Molecular Dynamics simulations of sulfuric acid cluster collisions

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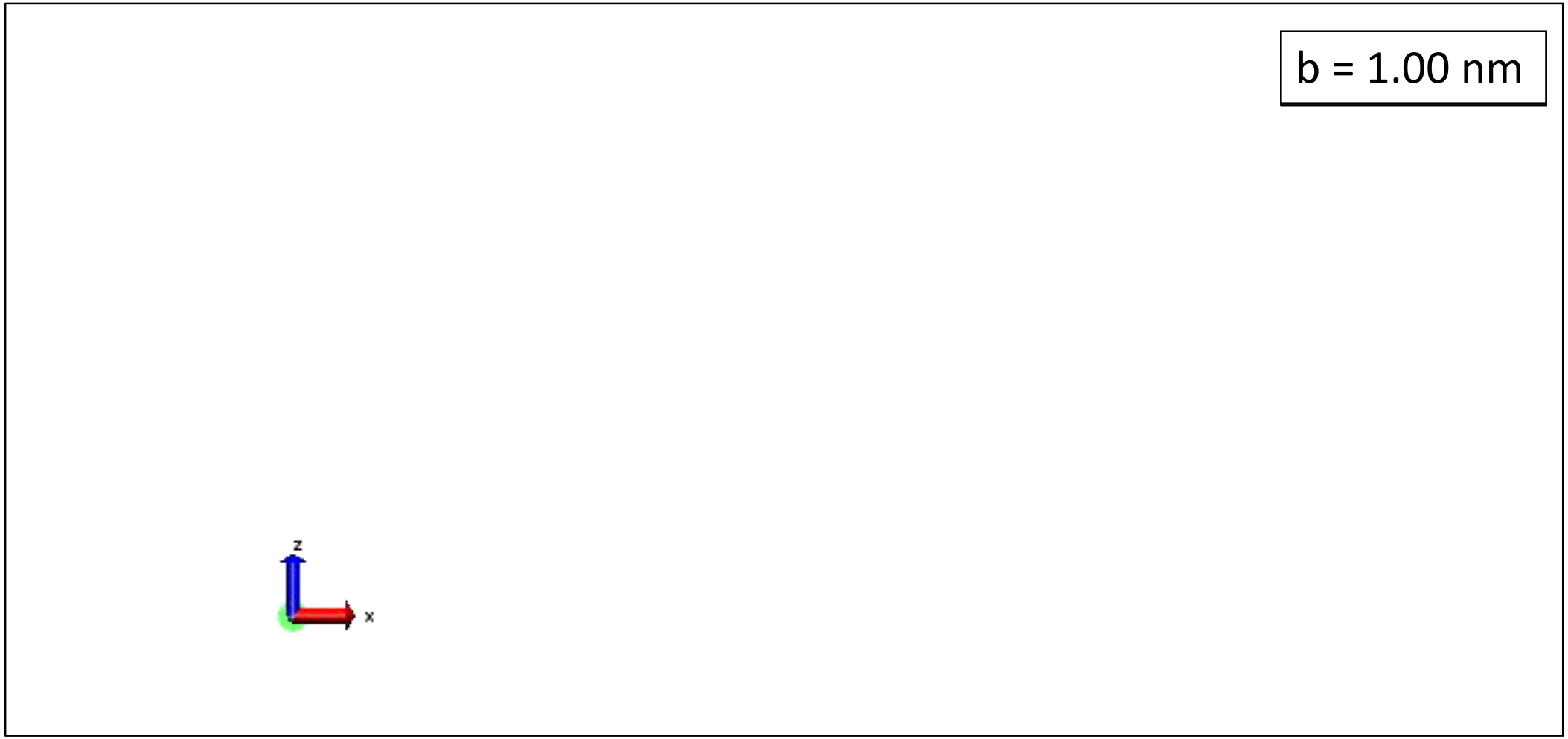
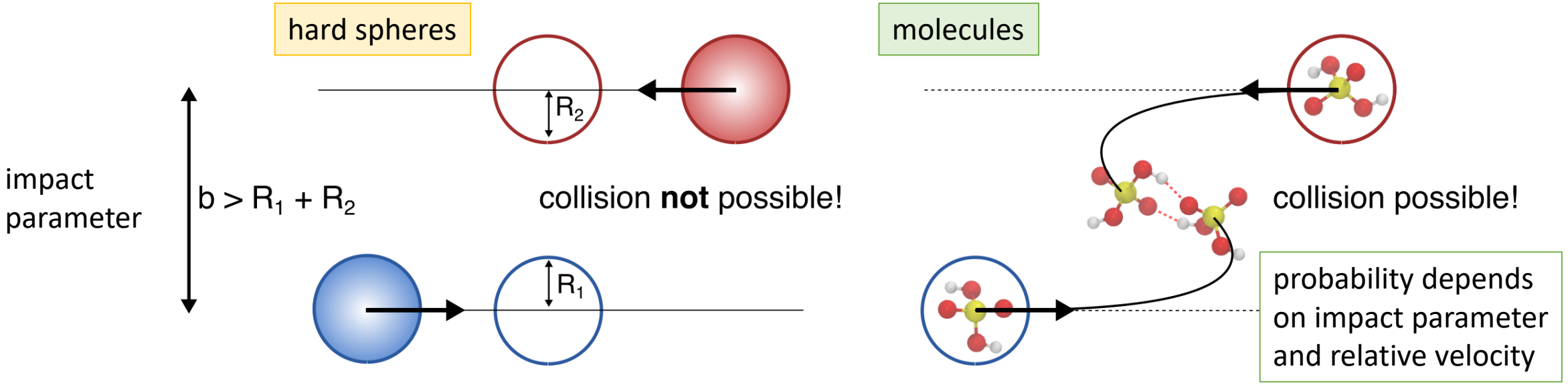
Molecular Dynamics of two H_2SO_4 molecules colliding



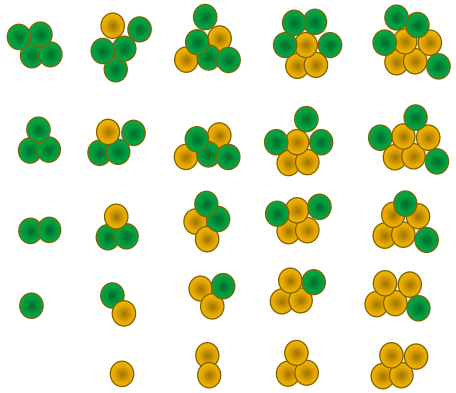
- v_{rel} = 200 m/s, OPLS-AA force field (sulfuric acid dipole moment = 3.07 Debye)

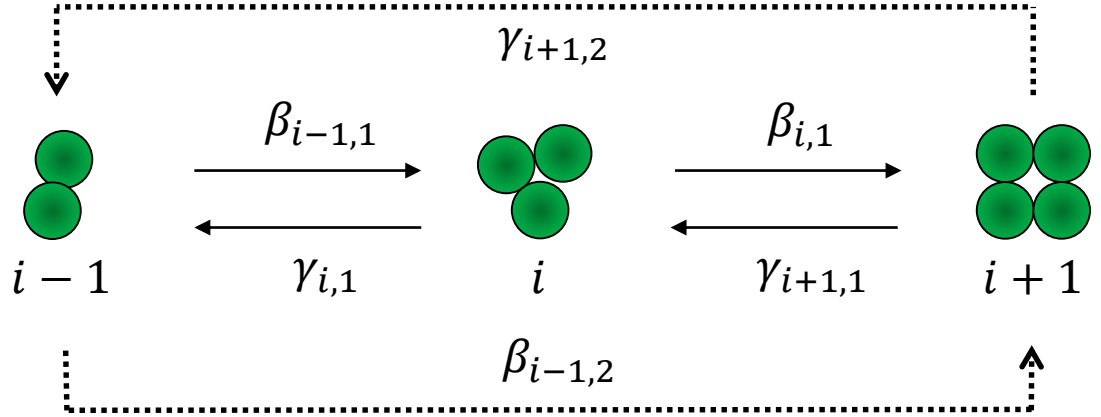


- Molecules have long-ranged attractive interactions:
  - Charge – charge (Coulomb): $U(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$
  - Charge – dipole: $U(r) = -\frac{q_1^2 \mu_2^2}{6(4\pi\varepsilon_0)^2 kT r^4}$
  - Dipole – dipole (Keesom): $U(r) = -\frac{\mu_1^2 \mu_2^2}{3(4\pi\varepsilon_0)^2 kT r^6}$
  - Induced dipole – dipole (Debye): $U(r) = -\frac{\mu_1^2 \alpha_2}{(4\pi\varepsilon_0)^2 r^6}$
  - Induced dipole – induced dipole (London dispersion): $U(r) = -\frac{4}{3}\frac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2 r^6}$

  } Van der Waals interaction

Motivation: collision coefficients for ACDC code

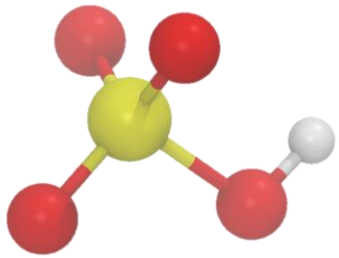




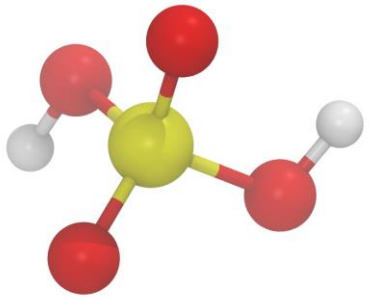
$$\frac{dc_i}{dt} = \frac{1}{2}\sum_{i'<i} \beta_{i',(i-i')}\, c_{i'}\, c_{(i-i')} + \sum_{i'} \gamma_{(i+i'),i'}\, c_{(i+i')} - \sum_{i'} \beta_{i,i'}\, c_i\, c_{i'} - \frac{1}{2}\sum_{i'<i} \gamma_{i,i'}\, c_i - \text{sinks} \,(+\text{ sources})$$

- cluster concentrations c_i
- **collision coefficients $\boldsymbol{\beta_{i,j}}$**
- evaporation coefficients $\gamma_{i,j}$ (lifetime = $1/\gamma_{i,j}$)
- sinks: coagulation sink to larger particles, wall losses (in the lab)
- sources: for example single vapour molecules can have sources (emissions, air chemistry)

1. Force Field validation



HSO_4^-



H_2SO_4

$$U(R) = \sum_{bonds} k_r (r - r_{eq})^2 \qquad \textit{bond}$$

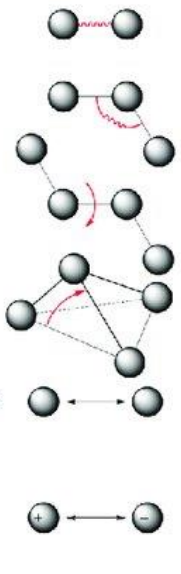
$$+ \sum_{angles} k_\theta (\theta - \theta_{eq})^2 \qquad \textit{angle}$$

$$+ \sum_{dihedrals} k_\phi (1 + \cos[n\phi - \gamma]) \qquad \textit{dihedral}$$

$$+ \sum_{impropers} k_\omega (\omega - \omega_{eq})^2 \qquad \textit{improper}$$

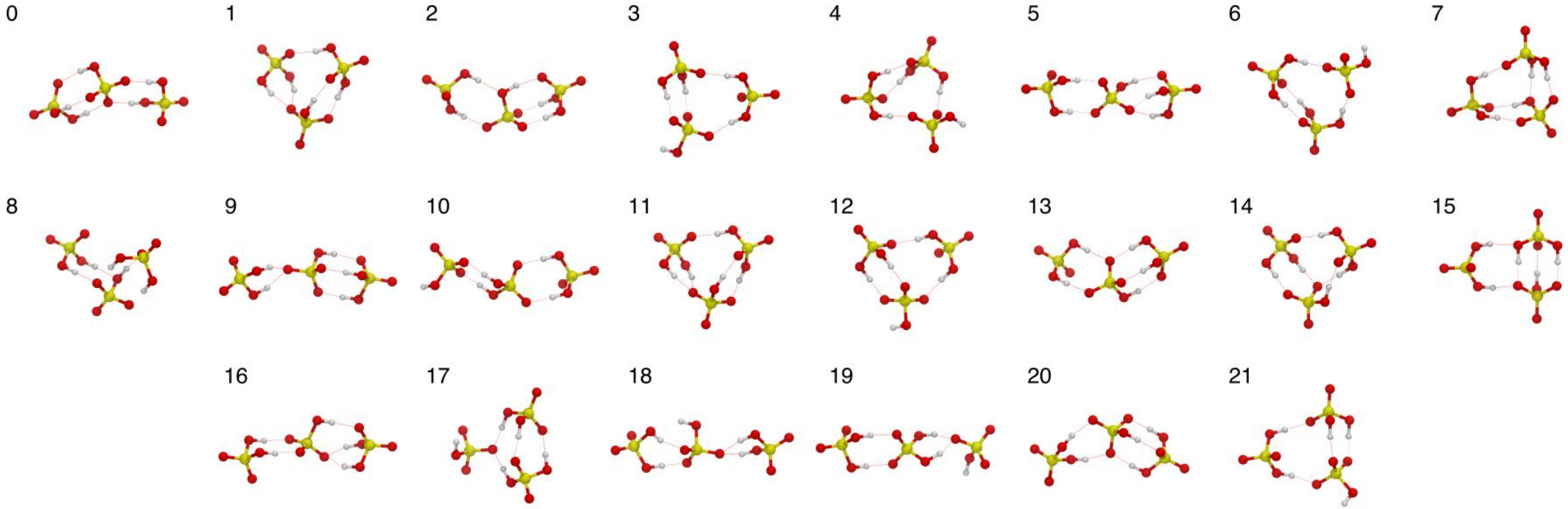
$$+ \sum_{i<j}^{atoms} \varepsilon_{ij} \left[\left(\frac{r_m}{r_{ij}} \right)^{12} - 2 \left(\frac{r_m}{r_{ij}} \right)^{6} \right] \qquad \textit{van der Waals}$$

$$+ \sum_{i<j}^{atoms} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \qquad \textit{electrostatic}$$



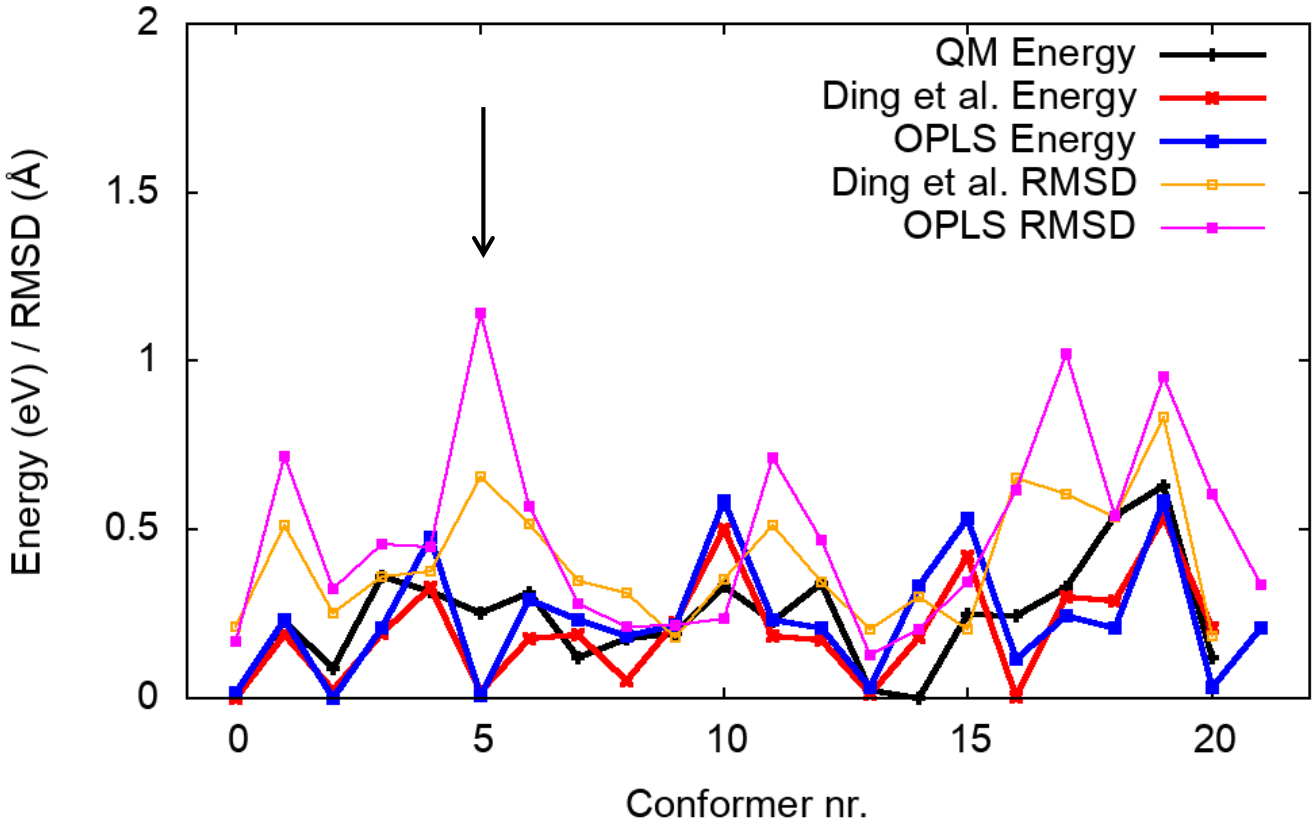
Benchmark set: 22 conformers of $[(H_2SO_4)_2,HSO_4]^-$ trimer

- QM structures optmised using B97X-D / 6-31++G(d,p)
- Two force fields tested:
  - Ding et al. [1] : fitted to DFT calculations of clusters containing sulfuric acid, bisulfate and water
  - OPLS-AA [2] : transferable potential for biological systems



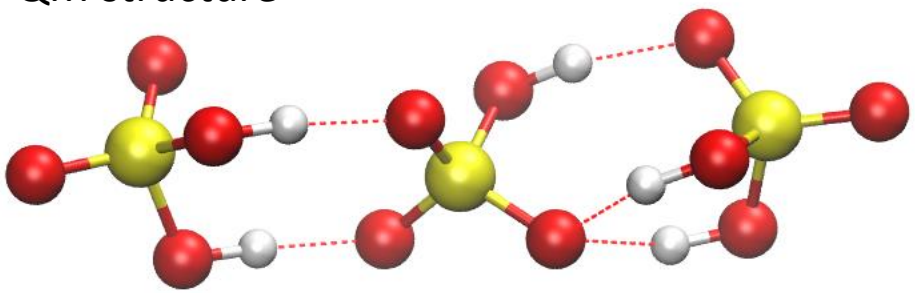
[1] C. G. Ding, T. Taskila, K. Laasonen and A. Laaksonen, Chem. Phys. 287, 7 (2003).
[2] W. L. Jorgensen, D. S. Maxwell and J. Rives-Tirado, J. Am. Chem. Soc. 118(45), 11225 (1996).

Forcefield benchmark results: energies and structures

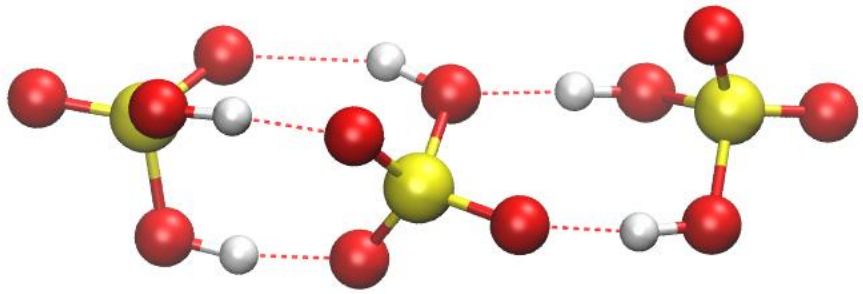


Ex. Conformer nr. 5

QM structure



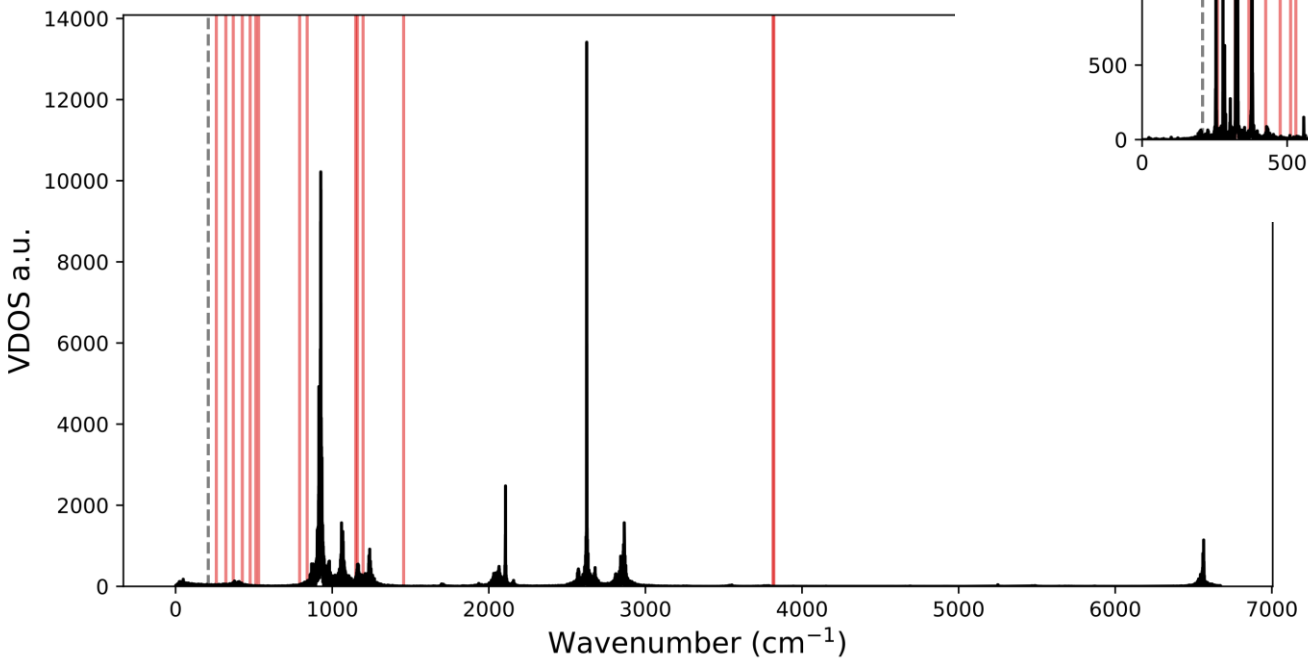
OPLS energy minimized

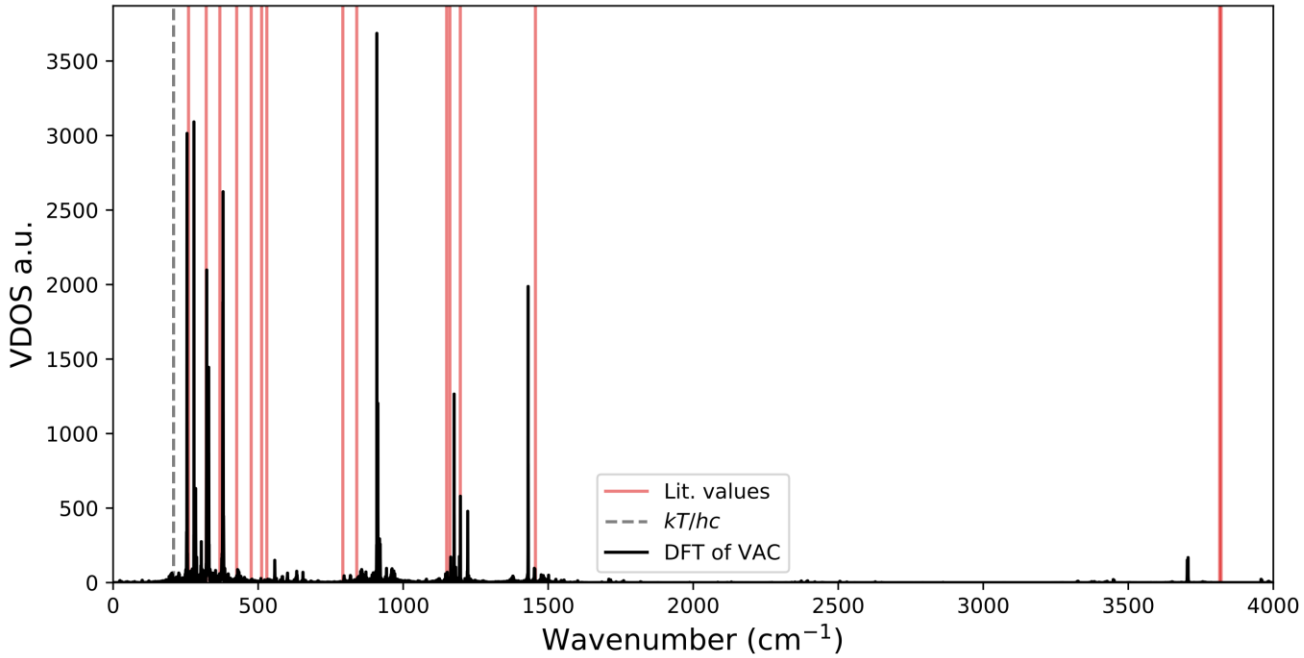


- Force field energies agree better between themselves than with QM energies
- Cases of bad structural match appear to be due to bifurcated hydrogen bonds, unfavorable in both FFs

H_2SO_4 vibrational spectra from FT of velocity ACF

Force field by Ding et al. (structure fitted to DFT of clusters of sulfuric acid/bisulfate/ water) does a very bad job…





OPLS-AA (fitted to gas phase vibrations) reproduces experimental spectra reasonably well!

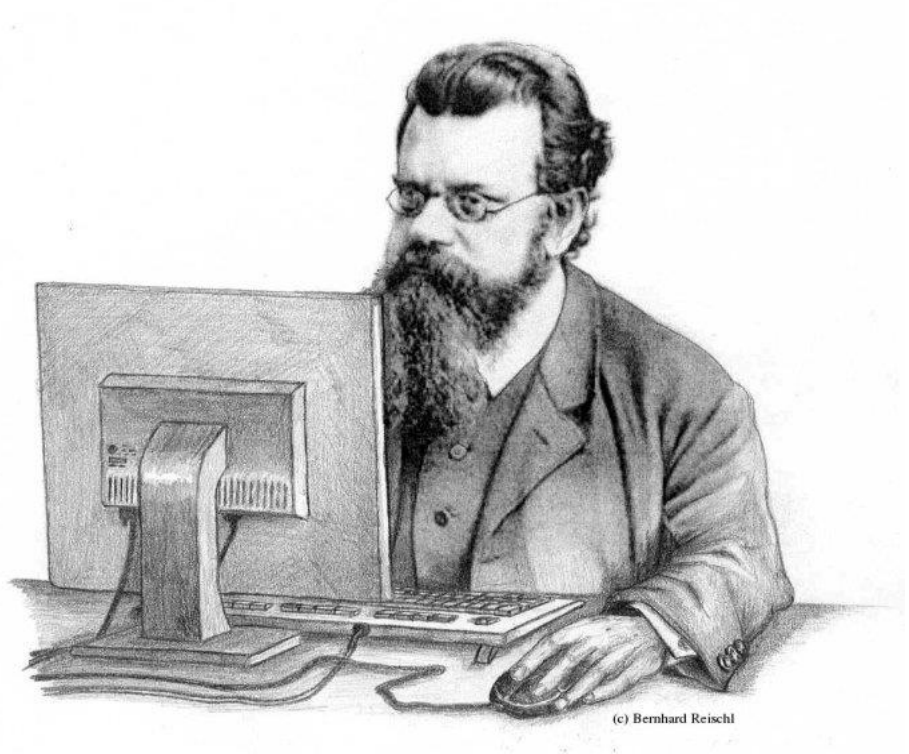
Forcefield benchmark: summary

- Ding et al.
  - Fitted explicitly to sulphuric acid/bisulphate/water cluster structures from DFT
  - Crude molecular mechanics model – no angles and dihedrals fitted, only bonds
  - Gas phase geometries correct; dipole of 3.7 Debye
  - Vibrational spectra horrible
  - No transferability

- OPLS-AA
  - Gas phase geometries correct, dipole of 3.1 Debye
  - QM benchmark a bit worse than Ding et al.
  - Vibrational spectra good
  - Transferable potential

- **OPLS-AA will be used for collision simulations**

2. Collision statistics in molecular dynamics simulation



Hard sphere diameter vs. dimer PMF from simulation

- Hard sphere model of H_2SO_4

  M = 98.09 g/mol, ρ = 1.84 g/cm^3
  --> V/molecule $= M/(\rho \cdot N_A) = 8.8516 \times 10^{-23}$ cm^3

  Volume fraction = 1

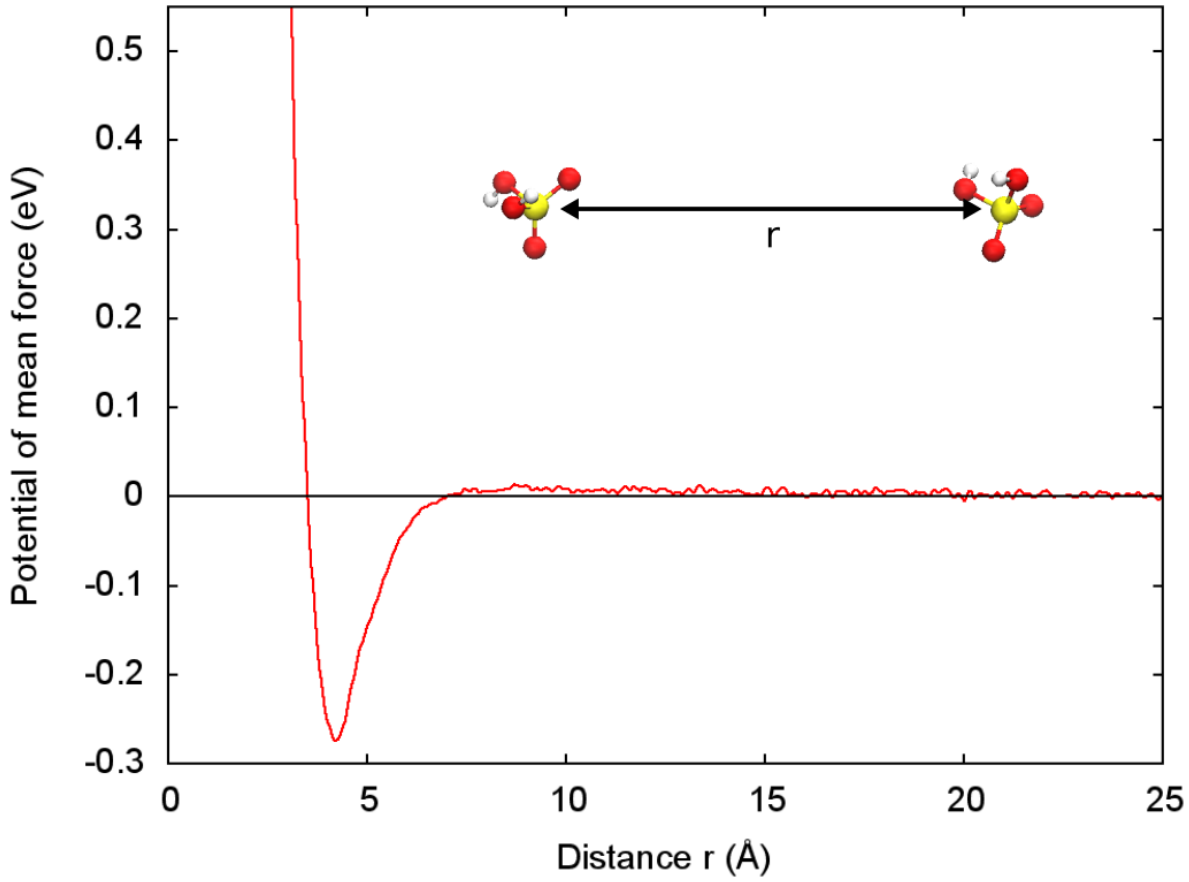
  --> $R = \sqrt[3]{\frac{1 \cdot V \cdot 3}{4\pi}} = 2.76 \times 10^{-8}$ cm = 2.76 Å

  Random close packing: Volume fraction = 0.64

  --> $R = \sqrt[3]{\frac{0.64 \cdot V \cdot 3}{4\pi}} = 2.38 \times 10^{-8}$ cm = 2.38 Å

  Hard sphere diameter: 4.8 – 5.5 Å

- PMF from Metadynamics simulation at 300 K,
  OPLS-AA force field (dipole moment = 3.07 Debye)



PMF has minimum at 4.2 Å, but is attractive to much larger distances!

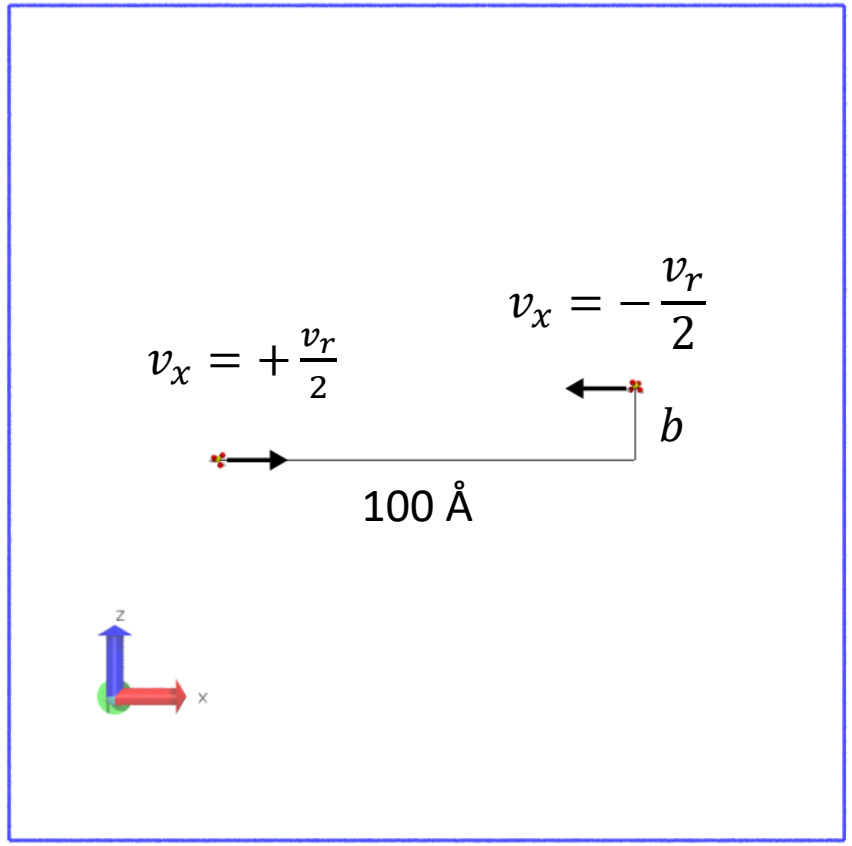
Setup for collision simulations

- OPLS-AA force field, LJ cutoff at 14 Å, Coulomb cutoff at 120 Å
- Assign atomic velocities from Maxwell-Boltzmann distribution
- Remove c.o.m. motion of each molecule individually
- Equilibrate/randomise for 50 ps in **NVE**
- Add translational velocities $v_x = \pm\frac{v_r}{2}$ to the molecules
- Run NVE MD for collision

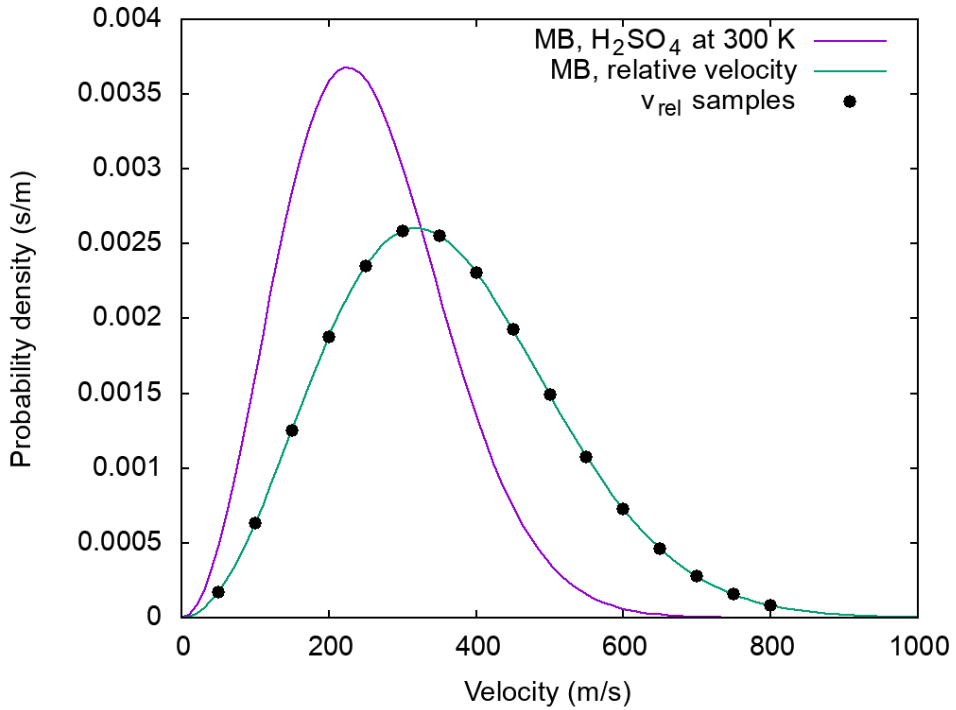
- Sample impact parameter b from 0 to 17.5 Å in steps of 0.5 Å
  - 1000 runs for each value of b

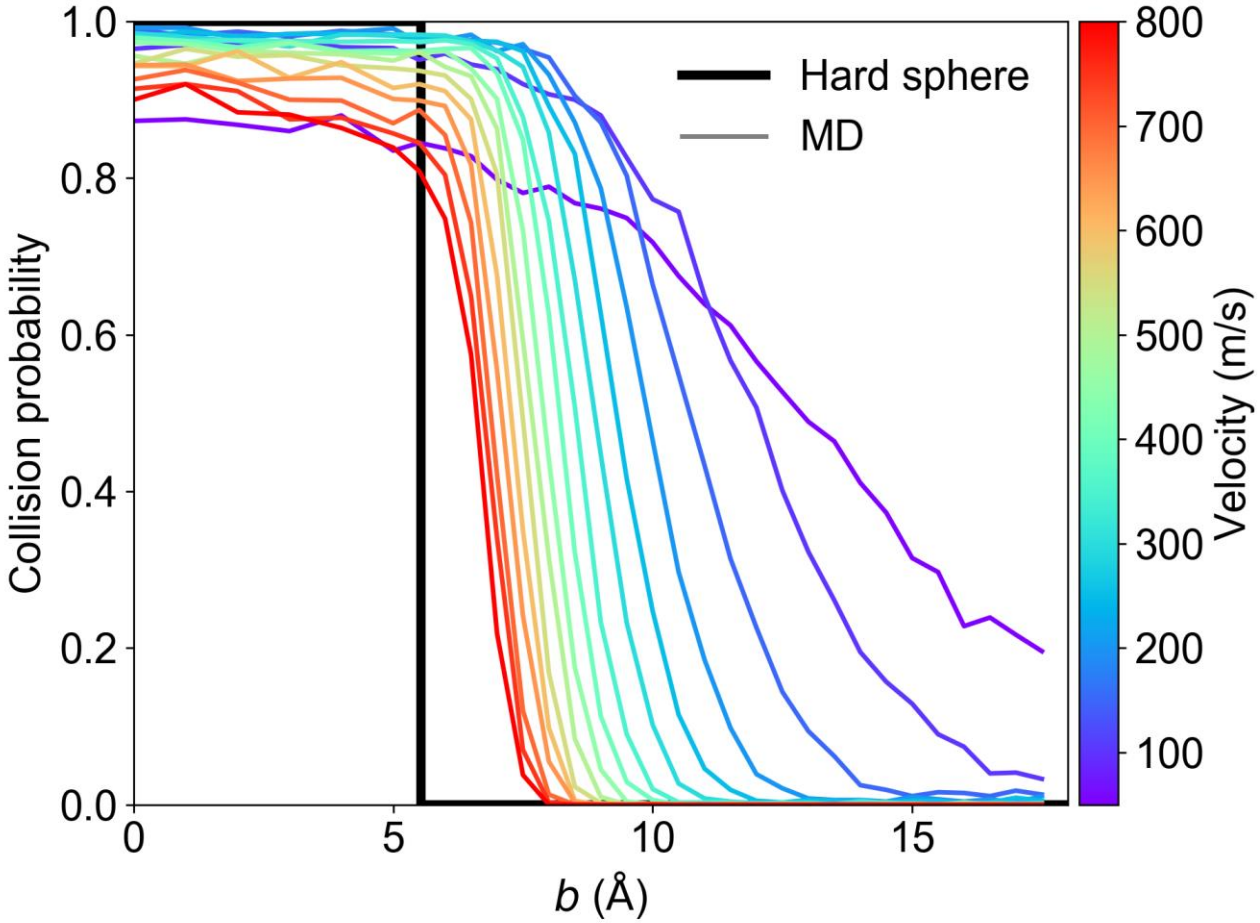
- Sample relative velocities v_r according to Maxwell-Boltzmann distribution, from 50 to 800 m/s in steps of 50 m/s

- Obtain statistics on collision and sticking probability as function of b and v_r



Collision probability: impact parameter and relative velocity





Two molecules colliding with relative velocity v_r :

Reduced mass $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} = \frac{m}{2}$, for $m_1 = m_2 = m$

$$v_r^p = \sqrt{\frac{2kT}{\mu}} = \sqrt{\frac{2 \cdot 2kT}{m}} = \sqrt{2} v^p$$

Collision coefficients

- Identical hard spheres:

$$\beta_{HS} = \sqrt{\frac{16kT}{\pi m}}\pi(2r)^2$$

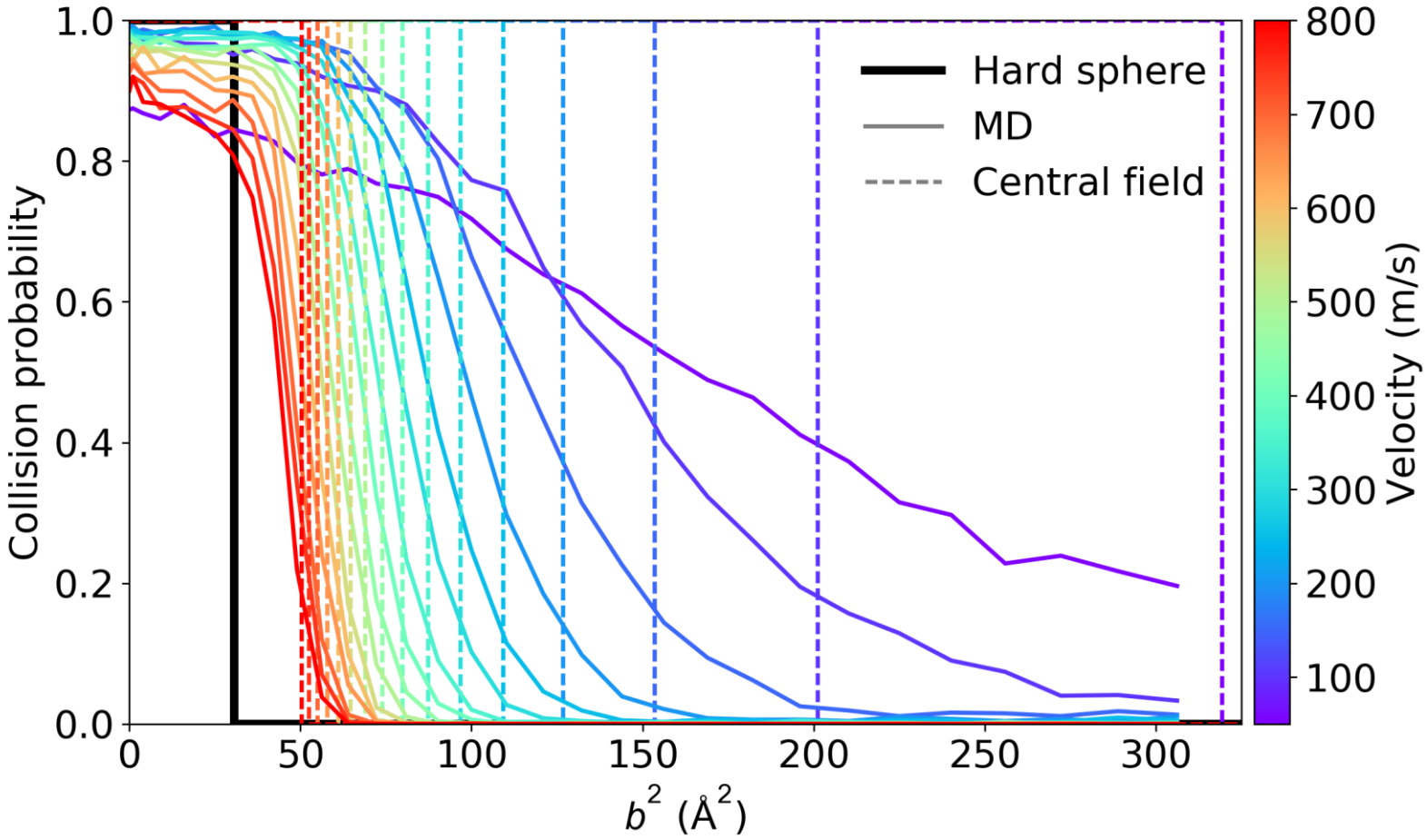
- Molecular dynamics:

$$\beta_{MD} = \pi \int_0^\infty dv \int_0^\infty db^2 \, v f(v) \, P(b)$$

- Central field theory:

$$\beta_{CF} = \pi \int_0^\infty v \, f(v) \, b_{max}^2 \, dv$$

$$\beta_{MD} \approx 2.2 \ \beta_{HS}$$
$$\beta_{CF} \approx 2.7 \ \beta_{HS}$$



”The factor of 2.3 has previously been shown to give good agreement between measured and modeled cluster and particle concentrations for the chemical system of sulfuric acid and DMA” A. Kürten et al., Atmos. Chem. Phys., 18, 845 (2018).

Summary and Outlook

- **Force field benchmark against QM optmised structures of 22 sulfuric acid trimers**
  - OPLS-AA suitable for collision simulations

- **Simulation of collisions of two sulfuric acid molecules**
  - Collisions simulated over a range of impact parameters and relative velocities
  - Need to sample from correct distributions of energies of intramolecular degrees of freedom

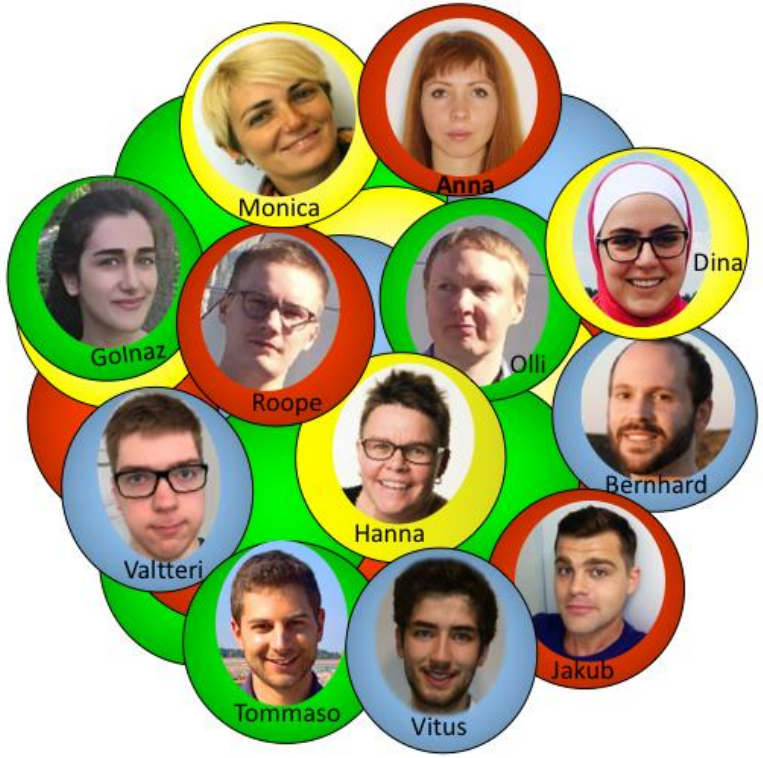
- **Collision coefficient from simulation is more than twice as large as the current value used in ACDC**

- **Outlook**
  - Need to double (and triple) check that this is not an artefact
  - Study collision / fragmentation probabilities of sulfuric acid clusters
  - Study statistics of energy transfer between internal degrees of freedom during collisions

Acknowledgments

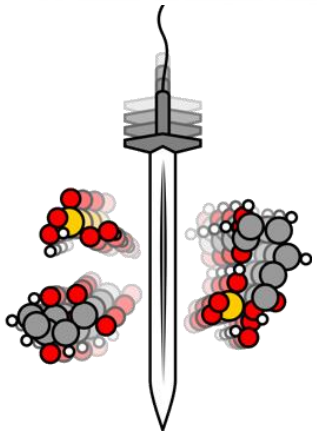
Computational Resources

CSC



The Computational Aerosol Physics Group

Funding



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