A Generalized Empirical Force Field for Glassy and Crystalline Sulfide Electrolytes

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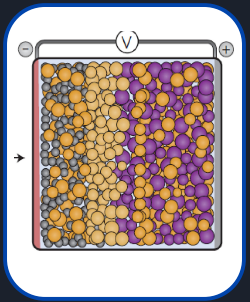
Context

Why sulfide solid electrolytes?

✔ **All-solid-state batteries** aim to replace flammable liquid electrolytes

✔ **Sulfide glasses and crystals** (SiS_2–Li_2S, P_2S_5–Li_2S, etc.) are **excellent Li^+ conductors**

✔ **Na**-based electrolytes are **promising alternative** to Li-ion

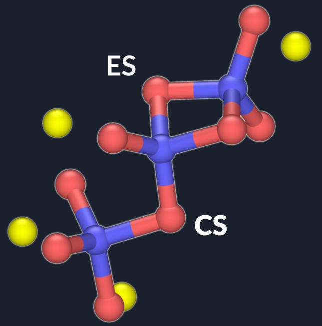


Why a classical force-field for simulation ?

- Quantum calculations (DFT):
  ✗ accurate but too slow for **large systems**

- Existing empirical models for sulfides:
  ✗ poor structure factors **S(k)** (X-ray/neutron diffraction experiments)

  ✗ failure to reproduce **edge-sharing tetrahedra**



Methodology: BM3PM force-field

- **Two-body term:**

$$V_{ij}(r) = A_{ij}e^{-r/\rho_{ij}} + \frac{q_i q_j}{r} - \frac{C_{ij}}{r^6}$$

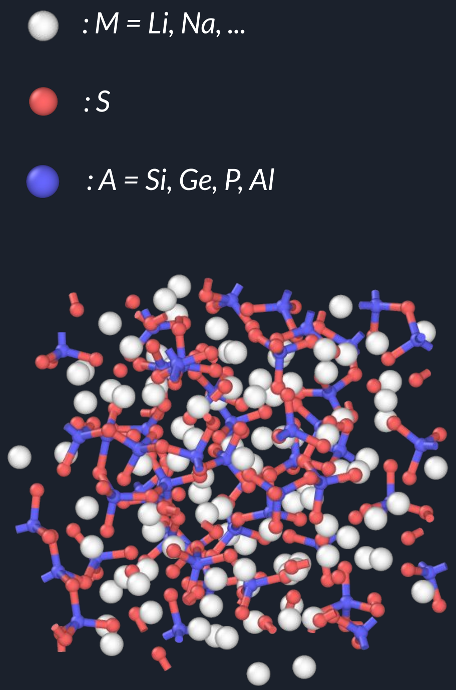
Born–Mayer repulsion + Coulomb + dispersion for all pairs (A–S, M–S, etc.)

- **Three-body term**:

$$V_3(\theta) = k_b(\theta - \theta_0)^2$$

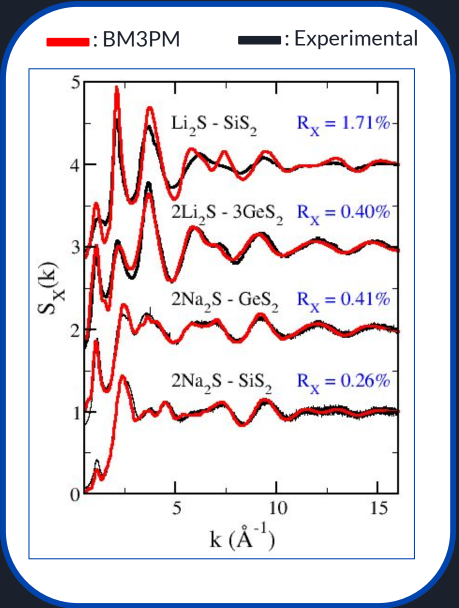
A–S–A (A = Si, Ge, P, Al) for bridging sulfurs

The parameters are then **fitted in two steps**: first to **crystal structures**, to reproduce lattice parameters, densities and vibrational stability; and second to glass data, by **matching the experimental structure factors S(k)**

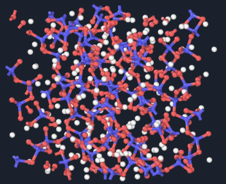


Results

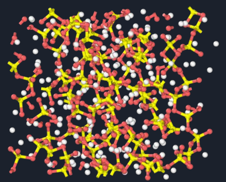
Glasses:



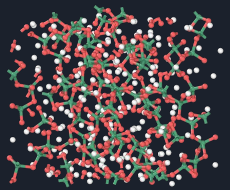
Na_2S - SiS_2



Na_2S - GeS_2



Na_2S - P_2S_5

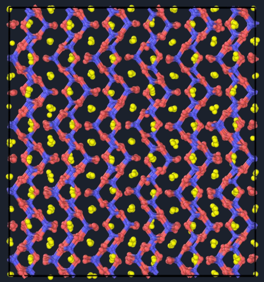


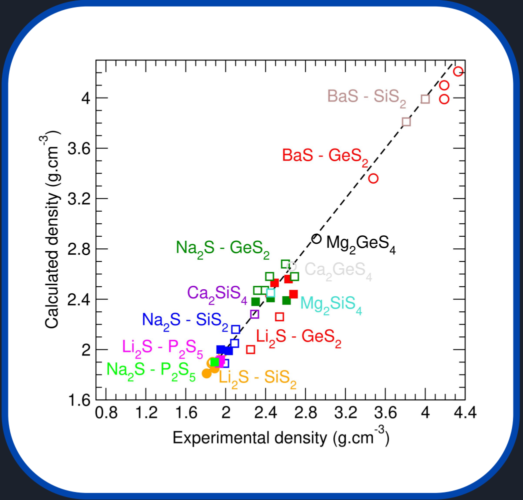
X-ray and neutron structure factors S(k) are reproduced with high accuracy, **outperforming** earlier classical potentials and some DFT-based models.

Crystals:

Quantitative agreement:

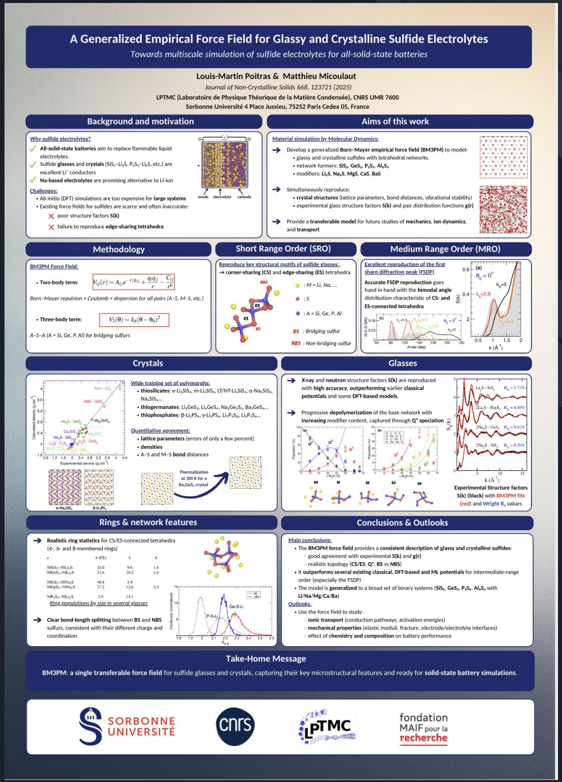
- ✔ lattice parameters
- ✔ densities
- ✔ A–S and M–S bond distances





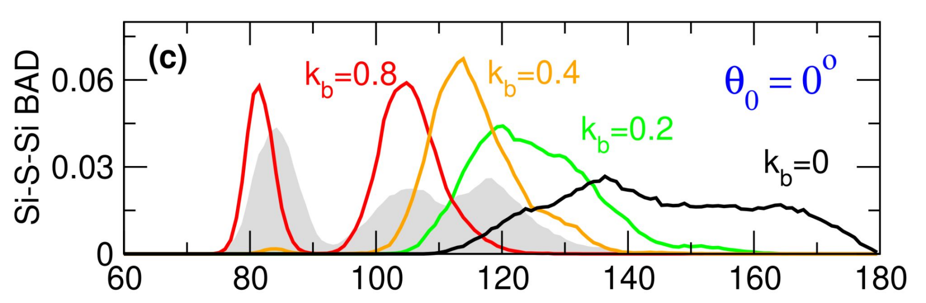
Thank you for your attention !

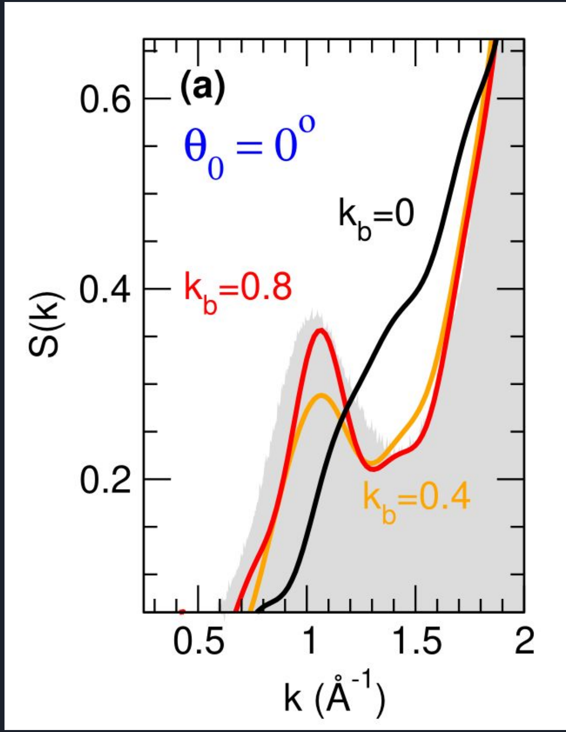
And come see my poster



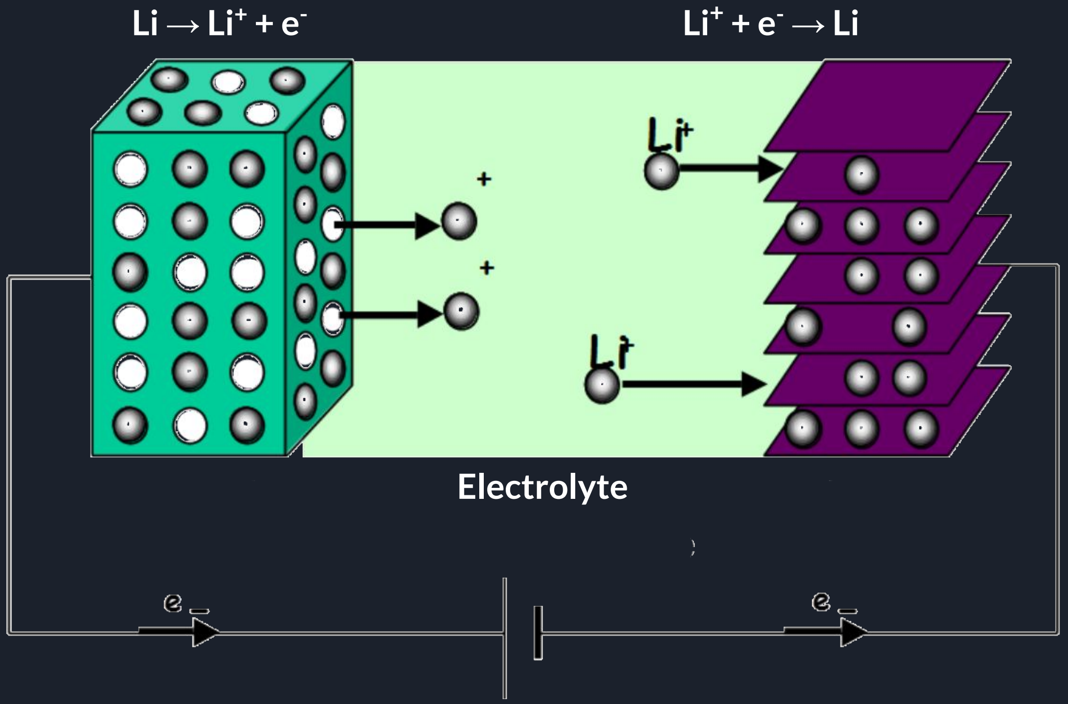
Effect of the 3-body term

➔ Accurate **first sharp diffraction peak (FSDP)** reproduction goes hand in hand with the bimodal angle distribution characteristic of **CS- and ES-connected tetrahedra**





⚙️ Une batterie... quésaco ?



💡 Autoroute à 2 voies :

- ➔ à l'intérieur, les ions Li^+ voyagent dans l'électrolyte
- ➔ à l'extérieur, les électrons e^- circulent dans le circuit.

🔄 Ce flux combiné fait fonctionner la batterie.