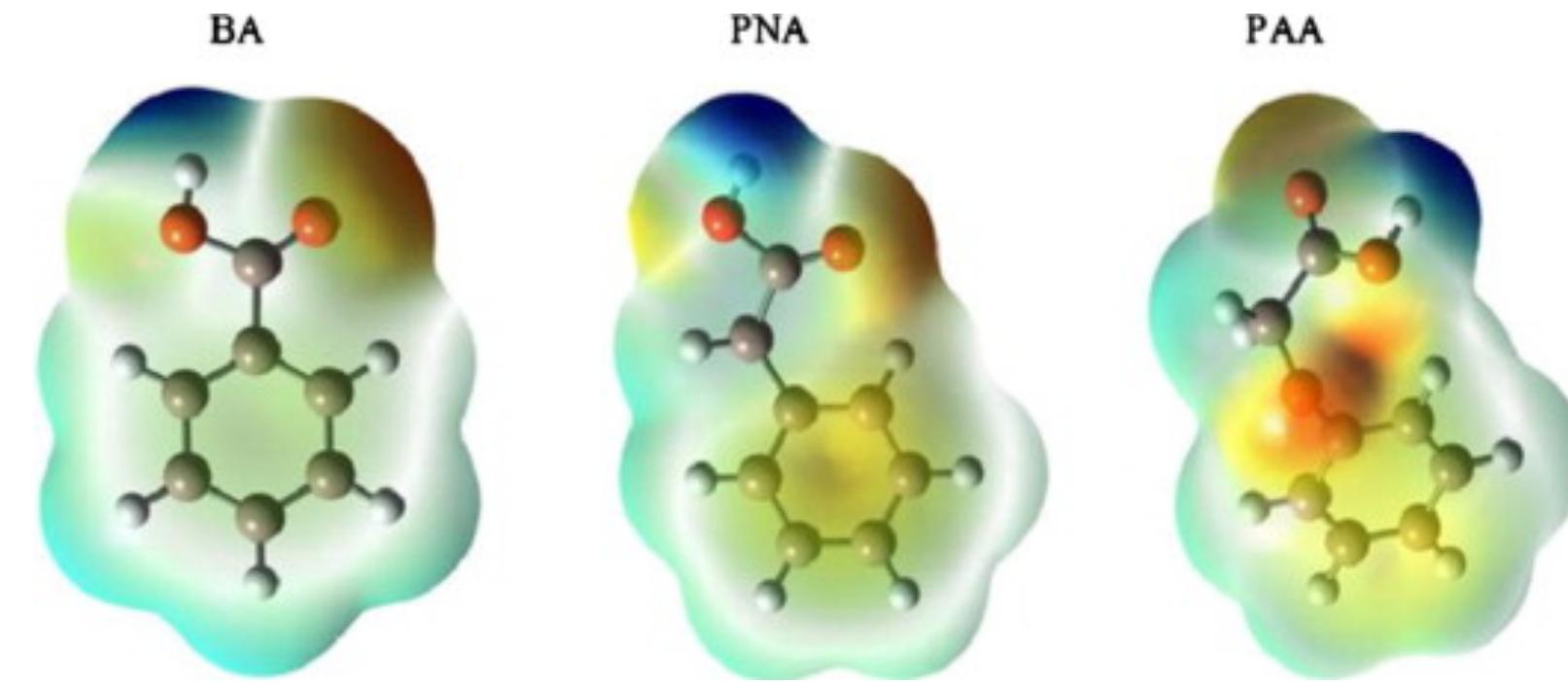
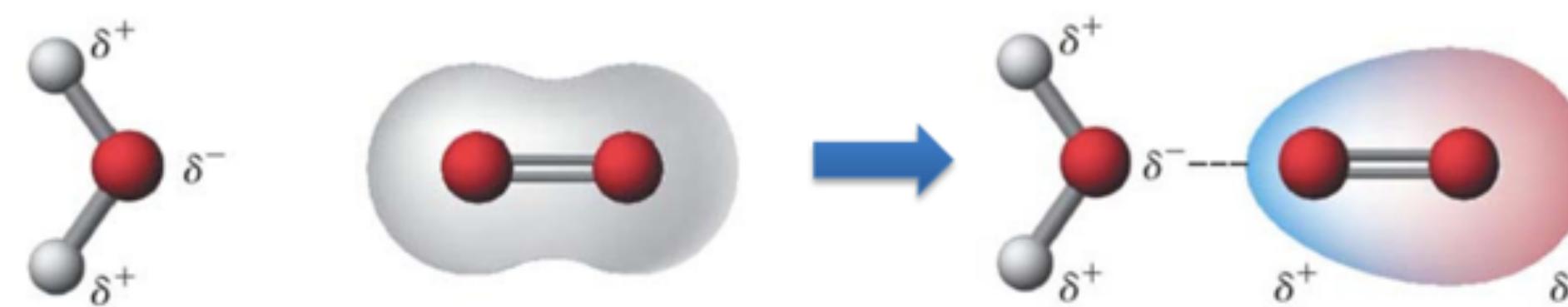


$$U = \sum k_b (b_{ij} - b_0)^2 + \sum k_\theta (\theta_{ijk} - \theta_0)^2 \\ + \sum k_\phi [1 + \cos(n\phi_{ijkl} - \phi_0)]^2$$

$$+ \sum \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^6} + \sum \frac{q_i q_j}{r_{ij}}$$



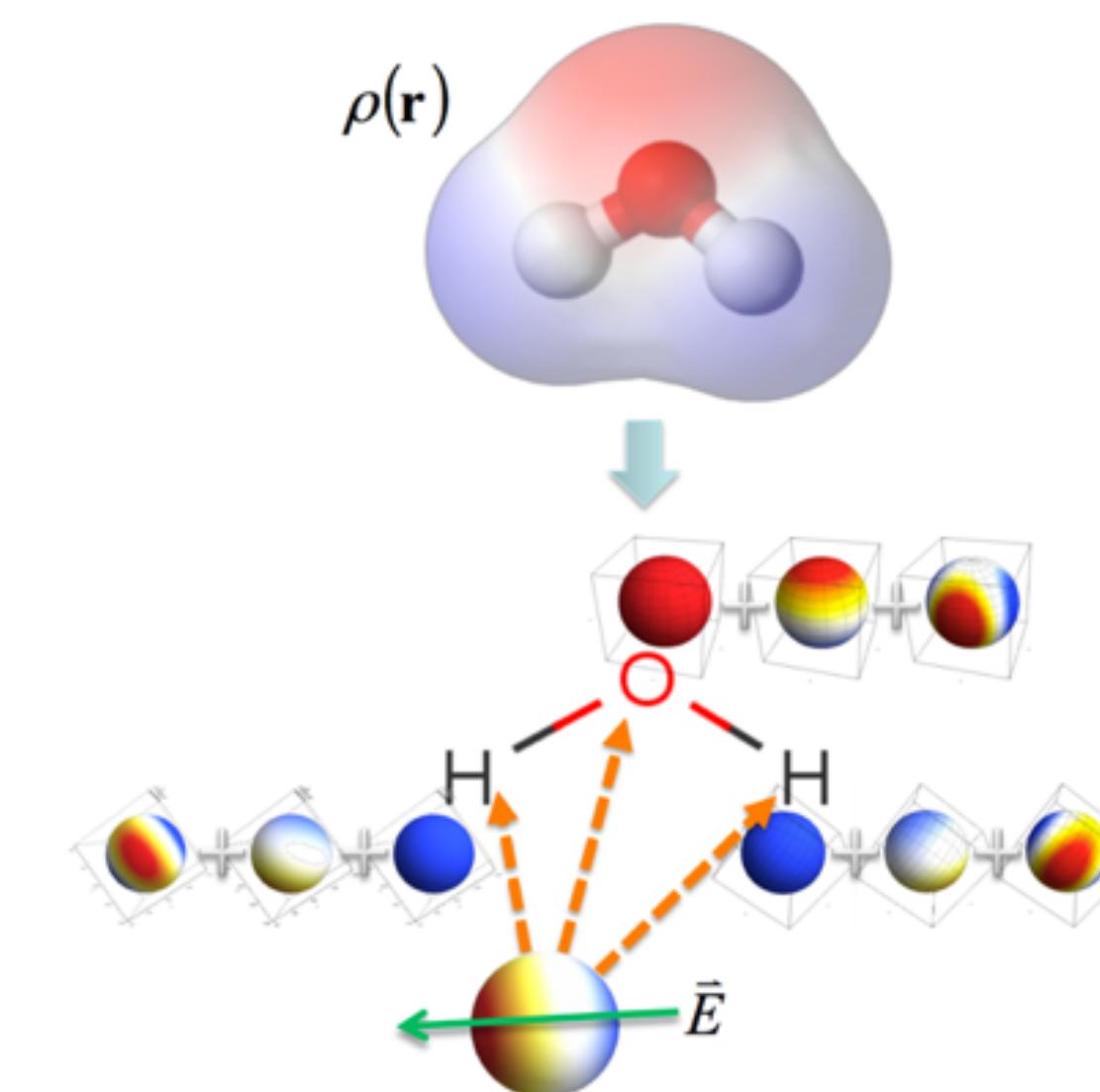
Polarisable forcefield



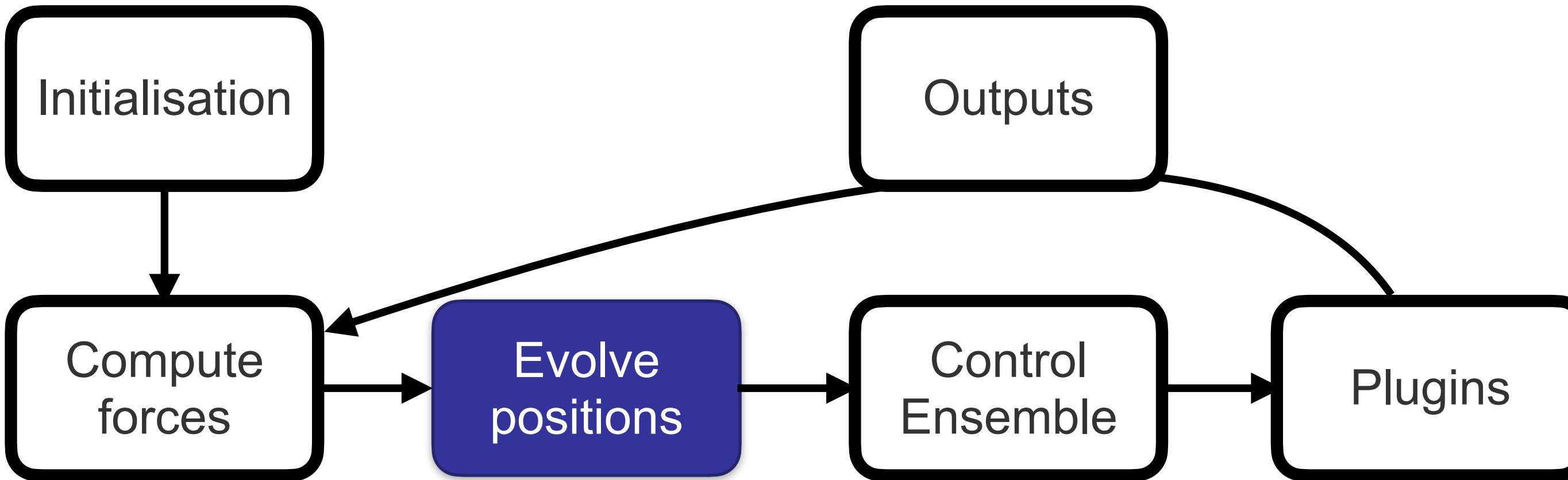
DOI: j.saa.2013.09.127

$$U = \sum k_b(b_{ij} - b_0)^2 + \sum k_\theta(\theta_{ijk} - \theta_0)^2 + \sum k_\phi[1 + \cos(n\phi_{ijkl} - \phi_0)]^2$$

$$+ U_{vdW} + U_{elec}^{perm} + U_{elec}^{ind}$$



Molecular Dynamics



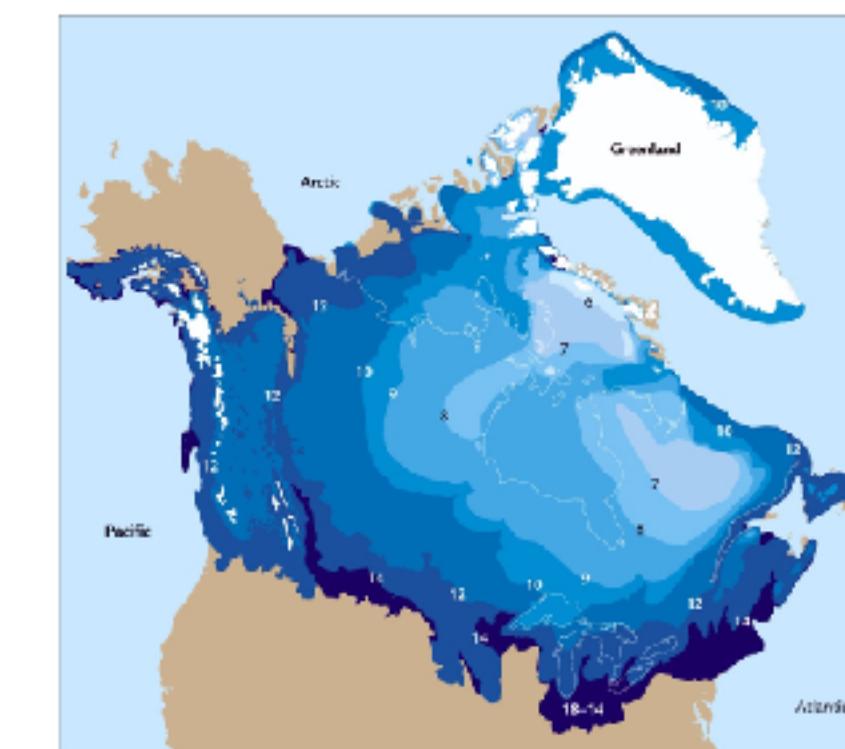
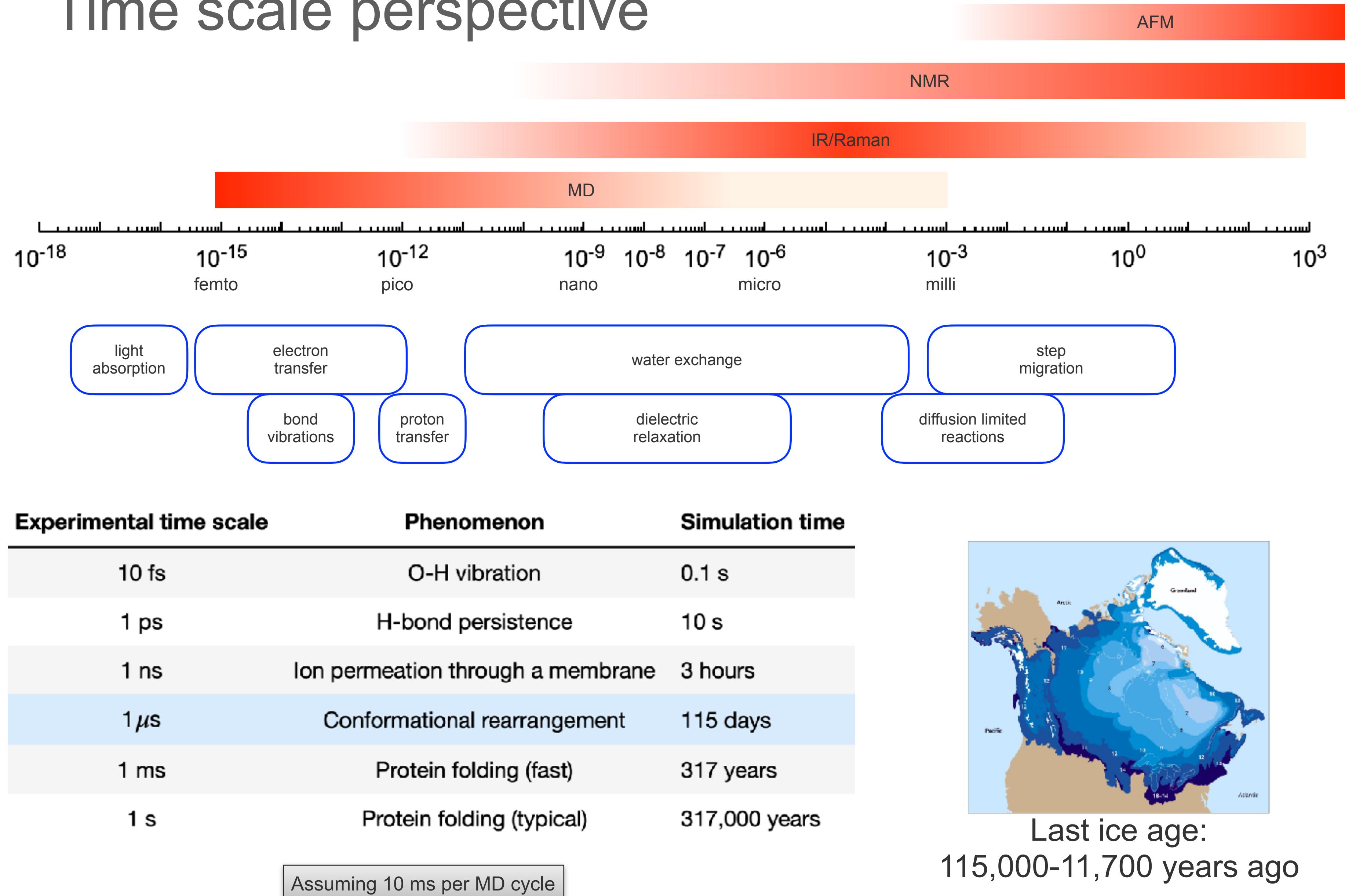
$$\vec{a}(t) = F(t) = -\frac{\partial U}{\partial \vec{r}}$$

timestep

Verlet algorithm $\vec{v}(t + \Delta t) = \vec{v}(t) + \vec{a}(t)\Delta t$ $\Delta t \approx 0.5 - 5 \text{ fs}$

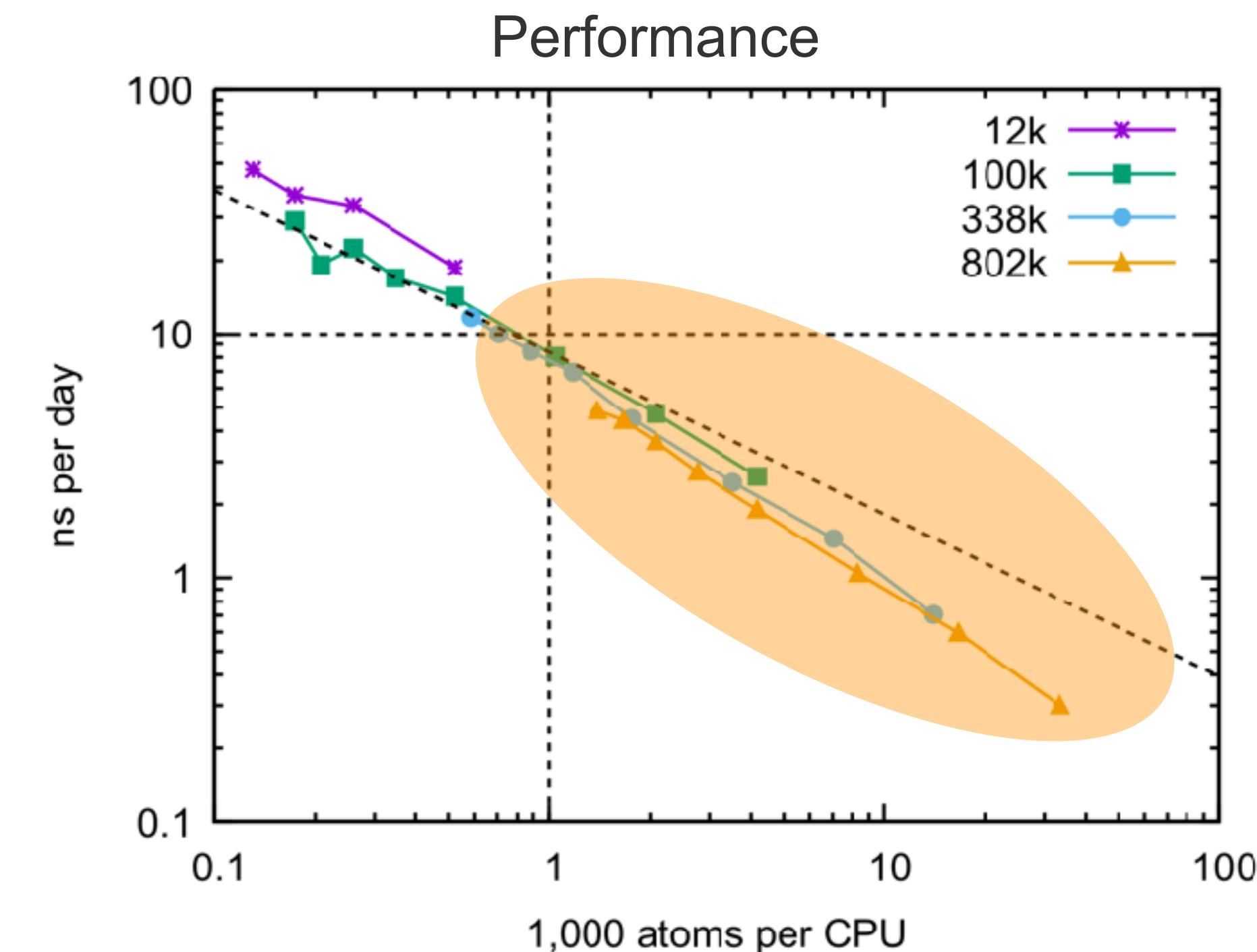
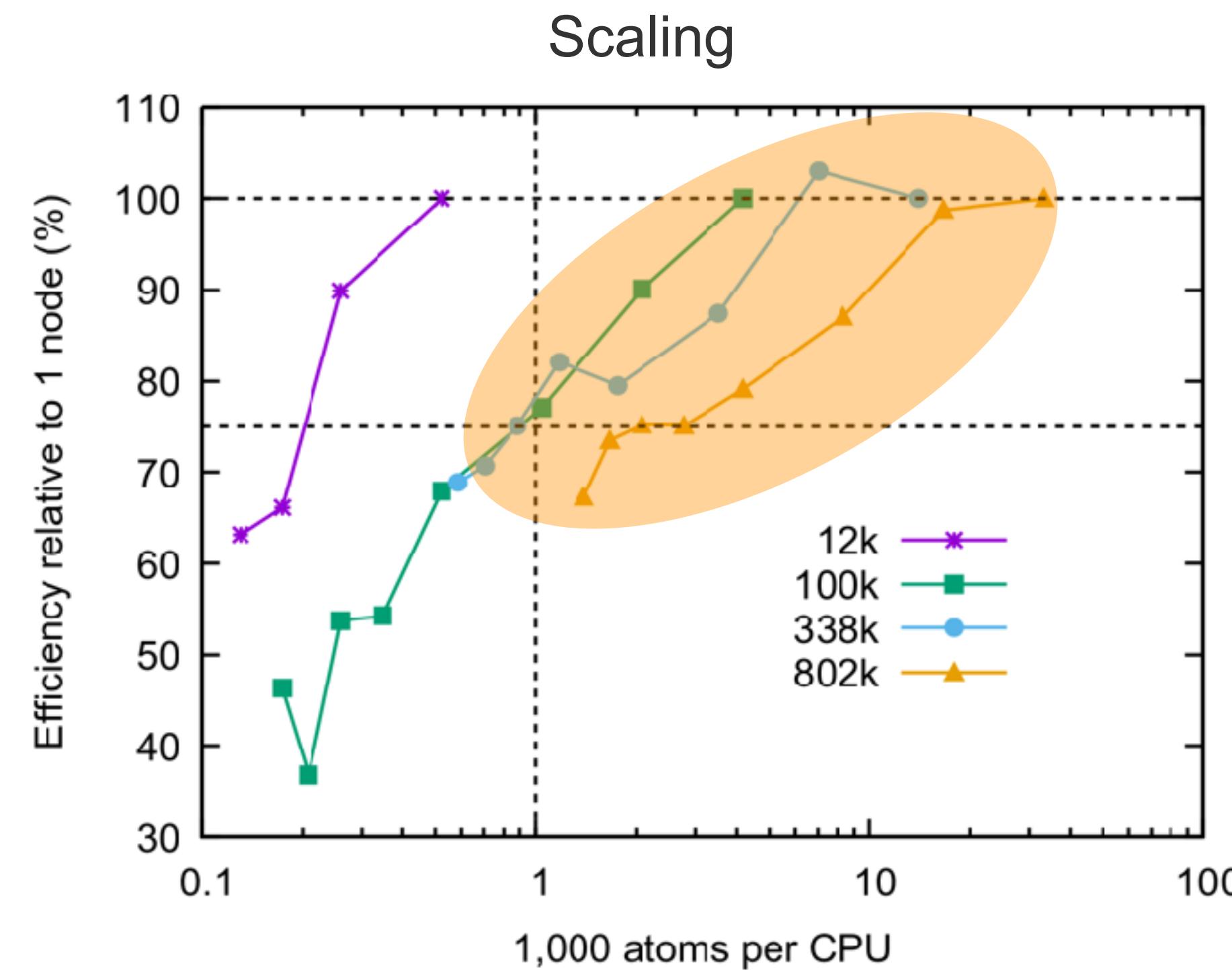
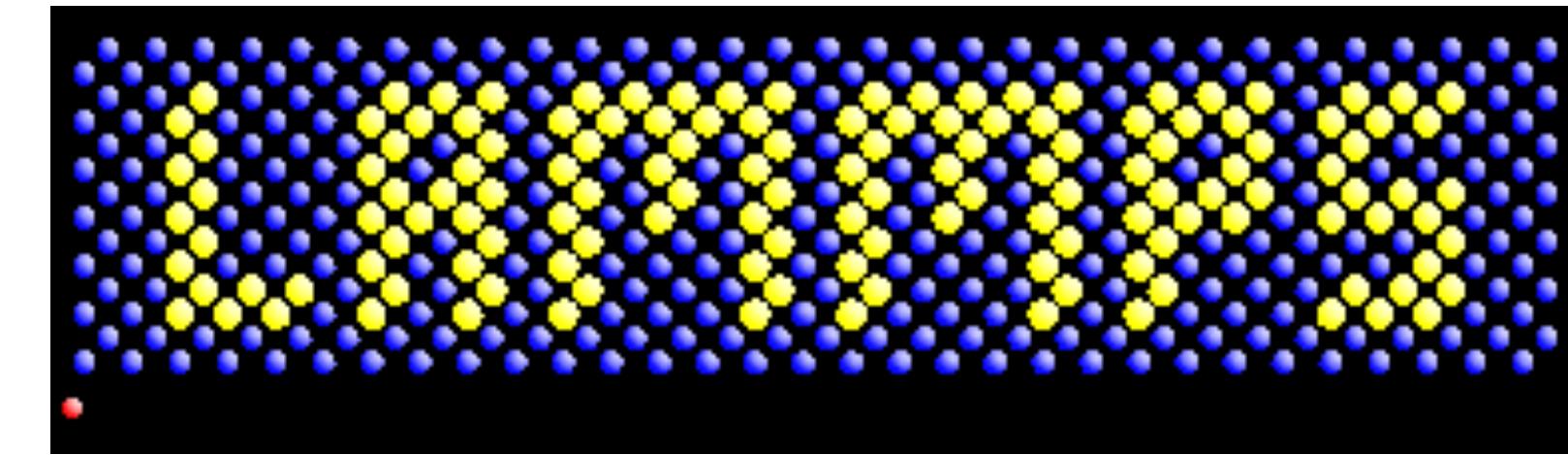
$$\vec{r}(t + \Delta t) = \vec{r}(t) + \vec{v}(t) \Delta t + \frac{1}{2} \vec{a}(t) \Delta t^2$$

Time scale perspective



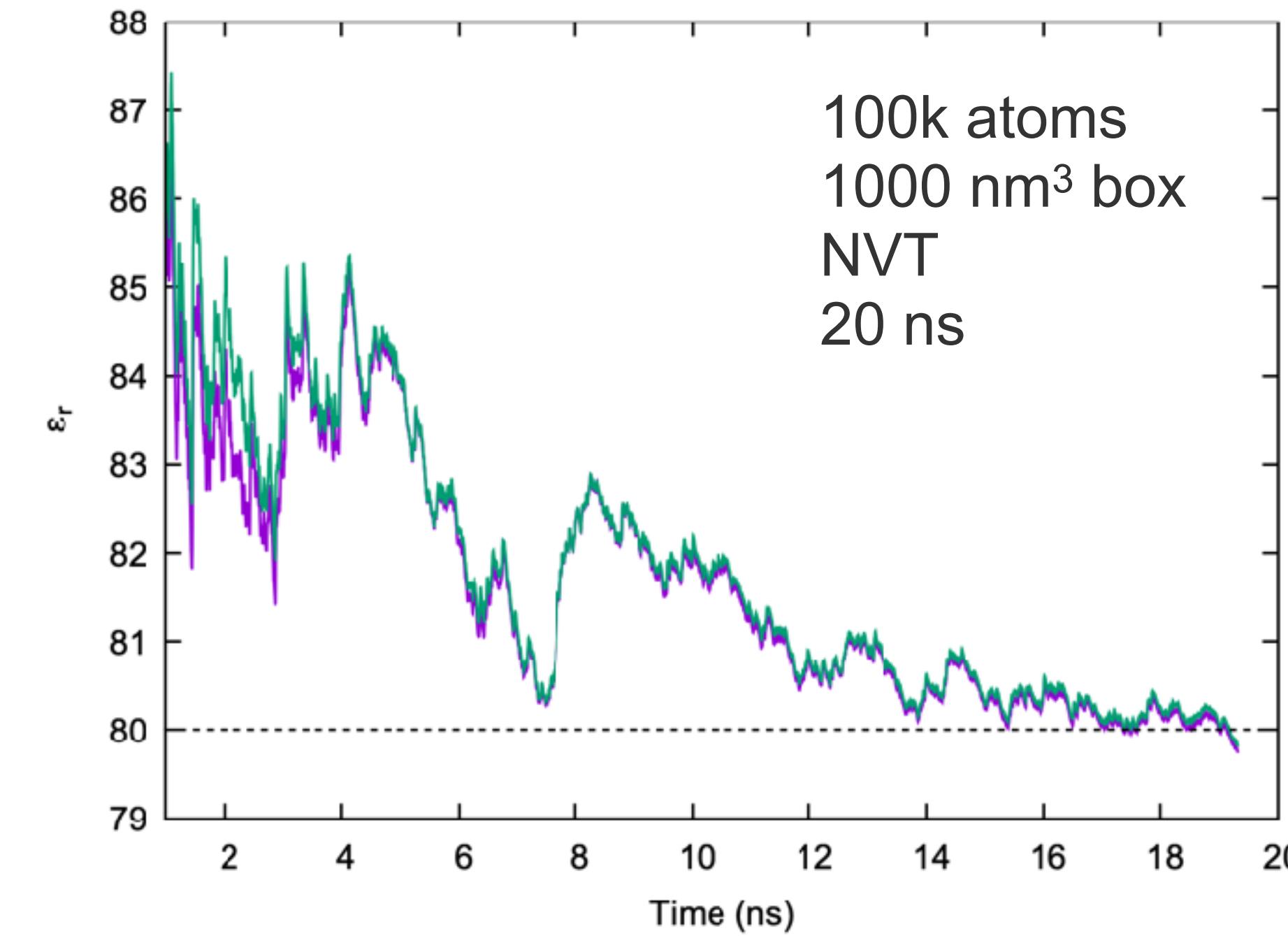
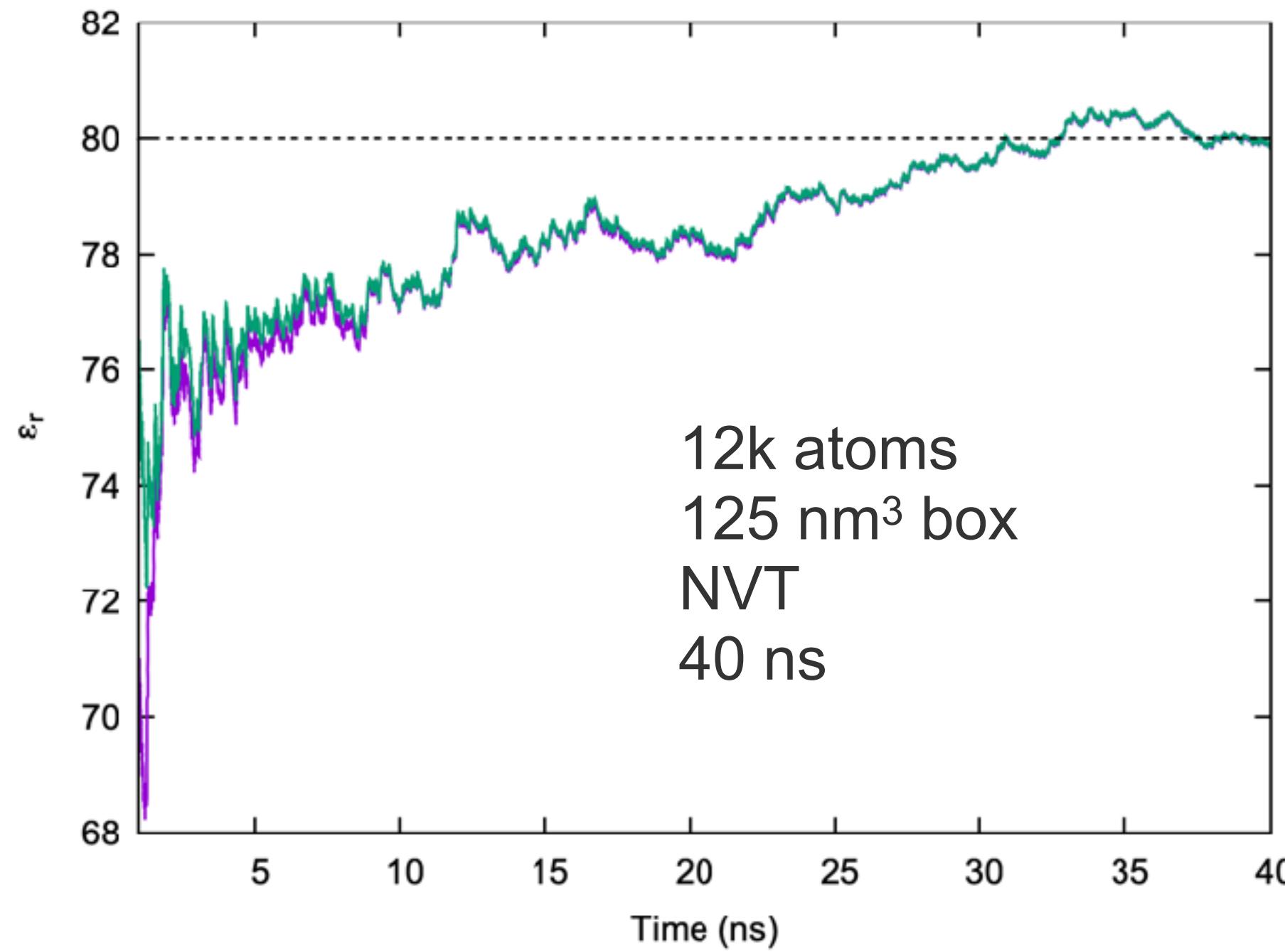
Last ice age:
115,000-11,700 years ago

LAMMPS on magnus

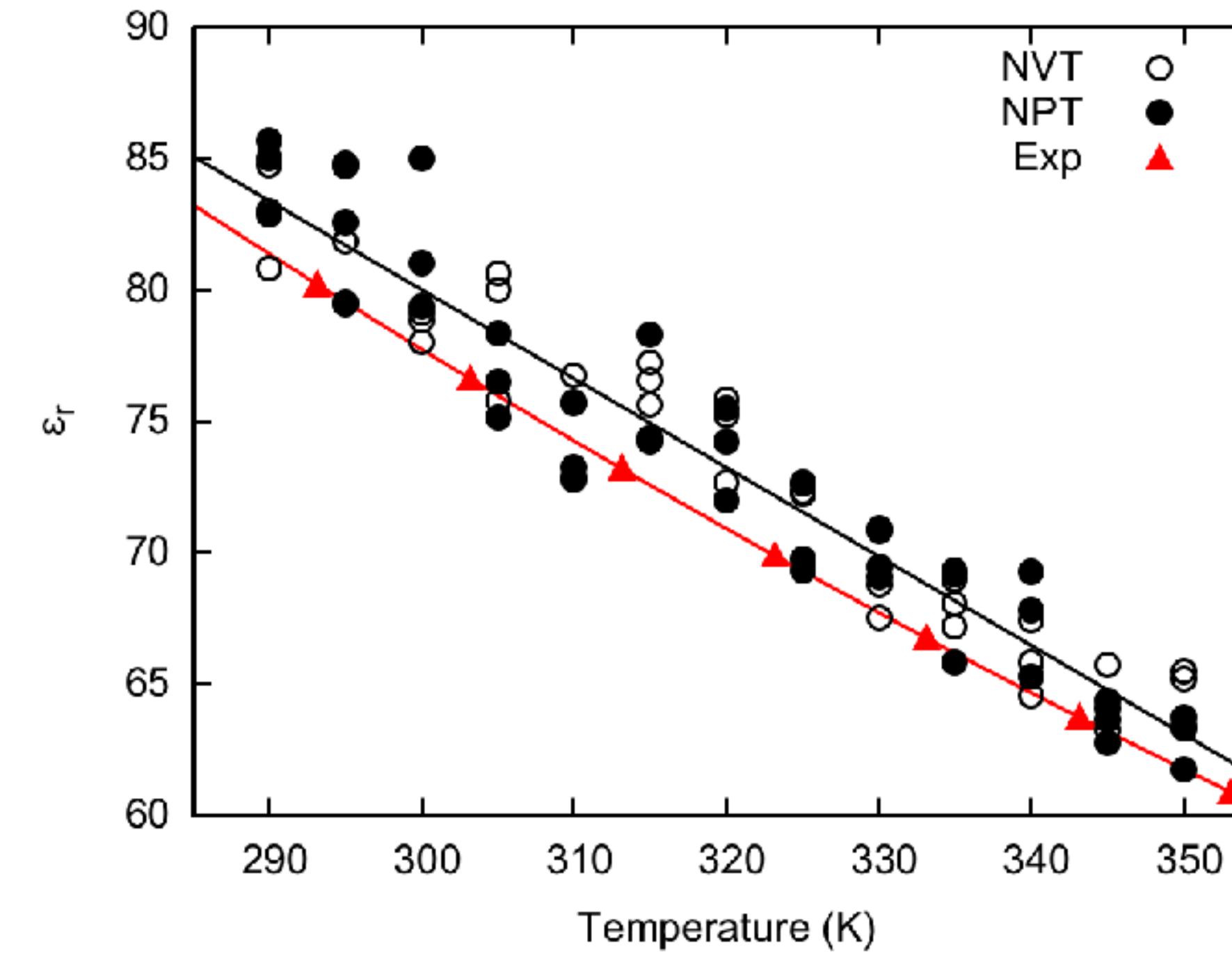
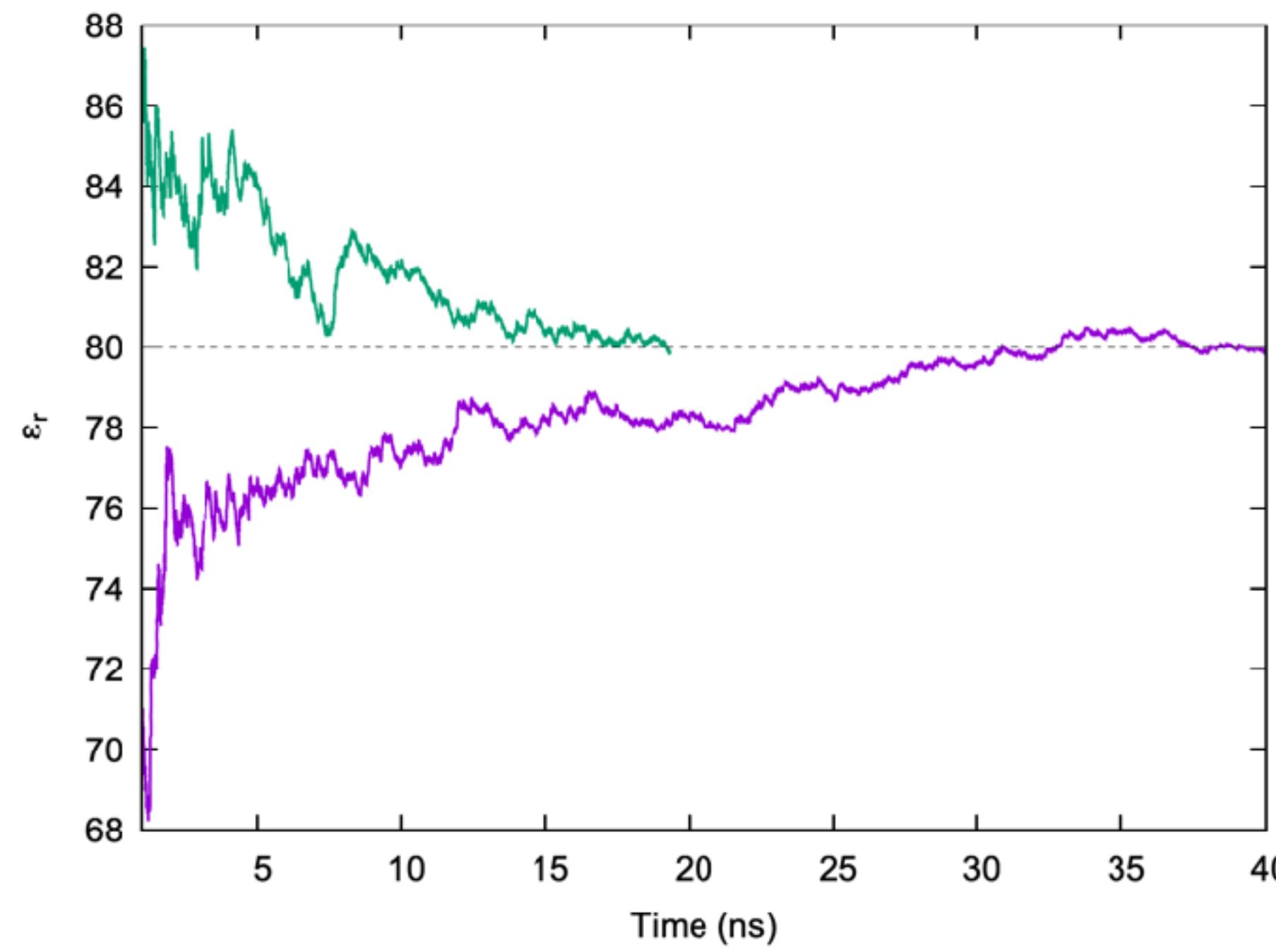


Number of nodes used:
1 - 2 - 3 - 4 - 8 - 12 - 16 - 20 - 24

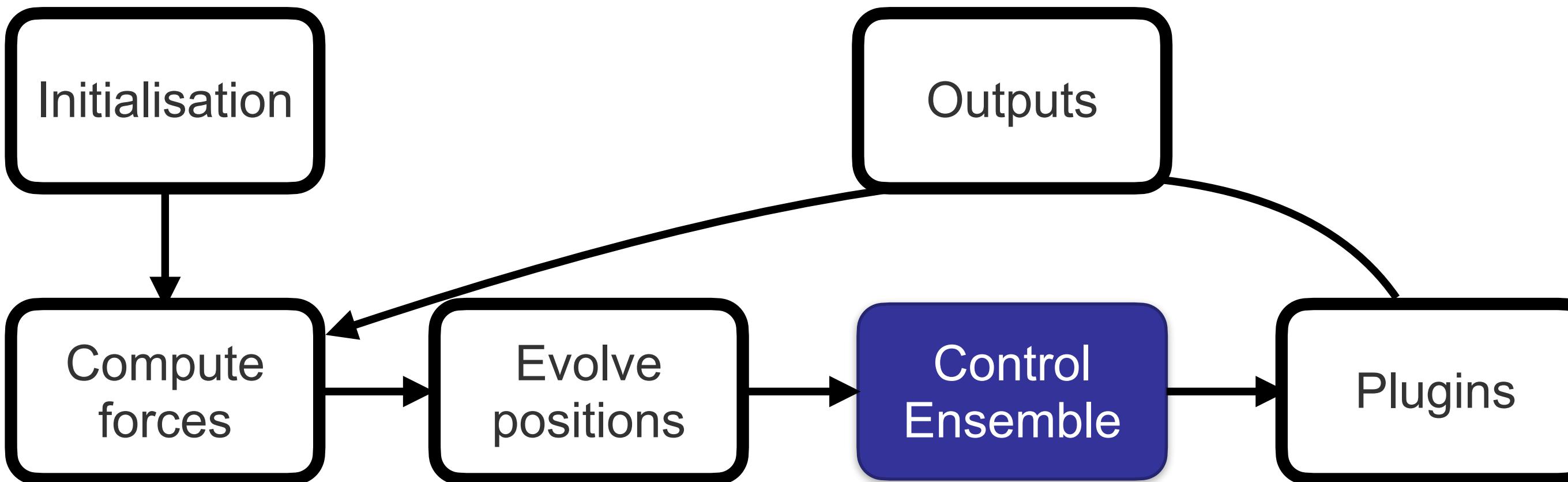
Finite time - Dielectric constant



Finite time - Dielectric constant



Molecular Dynamics



N : Number of atoms

μ : Chemical potential

V : Volume

P : Pressure

E : Energy

H : Enthalpy

T : Temperature

Choose (any) 3

NVE → Isolated system

NVT → Isothermal – Isochoric

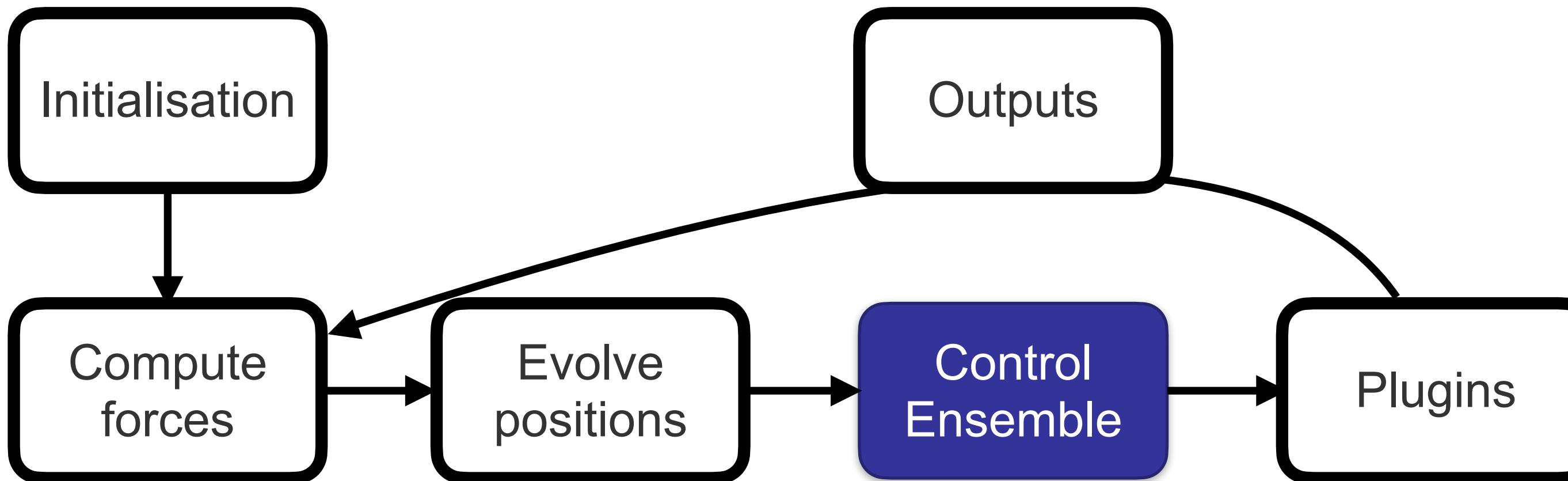
NPH → Isoenthalpic – Isobaric

NPT → Isothermal – Isobaric

μPT → Open system

C S
L Y
O S
S T
E E
D M

Molecular Dynamics



$$K(t) = \frac{1}{2} \sum_{i=1}^N m_i v_i^2(t) = \frac{3}{2} N k_B T(t)$$

Velocity Rescaling

$$\frac{1}{2} \sum_{i=1}^N m_i \lambda^2 v_i^2(t) = \frac{3}{2} N k_B T_{NVT}$$
$$\lambda = \sqrt{\frac{T_{NVT}}{T(t)}}$$

Specific heat

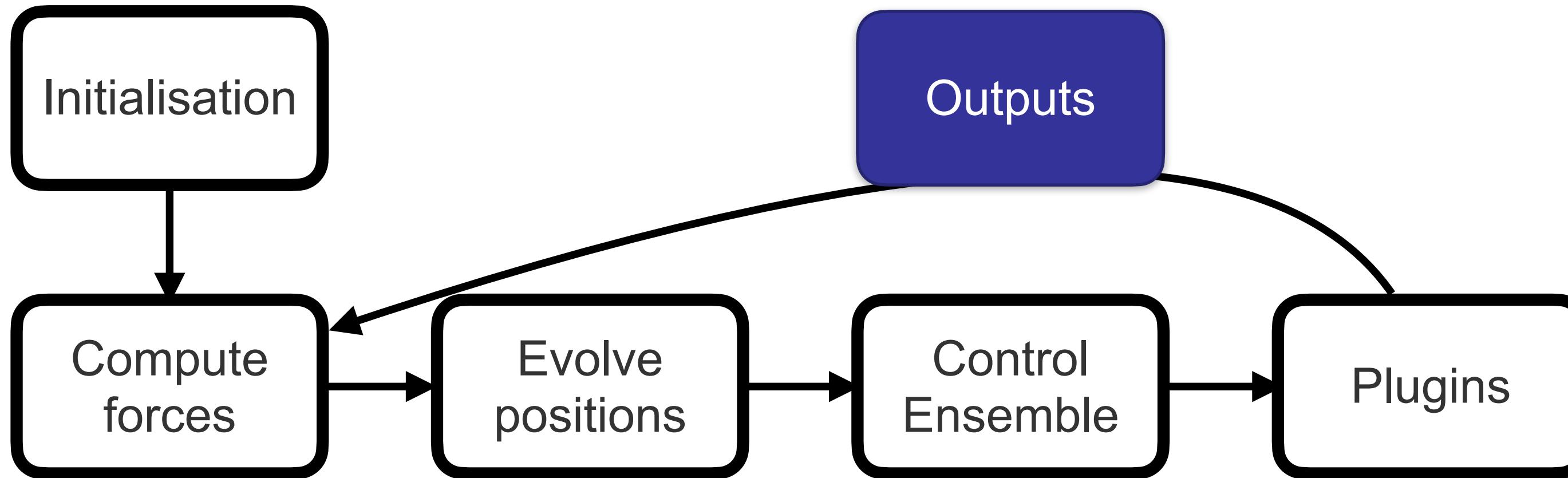
$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \frac{\langle \delta H^2 \rangle_{NPT}}{k_B T^2}$$

	slope	fluct.
Berendsen	31.98	4.36
Andersen	31.89	24.76
CSVР	32.07	32.80
Langevin	32.16	34.83
Exp.	29.71	

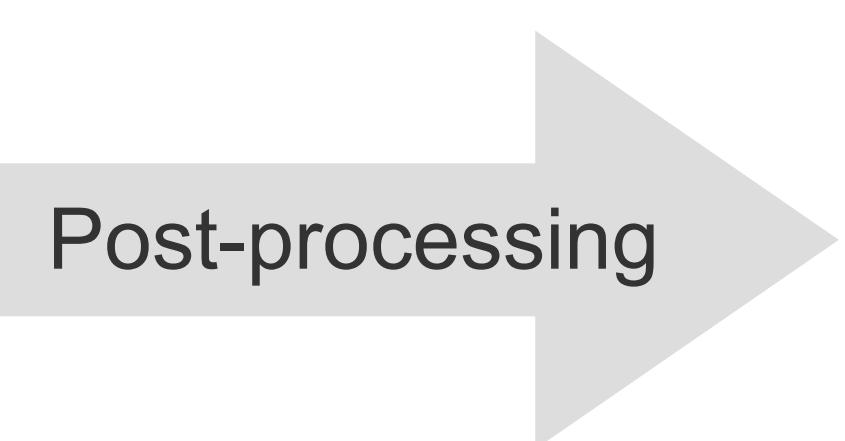
Self Diffusion coefficient

	D [10 ⁻⁵ cm ² /s]
Experiment	2.30
NVE	2.45
NVT - Berendsen	2.4
NVT - CSVР	2.47
NVT - Nosé-Hoover	2.46
NPT - MTTK	2.44
NVT - Langevin	1.09*

Molecular Dynamics



- *Energy*
- *Temperature*
- *Pressure*
- *Volume*
- ...
- *Atomic coordinates*
- ...



- *Density*
- *Structural properties* [$g(r)$]
- *Dynamical properties* [D_0]
- ...
- *Phase changes*
- ...
- *Free energies*
- *Reaction rates*