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Mathieu Cancade, Margarida Costa Gomes, Agilio A. H. Padua. Investigating electrolytes for divalent ion batteries: from molecular dynamics to experiments. Journée de Printemps SCF Rhône-Alpes, Jun 2024, Grenoble, France. . hal-04734964

HAL Id: hal-04734964

<https://hal.science/hal-04734964v1>

Submitted on 14 Oct 2024

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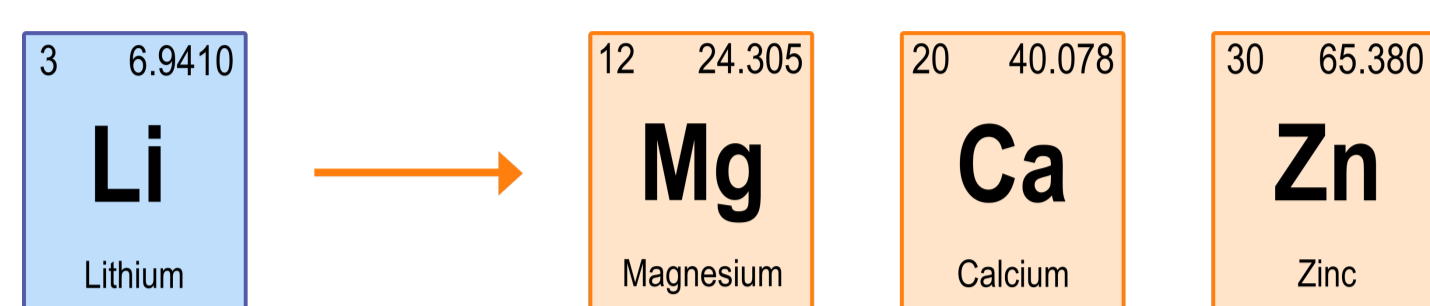


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Investigating electrolytes for divalent ion batteries: from molecular dynamics to experiments

Mathieu Cancade, Margarida Costa Gomes, Agílio A. H. Pádua

Université de Lyon, ENS Lyon, CNRS Laboratoire de Chimie, F69342 Lyon, France
mathieu.cancade@ens-lyon.fr

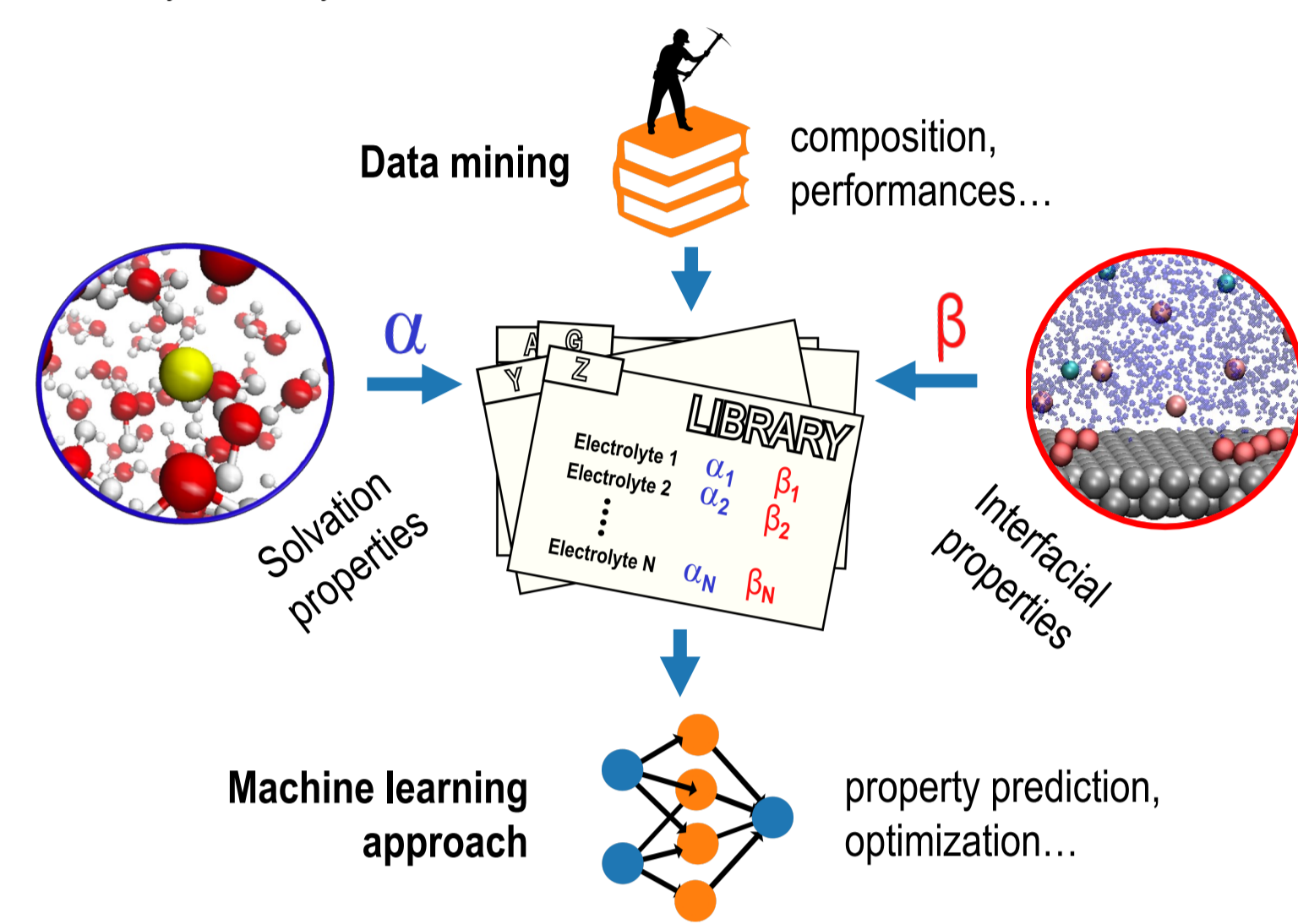


Issues to overcome:

Anarchic deposition on metallic anodes (dendrites)
Side reactions with the electrolyte, creation of a passivation layer

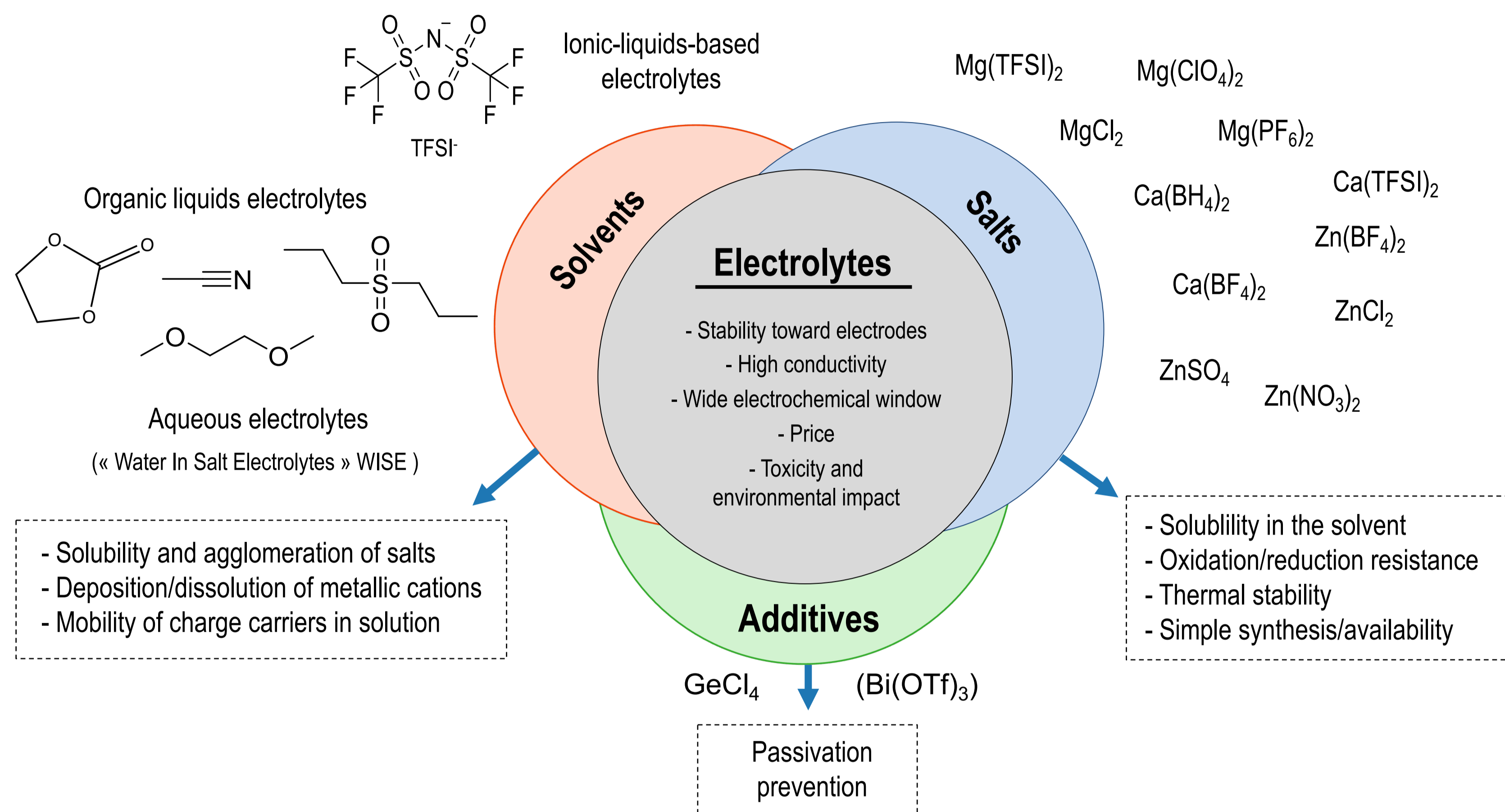
LEGEND Project

An Electrolyte Library for the Next Generation of Divalent Ion Batteries



Objective: build an electrolyte library by combining microscopic simulations, experiments and machine learning.

Electrolytes for Divalent Ion Batteries: Composition and Characteristics



Selected References: 1. Rajput, N. N. *et al. J. Am. Chem. Soc.* **2015**, 137 (9), 3411–3420. 2. Man, Y. *et al. Sci. Bull.* **2023**, 68 (16), 1819–1842.

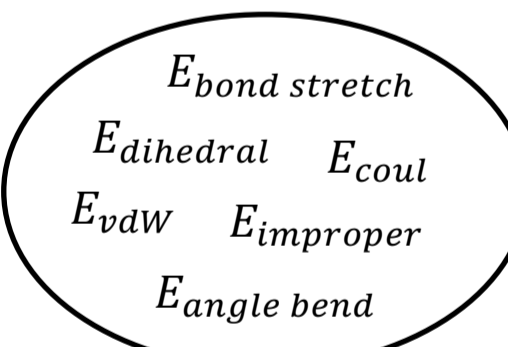
From Polarizable Molecular Dynamics (MD)...

Compared to classical force fields for molecular simulations, **polarizable molecular dynamics (MD)** offers a gain of accuracy and realism by describing **explicitly** many-body polarization effects *i.e.* modeling how the electrostatic charge distribution responds to a change in the surrounding electric field. This method provides a compromise between two levels of description: quantum calculations where the electrons are described explicitly and atomic simulations in which the atoms are considered as a whole.

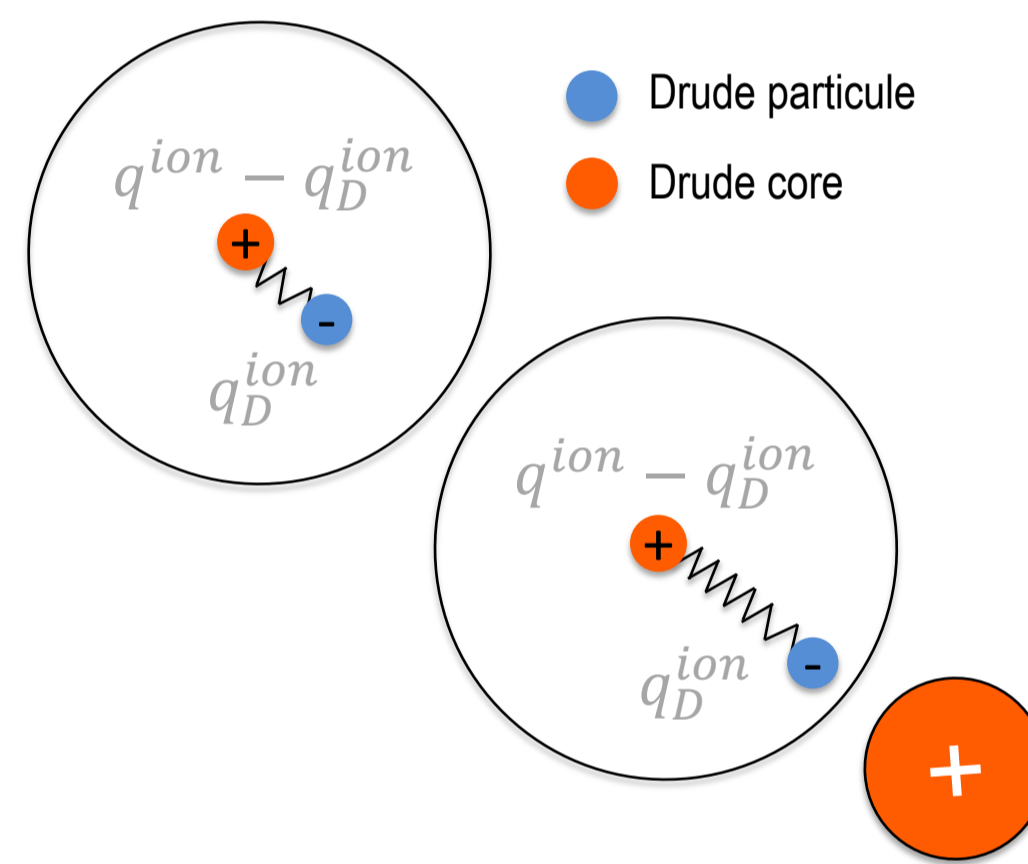
$$\begin{cases} m_i \frac{d^2 r_i(t)}{dt^2} = f_i(t) \\ f_i(t) = -\frac{\partial v(r)}{\partial r_i(t)} \end{cases}$$

m_i atomic masses r_i atomic positions

Potential energy function $v(\mathbf{r})$



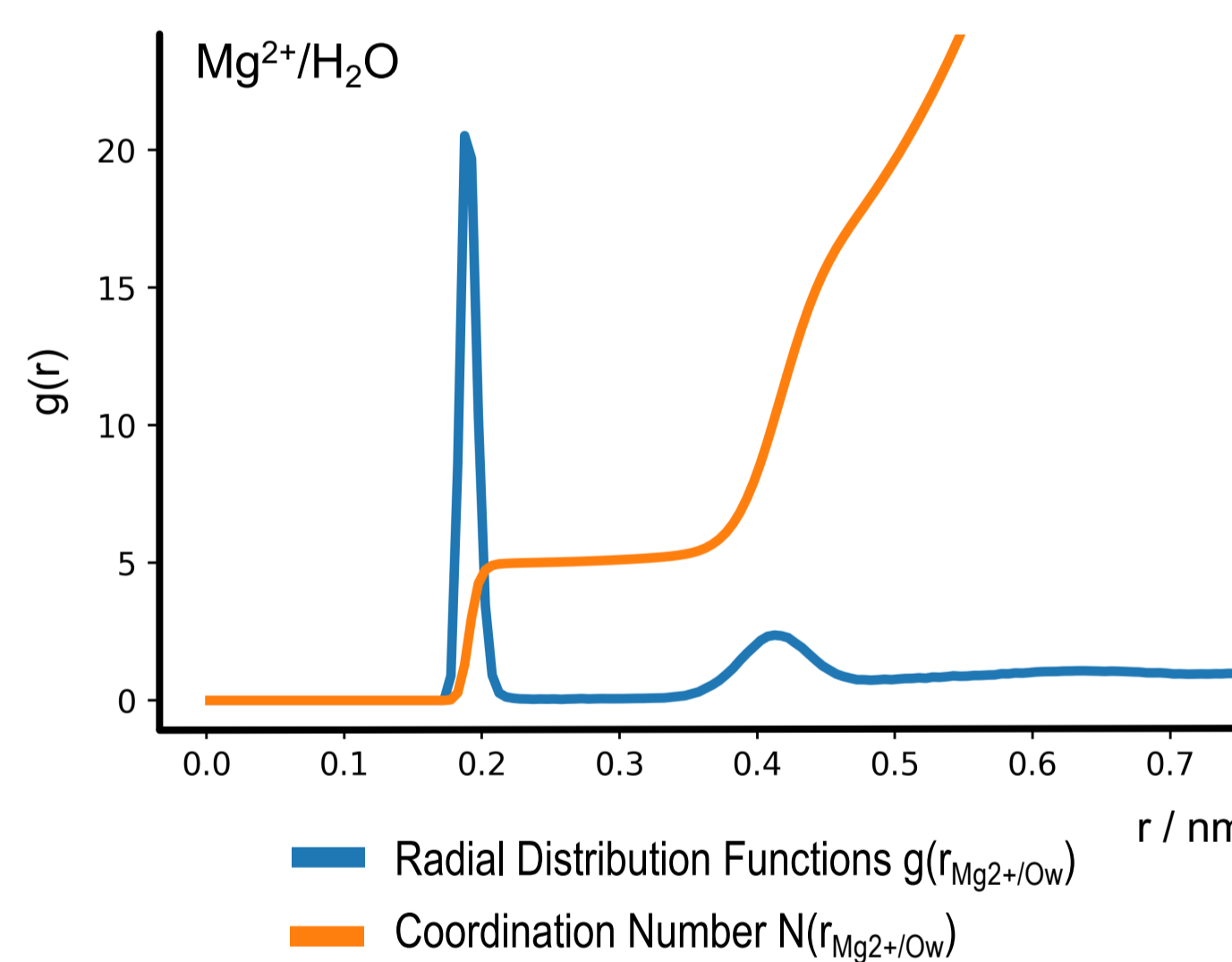
As for classical MD, the description of the system is based on the parametrization of potentials describing the interactions between bonded and non-bonded atoms. The dynamic evolution of the system is determined from the integration of **Newton's second law of motion**. This simple representation allows to simulate systems with a **large number of atoms** – not reachable with calculations at the quantum level – while reproducing the behavior of the electrostatic charge distribution, what is impossible with classical MD.



The **classical Drude oscillator model** is a way to depict explicitly these polarization effects. To do so, a slightly charged Drude particle is linked to a core via an harmonic potential. A change in the electric field of the environment creates a displacement of the particle, and a modification of the global charge distribution. Dipole/dipole or charge/dipole interactions can lead to **over-polarization issues**, which are avoidable using damping functions (Thole, Tang-Toennis).

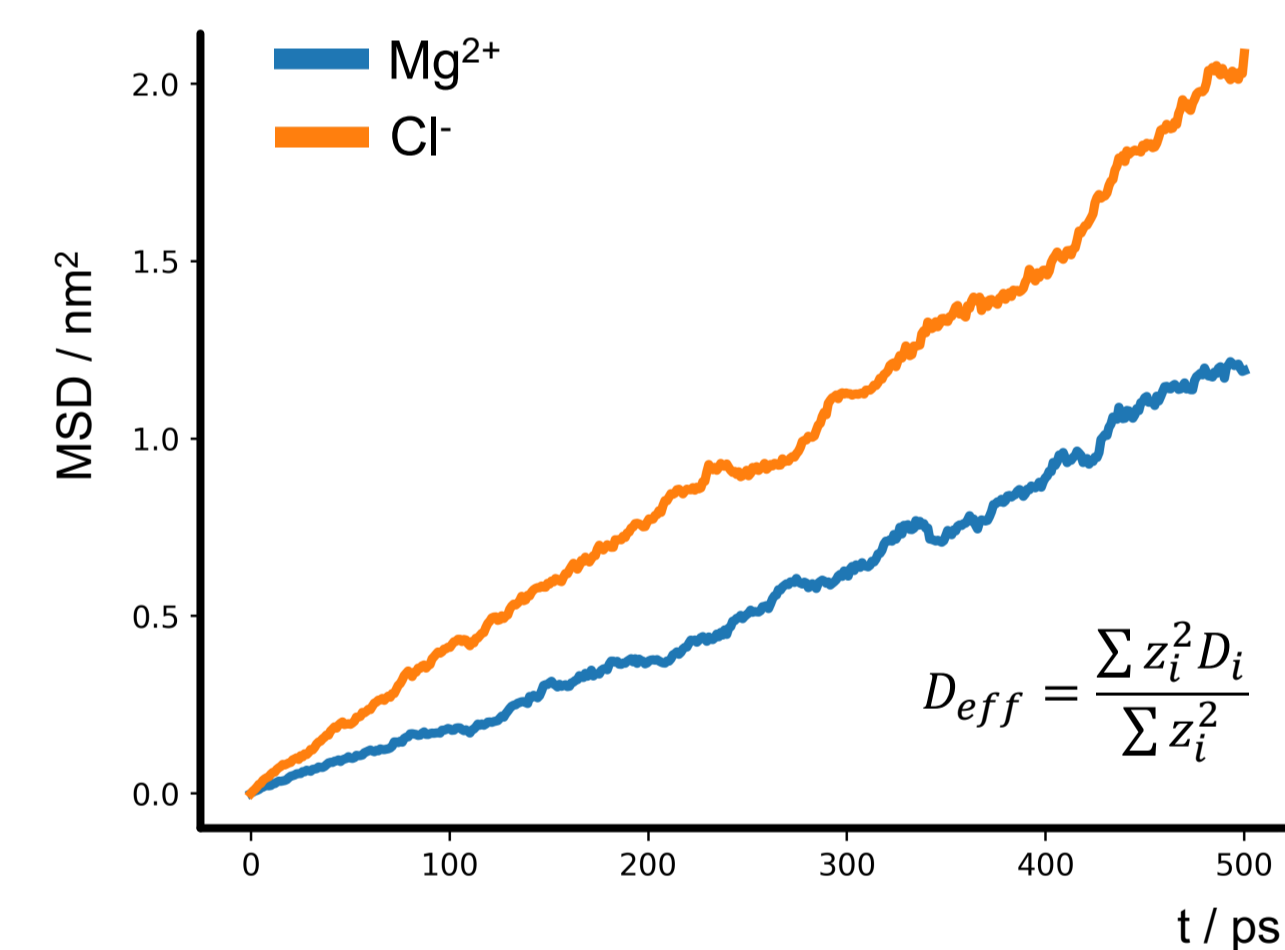
Static properties

Descriptors of the **solvation environment** (such radial distribution functions or coordination numbers) are paramount to understand how charge carriers are surrounded and stabilized within the electrolyte. In addition to this static view of solvation shells, thermodynamic calculations such free-energy ones rationalize solvation/de-solvation processes.



Dynamic properties

Time-dependent properties (such self-diffusion coefficients) depict the evolution and movement of electrolyte components. The use of big systems is an advantage for relevant statistical averages.



	D_{eff} (10^{-5} cm ² s ⁻¹)	
	Experiment	This study
Ca ²⁺ + 2 Cl ⁻	1.20	1.06 ± 0.40
Mg ²⁺ + 2 Cl ⁻	1.15	1.15 ± 0.34
Zn ²⁺ + 2 Cl ⁻	1.14	1.17 ± 0.36

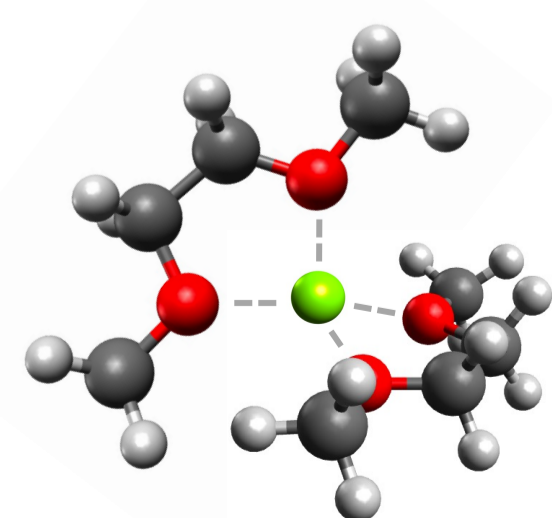
Selected References: 1. Goloviznina, K. *et al.*, Transferable, Polarizable Force Field for Ionic Liquids. *J. Chem. Theory Comput.* **2019**, 15, 5858–5871. 2. Dequidt, A. *et al.* Thermalized Drude Oscillators with the LAMMPS Molecular Dynamics Simulator. *J. Chem. Inf. Model.* **2016**, 56, 260–268.

... to Calorimetry Experiments

Isothermal titration calorimetry (ITC) is one of the first-choice techniques to **quantify molecular interactions in solution**. The cell where the study takes place is in contact with an isothermal environment: the calorimeter's oil bath. Throughout the experiment, injections of known volumes of titrant are performed and the heat exchanged between the cell and the bath is measured and converted into a voltage by the thermopiles, an assembly of thermocouples in series. A reference cell, filled with titrate solution, is used as a point of comparison.

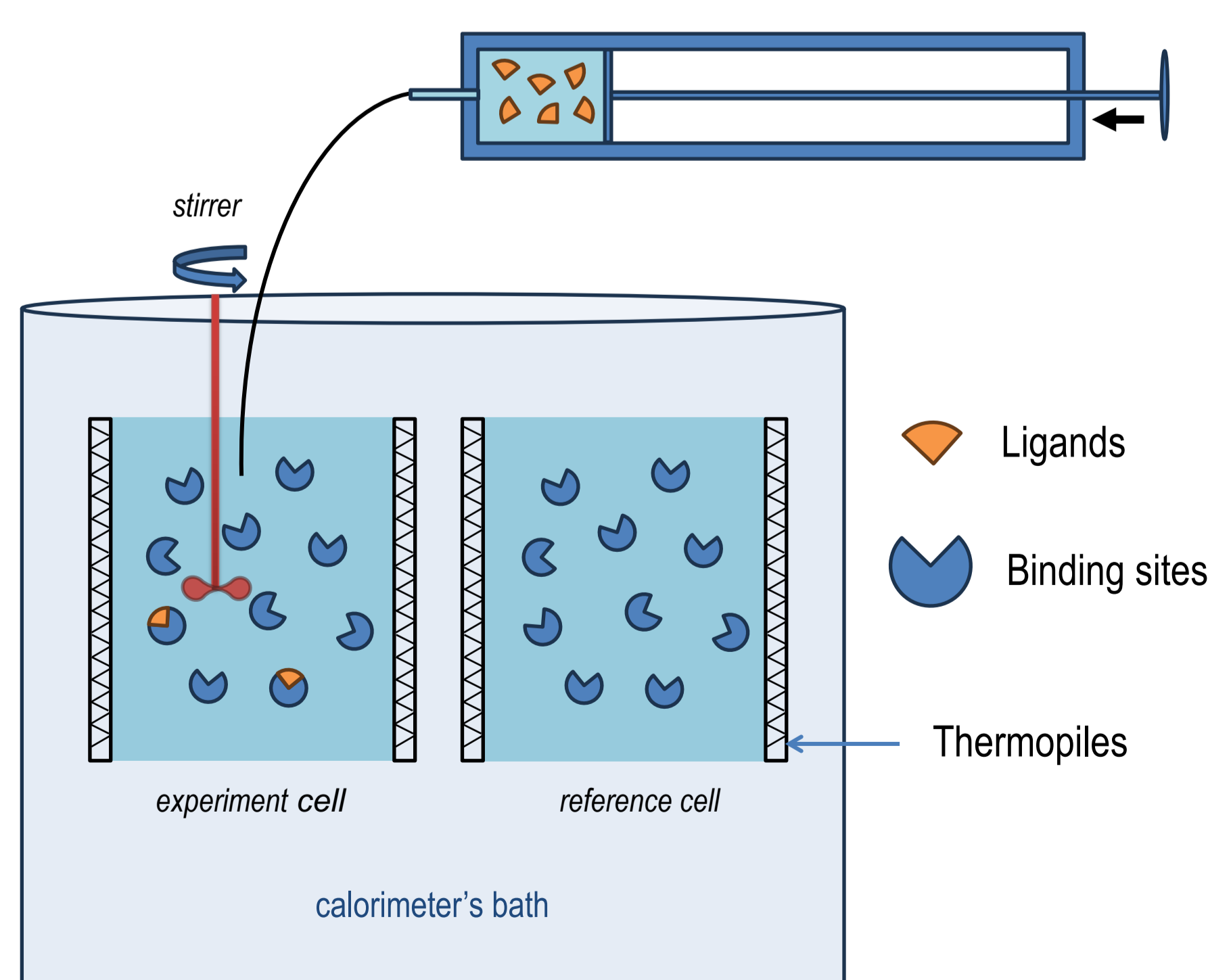
The total heat flow, plotted as a function of time, is the immediate result given by the instrument. Classically, this thermogram shows a peak after each injection, as long as binding sites are available. The thermogram integration gives access to thermodynamic descriptors of the process (stoichiometry of the interaction, binding affinity etc.)

In the case of electrolytes, ITC can provide **binding constants**, **coordination stoichiometries** or **enthalpies** resulting from the interactions between solvent molecules and charge carriers, in support of theoretical calculations. These investigations are in progress, only the principle is presented here.

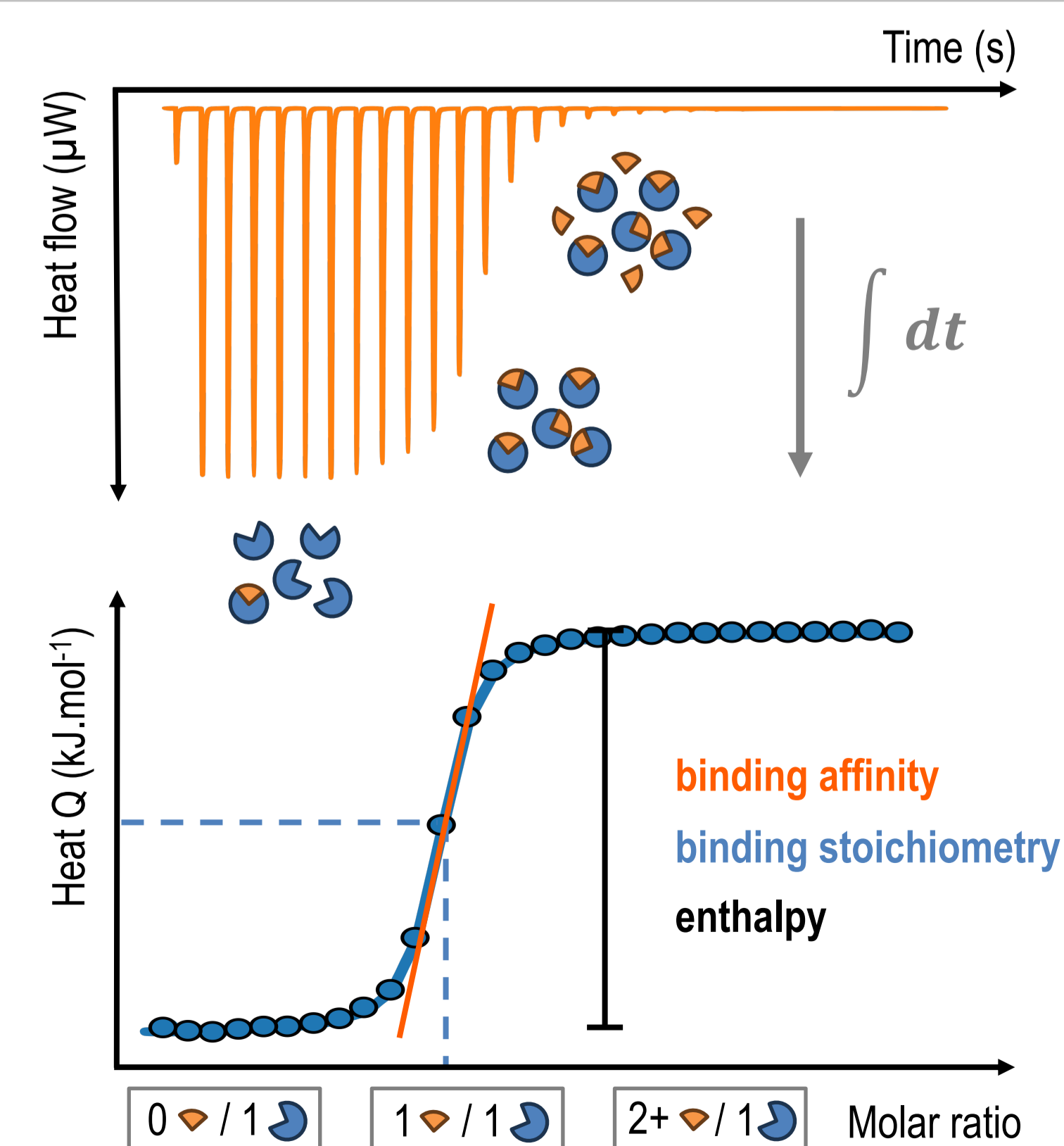


Selected Reference: Bastos, M. *et al.*, Isothermal titration calorimetry. *Nat Rev Methods Primers* **2023**, 17.

Isothermal titration calorimetry set-up



Data analysis



Acknowledgements

anr

PEPR BATTERIES

CBPsmn
Centre Saint-Pascal de Simulation et de Modélisation Numérique

Ionic Liquids Group:
website



Personal website:



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UPE Lyon 1

CNRS

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