redoxSQE

Toward modeling redox reactions with empirical potentials

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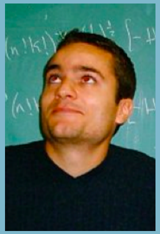


JSC, November 4, 2014 | **Wolf Dapp**

Outline

Introduction and motivation

- fixed / variable charge models (QE, AACT, SQE)
- split-charge equilibration (SQE)
- ions and charges, RedoxSQE

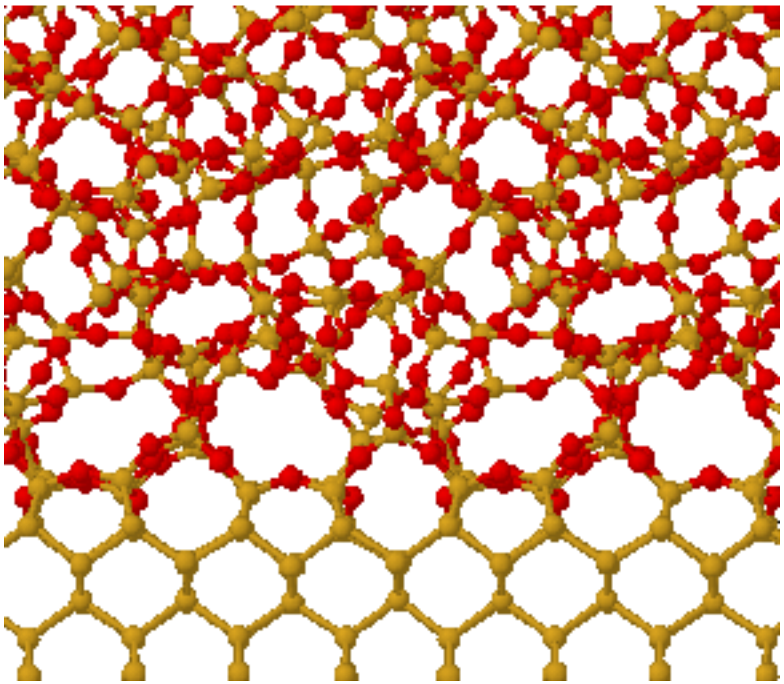
RedoxSQE

Proof of concept application: contact electrification

Proof of concept application: atomistic battery discharge

Why variable charge methods?

(effective) charge of a given atom unknown before simulation



Tu & Tersoff, PRL **84** (2000)

Si-SiO_2 interface

Si atom in bulk SiO_2:
Q(formal) = 4e
***Q*(effective) ≈ 2.6e**

continuous transition

Si atom in Si bulk (with SiO_2 interface):
Q(formal, or in pure Si) = 0e
***Q*(effective) << 1e**

For any chemically heterogeneous system
➔ **must adjust charges on the fly** (in particular for redox)

Justification / falsification of variable-charge models

Bottom-up approach

relate terms in the models to matrix elements or electronic densities of a DFT formulation

for SQE: Verstraelen *et al.;* JCP **138**, 074108 (2013), see his talk later

Top-down approach

match *ab initio* **computed charges** & **polarizabilities** or **experimental data**

investigate generic properties of the model, i.e., what are generic (macroscopic) **response functions**

Charge equilibration models

$$V = V_{\text{short}}$$
$$+ \sum_{i,j} \frac{Q_i Q_j}{4\pi\epsilon_0} J(|r_{i,j}|)$$
$$+ \sum_i \chi_i Q_i$$
$$+ \sum_i \frac{\kappa_i}{2} Q_i^2$$

short-ranged

(screened) Coulomb

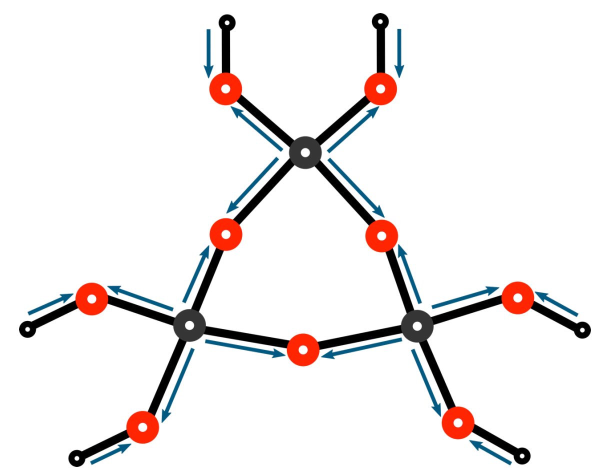
electronegativity

atomic hardness

QE (reax-FF)

$$Q_i = \sum_j q_{i,j}$$

charge is shared across a bond



Charge equilibration models

AACT (MM3-FF)

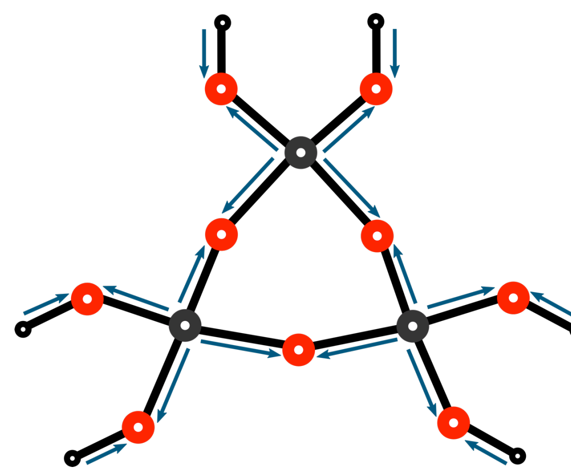
$$V = V_{\text{short}} + \sum_{i,j} \frac{Q_i Q_j}{4\pi\epsilon_0} J(|r_{i,j}|) + \sum_i \chi_i Q_i + \sum_i \frac{\kappa_i}{2} Q_i^2 + \sum_{i,j,j<i} \frac{\kappa_{i,j}}{2} q_{i,j}^2$$

- short-ranged
- (screened) Coulomb
- electronegativity
- atomic hardness
- bond-hardness

QE (reax-FF)

$$Q_i = \sum_j q_{i,j}$$

charge is shared across a bond



Comparison between generic properties of QE and AACT

	atom-based QE (e.g., reax-FF)	bond-based QE (e.g., MM3-FF)
oligomer polarizability	correct	**wrong**
skin depth	correct	**wrong**
dissociation	**wrong**	correct
polymer polarizability	**wrong**	correct
dipoles of long alcohol chains	**wrong**	correct
materials	**only metals**	**only ultra low-k**

zero bond hardness

zero atomic hardness

Charge equilibration models

AACT (MM3-FF)

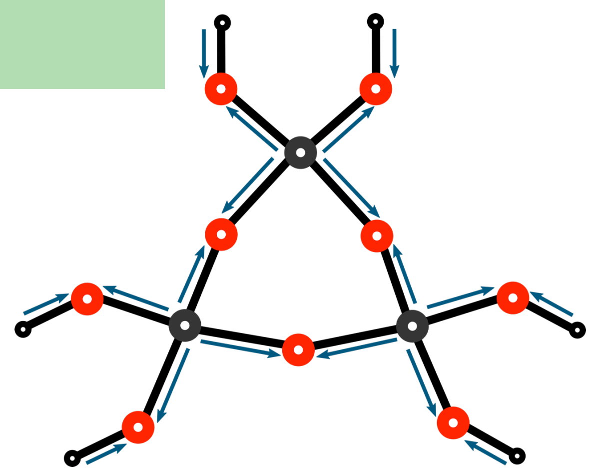
$$
\begin{aligned}
V &= V_{\text{short}} && \text{short-ranged} \\
&+ \sum_{i,j} \frac{Q_i Q_j}{4\pi\epsilon_0} J(|r_{i,j}|) && \text{(screened) Coulomb} \\
&+ \sum_{i} \chi_i Q_i && \text{electronegativity} \\
&+ \sum_{i} \frac{\kappa_i}{2} Q_i^2 && \text{atomic hardness} \\
&+ \sum_{i,j,j<i} \frac{\kappa_{i,j}}{2} q_{i,j}^2 && \text{bond-hardness}
\end{aligned}
$$

QE (reax-FF)

SQE (split charge equilibration)

$$Q_i = \sum_j q_{i,j}$$

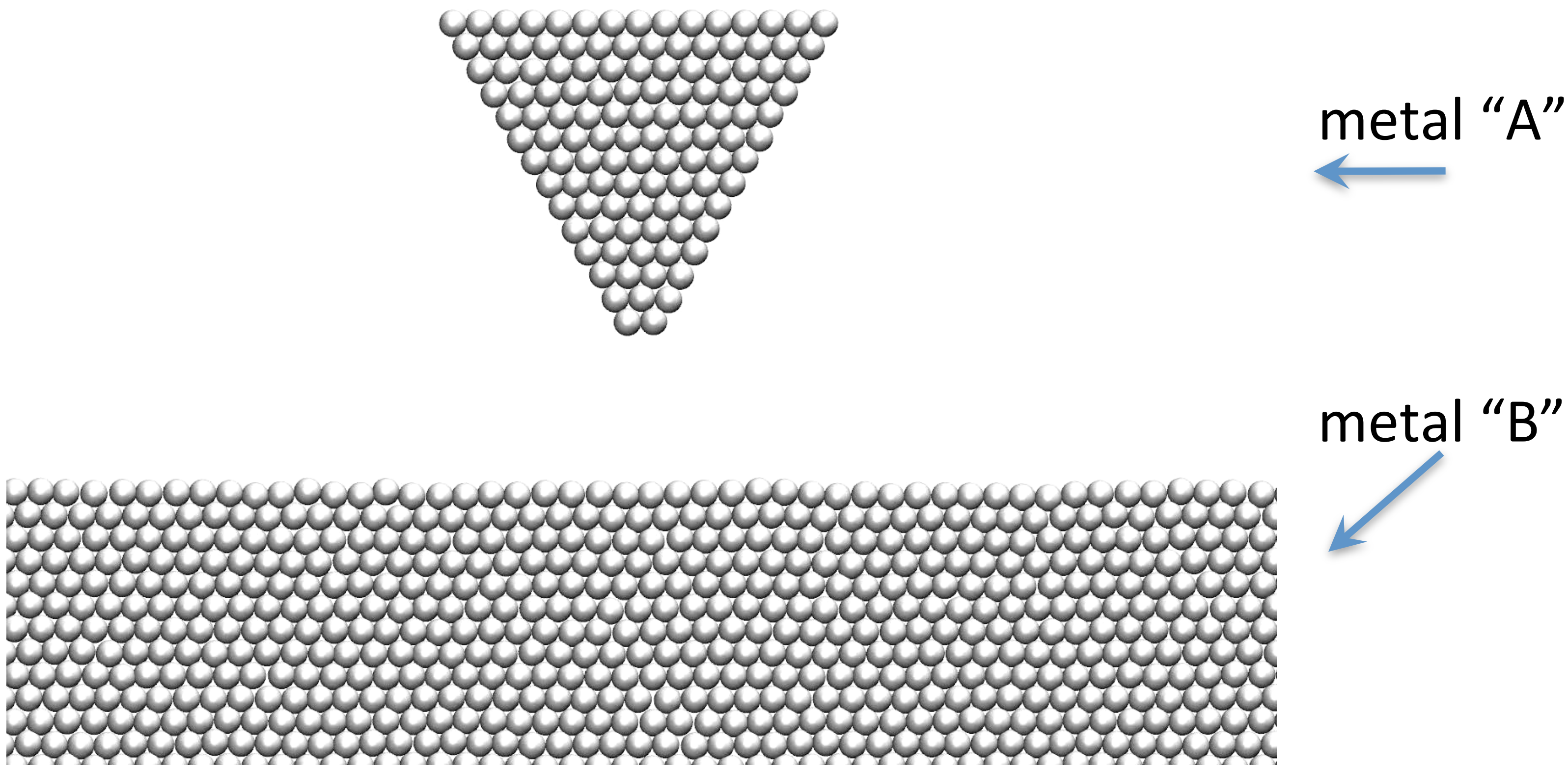
charge is shared across a bond



Comparison between generic properties of QE, AACT, and SQE

	atom-based QE (e.g., reax-FF)	bond-based QE (e.g., MM3-FF)	SQE
oligomer polarizability	correct	**wrong**	**correct**
skin depth	correct	**wrong**	**correct**
dissociation	**wrong**	correct	**correct**
polymer polarizability	**wrong**	correct	**correct**
dipoles of long alcohol chains	**wrong**	correct	**correct**
materials	**only metals**	**only ultra low-k**	**any ε_r**
errors for partial charges	**30%**	**30%**	**10%**

… but SQE still cannot describe "true" ions, nor permanent charge transfer…

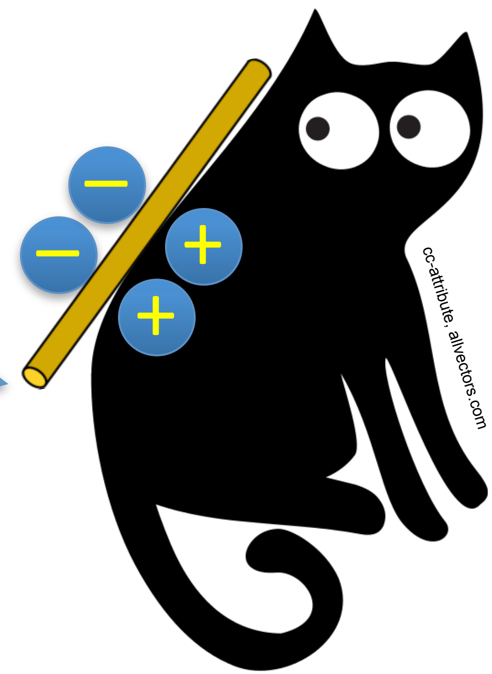


like any other method using energy minimization based **uniquely** on atomic positions, including some so-called "reactive" force fields

… subject of one of oldest basic-science experiments…

Thales of Miletus
624—546 B.C.
… replaced mythology with empiricism

amber stick



…still very relevant, for instance in copiers / laser printers

… enter redoxSQE

M. H. Müser, Eur. Phys. J. B **85**, 135 (2012)

Introduce **oxidation state** n_i as a discrete state variable

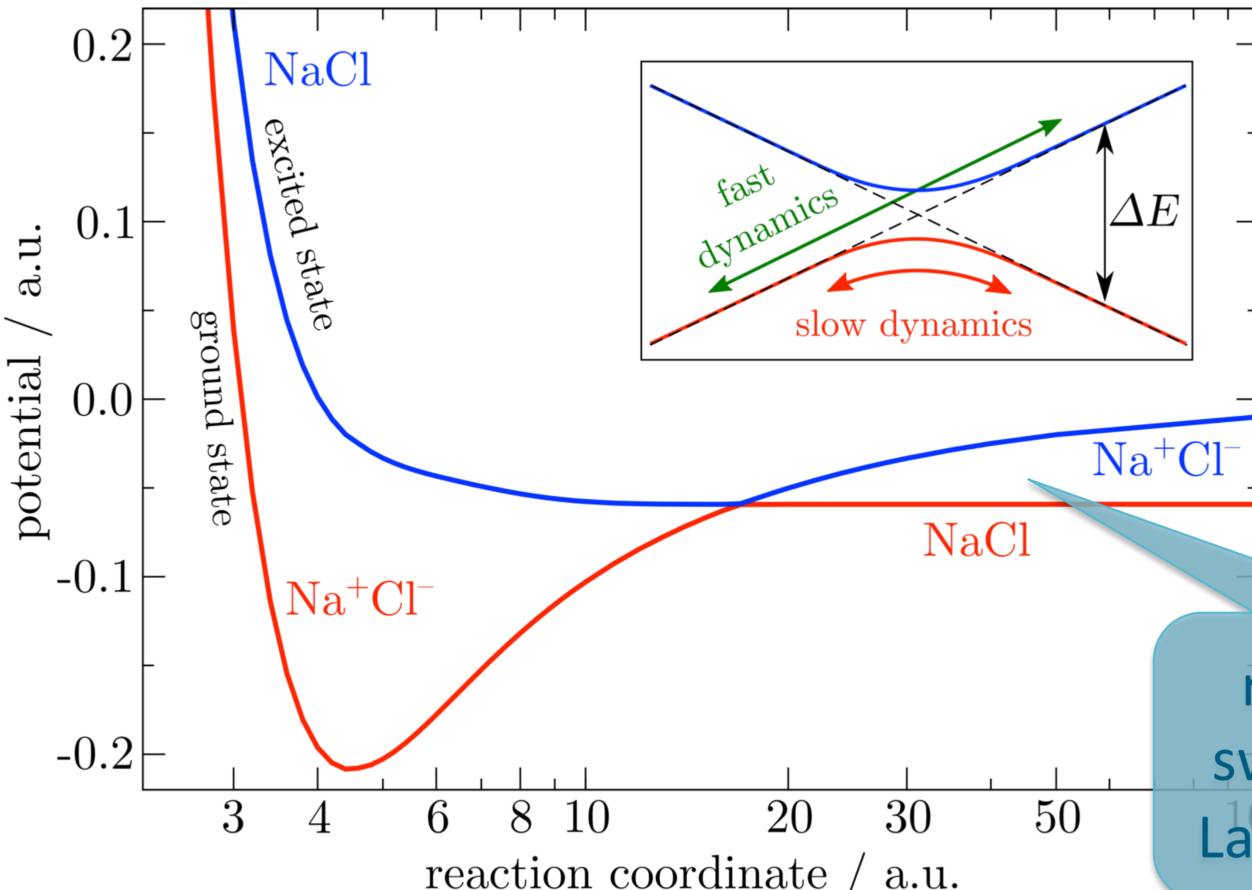
$$Q_i = n_i e + \sum_j q_{i,j}$$

not subject to bond hardness

describes **ionization** / **excess electrons**

trial redox moves (incrementing n_i , decrementing n_j)
are accepted according to a Metropolis condition on energy.

Consequences of "oxidation state"

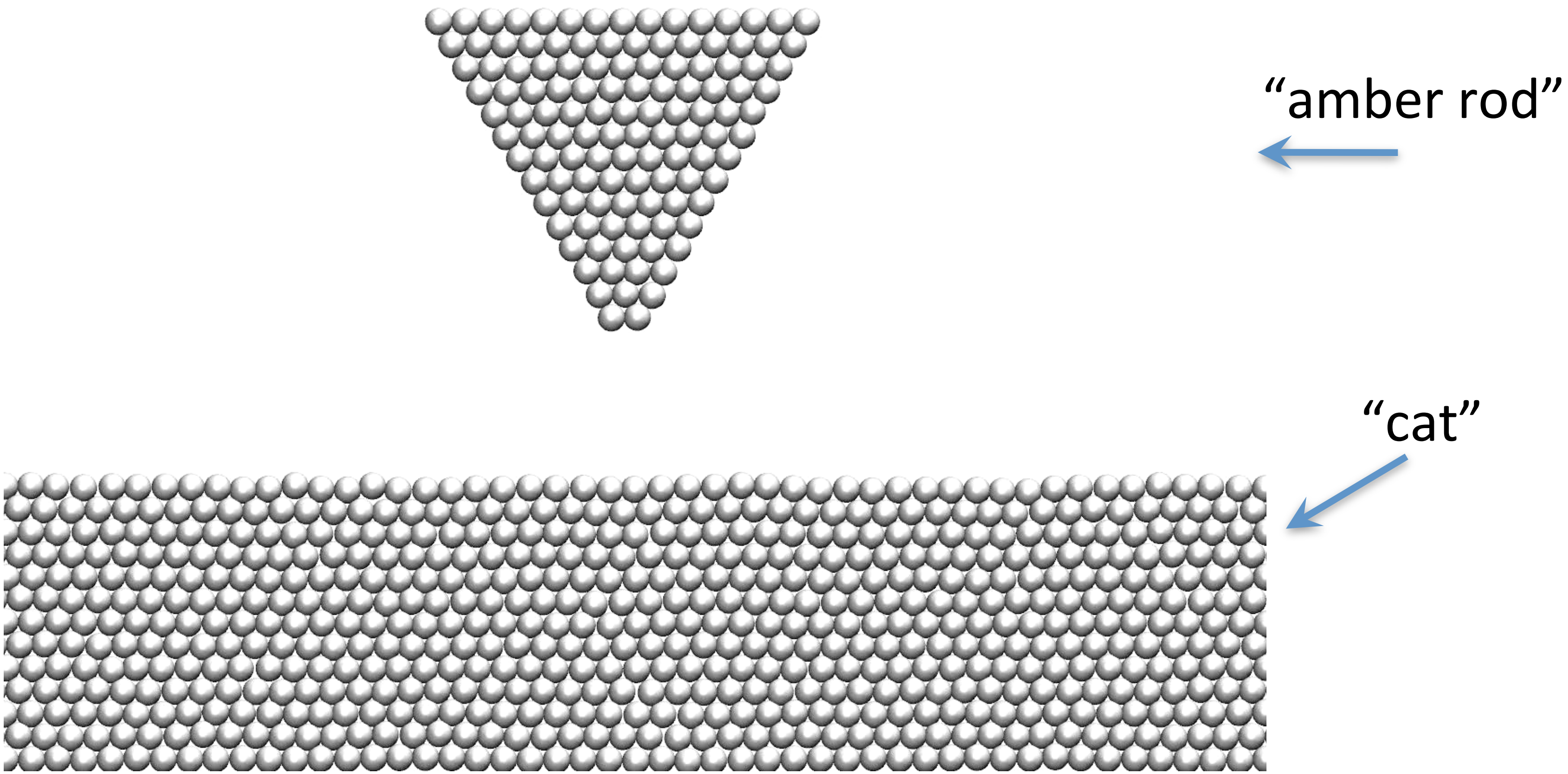


Landau-Zener dynamics when dissociating NaCl

energy levels are shifted in the presence of **polarizable solvent**

redoxSQE allows switching between Landau-Zener levels

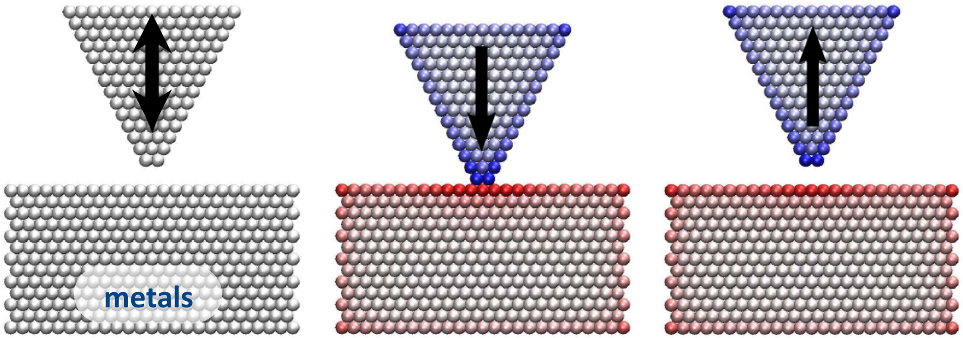
Toward the simulation of tribo-electricity



STATIC ELECTRICITY

"Yeah, really funny... rub me on the carpet and then put me in the shipping box... You will pay for this!"

Proof-of-concept application: contact electrification

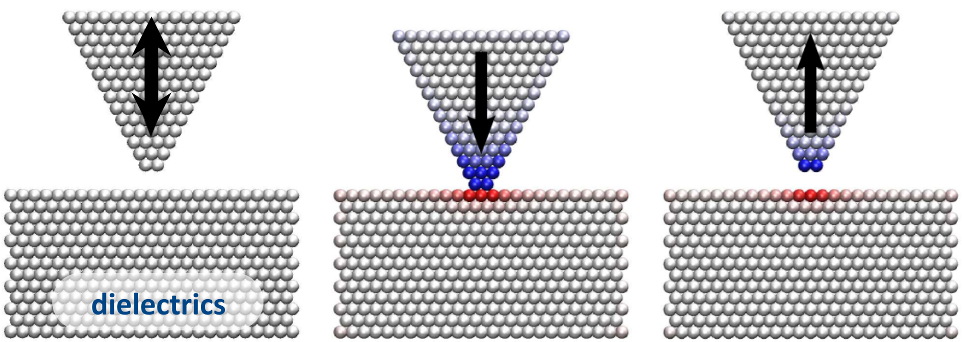


neutral bodies are brought into contact, and back

fractional charges are exchanged upon contact

reality / with RedoxSQE: parts retain charge after separation

without RedoxSQE: bodies neutral again upon separation



Dapp & Müser, EPJB **86**, 337 (2013)

QE/DFT: long-range charge transfer, no neutral bodies possible (without artificial constraints)

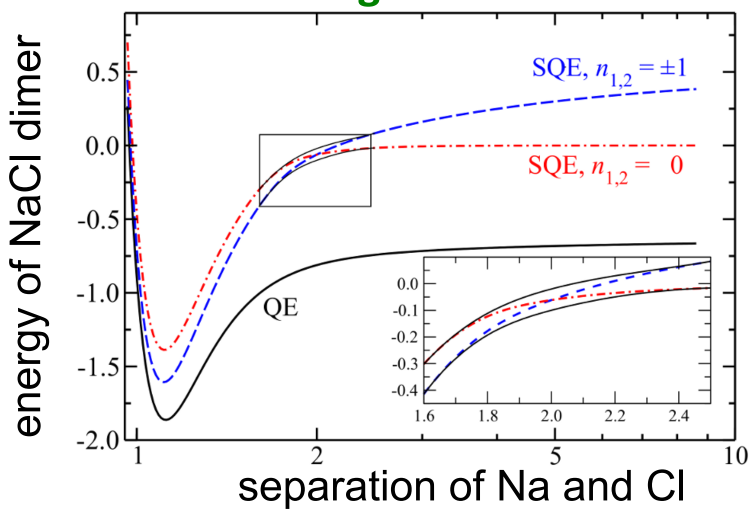
AACT/SQE: parts neutral before *and* after separation

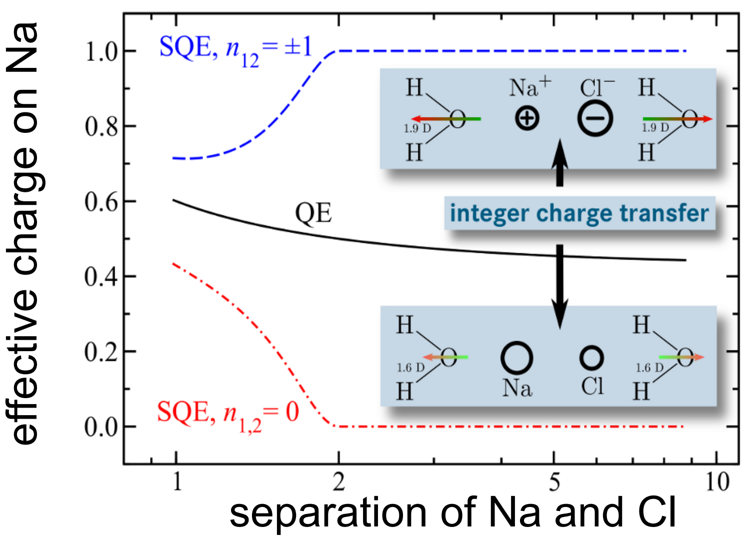
redoxSQE: despite **identical** atomic positions, forces are **different** before / after contact

→ captures history dependence
(also: polarization charges, metallic charge behavior, ...)

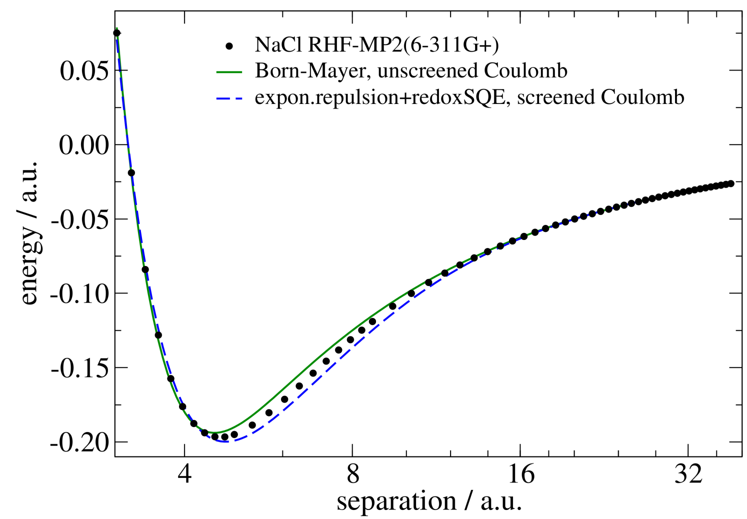
Parametrizing redoxSQE for NaCl

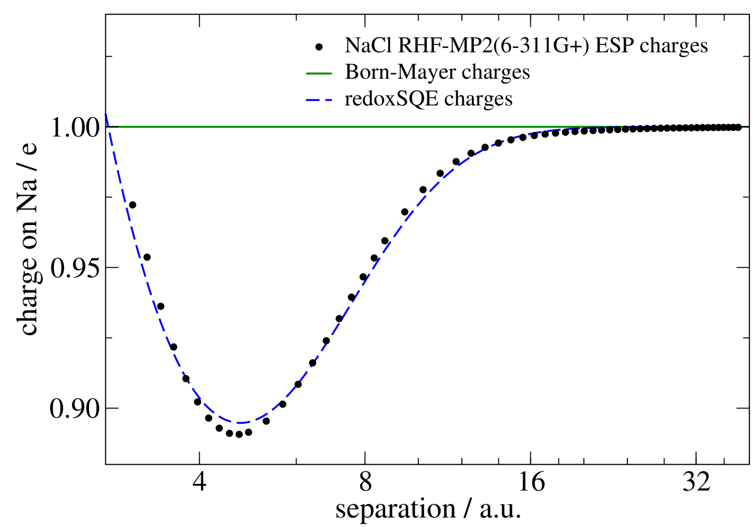
generic





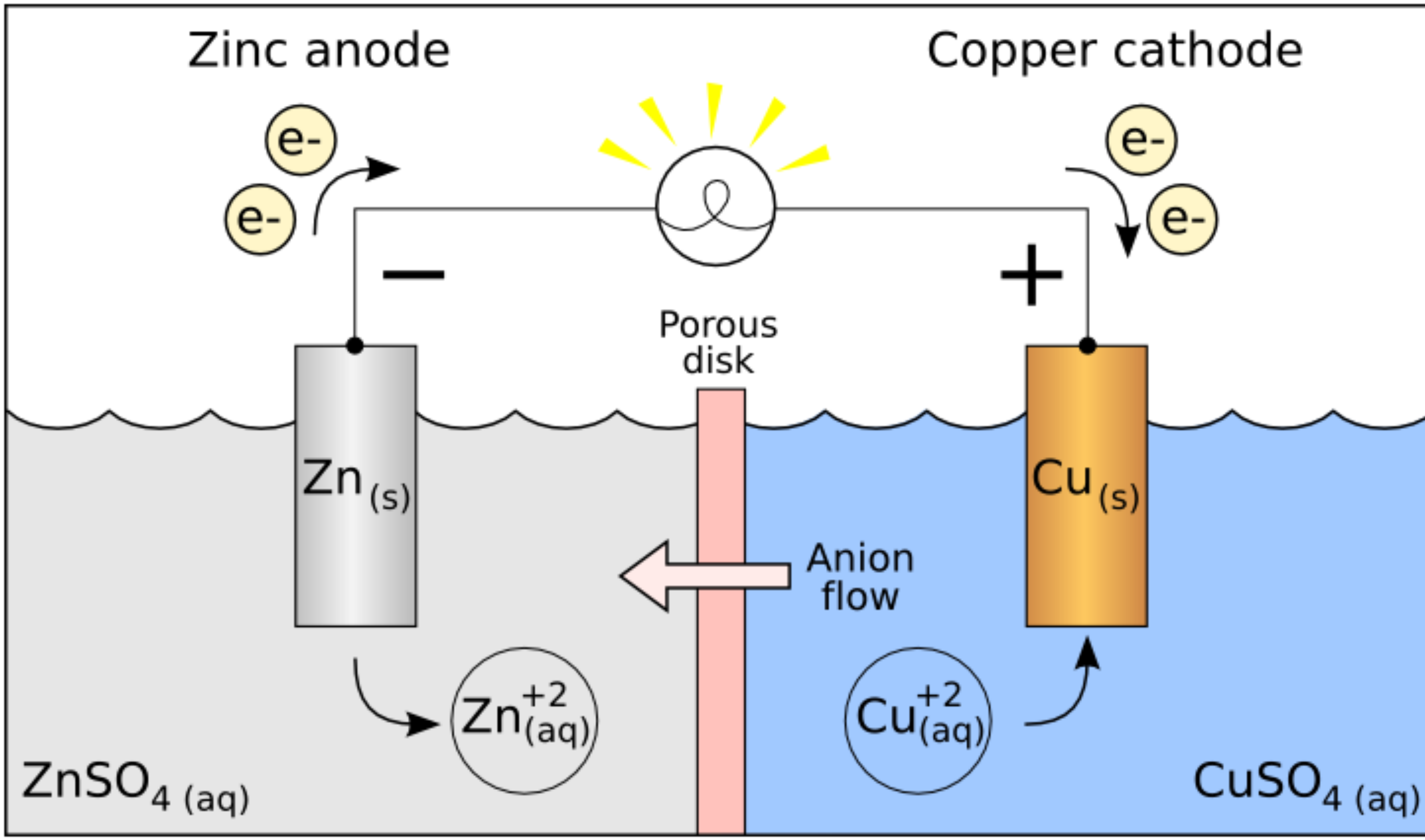
quantum chemistry





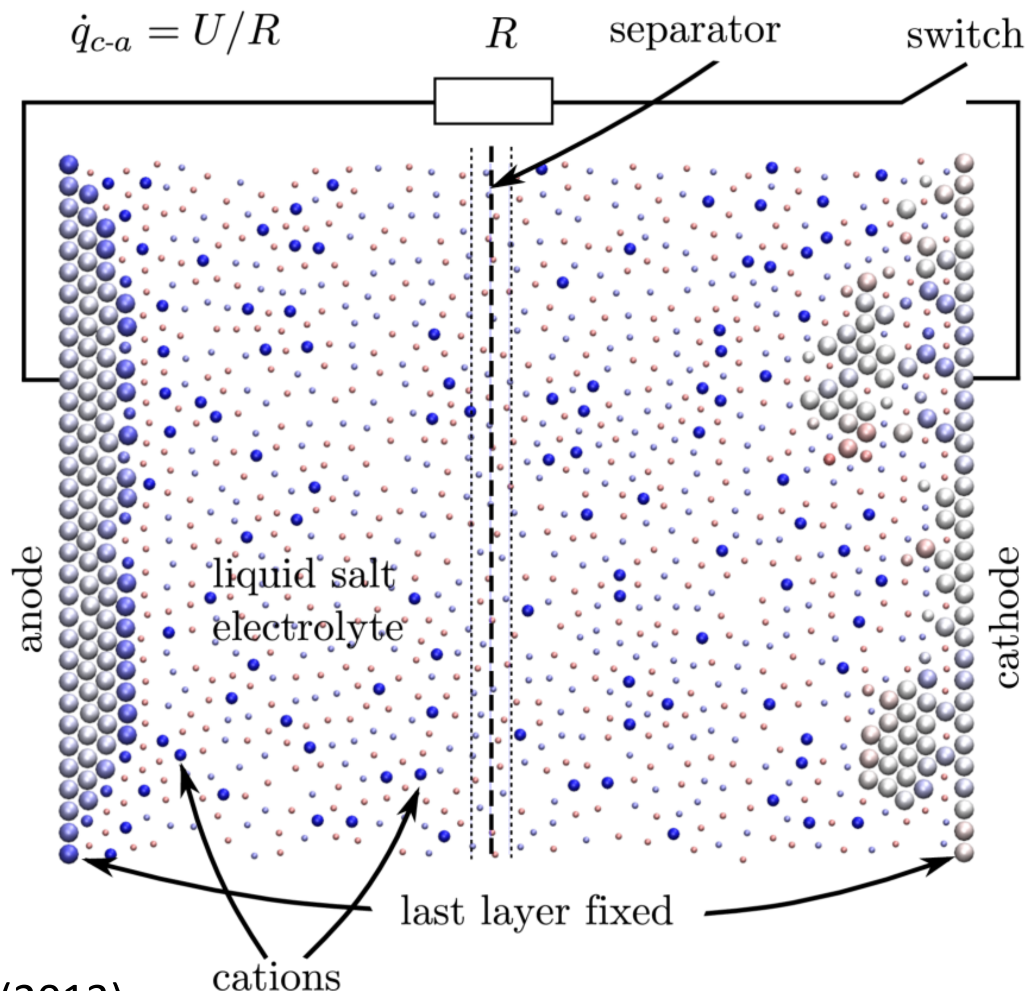
Dapp & Müser, EPJB **86**, 337 (2013)

Proof-of-concept application: atomistic battery discharge



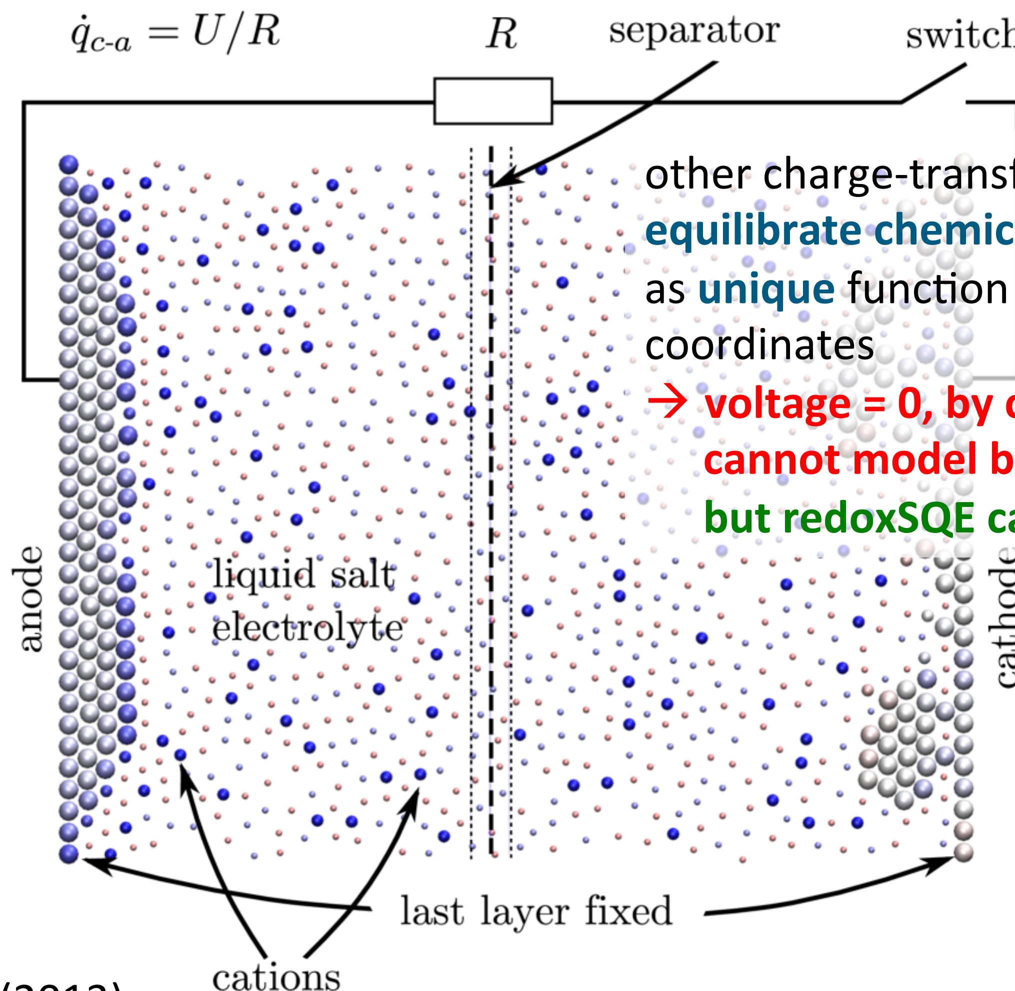
http://en.wikipedia.org/wiki/Galvanic_cell

Proof-of-concept application: atomistic battery discharge



Dapp & Müser,
JCP **139**, 064106 (2013)

Proof-of-concept application: atomistic battery discharge



other charge-transfer force fields **equilibrate chemical potential** as **unique** function of atomic coordinates

→ **voltage = 0, by construction, cannot model batteries, but redoxSQE can**

Dapp & Müser,
JCP **139**, 064106 (2013)

Model battery discharge

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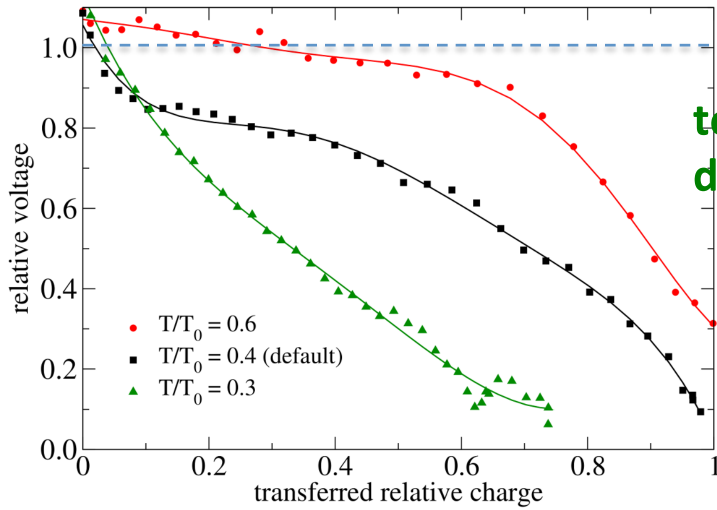
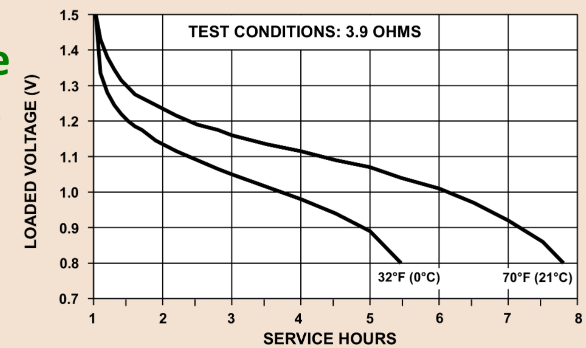
comparison: Duracell MN1500 Alkaline battery

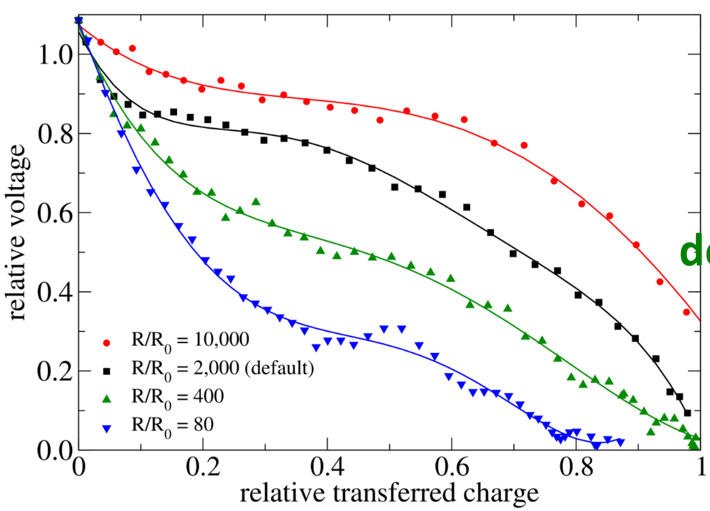


temperature dependence

Figure 9a

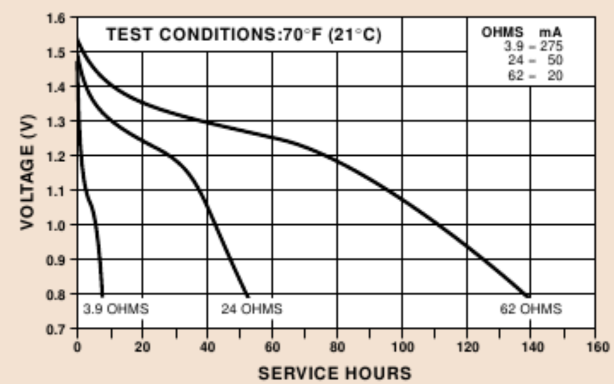


Comparison of the effects of temperature on the voltage profile of the DURACELL® alkaline MN1500 ("AA" size) cell.



load dependence

Figure 2

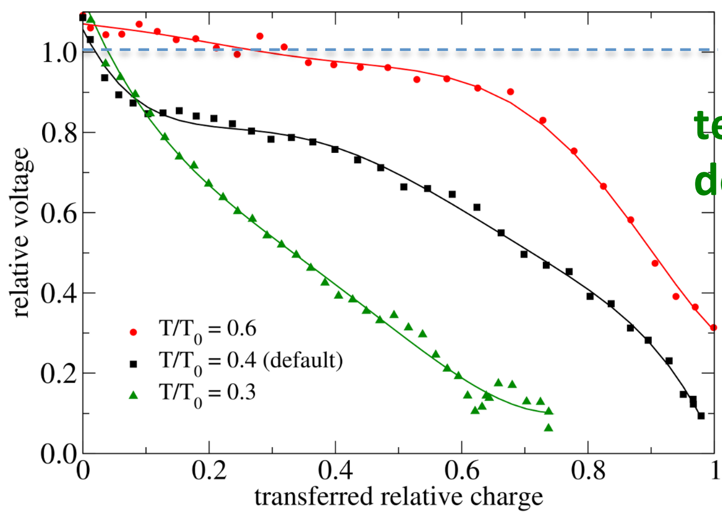


Typical discharge profile of the DURACELL® alkaline MN 1500 ("AA" size) cell.

Dapp & Müser, JCP **139**, 064106 (2013)

Model battery discharge

comparison: Duracell MN1500 Alkaline battery



temperature dependence

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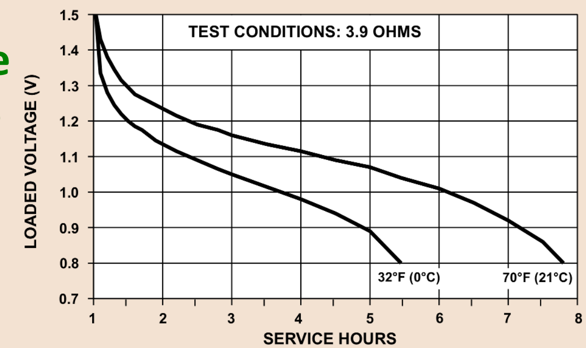

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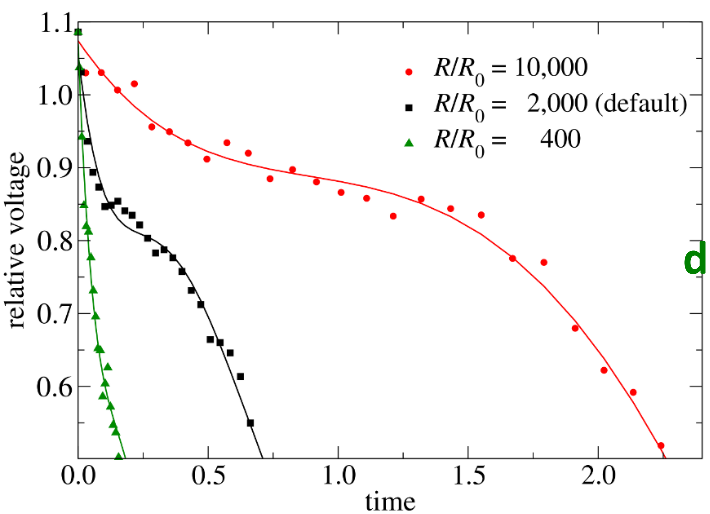

load dependence

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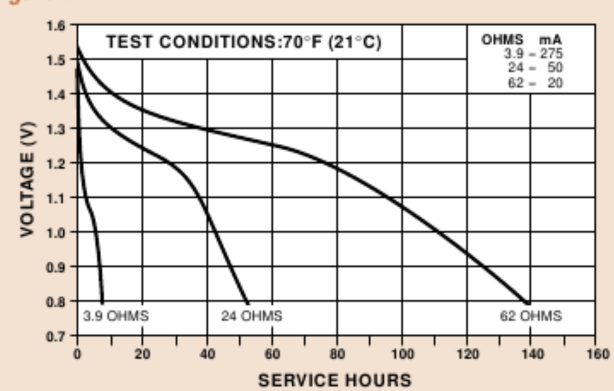
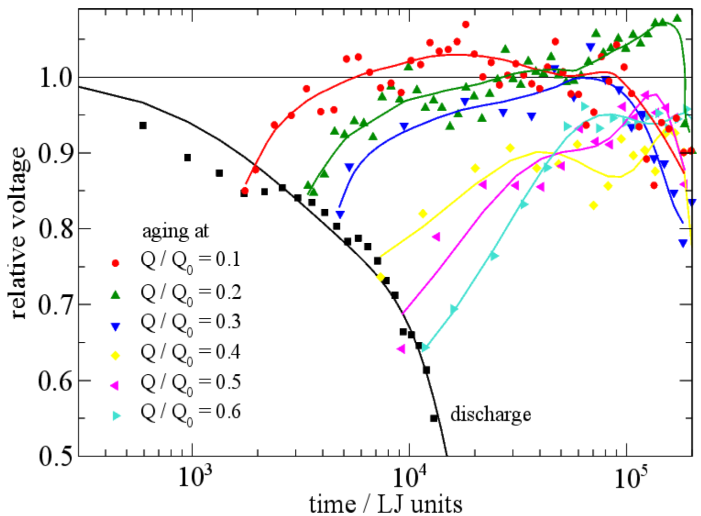


Typical discharge profile of the DURACELL® alkaline MN 1500 ("AA" size) cell.

Dapp & Müser, JCP **139**, 064106 (2013)

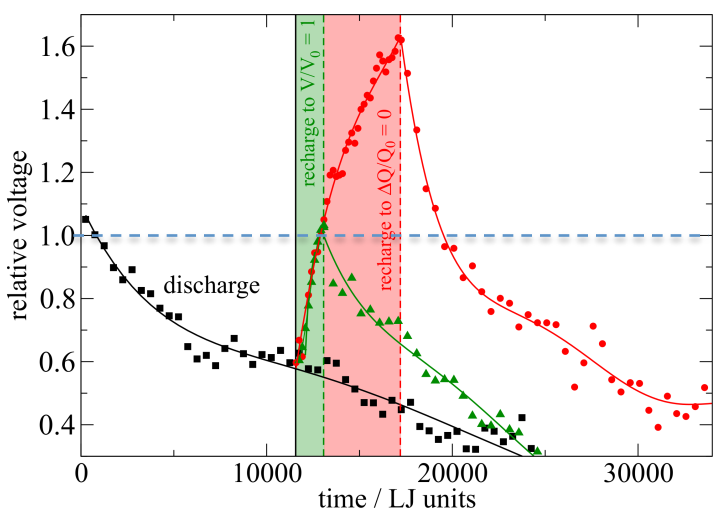
Pulsed discharge and recharge



pulsed discharge:

- relaxation effects, recovery of voltage
- self-discharge in the case of long storage
- typical usage case: communication devices

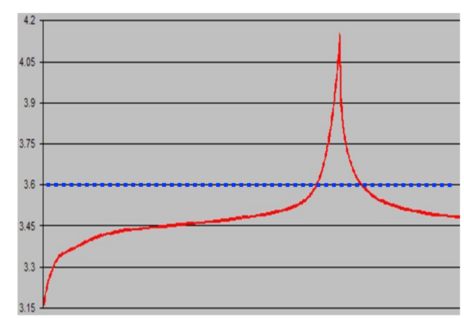
Dapp & Müser, JCP **139**, 064106 (2013)



recharge:

- overshoots nominal voltage (OCV)
- degeneration across multiple cycles

comparison:
charge curve
$LiFePO_4$ battery,
nominal voltage **3.6V**



Caveats

presently: proof-of-concept only

- microscopic battery: **≈ 1000 atoms**, in **monolayer setup**
- "Lennard-Jonesium"+RedoxSQE,
  not parametrized for **specific** material (parameters ≈ Cu)
- short-range interactions two-body only

reference values

nano battery:
("Cu" battery with liquid salt electrolyte, except for atomic hardness)

- 1.3 V open circuit voltage,
- 0.7 nA mean current,
- 0.7 GΩ external resistance

"scaled" battery:

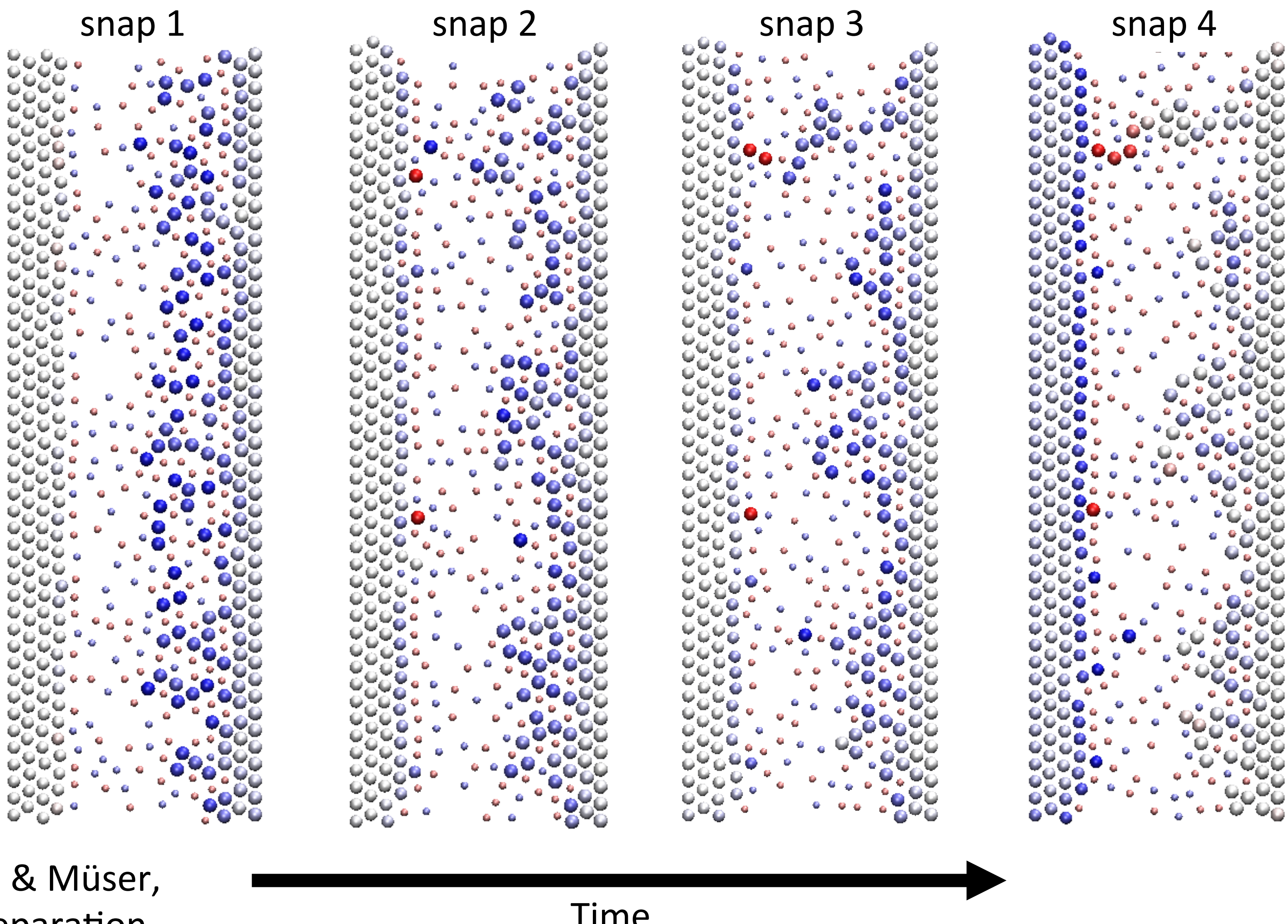
- 1.3 V OCV,
- 7 mA ≈ 60 Ω,
- 2400 mAh capacity,
- 2 Wh energy

Alkaline / NiMH:

- 1.5 / 1.2 V OCV,
- 30 mA ≈ 40 Ω,
- 2800 mAh,
- ≈3 Wh

outlook: electrochemical memory cells

see also talk by Alejandro Strachan tomorrow



Dapp & Müser,
in preparation

outlook: electrochemical memory cells

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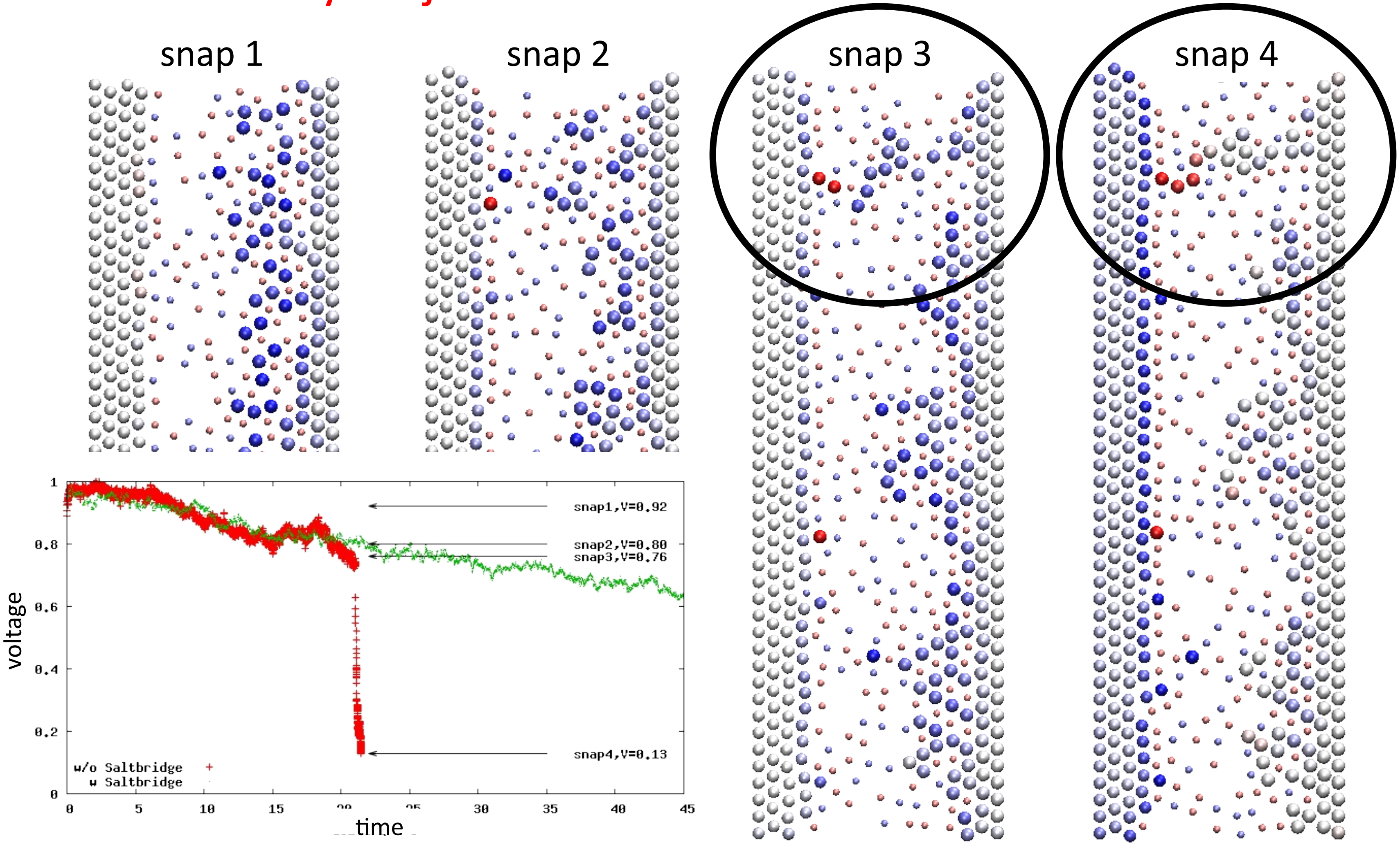

Time

Dapp & Müser,
in preparation

Summary and conclusions

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Original split-charge method (SQE):

- reliable and **transferable** charges for molecular systems
- tunable dielectric constant and penetration depth
- **correct** scaling of dipoles and polarizability with chain length

RedoxSQE

- can model “true” ions (zwitterions) & **time dependence**
- describes **redox reactions**
- extends applicability of SQE to **non-equilibrium** situations, such as **tribo-electricity**, **Galvanic cells**
- reproduces generic characteristics of **battery discharge** and allows to study electrolyte-electrode interface, etc.