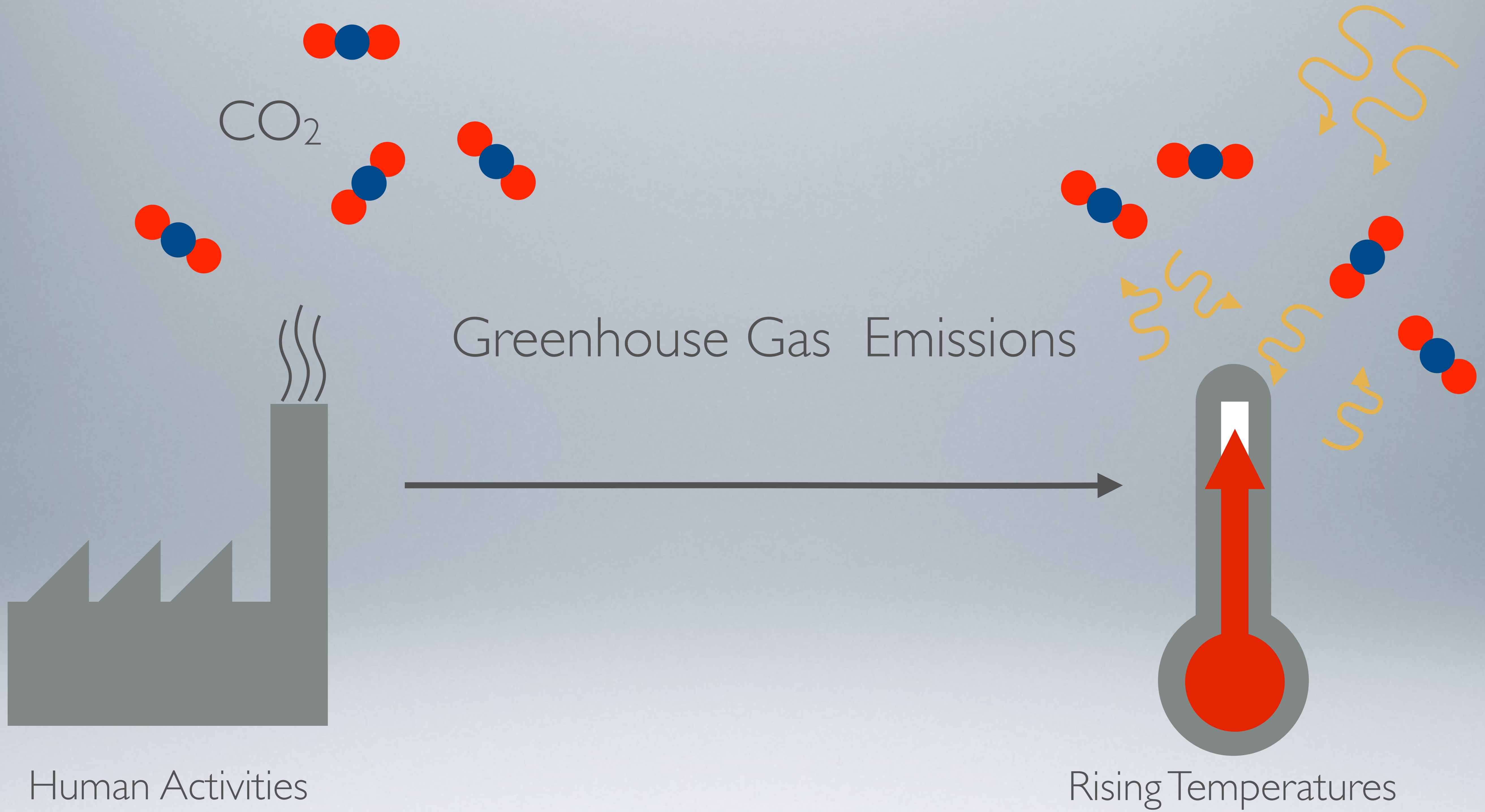
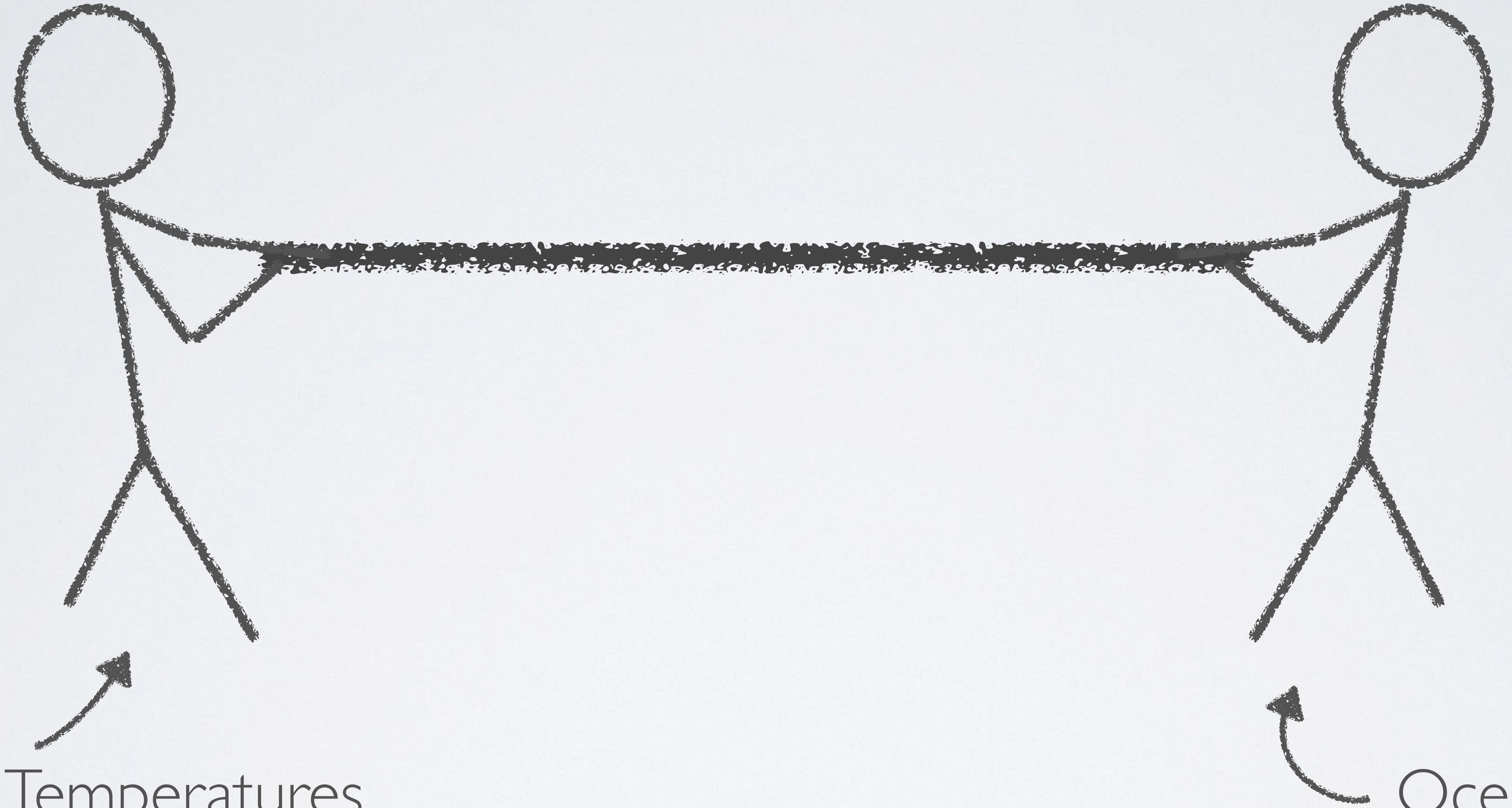
DEEP OCEAN THERMODYNAMICS AND CLIMATE CHANGE

Edoardo Savoia

Swinburne University of Technology



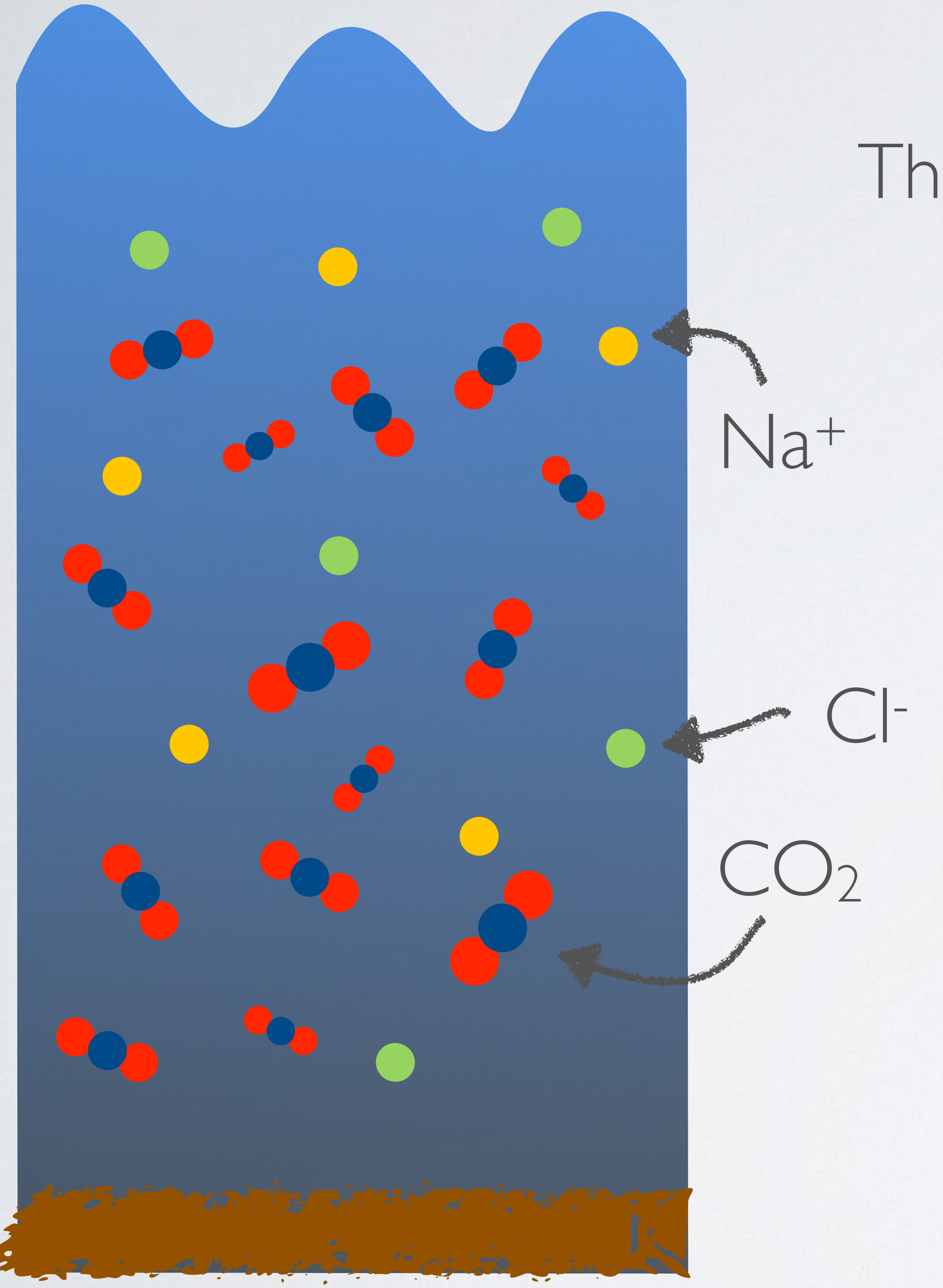
CO_2
Greenhouse Gas Emissions
Human Activities
Rising Temperatures



Rising Temperatures

Oceans

Thermodynamic & Transport properties
(heat capacity, diffusivity, …)



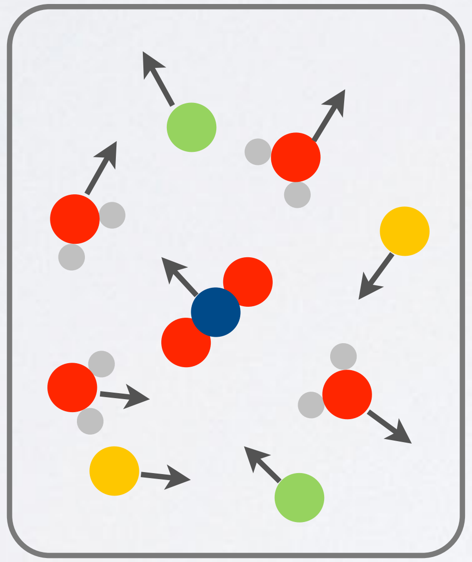
Thermodynamic & transport properties of seawater depend on **composition**

current knowledge is **limited***

* IAPWS, 2017: "Certified Research Need - Thermophysical Properties of Seawater"

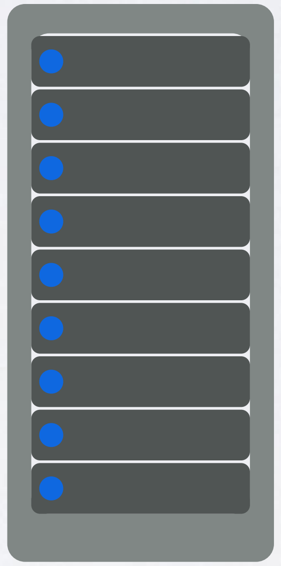
OBJECTIVE

Study thermodynamic and transport properties of mixtures of seawater and carbon dioxide at different temperatures, pressures at various concentrations of CO_2

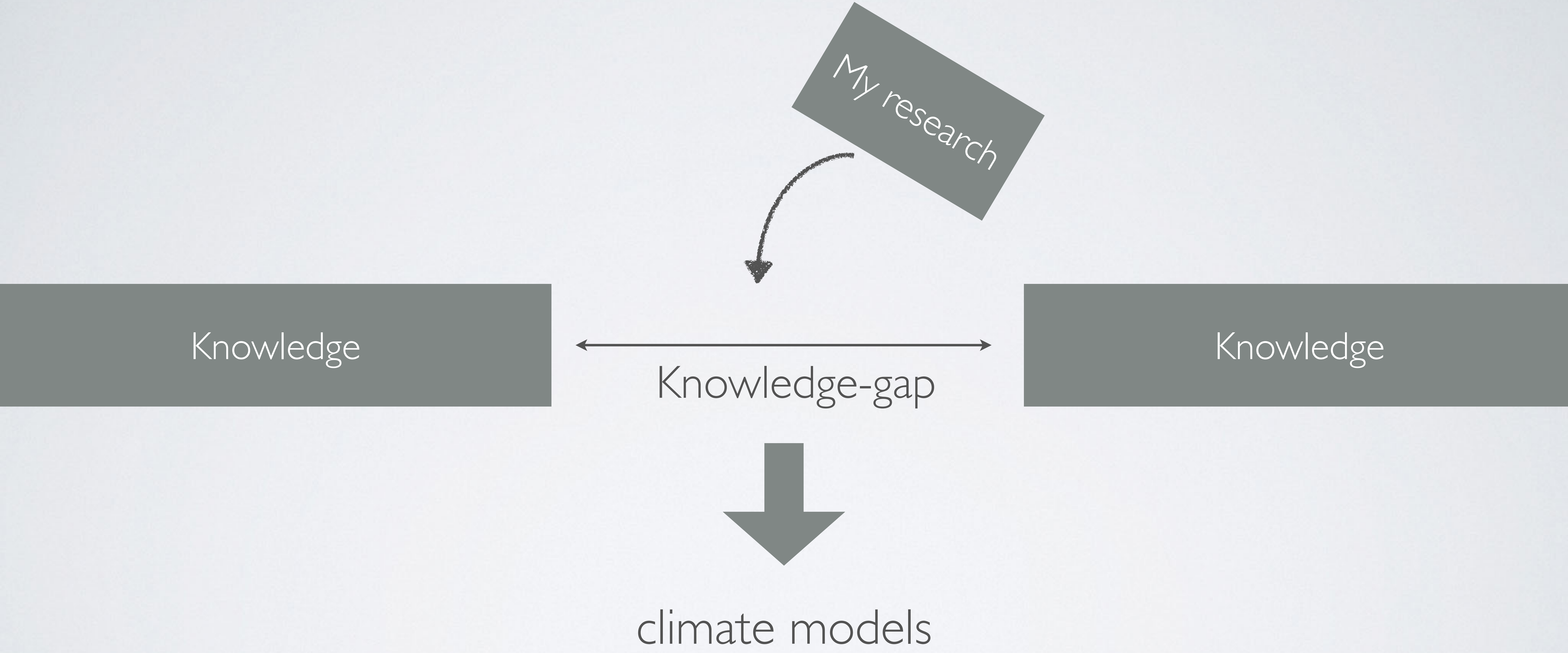


Molecular Dynamics

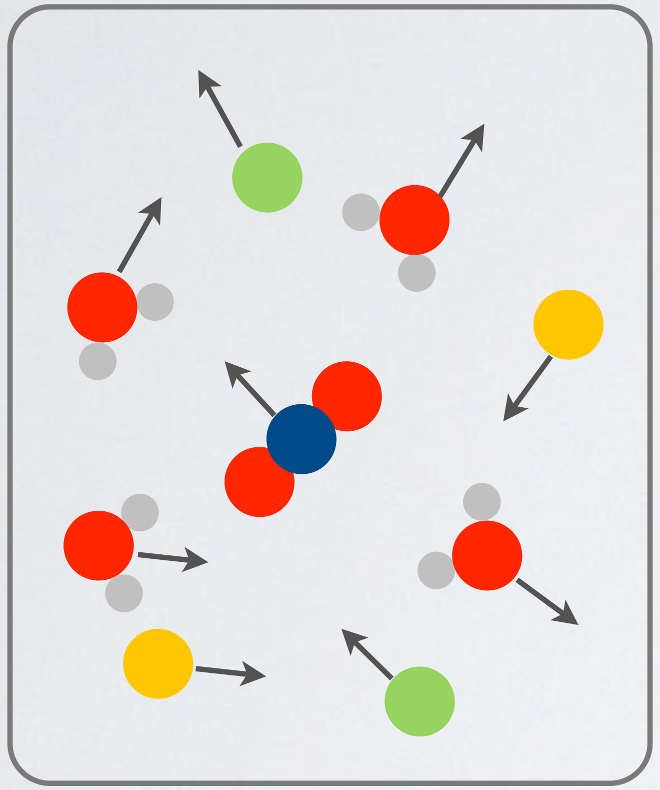
@



OzStar HPC


My research
Knowledge
Knowledge-gap
Knowledge
climate models

RESEARCH METHODS



Seawater is a complex mixture

modelled as a mixture of water and sodium chloride

Molecular Dynamics Tools

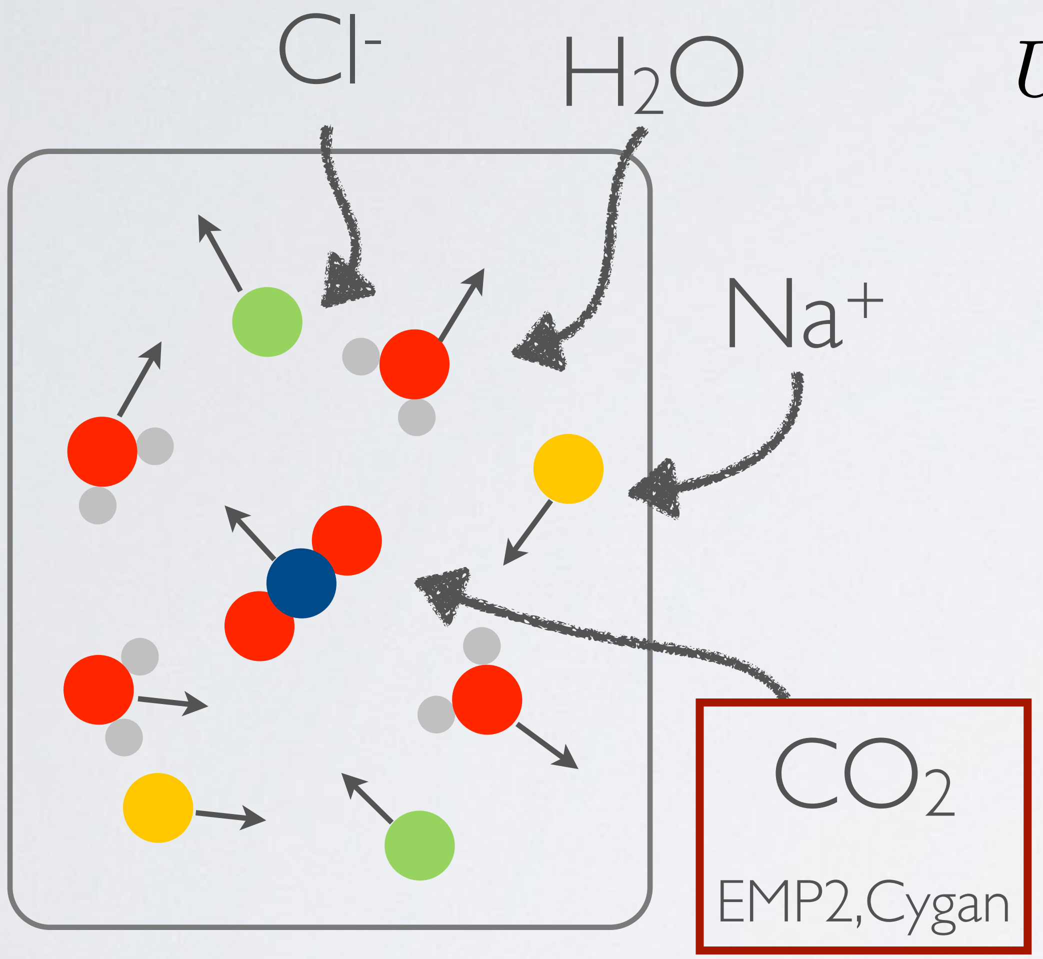
provide a thermophysical characterisation of the system

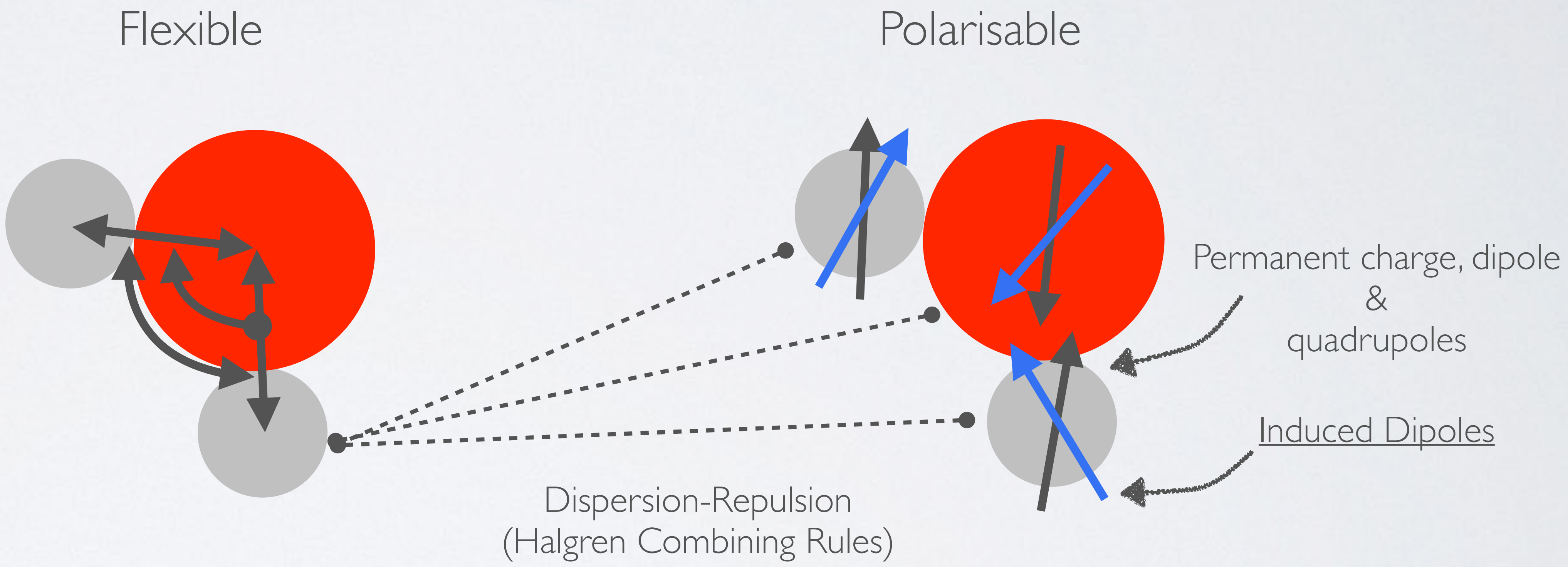
Numerical simulations

Temperature range: 273 K - 313 K
Pressure range: 1 atm - 1000 atm

WATER MODELS: AMOEBA FAMILY

$$U = U_{\text{bond}} + U_{\text{angle}} + U_{\text{bond-angle}} + U_{\text{vdW}} + U_{\text{ele}}^{\text{perm}} + U_{\text{ele}}^{\text{ind}}$$





Original AMOEBA 2003 [1] & inexpensive-AMOEBA [2]

[1] Ren P, Ponder JW. 2003 Polarizable Atomic Multipole Water Model for Molecular Mechanics Simulation. The Journal of Physical Chemistry B 107, 5933–5947.

[2] Wang LP, et. al. 2013 Systematic improvement of a classical molecular model of water. The Journal of Physical Chemistry B 117, 9956–9972.

WATER MODELS

Original AMOEBA 2003: self consistent induced dipoles

$$\mu_{i,\alpha}^{\text{ind}} = \alpha_i \Big(\sum_{j \notin Mol_i} T_{\alpha}^{ij} M_j + \sum_{j' \neq i} T_{\alpha\beta}^{ij'} \mu_{j,\beta}^{\text{ind}} \Big), \qquad \alpha, \beta = x, y, z$$

Induced Dipoles

iAMOEBA: directly induced dipoles

$$\mu_{i,\alpha}^{\text{ind}} = \alpha_i \Big(\sum_{j \notin Mol_i} T_{\alpha}^{ij} M_j \Big), \qquad \alpha = x, y, z$$

Permanent multipoles

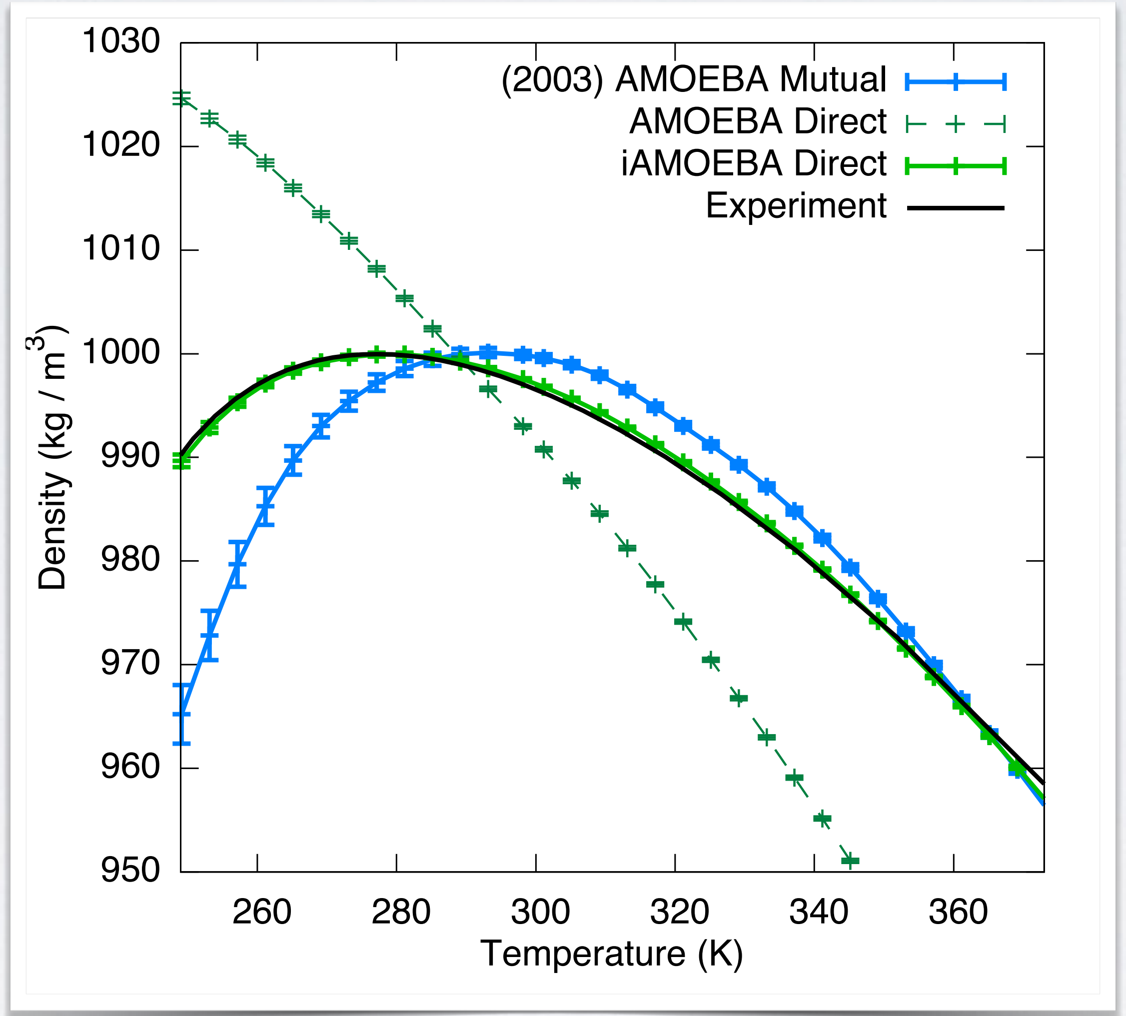
SIMULATION SETUP

NpT Simulations with TINKER 8.10.2 (customised)

Computed quantities:

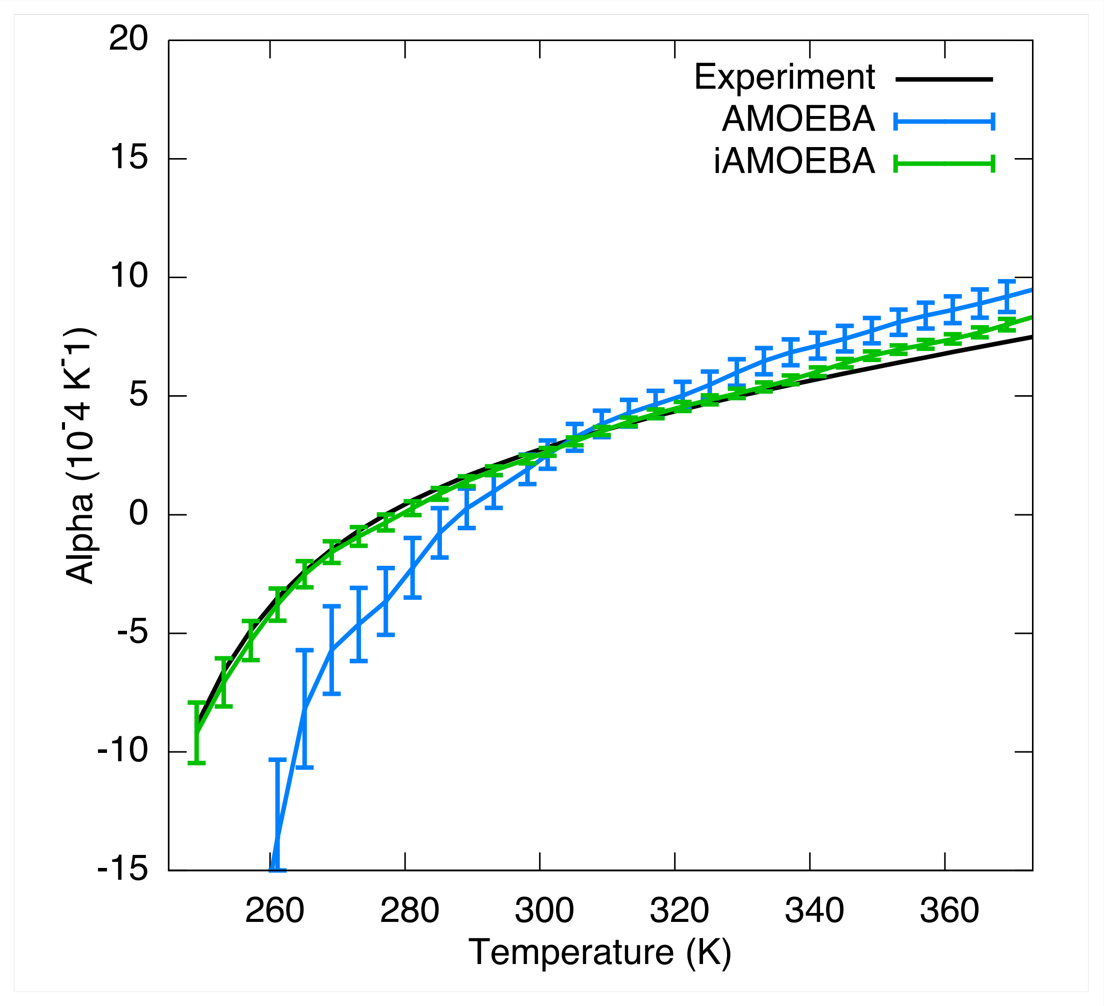
- Density
- Isothermal Compressibility
- Thermal Expansion Coefficient
- Isobaric Heat Capacity

DENSITY



* Wang LP, et. al. 2013 Systematic improvement of a classical molecular model of water. S.I. The Journal of Physical Chemistry B 117, 9956–9972.

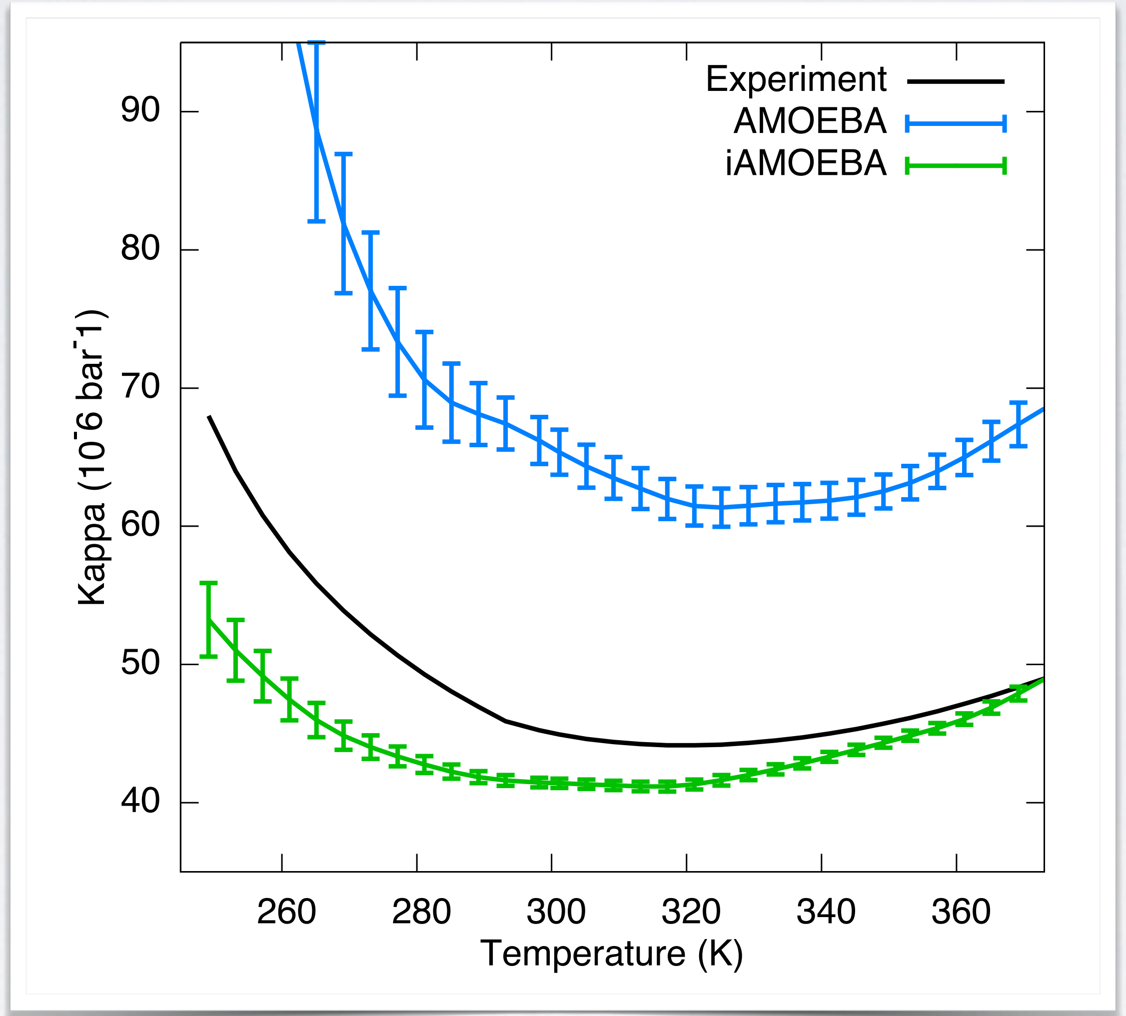
THERMAL EXPANSION COEFF.



$$\alpha_p = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{\langle \mathcal{H} V \rangle - \langle \mathcal{H} \rangle \langle V \rangle}{k_B \langle V \rangle T^2}$$

* Wang LP, et. al. 2013 Systematic improvement of a classical molecular model of water. S.I. The Journal of Physical Chemistry B 117, 9956–9972.

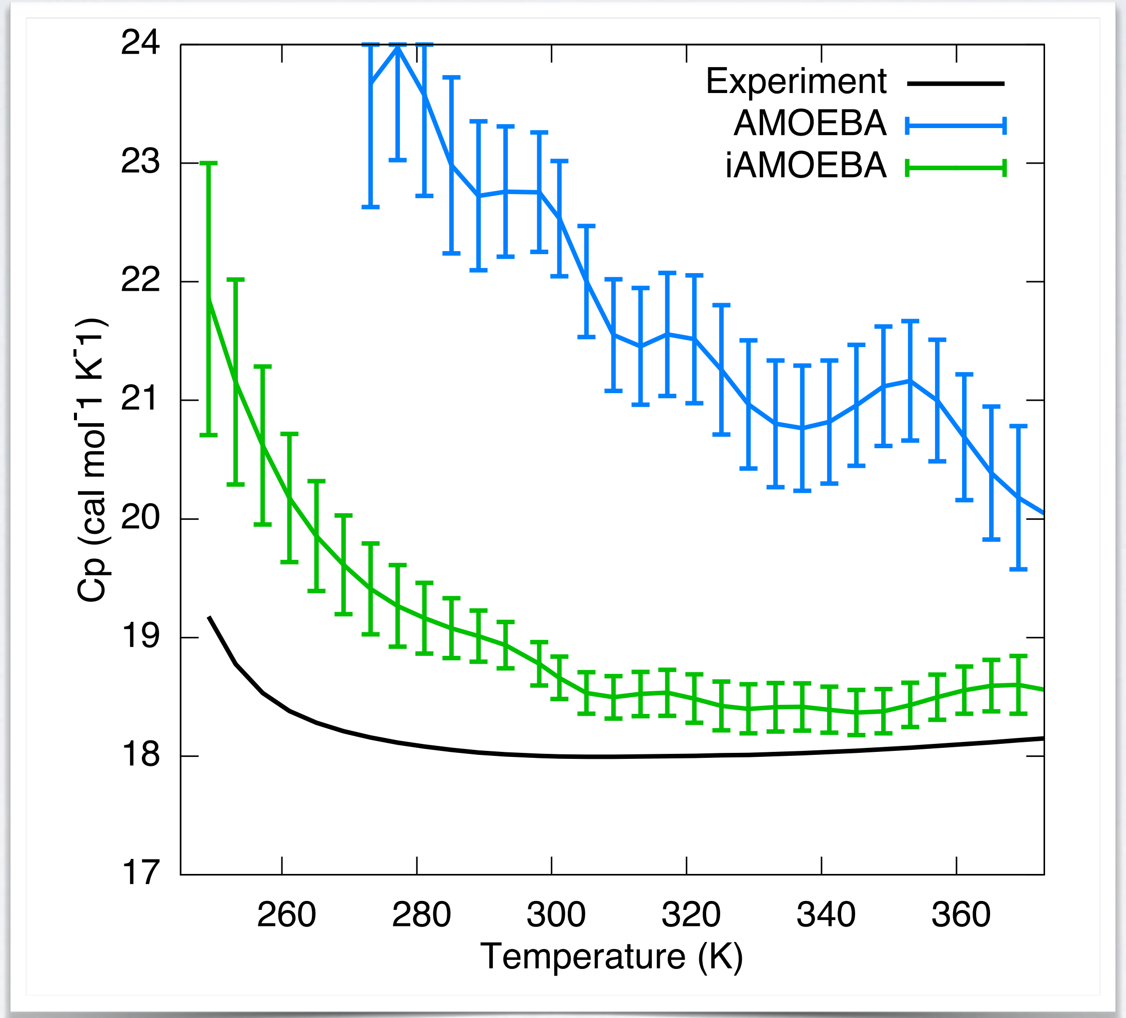
ISOTHERMAL COMPRESSIBILITY



$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{\langle V^2 \rangle - \langle V \rangle^2}{k_B \langle V \rangle T}$$

* Wang LP, et. al. 2013 Systematic improvement of a classical molecular model of water. S.I. The Journal of Physical Chemistry B 117, 9956–9972.

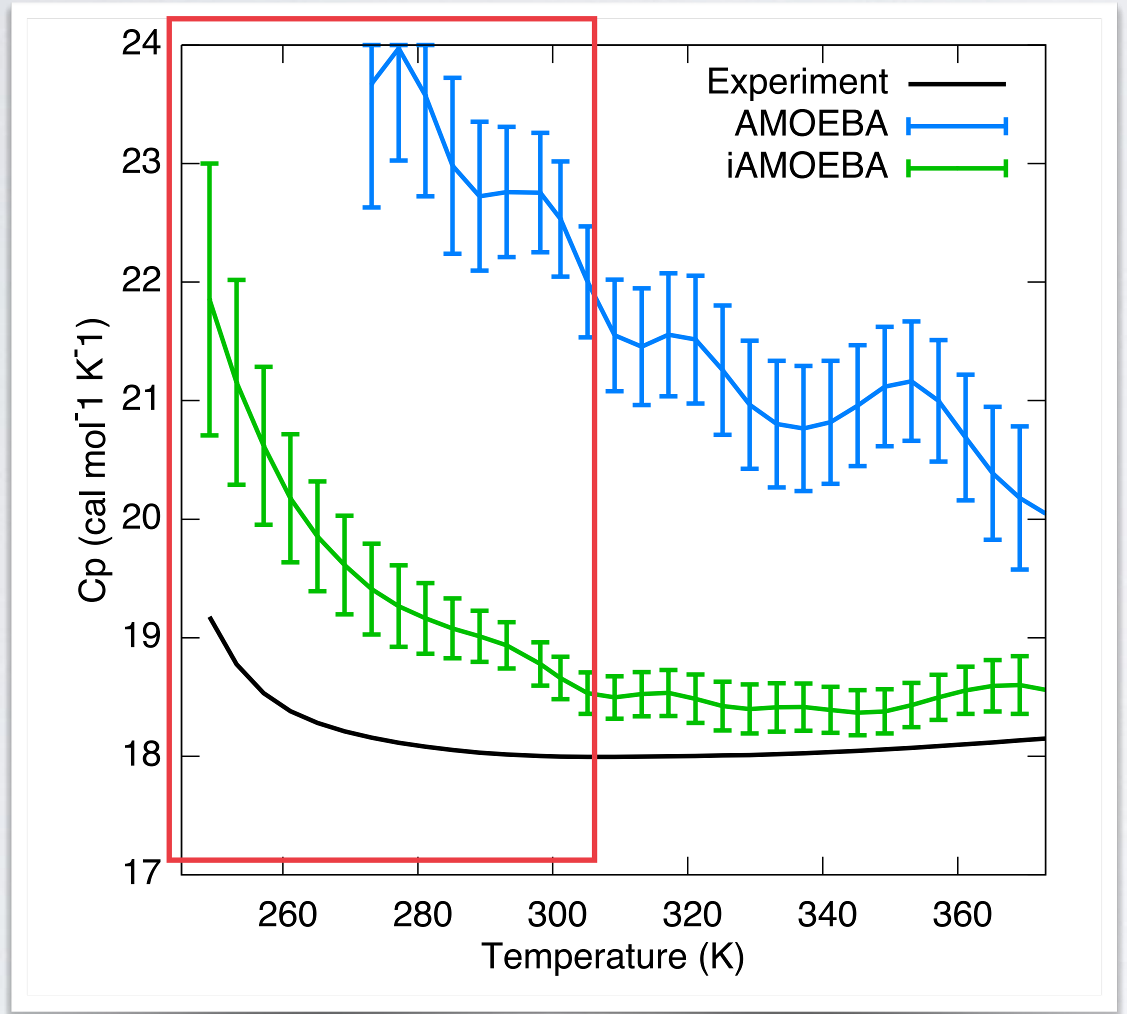
ISOBARIC HEAT CAPACITY

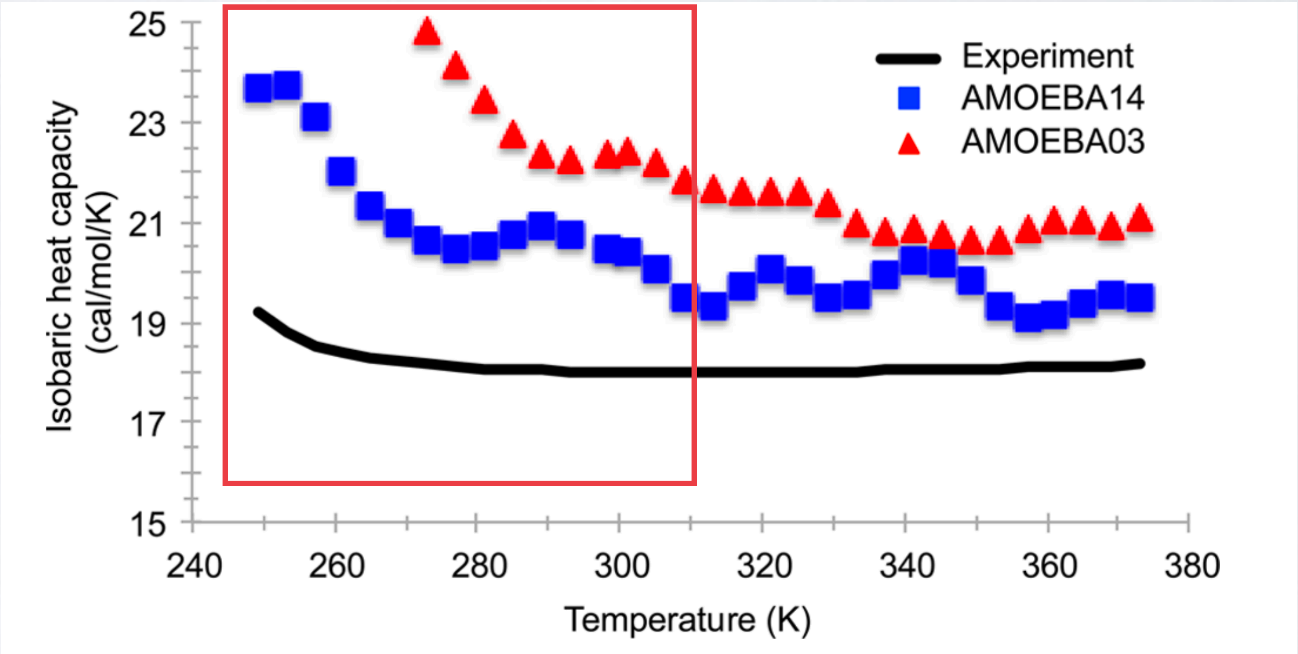


$$c_p = \left.\frac{\partial \mathcal{H}}{\partial T}\right|_p = \frac{\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2}{k_B N_{\mathrm{mol}} T^2}$$

* Wang LP, et. al. 2013 Systematic improvement of a classical molecular model of water. S.I. The Journal of Physical Chemistry B 117, 9956–9972.

ISOBARIC HEAT CAPACITY





Amoeba14*

$$c_p = \left.\frac{\partial \mathcal{H}}{\partial T}\right|_p = \frac{\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2}{k_B N_{\mathrm{mol}} T^2}$$

*Laury ML, et al. 2015 Revised parameters for the amoeba polarizable atomic multipole water model. J. Phys. Chem. B 119, 9423–9437.

Classical M.D. **can’t correctly reproduce** the temperature behaviour of heat capacity at low temperatures where quantum effects have to be considered.

QUANTUM CORRECTIONS

Harmonic oscillators

$$E_{\text{vib}}^{\text{CM}} = n_{\text{vib}} k_B T$$

Classical Oscillators

$$E_{\text{vib}}^{\text{QM}} = \sum_{i=1}^{n_{\text{vib}}} \left(\frac{h\nu_i}{2} + \frac{h\nu_i}{e^{h\nu_i / k_B T} - 1} \right)$$

Quantum Oscillator

$$c_p^{\text{MD}} + c^{\text{Correction}} = c_p^{\text{MD}} + (c_V^{\text{QM}} - c_V^{\text{CM}})$$

QUANTUM CORRECTIONS

Horn[1] :
Use a reduced number of frequencies obtained from experiments

Berens[2]:
Use the full vibrational spectrum computed from velocity autocorrelation function

[1] Horn HW et al. 2004 The Journal of Chemical Physics, vol. 120, pp. 9665-9678. [2] Berens PH et al. 1983 The Journal of Chemical Physics, vol. 79 pp. 2375-2389.

FULL SPECTRUM QUANTUM CORRECTIONS

velocity autocorrelation function

$$C(t) = \sum_s m_s C_s(t), \quad C_s(t) = \langle \boldsymbol{v}_s(t') \cdot \boldsymbol{v}_s(t'+t) \rangle_t$$

Vibrational spectrum:

$$S(\nu) = \frac{2}{k_B T} \int_{-\infty}^{-\infty} dt C(t) e^{-2\pi \imath \nu t}$$

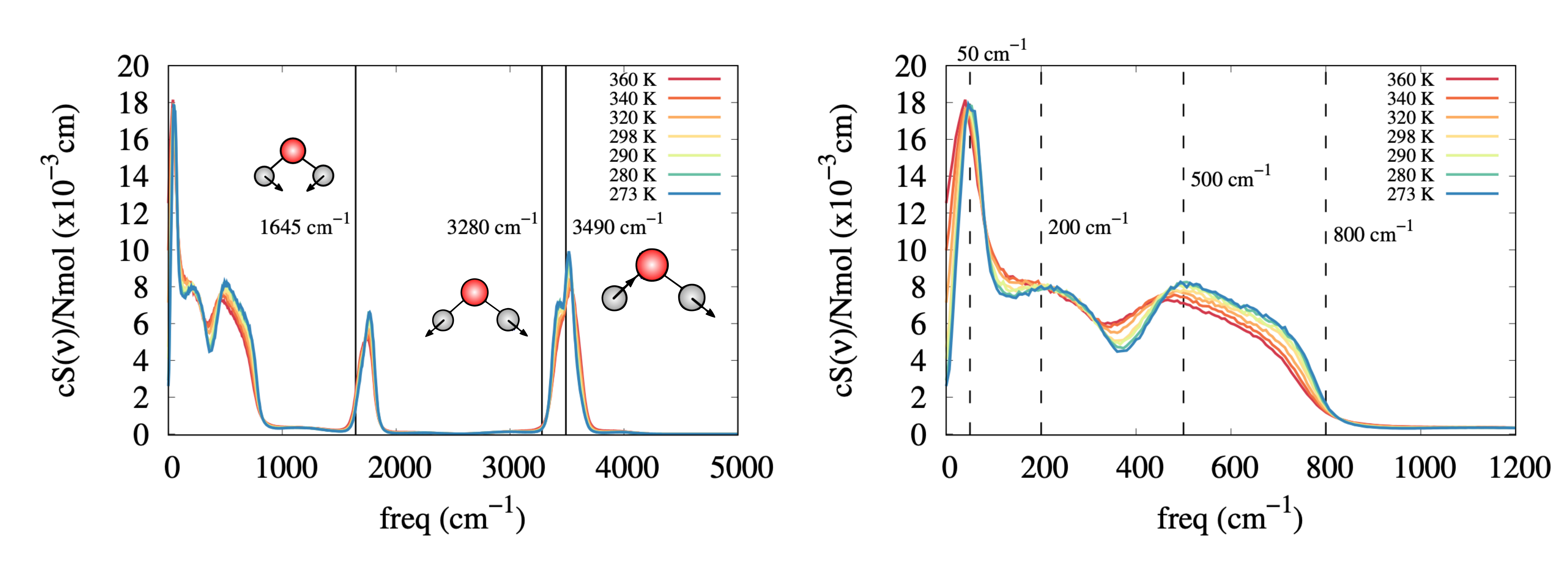
FULL SPECTRUM QUANTUM CORRECTIONS

Specific heat capacity correction

$$c_V^{Qm} - c_V^{Cl} = \frac{k_B}{N_{mol}} \int_0^\infty d\nu S(\nu) w_{c_V}(\nu)$$

$$w_{c_V}(\nu) = \frac{u^2 e^u}{(1 - e^u)^2} - 1, \; u = \beta h \nu$$

VIBRATIONAL SPECTRA



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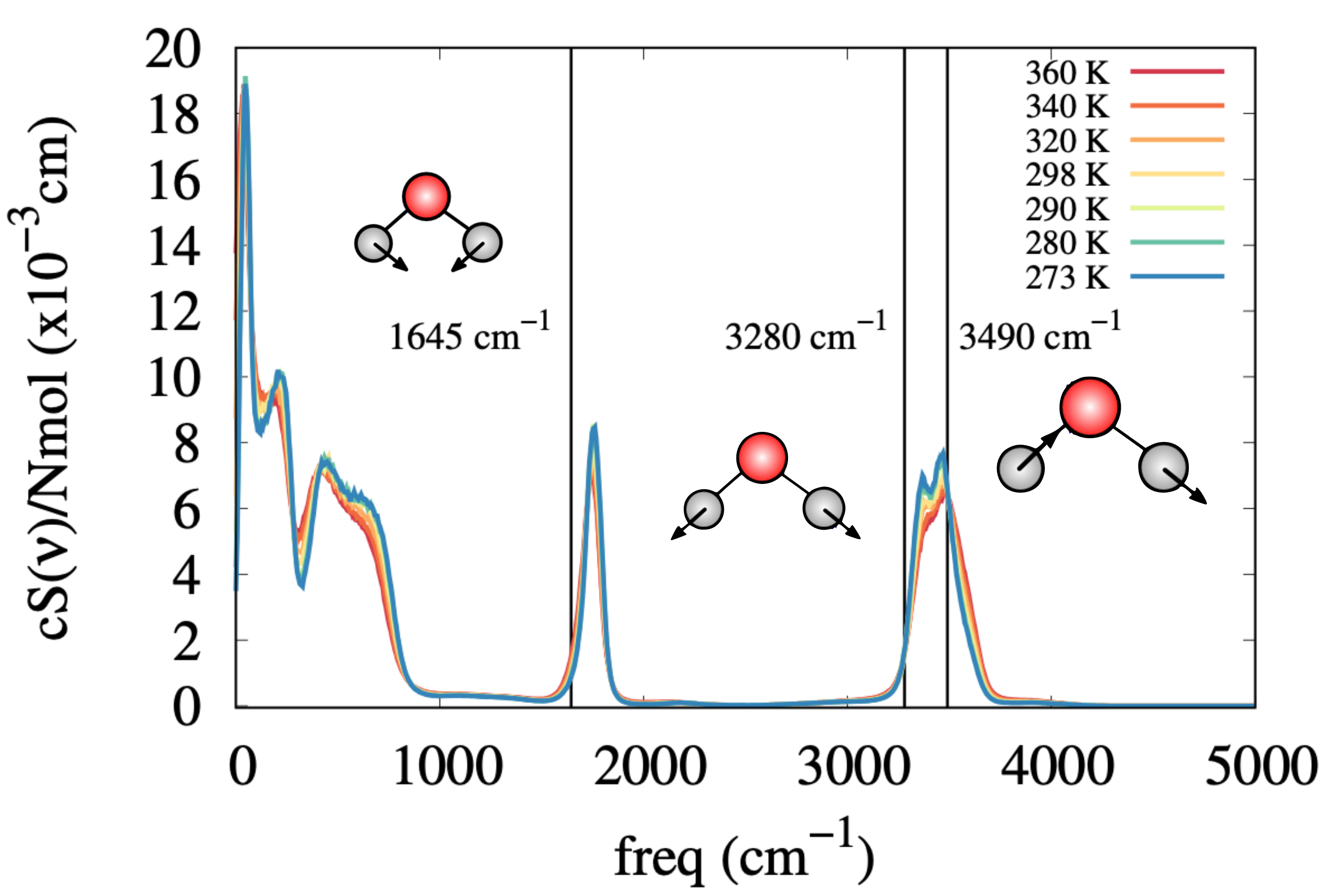
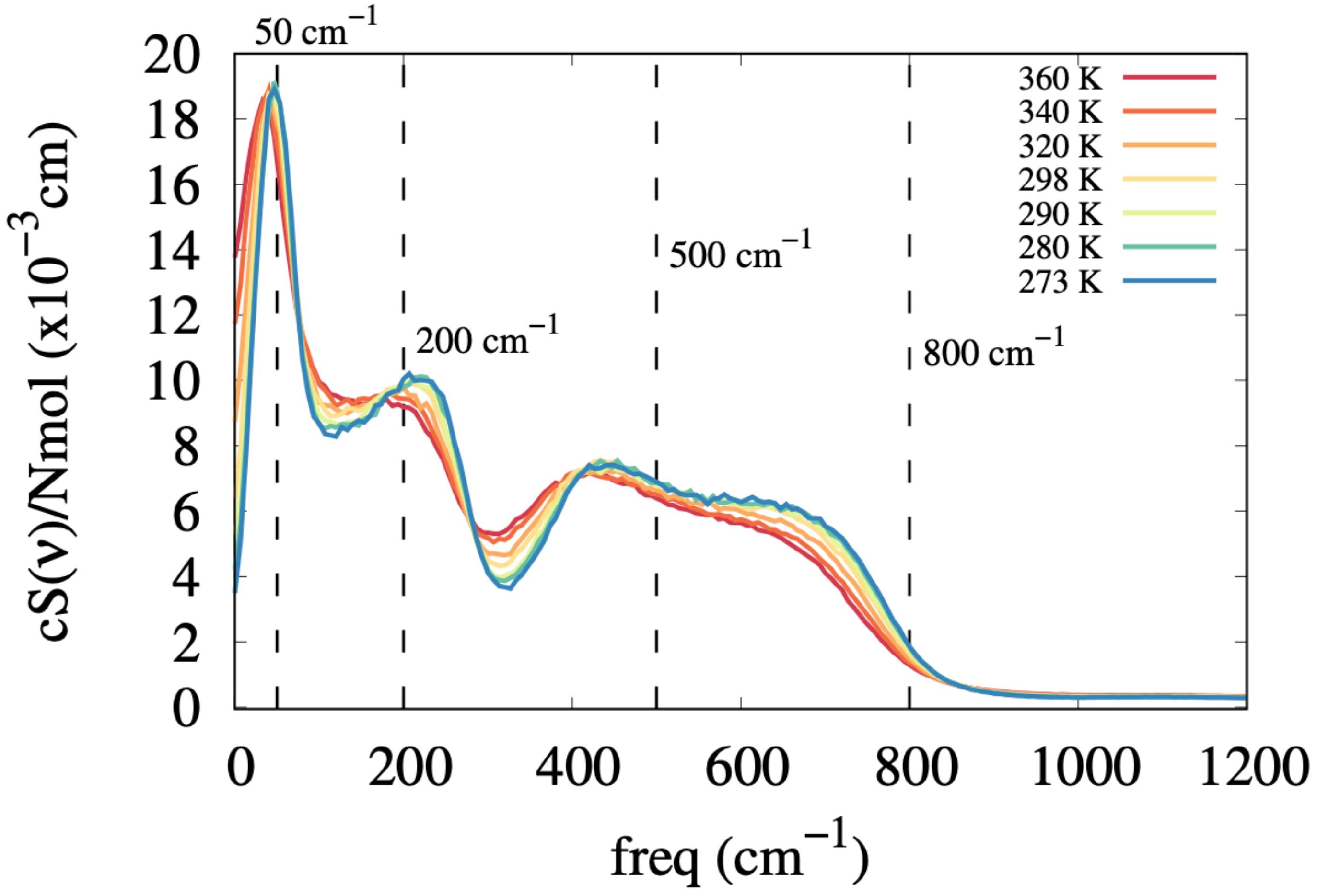
VIBRATIONAL SPECTRA





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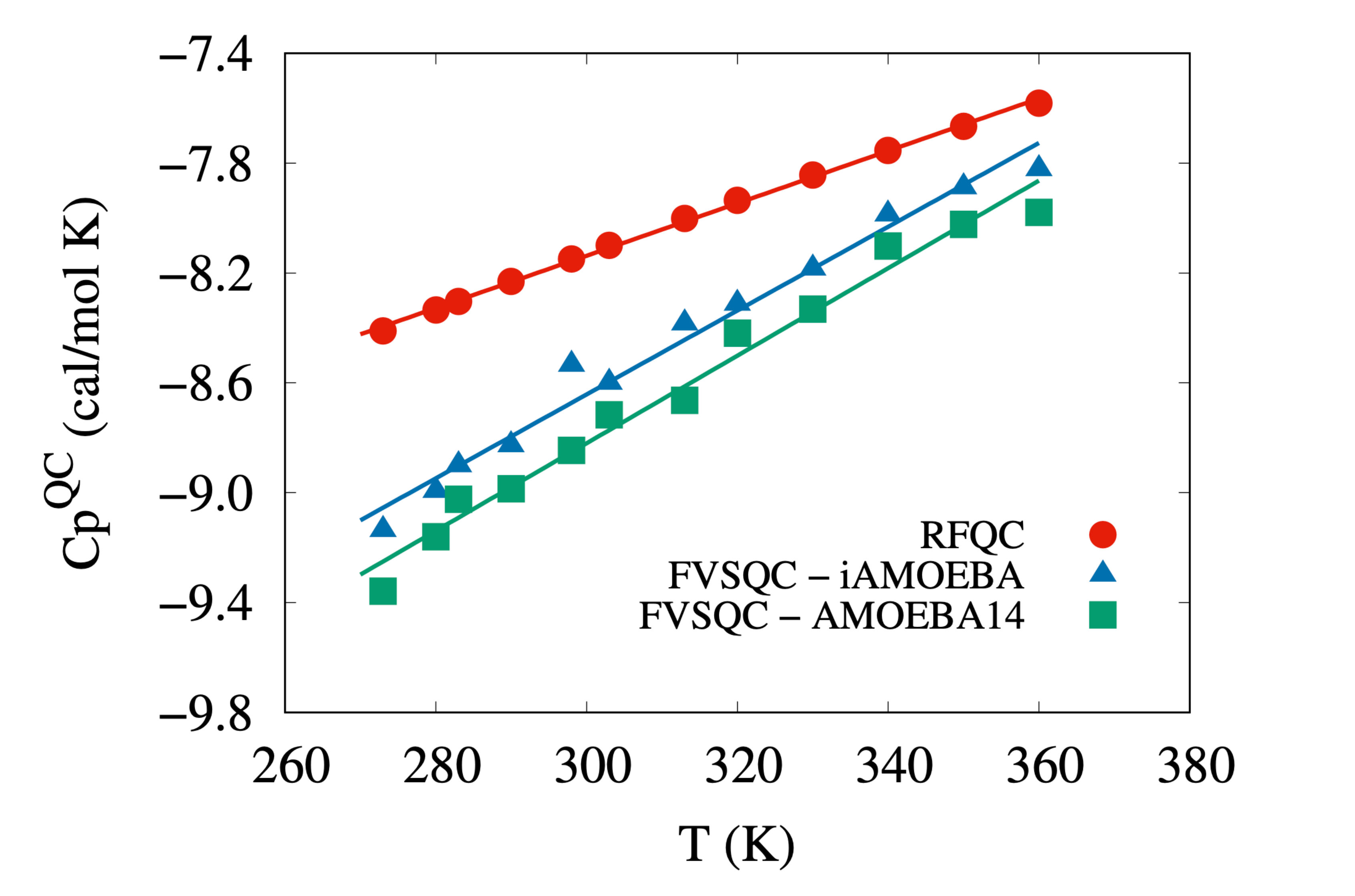
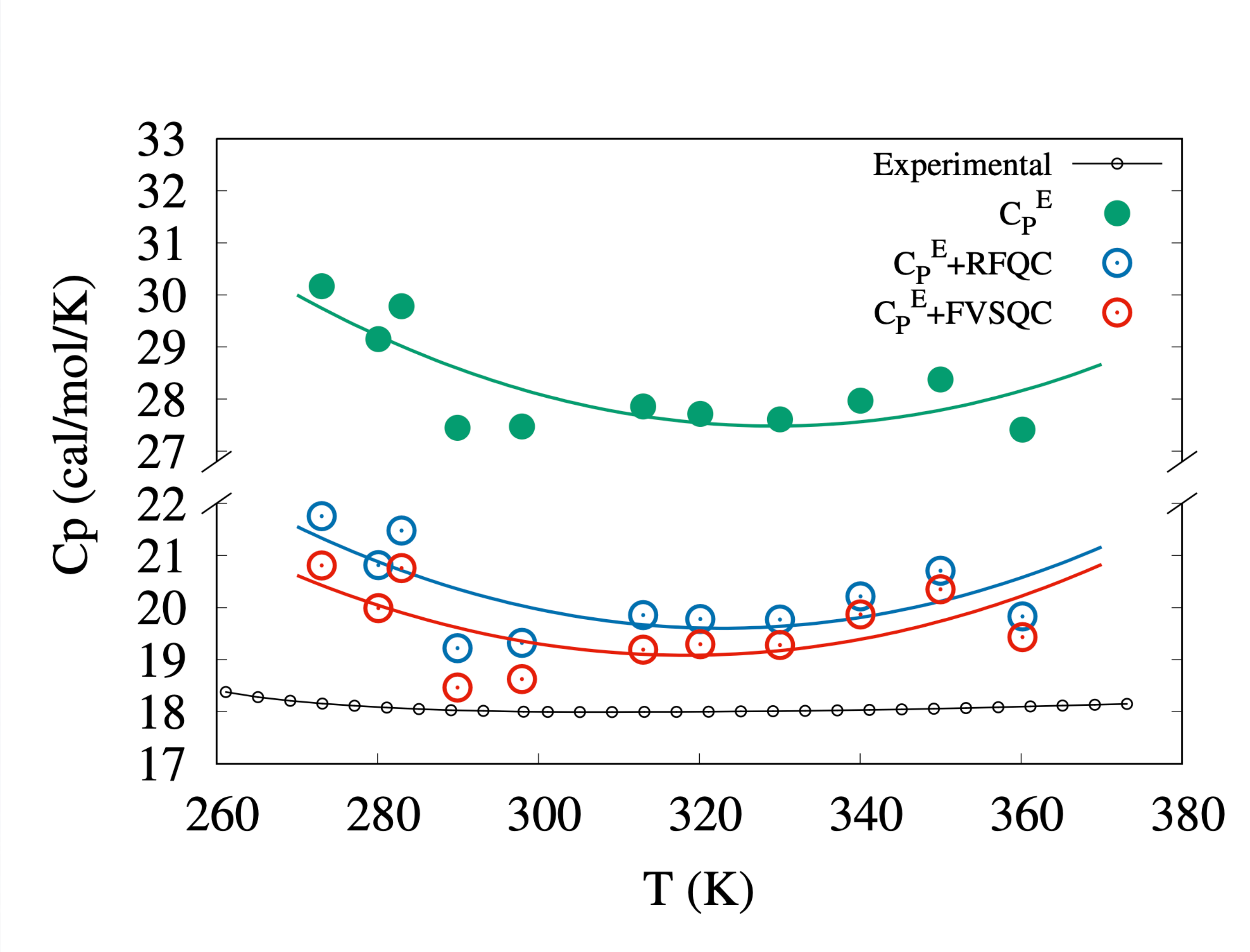
COMPARE QUANTUM CORRECTIONS



CORRECTED SPECIFIC HEAT CAPACITY



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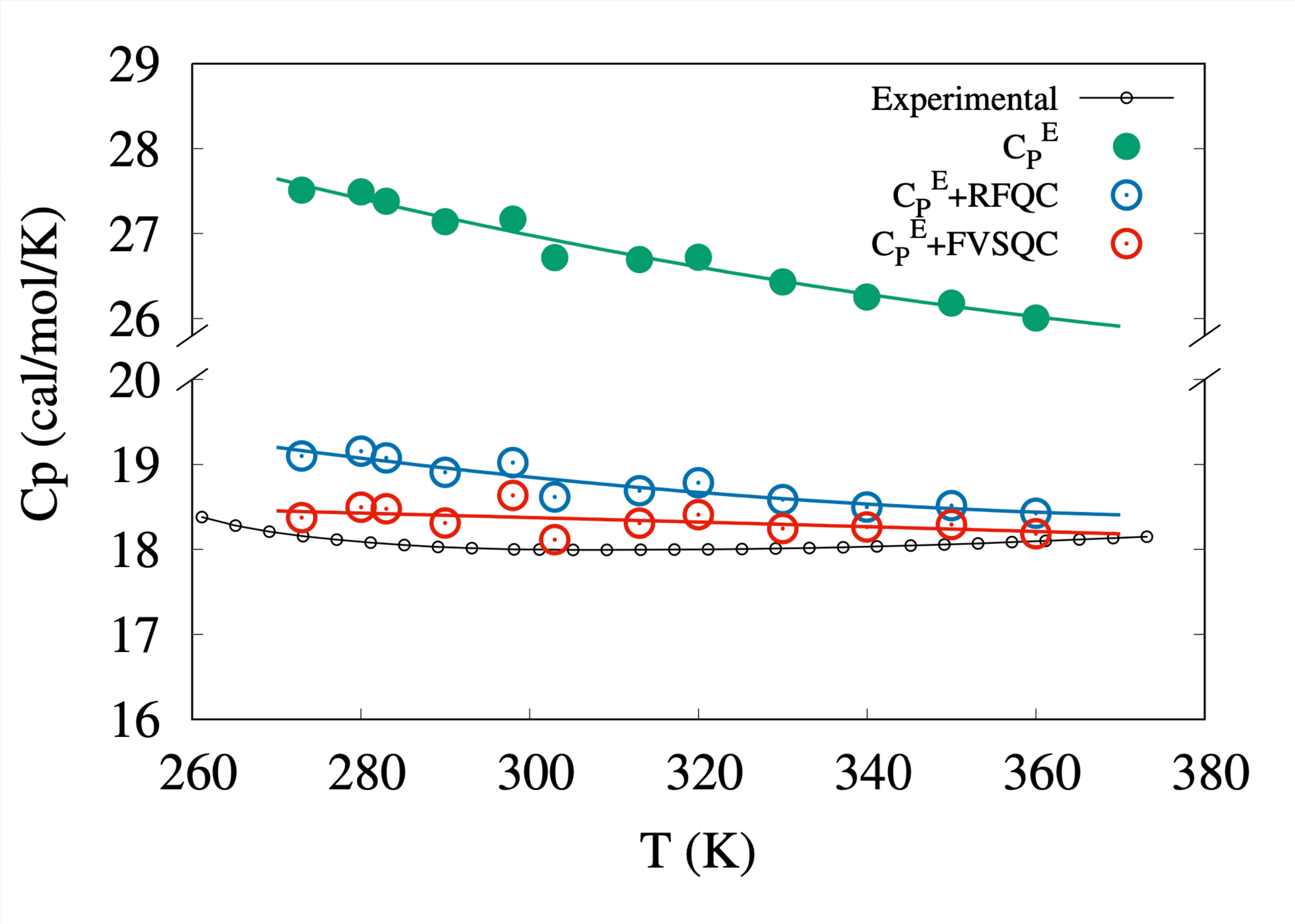
CORRECTED HEAT CAPACITY



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Thank you