Rate enhancement in collisions of sulfuric acid molecules due to long-range intermolecular forces

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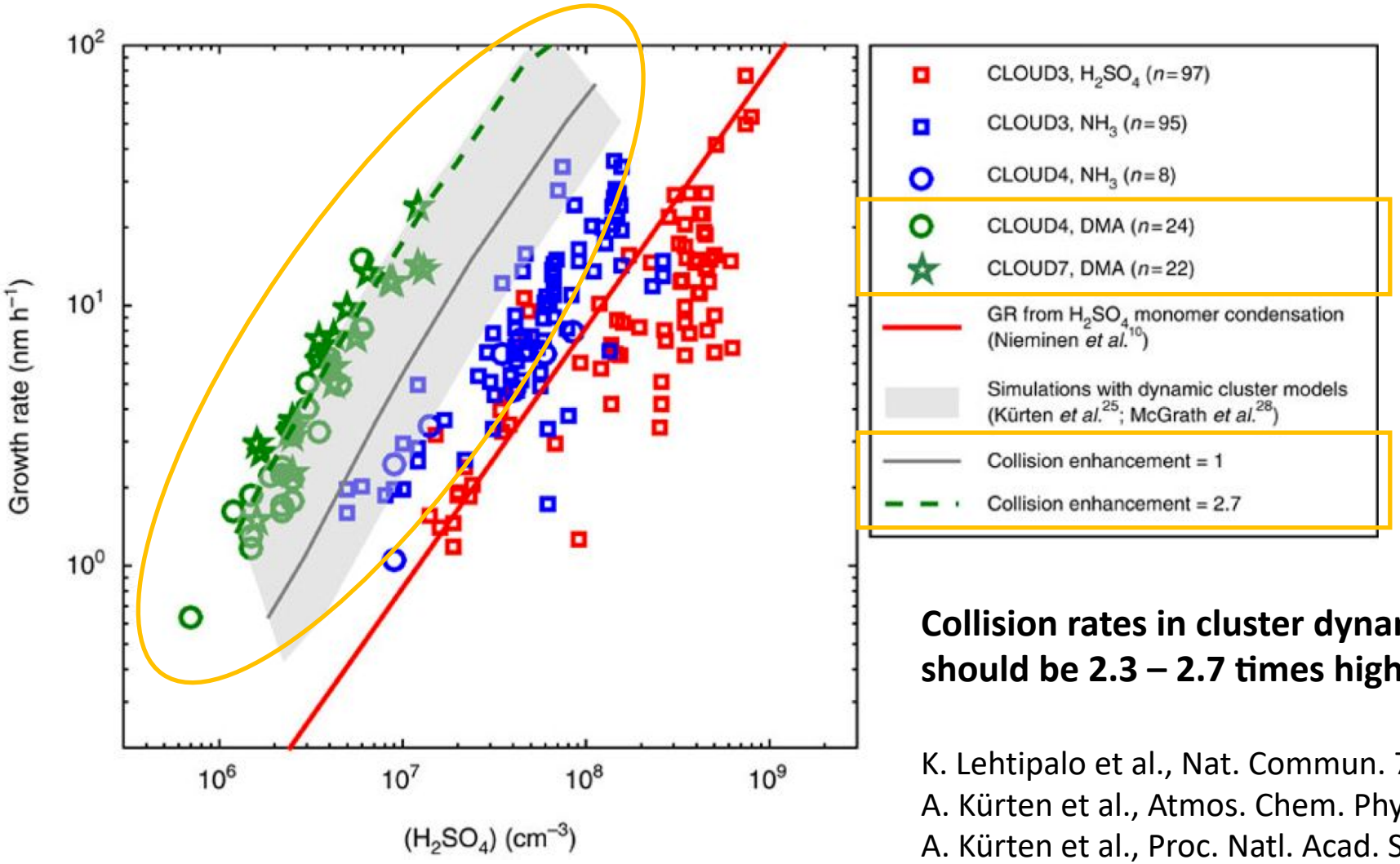
R. Halonen, E. Zapadinsky, T. Kurtén, H. Vehkamäki, B. Reischl, “Rate enhancement in collisions of sulfuric acid molecules due to long-range intermolecular forces”, Atmos. Chem. Phys. **19** (21), 13355-13366 (2019).

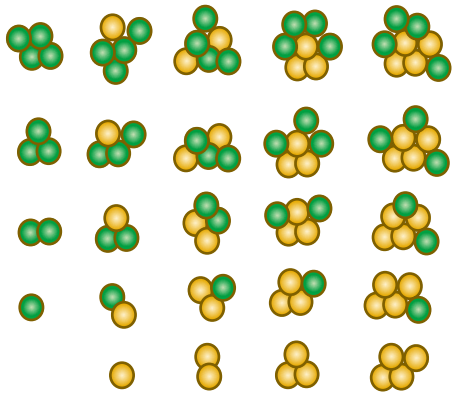
Motivation: discrepancy between particle growth rates in experiment and cluster dynamics simulations

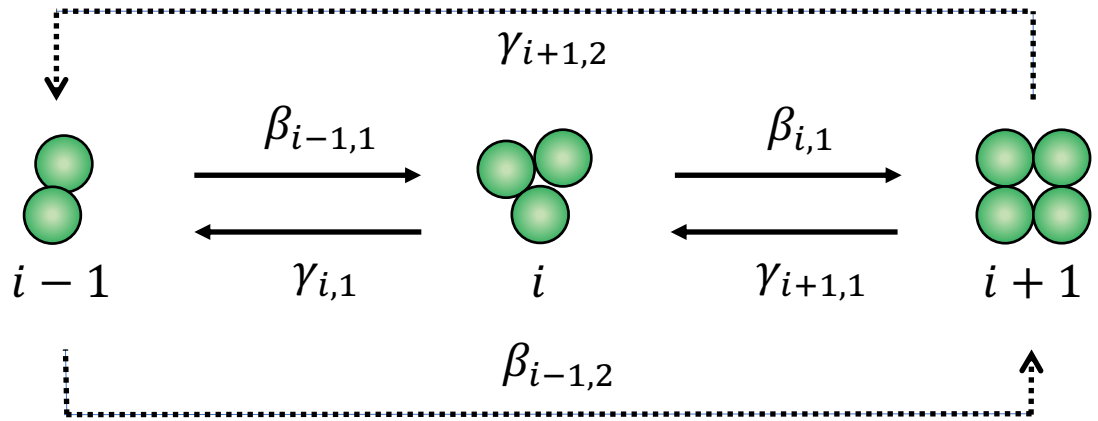


Collision rates in cluster dynamics models should be 2.3 – 2.7 times higher!

K. Lehtipalo et al., Nat. Commun. 7, 11594 (2016).
A. Kürten et al., Atmos. Chem. Phys., 18, 845 (2018).
A. Kürten et al., Proc. Natl. Acad. Sci. USA 111, 15019 (2014).

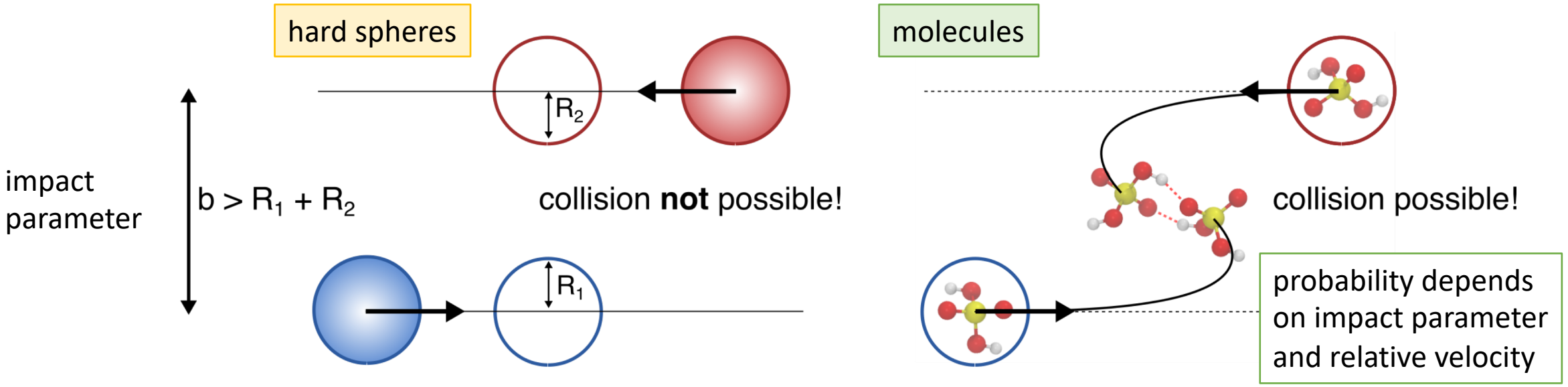
Collision rate coefficients for ACDC code





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

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



- Molecules have long-ranged attractive interactions:
  - Charge – charge (Coulomb): $U(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r} \propto r^{-1}$
  - Charge – dipole: $U(r) = -\frac{q_1^2 \mu_2^2}{6(4\pi\varepsilon_0)^2 kTr^4} \propto r^{-4}$
  - Dipole – dipole (Keesom): $U(r) = -\frac{\mu_1^2 \mu_2^2}{3(4\pi\varepsilon_0)^2 kTr^6} \propto r^{-6}$
  - Induced dipole – dipole (Debye): $U(r) = -\frac{\mu_1^2 \alpha_2}{(4\pi\varepsilon_0)^2 r^6} \propto r^{-6}$
  - Induced dipole – induced dipole (London dispersion): $U(r) = -\frac{4}{3}\frac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2 r^6} \propto r^{-6}$

  ”Van der Waals Interaction”

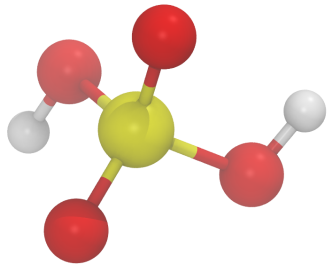
Validation of force fields for H_2SO_4

- Intermolecular interactions through Lennard-Jones and Coulomb interactions

$$U_{\text{inter}} = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

- Ding et al. [1]:
  - fitted to *ab initio* geometries of small clusters of H_2SO_4, and HSO_4^- and water
  - Intramolecular interactions through harmonic bonds only!
  - dipole = 3.52 Debye

$$U_{\text{intra}}^{\text{Ding}} = \sum_{i=1}^{N_1-1} \sum_{j=i+1}^{N_1} \frac{k_{ij}}{2} \left(r_{ij} - r_{ij}^0 \right)^2$$



- Loukonen et al. [2], using OPLS-AA doctrine [3]:
  - Transferable potential
  - Intramolecular interactions through harmonic bonds, angles and dihedrals
  - Molecular geometry, vibrations and charges fitted to ab initio calculation
  - dipole = 3.07 Debye

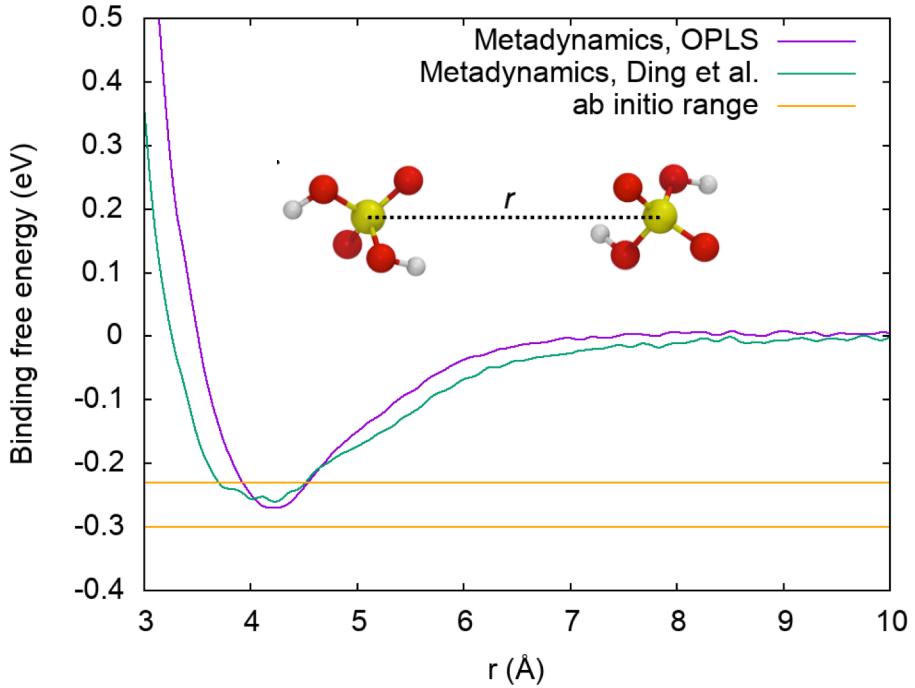
$$U_{\text{intra}}^{\text{OPLS}} = \sum_{i=1}^{N_{\text{bonds}}} \frac{k_i^b}{2} \left(r_i - r_i^0 \right)^2 + \sum_{j=1}^{N_{\text{angles}}} \frac{k_j^\theta}{2} \left(\theta_j - \theta_j^0 \right)^2 + \sum_{k=1}^{N_{\text{dihedrals}}} \sum_{n=1}^{4} \frac{V_n}{2} \left[1 + \cos(n\phi^k - \phi_n^k) \right]$$

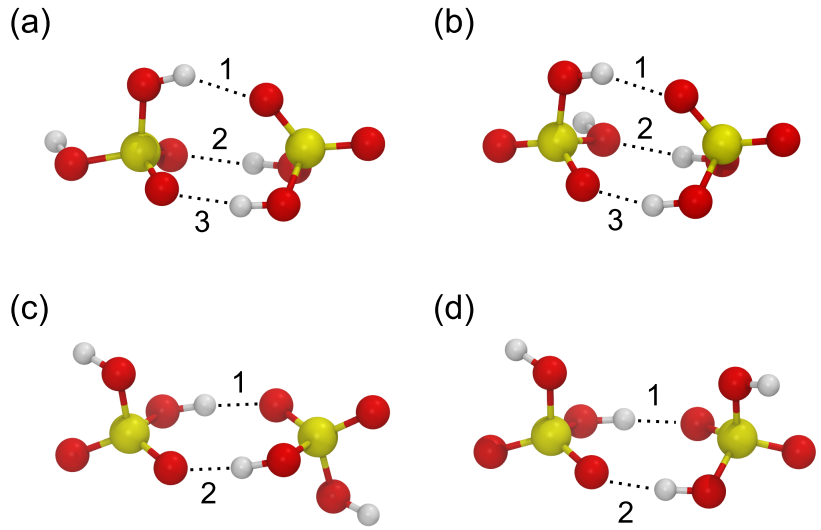
[1] C. G. Ding, T. Taskila, K. Laasonen and A. Laaksonen, Chem. Phys. 287, 7 (2003).
[2] V. Loukonen, T. Kurtén, I. K. Ortega, H. Vehkamäki, A. A. H. Pádua, K. Sellegri, and M. Kulmala, Atmos. Chem. Phys., 10, 4961 (2010).
[3] W. L. Jorgensen, D. S. Maxwell and J. Rives-Tirado, J. Am. Chem. Soc. 118(45), 11225 (1996).

Benchmark 1: conformers of the H_2SO_4 dimer

- Comparison of structures and energies of four conformers (a-d) obtained with force fields to ab initio results at (RI-MP2/CBS//MP2/6-31+G*) level [1]

- Comparison of binding free energies obtained from metadynamics simulations at 300 K





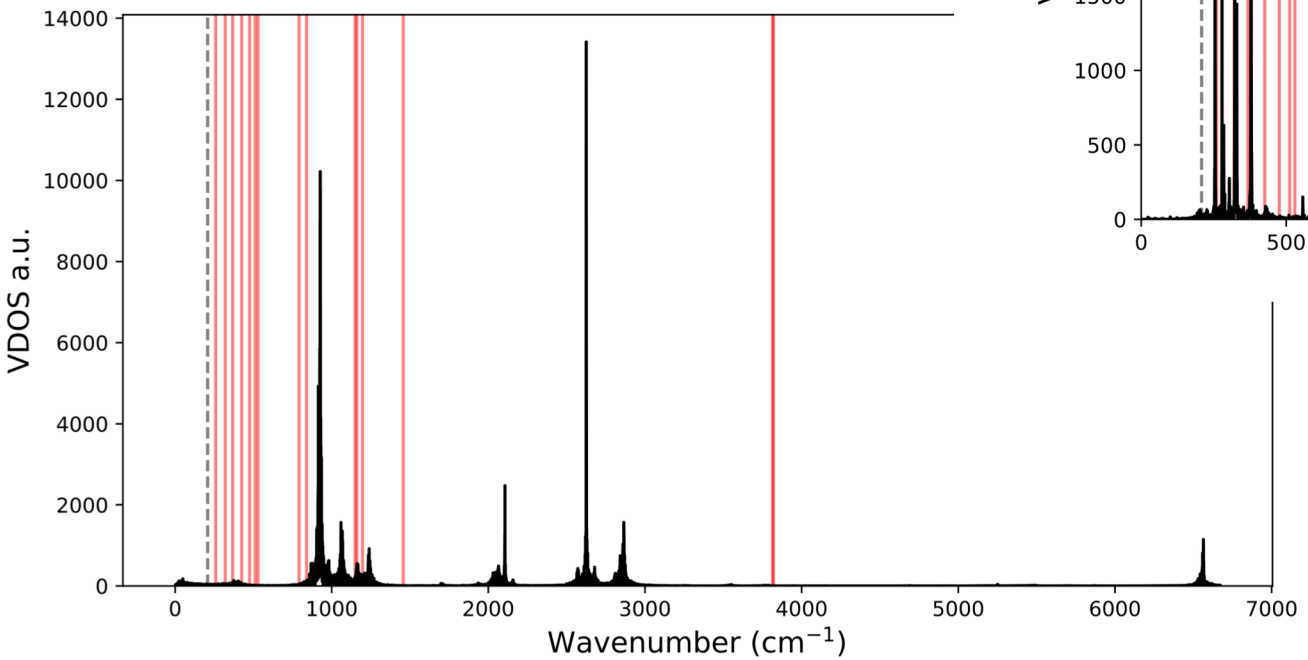
Structure			a	b	c	d
$\Delta\Delta E$	ab initio		0.000	0.032	0.036	0.048
	Ding et al.		0.000	0.081	0.052	0.045
	OPLS		0.180	0.099	0.004	0.000
$d_{O\cdots H}$	ab initio	1	1.82	1.74	1.75	1.75
		2	1.89	1.91	1.75	1.75
		3	1.90	1.87		
	Ding et al.	1	2.00	1.84	1.75	1.74
		2	1.87	2.31	1.74	1.74
		3	1.88	1.85		
	OPLS	1	1.91	1.84	1.72	1.72
		2	1.85	1.87	1.72	1.72
		3	1.83	1.83		

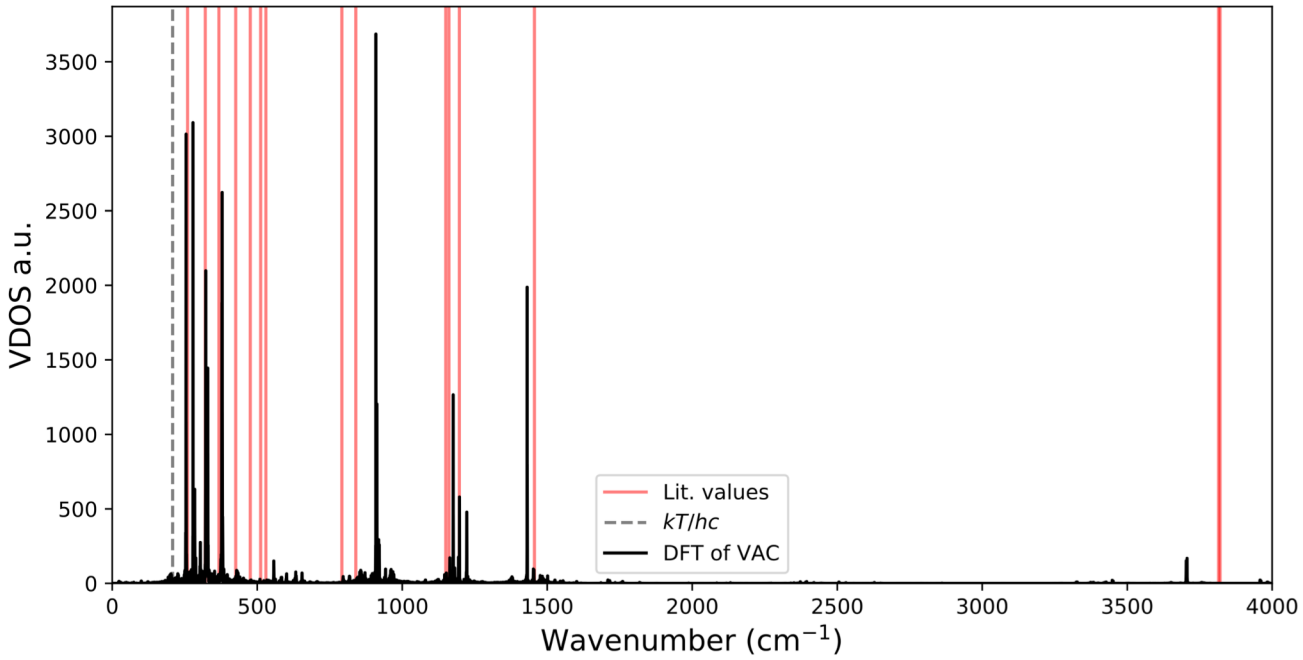
[1] B. Temelso, T. N. Phan and G. C. Shields, J. Phys. Chem. A 116, 9745 (2012).

Benchmark 2: H_2SO_4 vibrational spectra

Vibrational spectra from Fourier transform of velocity autocorrelation functions in MD simulation of individual H_2SO_4 at 300 K.

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!

Force field 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 harmonic bonds
  - Gas phase geometries correct; dipole of 3.7 Debye
  - Vibrational spectra horrible
  - Not transferable

- Loukonen et al. (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

Property	Ding et al.	OPLS
Molecular geometry	+	+
Dipole	+	+
Dimer structures	+	+
Dimer energies	+	~
Binding free energy	+	+
Vibrational spectra	--	+
Transferability	--	+

Hard sphere model and Langevin model of capture

- **Hard sphere model:**

  Molecule is considered as a spherical droplet with the bulk liquid density:

  ρ = 1.84 g/cm^3, M = 98.09 g/mol

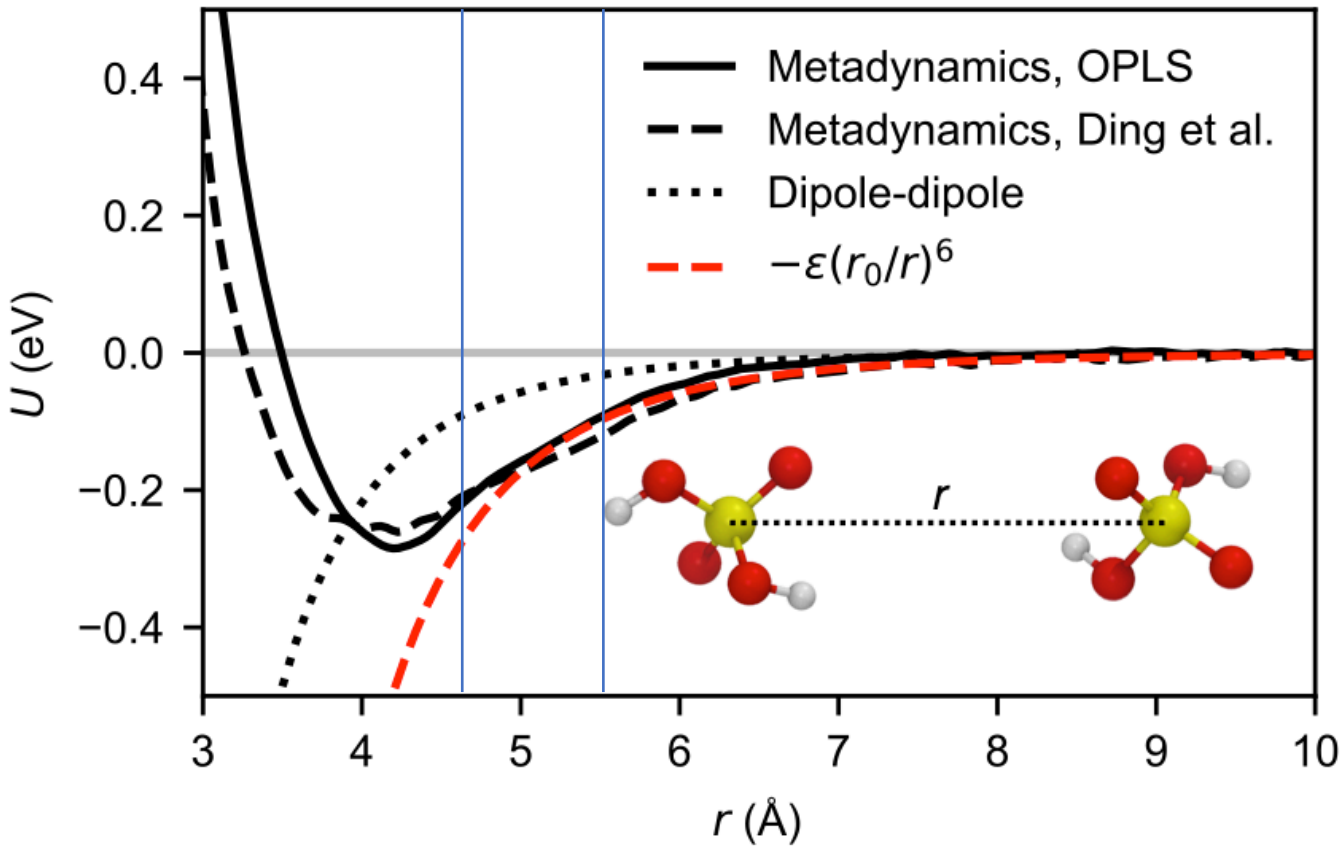
  --> R = 2.76 Å

- **Molecular dynamics:**
  PMF from Metadynamics simulation at 300 K has minimum at 4.2 Å, but is attractive to much larger distances!

- **Langevin model:**

  We can fit the attractive tail with $U(r) = -\varepsilon \left(\frac{r_0}{r}\right)^n$ for a Langevin model of capture in a central field:

  Collision if $b < b_{max} = \left(\frac{27\varepsilon r_0^6}{2\mu v^2}\right)^{1/6}$



Setup for collision simulations

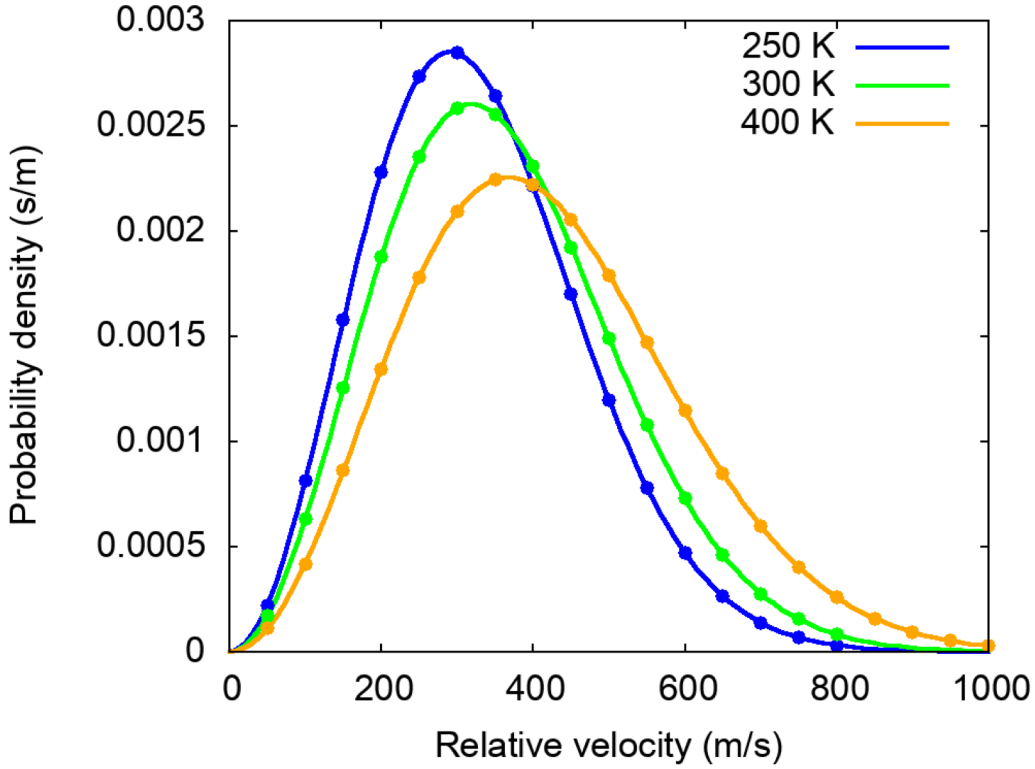
- OPLS-AA force field, LJ cutoff at 14 Å, Coulomb cutoff at 120 Å

- 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
- Sample relative velocities v_r according to Maxwell-Boltzmann distribution, from 50 to 800 (or 1000) m/s in steps of 50 m/s

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

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



Similar technique used recently in:
H. Yang, E. Goudeli, and C. J. Hogan Jr., J. Chem. Phys, 148, 164304 (2018).

Collision rate coefficients at T = 300 K

- Hard spheres:

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

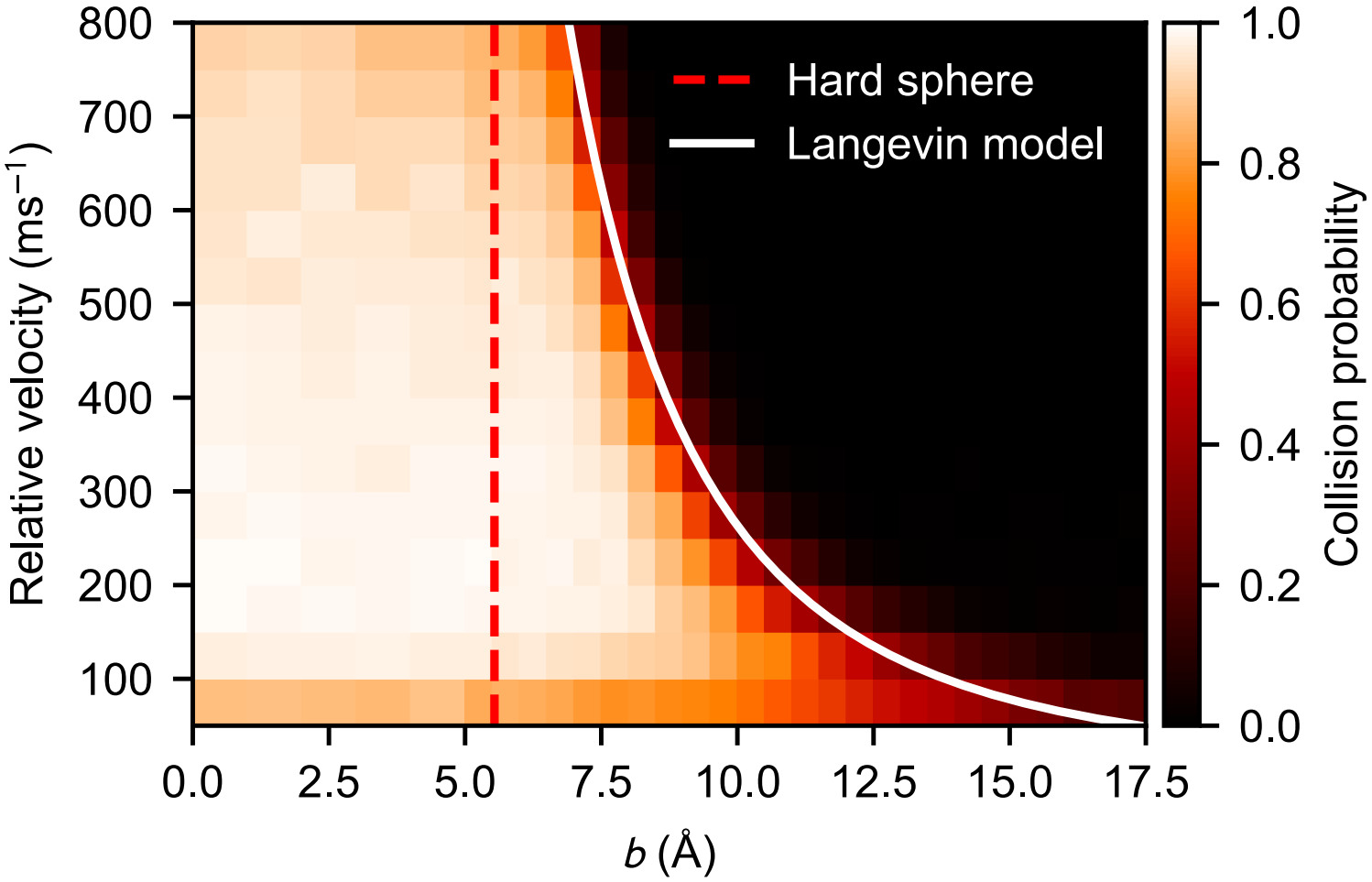
- Langevin model:

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

- Molecular dynamics:

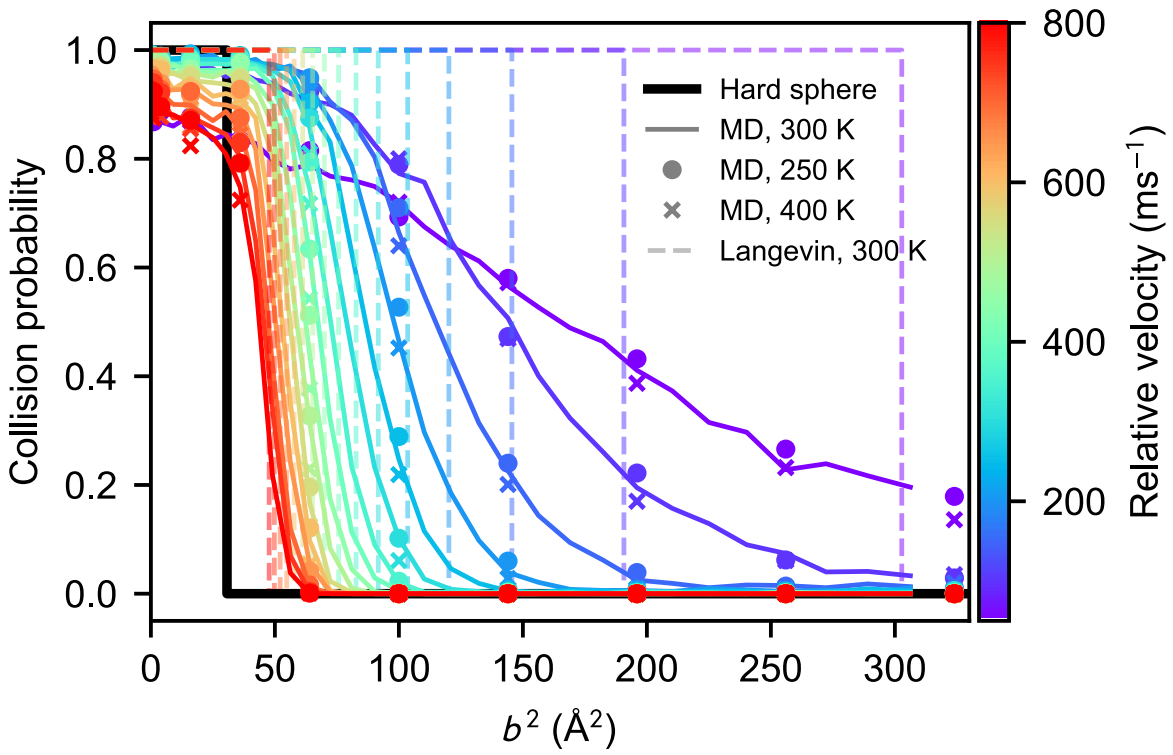
$$\beta_{MD} = \pi \int_0^\infty dv \int_0^\infty db^2\, v f(v)\, P(v,b)$$

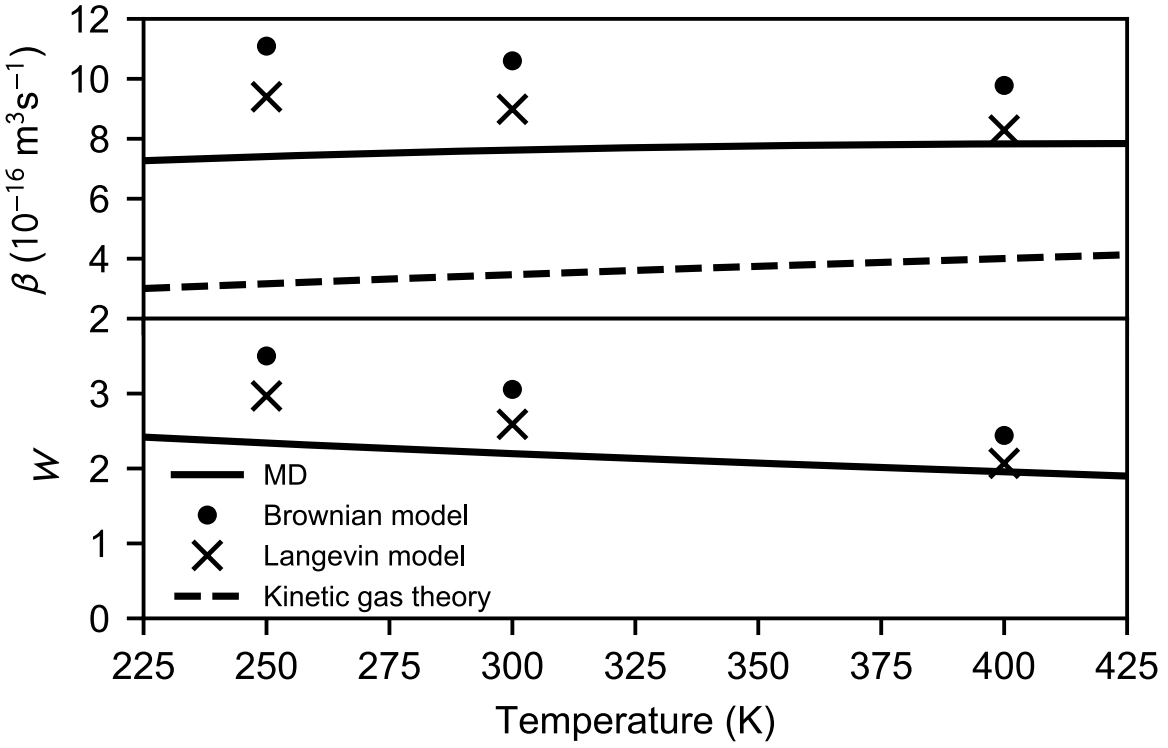
$$\beta_{MD} \approx 2.2\ \beta_{HS}$$
$$\beta_L \approx 2.7\ \beta_{HS}$$



"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).

Temperature dependence of collision rate coefficients





Collision rate enhancement is not very sensitve to temperature in atmospherically relevant temperature range of 250-400 K

Collision rate coefficents: β_x

Enhancement factors: $W_x = \frac{\beta_x}{\beta_{HS}}$

Summary and Outlook

- **All molecules – even neutral ones – interact at range!**

- **Force field benchmark against QM sulfuric acid dimers and vibrational spectra**
  - OPLS-AA suitable for collision simulations

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

- **Collision coefficient for two neutral H_2SO_4 molecules with dipole of 3 Debye is twice as large as kinetic gas theory value – even stronger enhancement expected for molecules/clusters with larger dipoles**

- **Outlook**
  - Statistics of energy transfer between internal degrees of freedom during collisions?
  - Study collision (and fragmentation) probabilities of larger clusters containing sulfuric acid, etc.
  - Vast number of compounds in the atmosphere – need a way to pre-screen & automate process

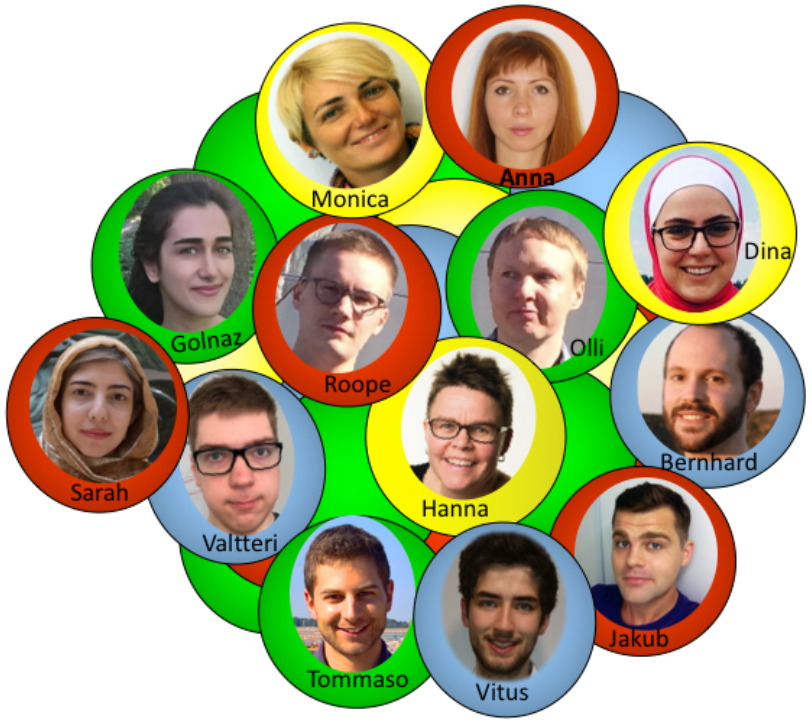
R. Halonen, E. Zapadinsky, T. Kurtén, H. Vehkamäki, B. Reischl, “Rate enhancement in collisions of sulfuric acid molecules due to long-range intermolecular forces”, Atmos. Chem. Phys. **19** (21), 13355-13366 (2019).

Acknowledgments

Computational Resources

CSC

The Computational Aerosol Physics Group



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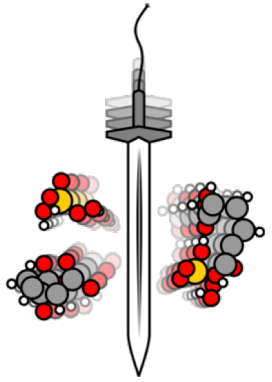

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