Lodz University of Technology
Institute of Applied Radiation Chemistry

A NEW DIBROMETHANE MODEL FOR SIMULATIONS IN LIQUID PHASE

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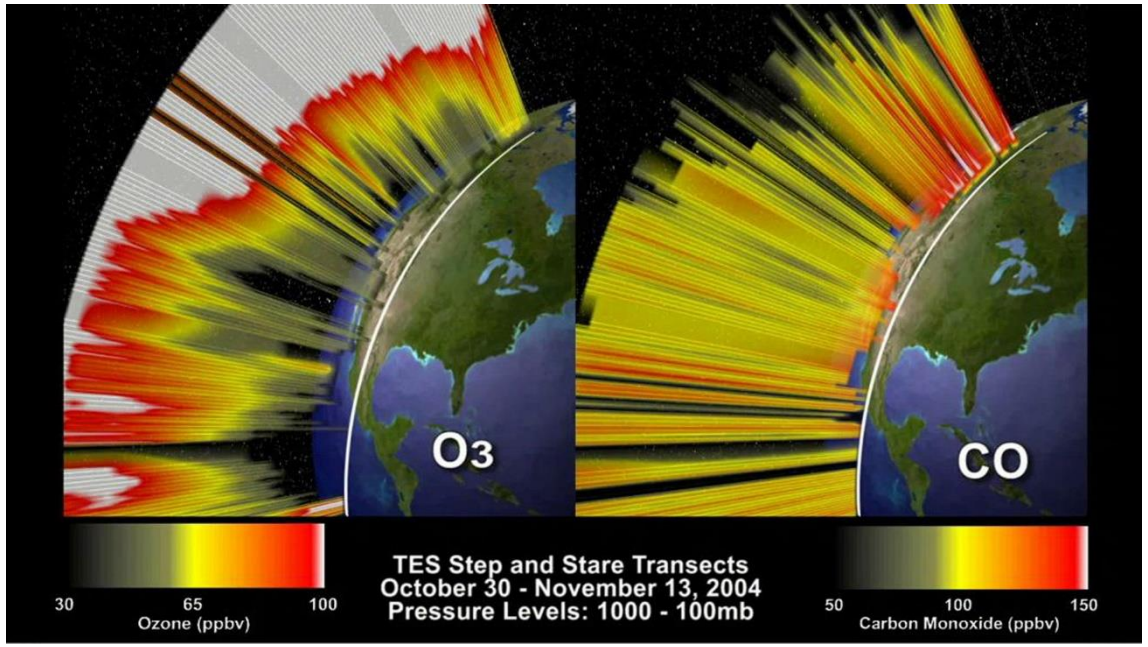
Dibromomethane (DBM)



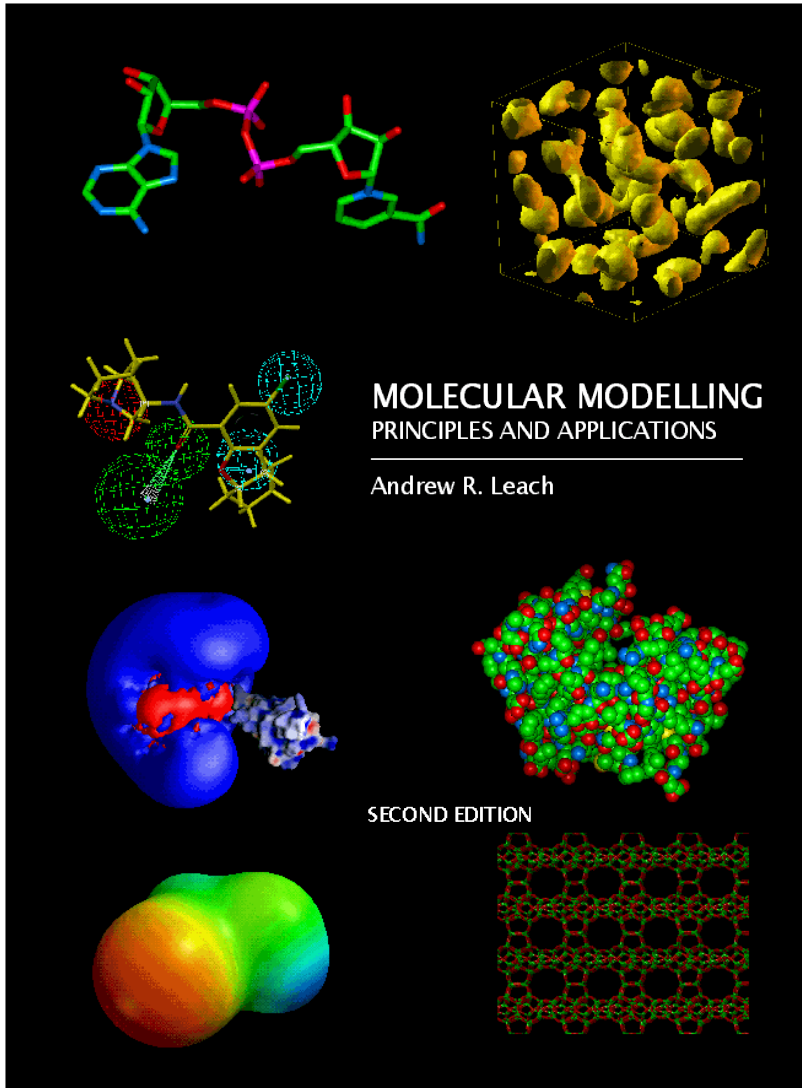
jpl.nasa.gov

www.biocean-algues-marines.com

Experimental density = 2.477 g/cm^3

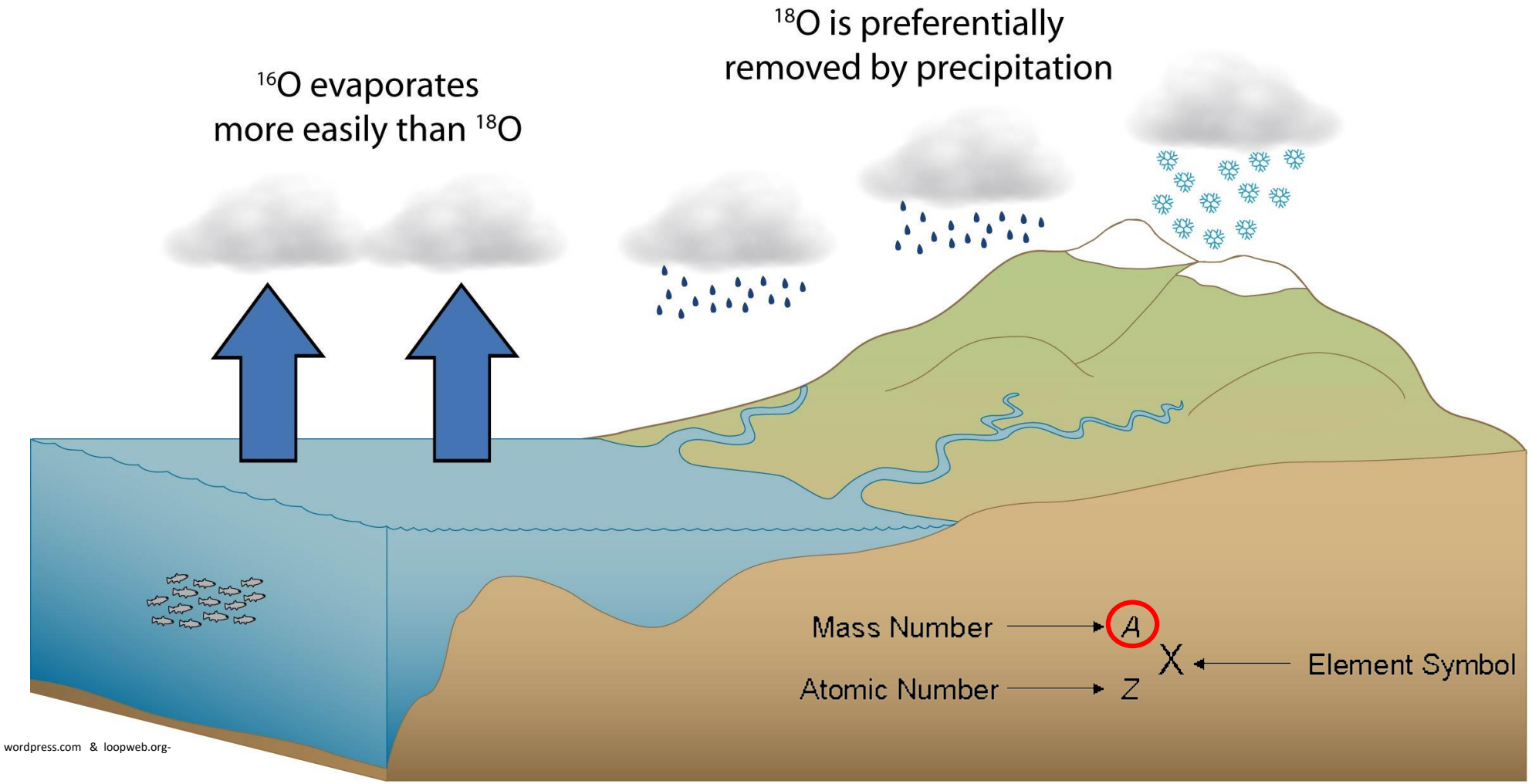
Experimental dipole moment = 1.43 D

Can they be reproduce ?



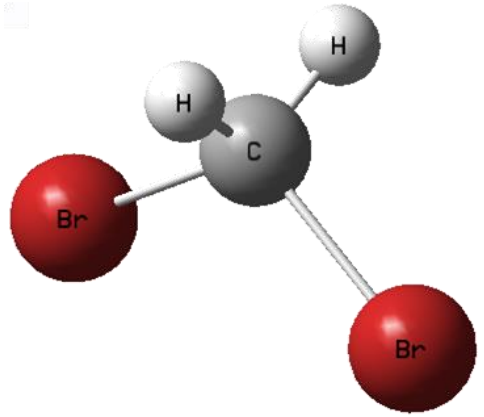
booksites.net

¿What is a isotope effect and why ought I to care ?



Geometry optimisation of DBM

- Density Functional Theory (DFT): **B3LYP & M06-2X**
- Coupled cluster (CC): **CCSD**
- Møller–Plesset perturbation theory (MP): **MP2**
- Basis set : 6-311+g(d,p)
- QM package : Gaussian 9 D.



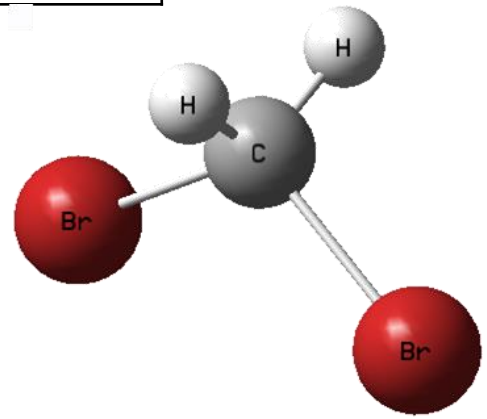
Atom type	Electrostatic partial charges			
	B3LYP	CCSD	M06-2X	MP2
CT	-0.638	-0.605	-0.664	-0.602
HC	0.315	0.316	0.327	0.315
HC	0.316	0.317	0.327	0.315
Br	0.003	-0.014	0.005	-0.014
μ (D)	1.79	2.00	1.85	1.99

Experimental dipole moment = 1.43 D

Level of theory	Bond length, Å		Bond angle (°)		
	CT - Br	CT - HC	HC - CT - HC	HC - CT - Br	Br - CT - Br
B3LYP	1.95	1.08	112.5	107.5	114.4
CCSD	1.94	1.08	111.5	107.9	114.0
M06-2X	1.93	1.08	112.1	107.8	113.8
MP2	1.93	1.09	111.5	107.9	114.0

Geometry vs general AMBER force field parameters of DBM

Level of theory	Bond length, Å		Bond angle (°)		
	CT - Br	CT - HC	HC - CT - HC	HC - CT - Br	Br - CT - Br
B3LYP	1.95	1.08	112.47	107.53	114.39
CCSD	1.94	1.08	111.5	107.86	113.95
M06-2X	1.93	1.08	112.14	107.75	113.78
MP2	1.93	1.09	111.52	107.86	113.96



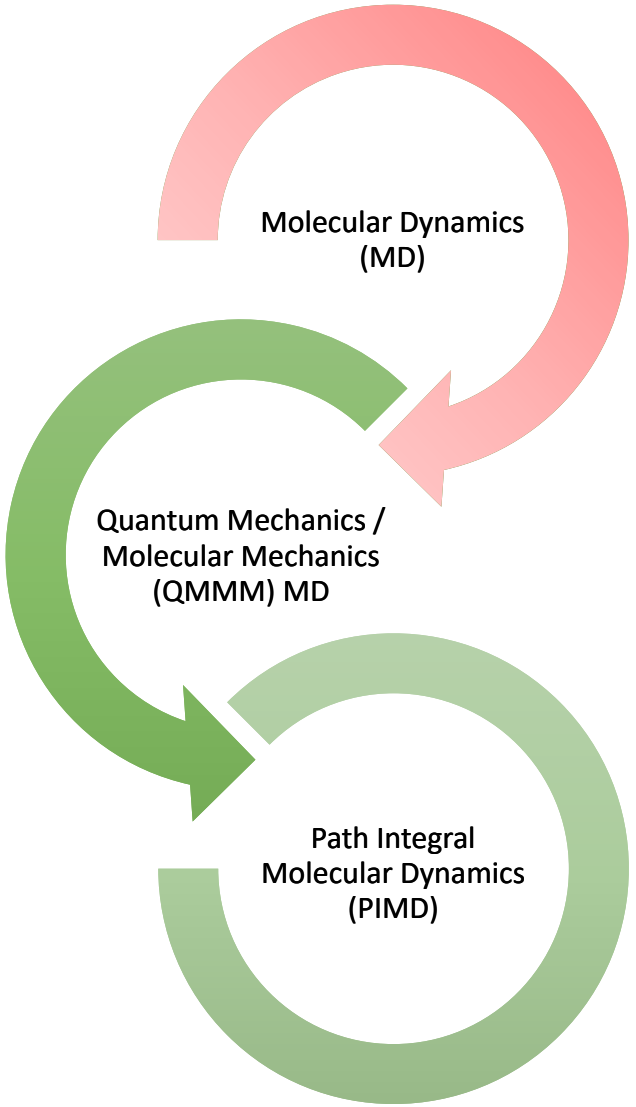
Bond Parameters		
BOND	K_b (kcal ·mol^{-1}·Å^2)	r_0 (Å)
Br - CT	159	1.944
CT - HC	340	1.09
Angle Parameters		
Angle	K_θ (kcal ·mol^{-1}·rad^2)	θ_0 (deg)
HC - CT - HC	35	109.5
HC - CT - Br	43.18	108.111
Br - CT - Br	66.91	113.001
Atom Van der Waals parameters		
Atom	ε (kcal ·mol^{-1})	R (Å)
CT	0.1094	1.908
HC	0.0157	1.287
Br	0.42	2.02

Simulation flow

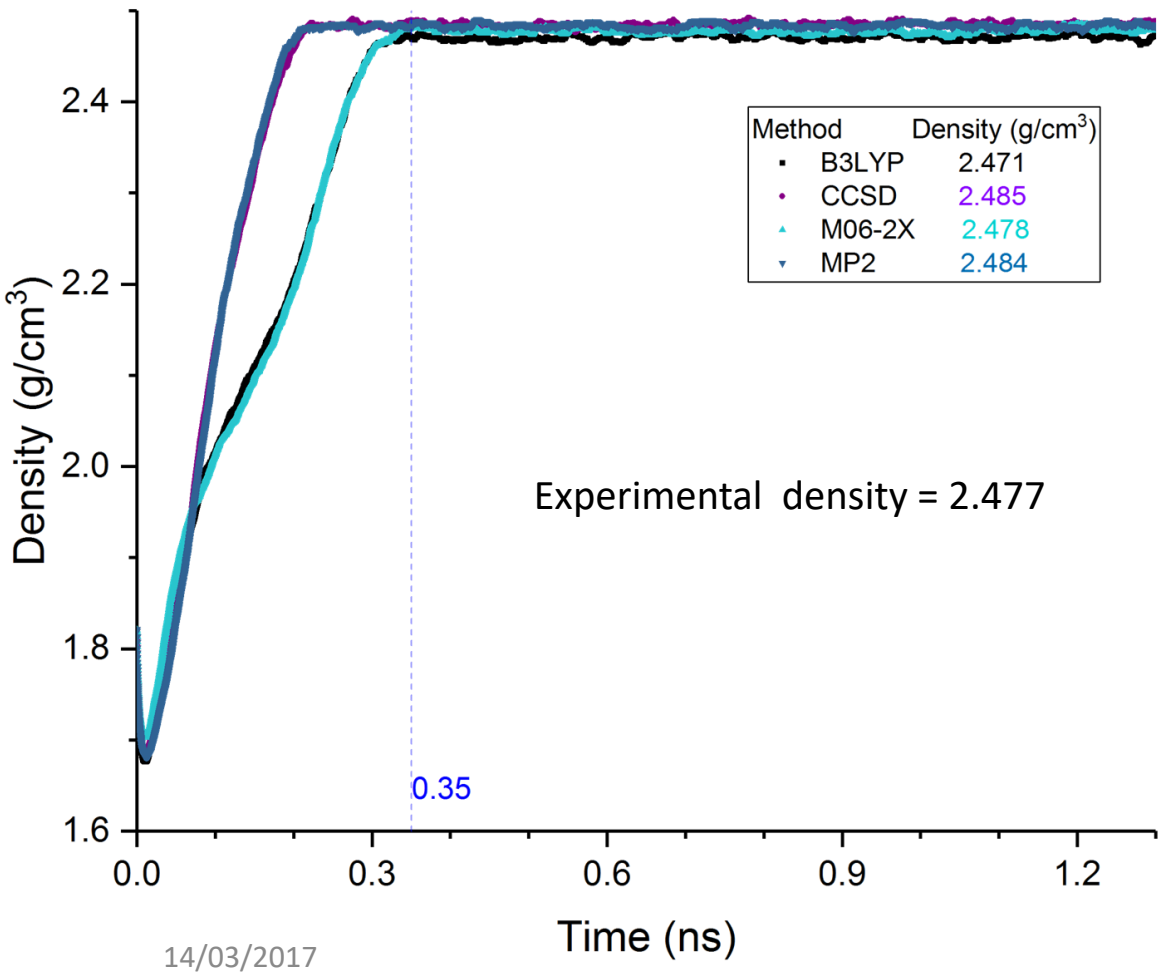
DBM system is named, based on the level of theory used for the geometry optimisation of the molecule:

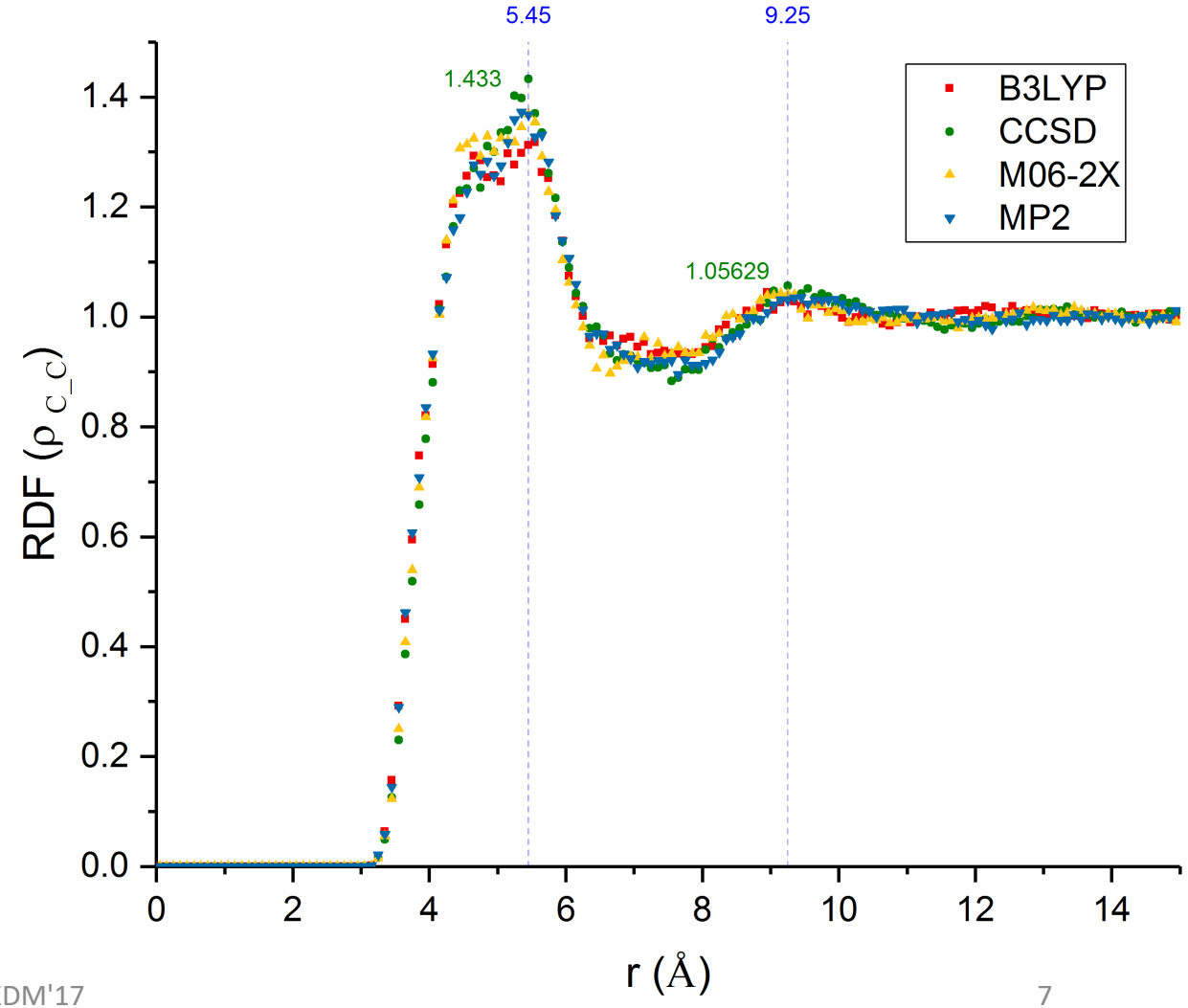
B3LYP - M06-2X - CCSD - MP2

40 Å box - Periodic
298.15 K
Time-step : 0.5 fs
Heating time : 0.3 ns
Langevin Thermostat
Simulation time : 2.2 ns
AMBER 14



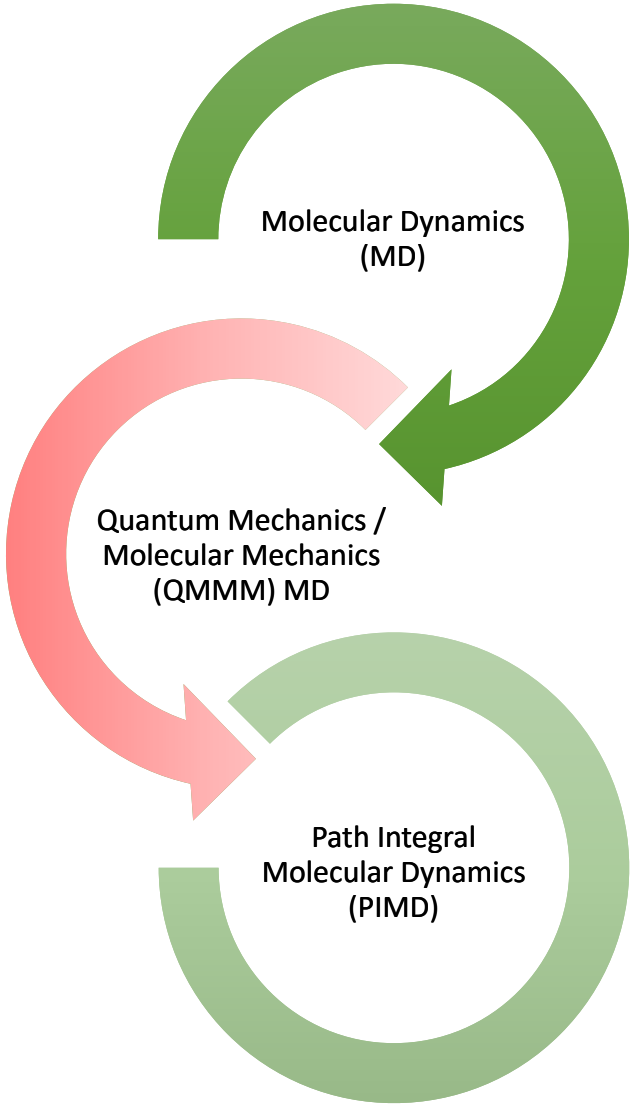
MD > density & radial distribution function



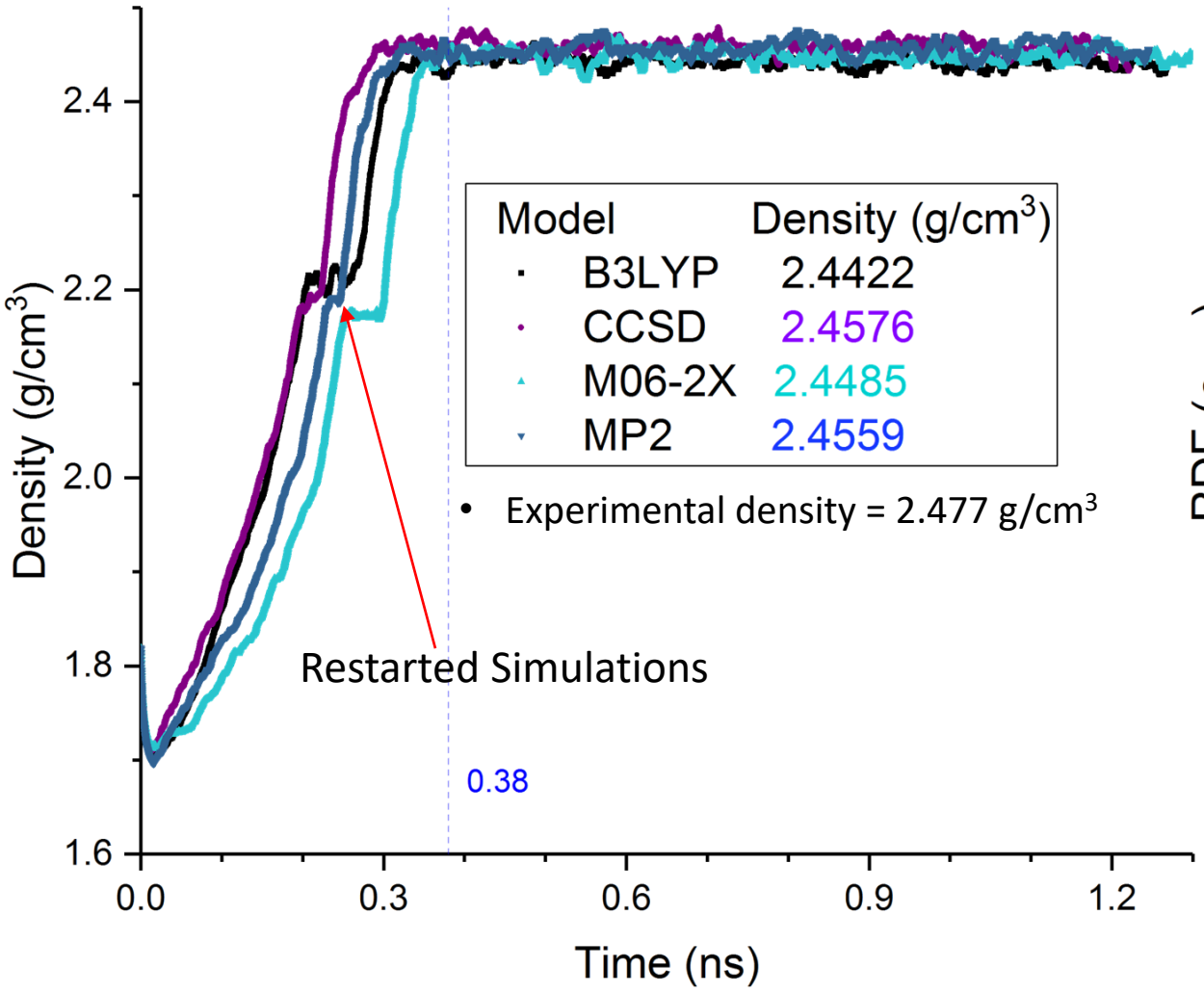


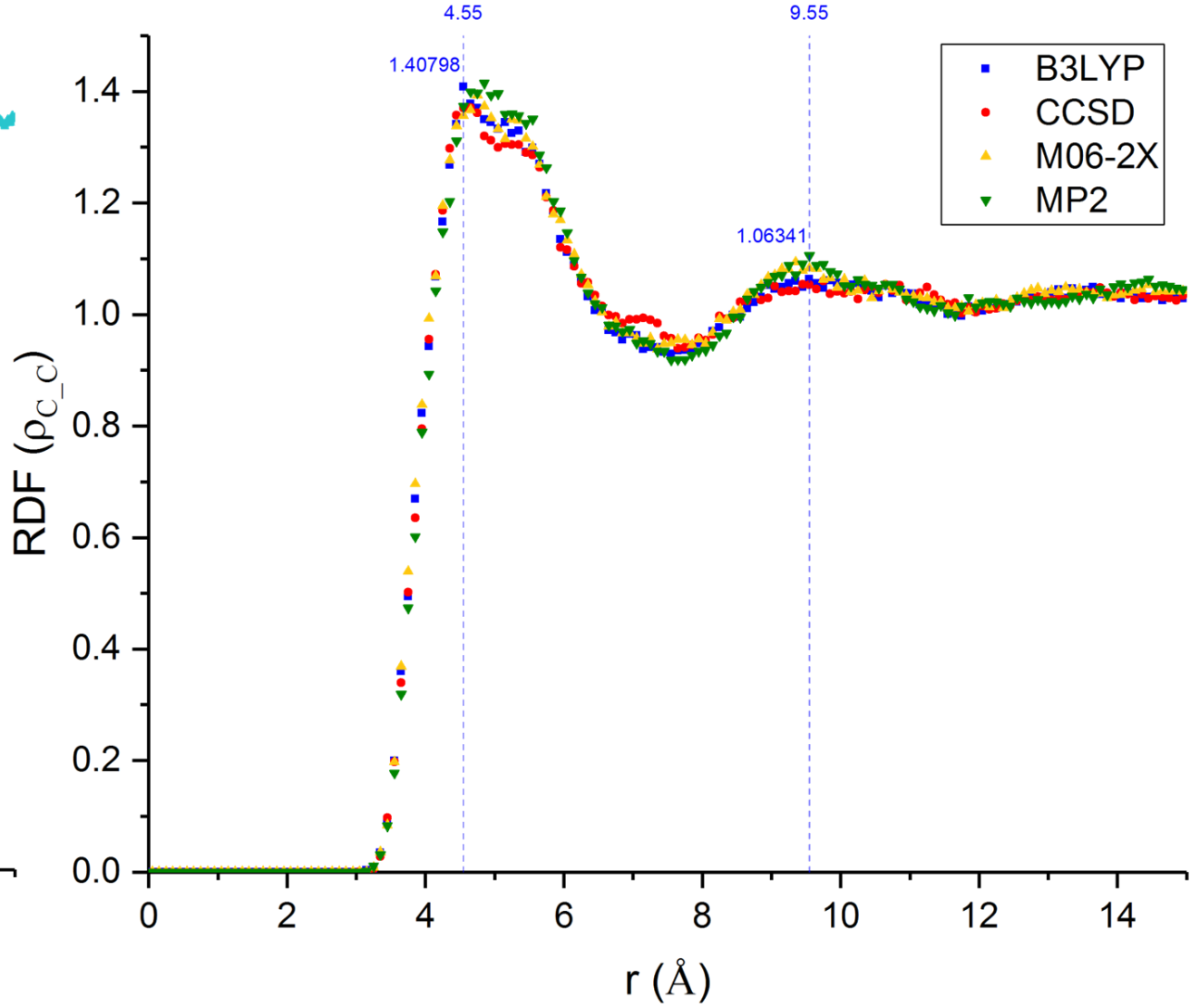
Simulation flow

40 Å box - Periodic
298.15 K
QM : PM6
Time-step : 0.5 fs
Heating time : 0.3 ns
Langevin Thermostat
Simulation time : 2.2 ns

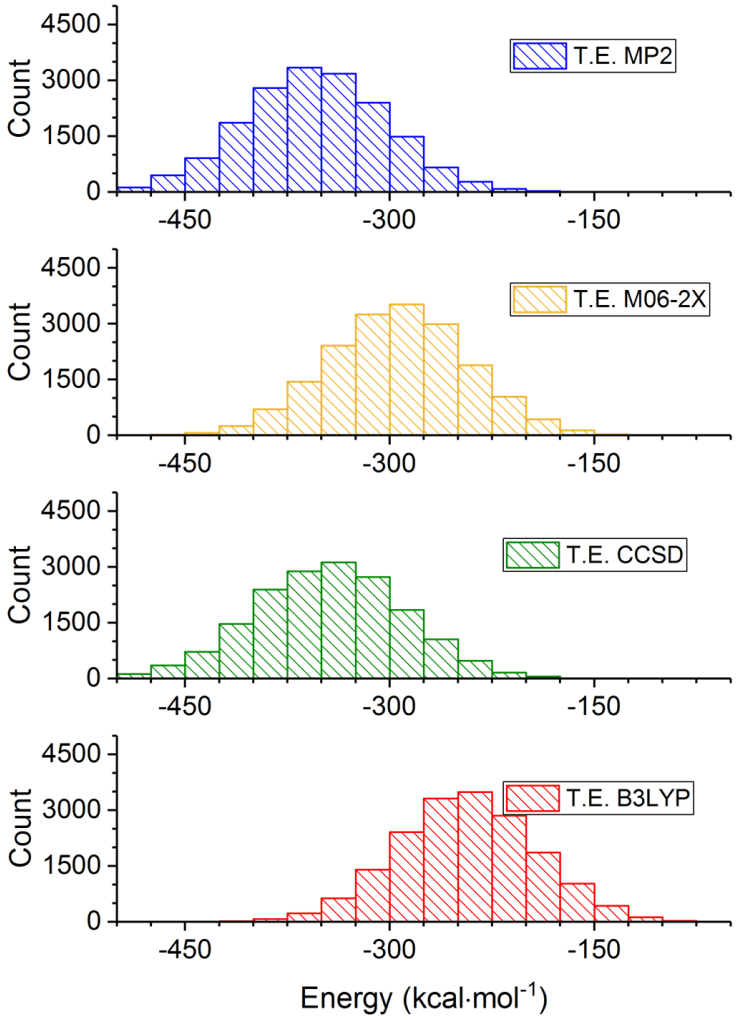


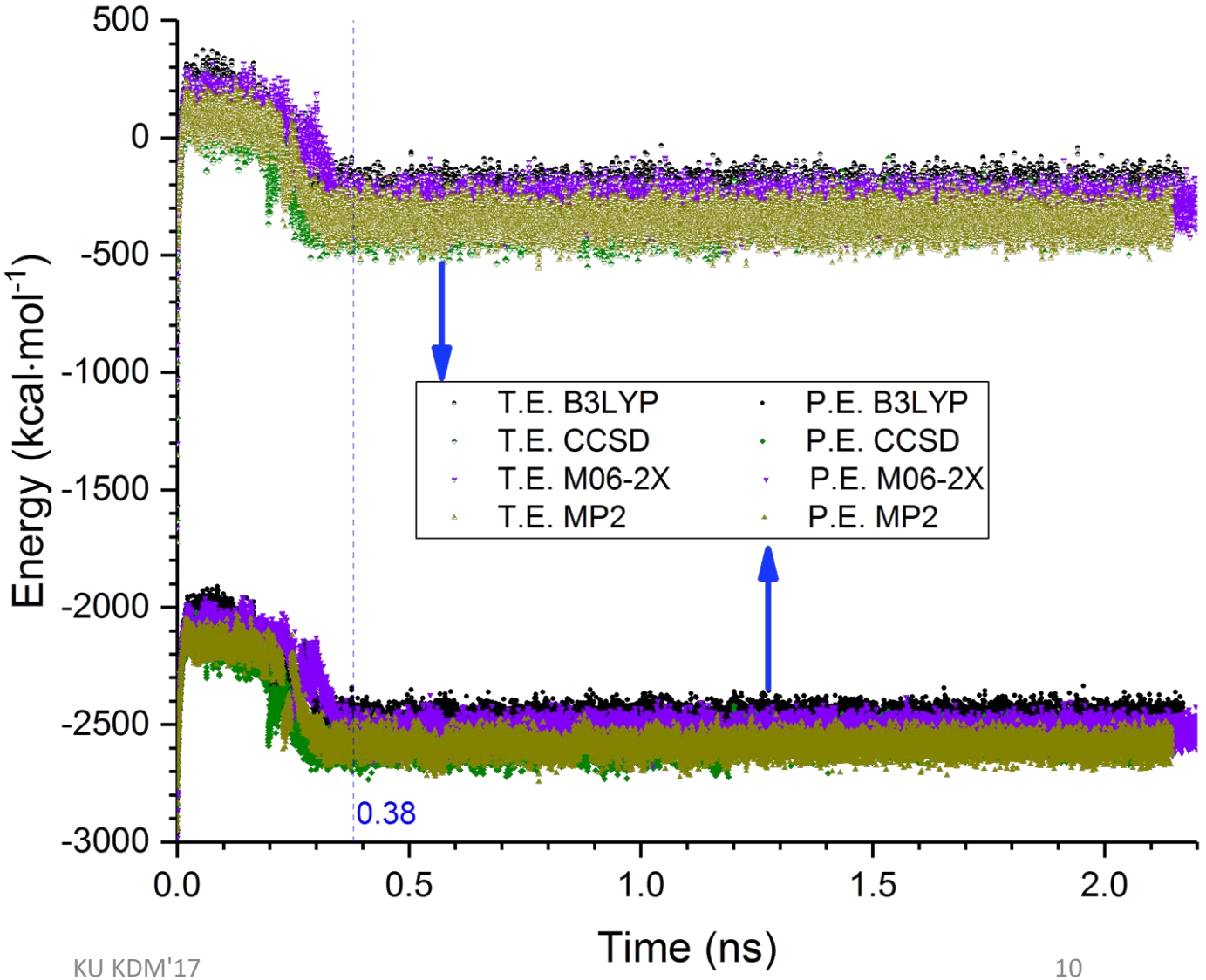
QM/MM MD > Density





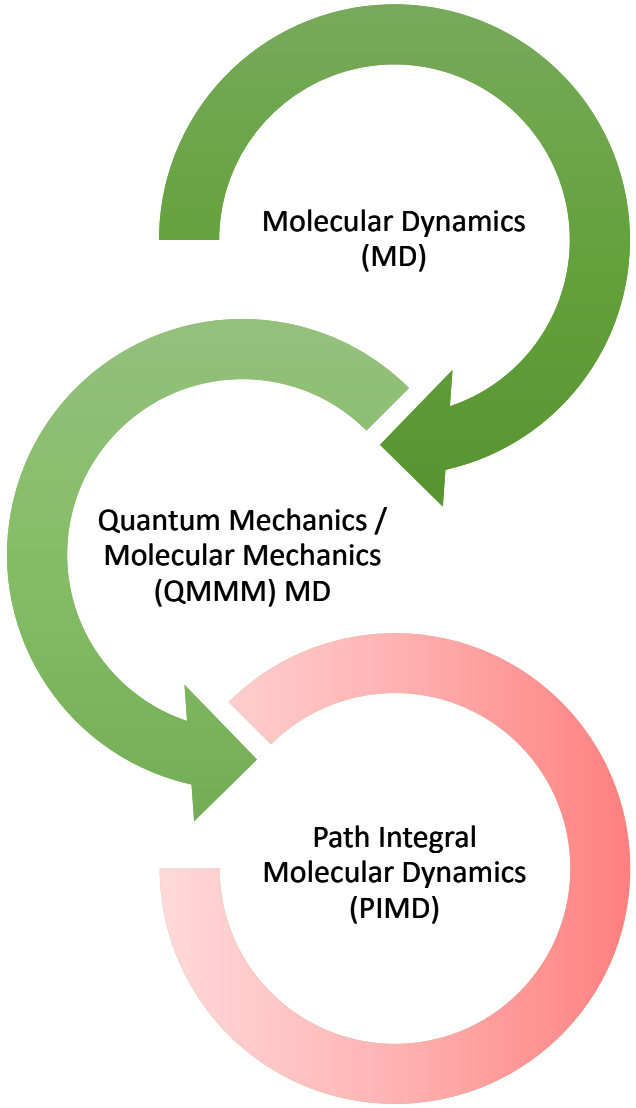
QM/MM MD > Energy of the system



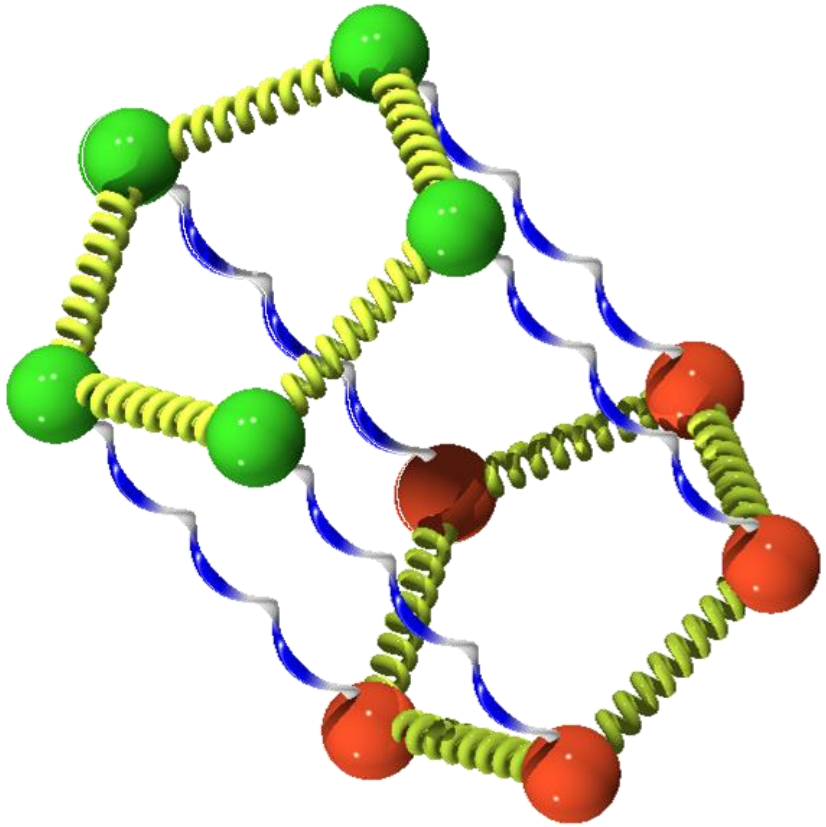


Simulation flow

Restart file from QM/MM MD
298.15 K
Time-step : 0.2 fs
Simulation time : 0.8 ns
Nosé-Hoover chain thermostat



Path Integral Molecular Dynamics (PIMD)



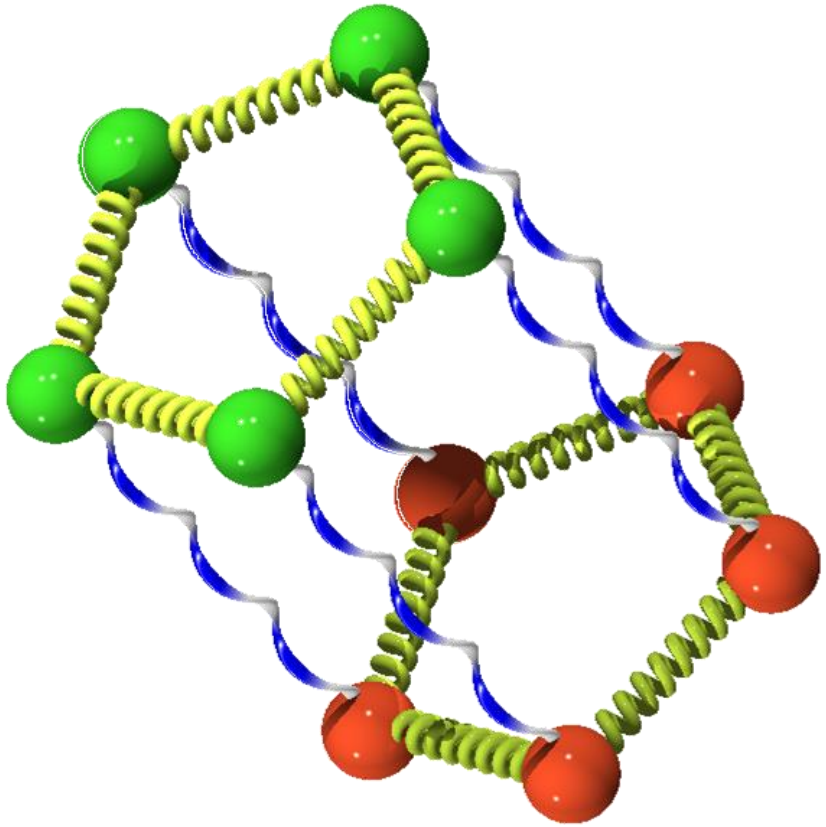
SklogWiki

Path integral formalism represents an isomorphism between a quantum system and an equivalent classical model system.

Hamiltonian for the one-dimensional system

$$H = \frac{p^2}{2m} + v(x) = T + V \qquad [T,V] =/ 0$$

Path Integral Molecular Dynamics (PIMD)



SklogWiki

Canonical partition function

$$Z(\beta) = \lim_{\mathrm{P}\to\infty} \left(\frac{m\mathrm{P}}{2\pi\beta\hbar^2}\right)^{\mathrm{P}/2} \int_{x_{\mathrm{P}+1}=x_1} dx_1 \cdots dx_{\mathrm{P}}\, e^{-\beta U_{eff}},$$

Effective potential

$$U_{eff} = \sum_{i=1}^{\mathrm{P}} \left[\frac{m\mathrm{P}}{2\beta^2\hbar^2}\left(x_{i+1} - x_i\right)^2 + \frac{1}{\mathrm{P}}U\left(x_i\right)\right],$$

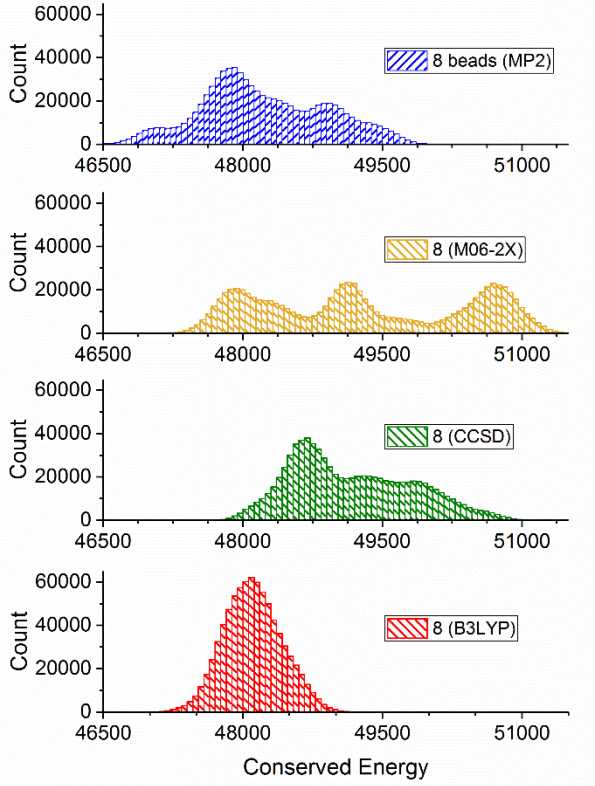
Harmonic springs

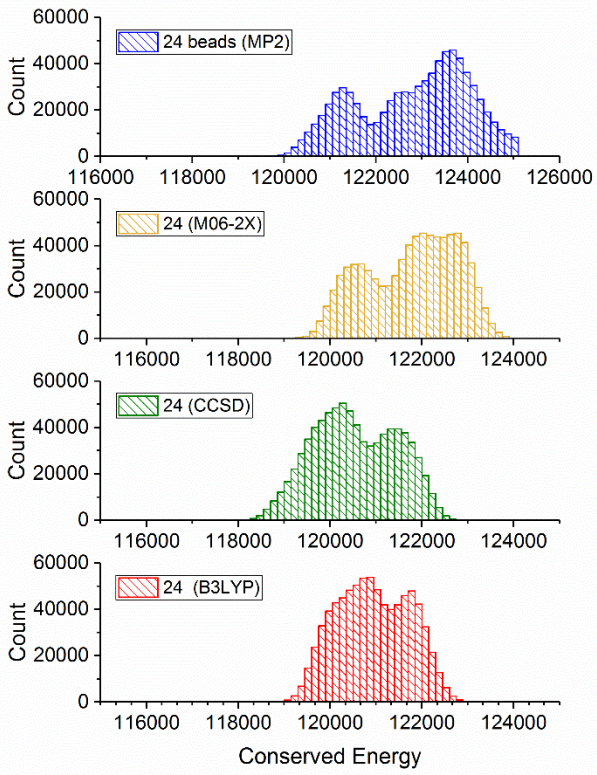
Classical Hamiltonian

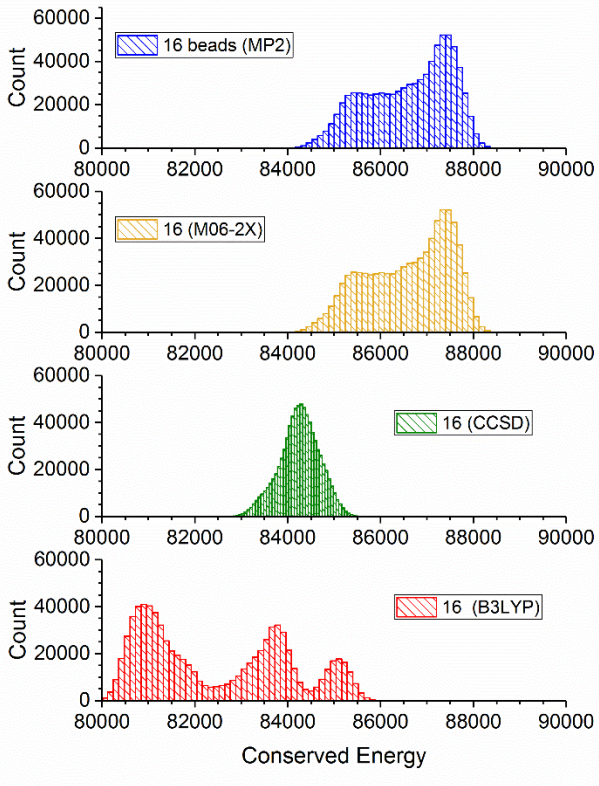
Spring constant $$k(P,\beta) = \frac{m\,P}{\hbar^2\,\beta^2} = \frac{m\,P\,k_B^2\,T^2}{\hbar^2}$$

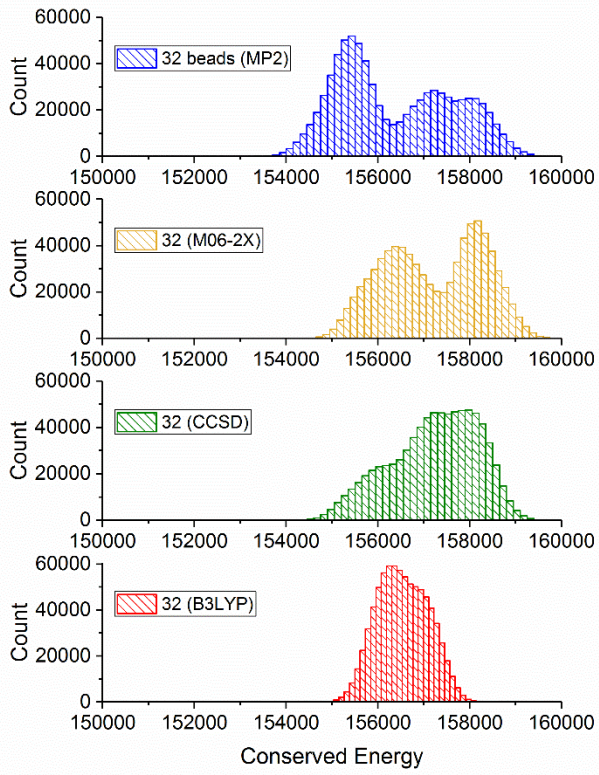
PIMD > Conserved Energy

- Performed simulations with 8, 16, 24 , & 32 “beads”

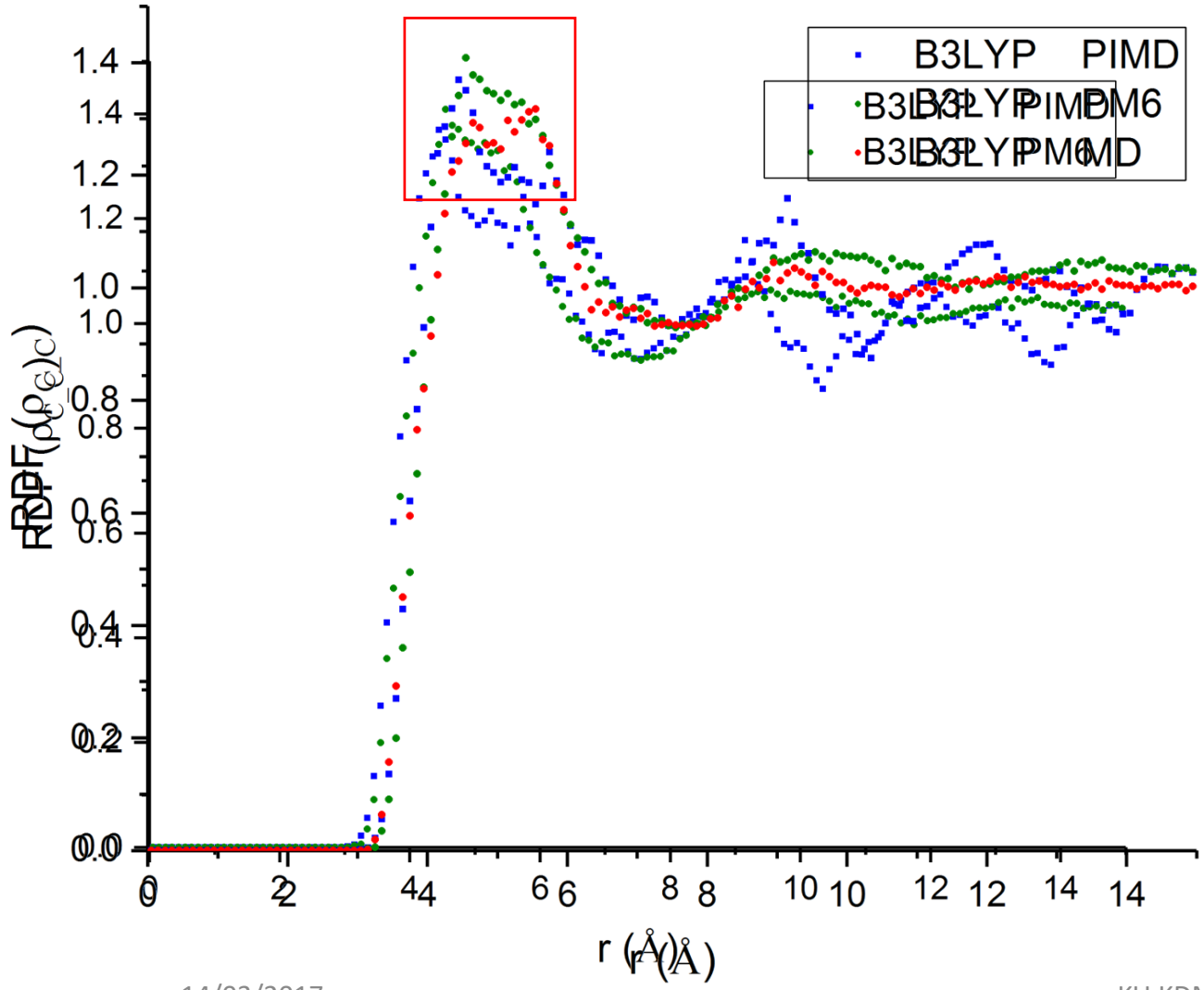


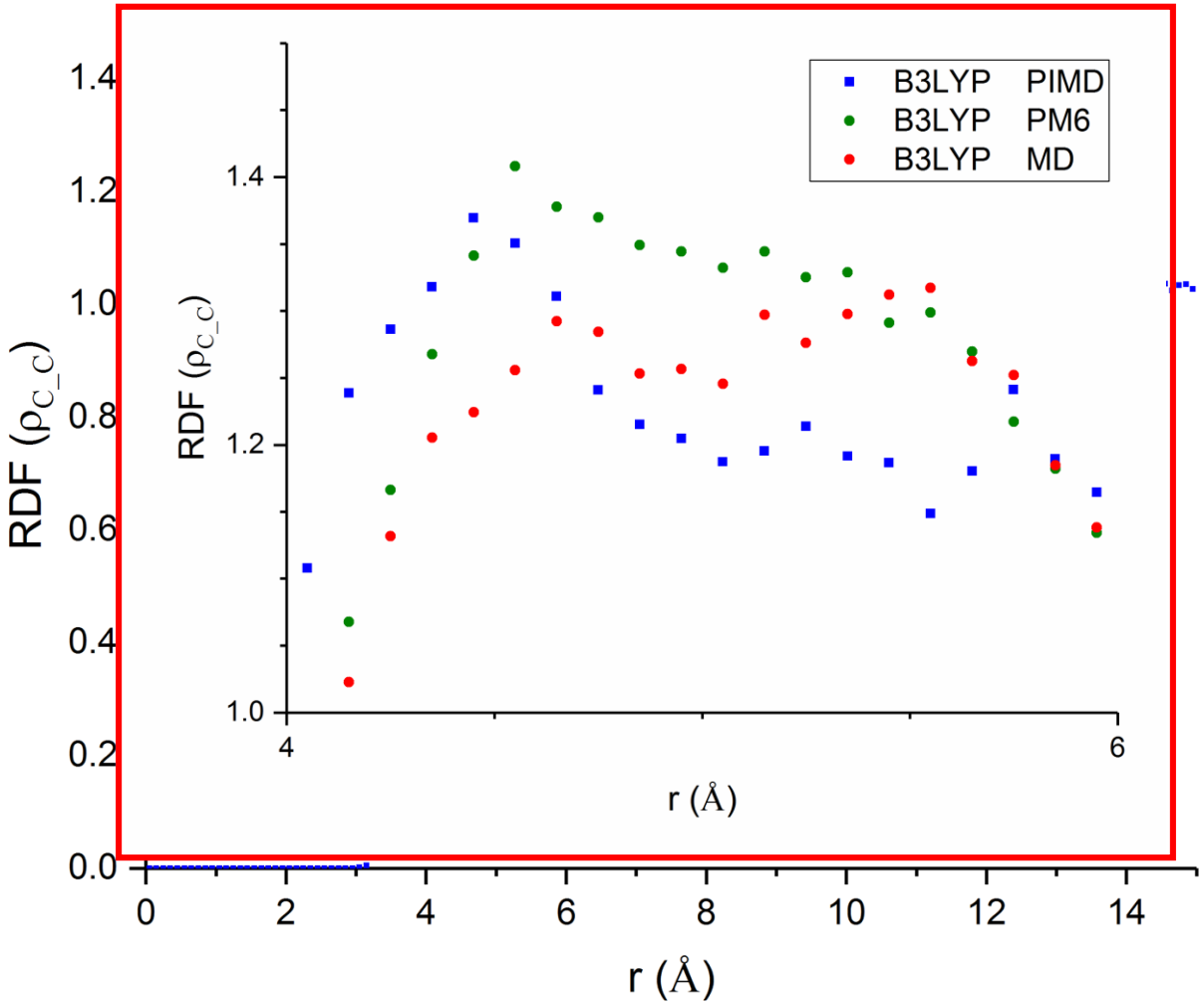




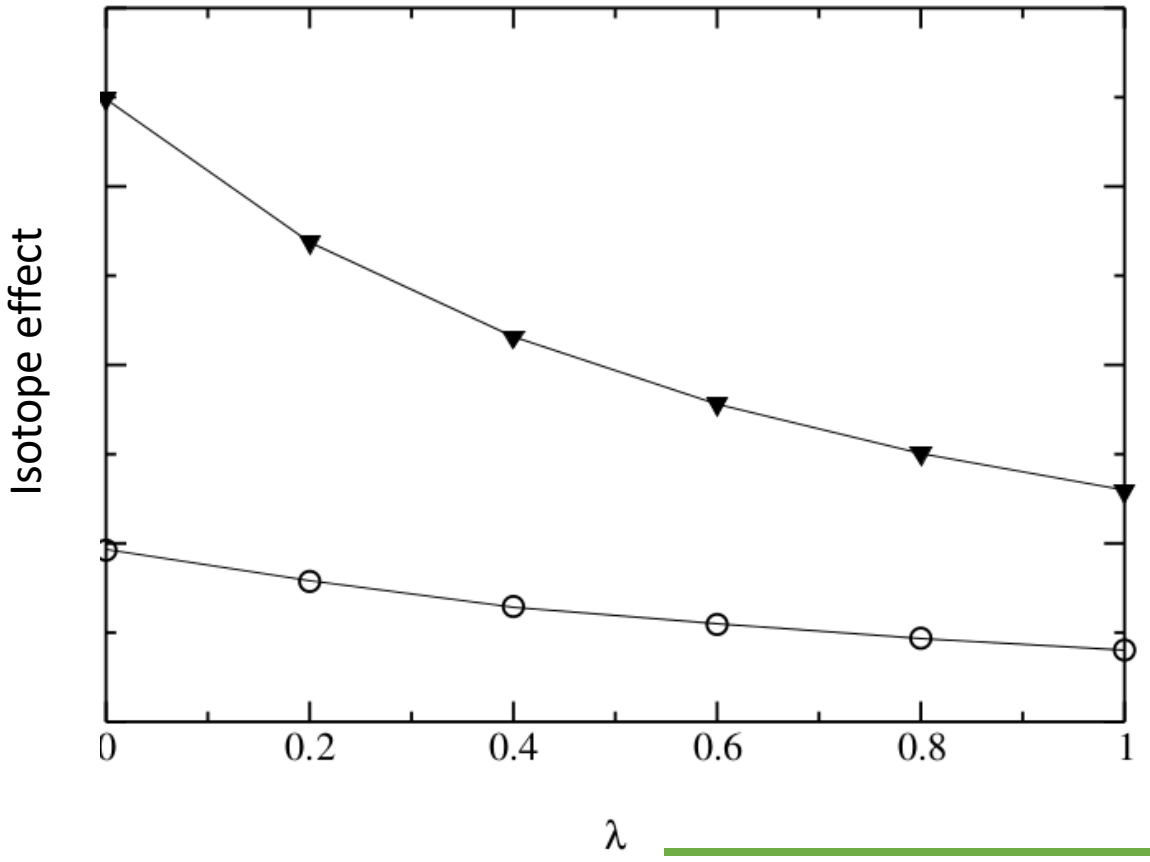


PIMD > RDF comparisons





Equilibrium Isotope Effects (EIE)



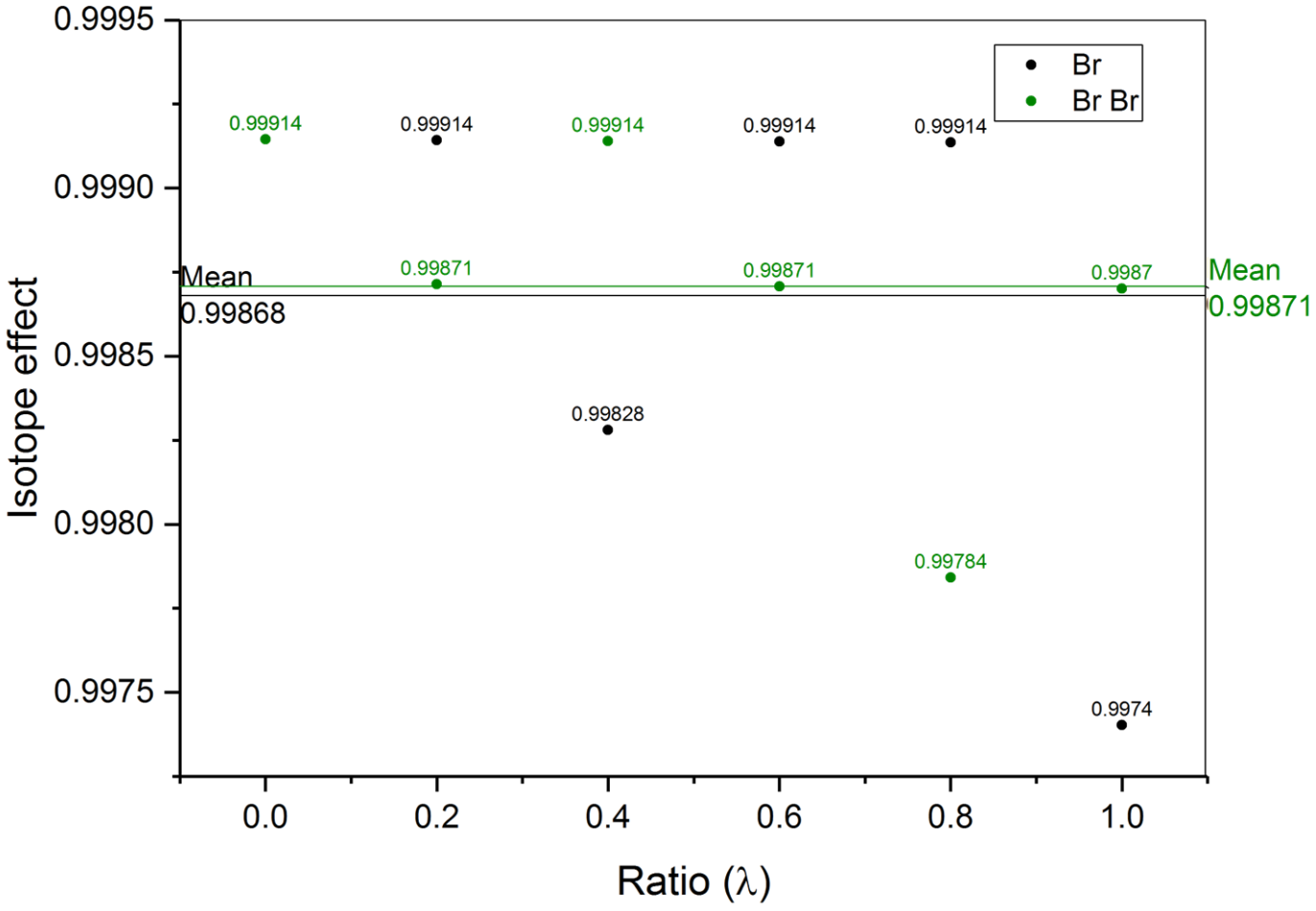
AMBER manual, 2014

$$\mathrm{EIE} := \frac{K^{(l)}}{K^{(h)}}.$$

$^{12}_{6}\mathrm{C}$ $^{13}_{6}\mathrm{C}$

Interpolation between the masses, lighter (λ = 0) and heavier (λ = 1)

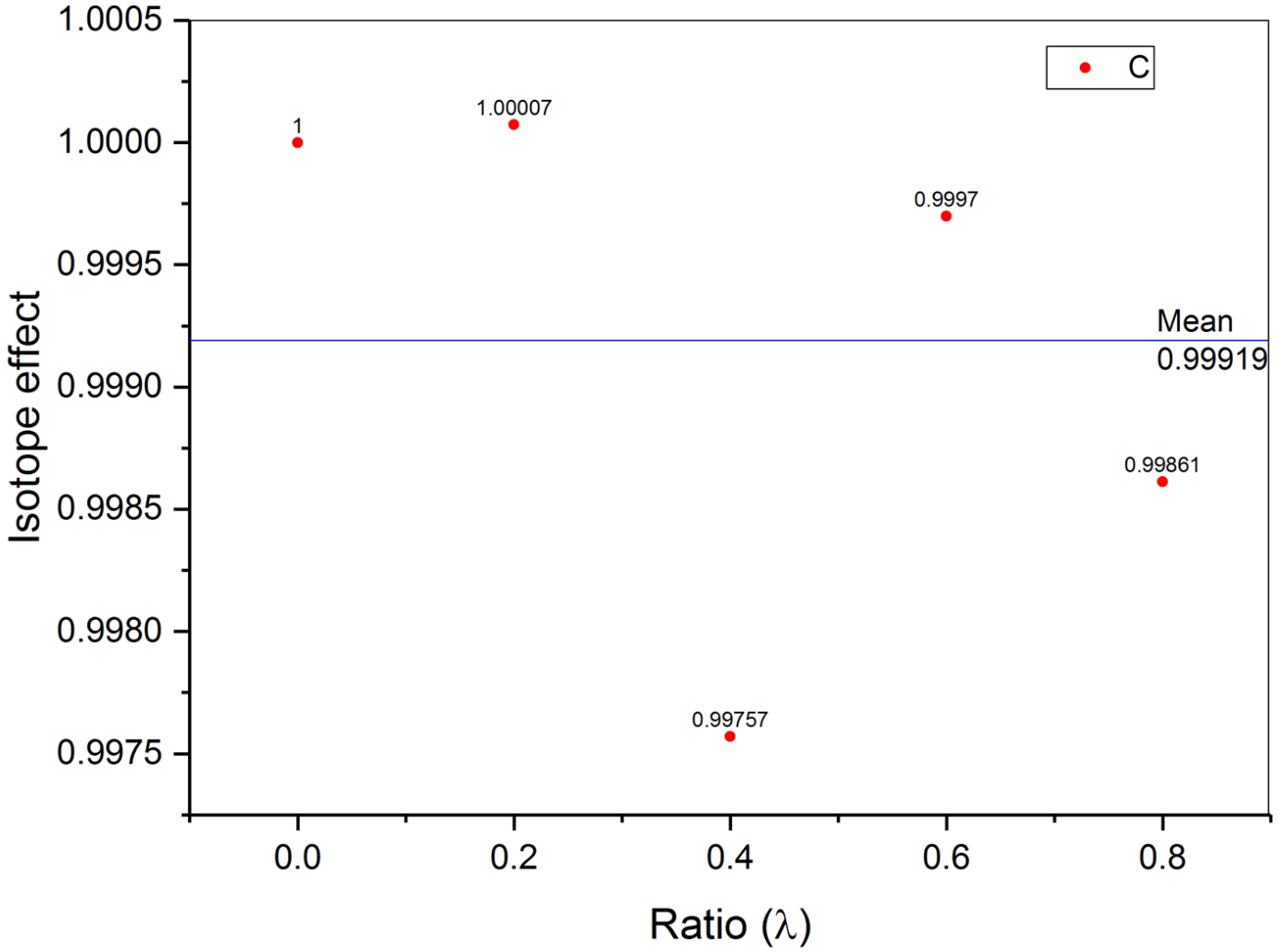
EIE> (Bromide)



$^{79}_{35}Br$ $^{81}_{35}Br$

Experimental value : 1.001

EIE> (Carbon)



$^{12}_{6}C$ $^{13}_{6}C$

Experimental value : 0.999

Acknowledgments

Present work was done thanks to the support of SONATA-BIS research grant funded by the National Science Centre, Poland (UMO-2014/14/E/ST4/00041).

Cyfronet – Plgrid.

Thanks for your attention ☺

EIE

means

Equilibrium Isotope Effect

by allacronyms.com