Karlsruhe Institute of Technology

Acceptance Rate Optimized Monte-Carlo Simulations

Multi-Scale-Modelling of Materials and Elements for Energy Conversion and Storage

Steinbuch Centre for Computing (SCC) & Institut für Nanotechnologie (INT)


ENERGY

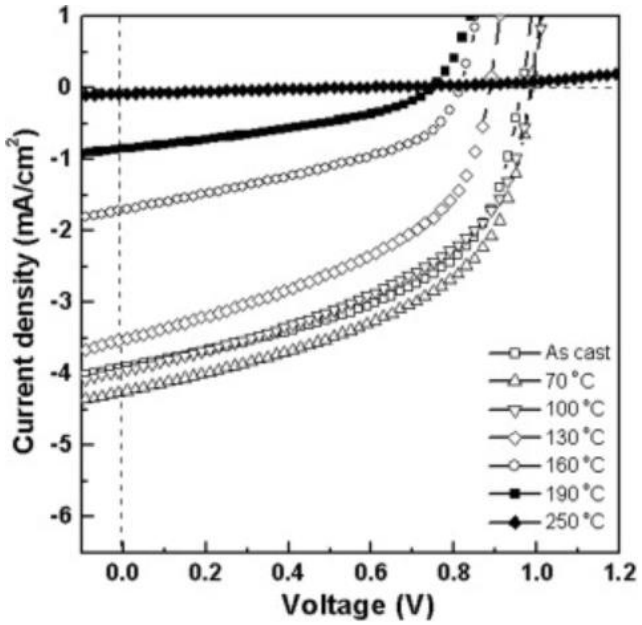
Energy is ubiquitous

- Generation

- Storage

Energy: Big Challenges

- Efficiency of solar cells



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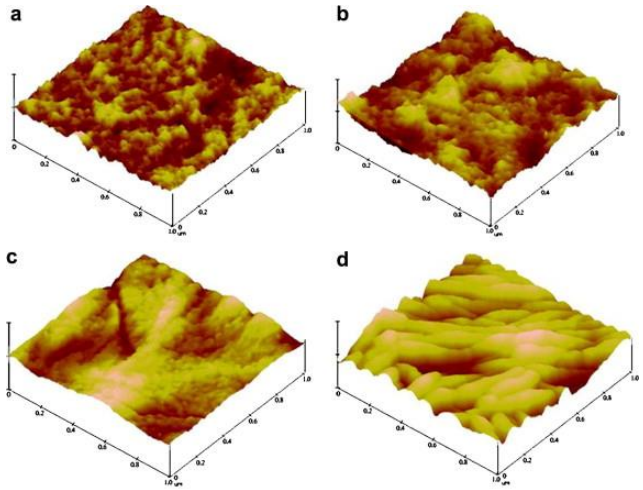
Changes of domain structures during tempering can have big effects on the efficiency.

- Safety of Li-Ion Batteries

Energy: Big Challenges

- Efficiency of solar cells



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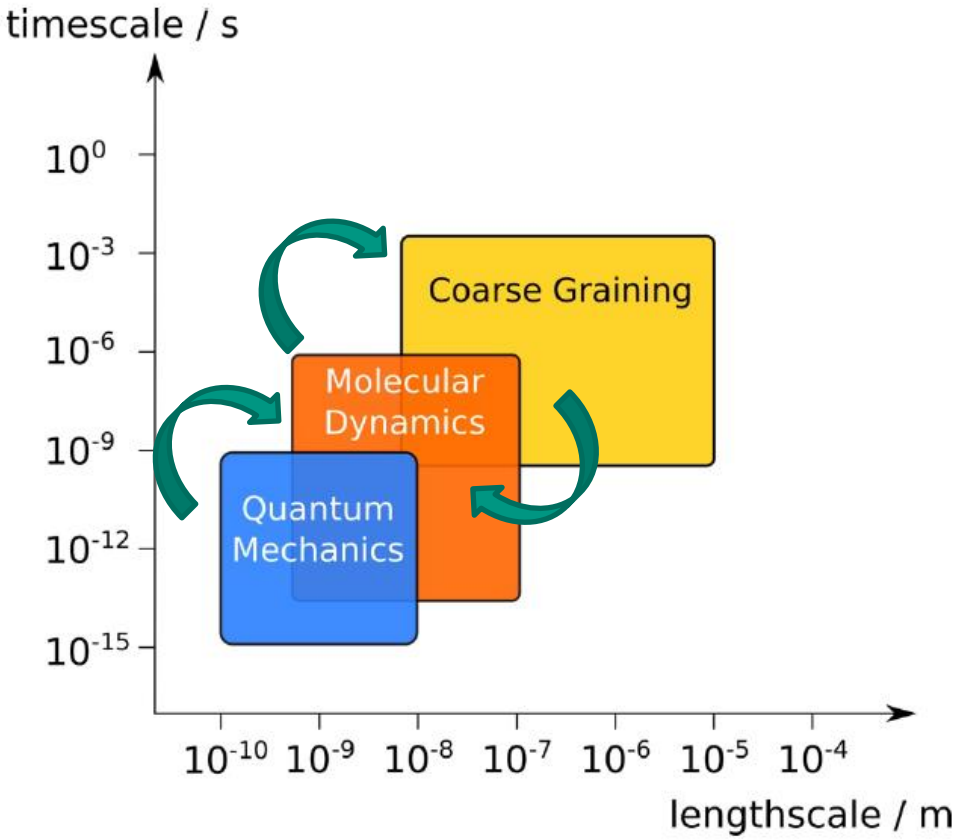
Changes of domain structures during tempering can have big effects on the efficiency.

- Safety of Li-Ion Batteries

Multiscale Simulations

- Coarse graining
- Use microscopic simulations to obtain parameters for less detailed simulation approaches.
- Use backmapping to obtain microscopic structures from coarse-grained simulations



Microscopic Simulations

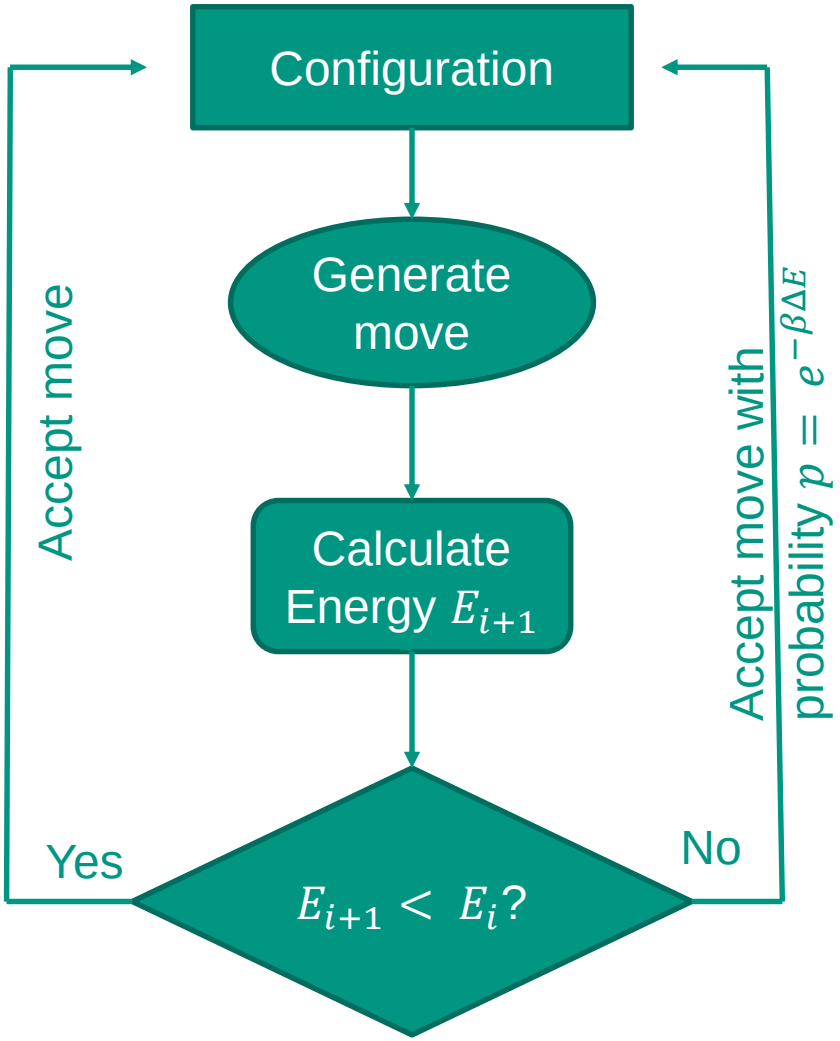
- Molecular Dynamics

- Full dynamics
- Tiny timesteps ~ 1fs
- Tiny displacements

- Monte Carlo

- Direct sampling of the canonical ensemble
  - No thermostat needed
- „unphysical“ moves permitted
- Larger displacements possible

Metropolis-Hastings MC



- Problem:

Small acceptance probability in molecular systems.

- Costs:

(Move generation + Energy calculation) * acceptance_rate^{-1}

- Ok für cheap energy evaluation (e.g. Ising model), not ok for expensive energy calculation (e.g. DFT)

A better way to generate MC Steps

- Detailed balance

Probability to suggest move

Probability to accept move

$$\frac{w(\boldsymbol{r} \to \boldsymbol{r}')\varphi(\boldsymbol{r} \to \boldsymbol{r}')}{w(\boldsymbol{r}' \to \boldsymbol{r})\varphi(\boldsymbol{r}' \to \boldsymbol{r})} = e^{-\beta \Delta E(\boldsymbol{r},\boldsymbol{r}')}$$

Metropolis-Hastings:

$$w(\boldsymbol{r} \to \boldsymbol{r}') = w(\boldsymbol{r}' \to \boldsymbol{r})$$

$$\phi(\boldsymbol{r} \to \boldsymbol{r}') = \min\{1, e^{-\beta \Delta E(\boldsymbol{r},\boldsymbol{r}')}\}$$

Ideal:

$$\frac{w(\boldsymbol{r} \to \boldsymbol{r}')}{w(\boldsymbol{r}' \to \boldsymbol{r})} = e^{-\beta \Delta E(\boldsymbol{r},\boldsymbol{r}')}$$

$$\phi(\boldsymbol{r} \to \boldsymbol{r}') \equiv 1$$

A better way to generate steps

- Ideal case:

$$w(\boldsymbol{r} \to \boldsymbol{r}') = e^{-\frac{1}{2}\beta \Delta E(\boldsymbol{r},\boldsymbol{r}')} \text{ as } \Delta E(\boldsymbol{r},\boldsymbol{r}') = -\Delta E(\boldsymbol{r}',\boldsymbol{r})$$

- Problem: We don‘t know the energy at every position.
- Solution: Local energy estimator:
  - 0th Order: $E(\boldsymbol{r}') \cong E(\boldsymbol{r})$ ➡ Metropolis-Hastings MC
  - 1st Order: $E(\boldsymbol{r}') \cong E(\boldsymbol{r}) - \boldsymbol{F}(\boldsymbol{r})^T \Delta\mathbf{r}$ ➡ Force-biased MC / AROMoCa v1
  - 2nd Order: $E(\boldsymbol{r}') \cong E(\boldsymbol{r}) - \boldsymbol{F}(\boldsymbol{r})^T \Delta\boldsymbol{r} + \frac{1}{2}\Delta\boldsymbol{r}^T \boldsymbol{H}(\boldsymbol{r}) \Delta\mathbf{r}$

    ➡ **AROMoCa 2. Ordnung**

    Hessian Matrix

Advantages of second order approximation

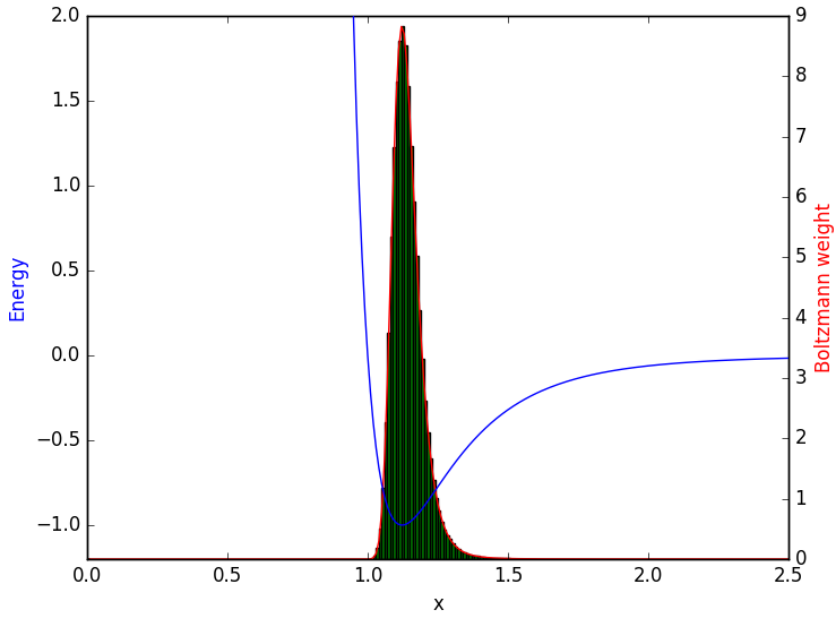
- Improved energy estimation.
- Fully correlated moves.
- Simple inter-molecular interactions well described by harmonic potentials (harmonic bonds, angles).
  - Here AROMoCa v2 should be exact!
- In many cases, dynamics at the minimum can be approximated by a harmonic potential.

Lennard-Jones Potential

- Common potential to model van-der-Walls interactions

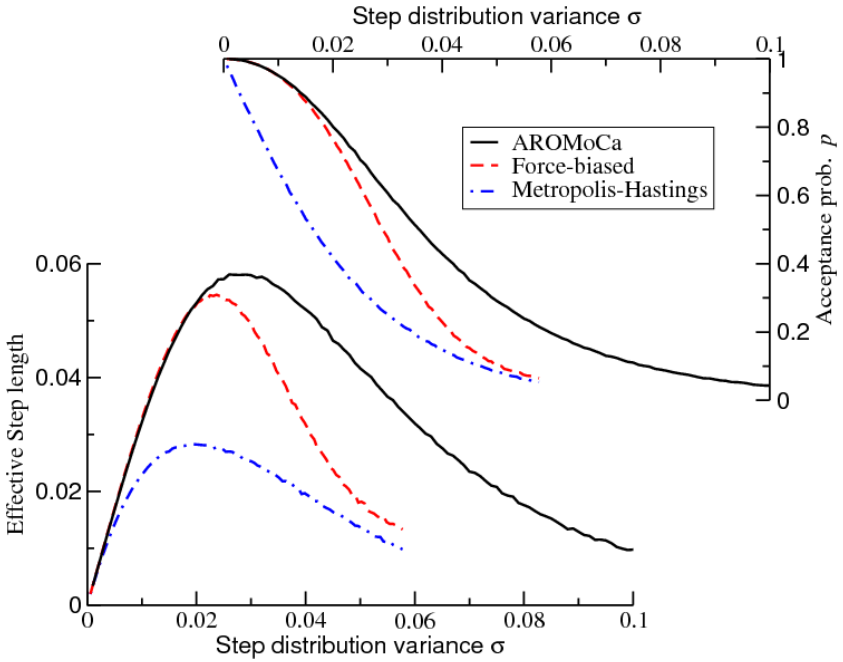
$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Samling is correct!



Lennard-Jones Potential

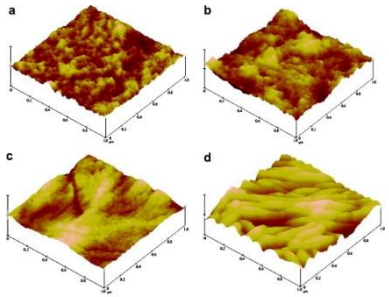
- Acceptance rate and effective step length



Improvement over Force-biased MC.

Summary

Solar cell efficiency is determined by the domain structure



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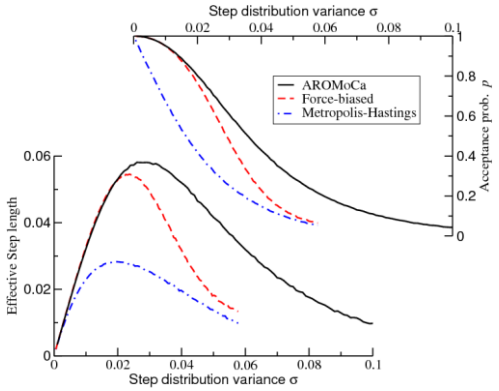
A task for a multiscale simulation approach.



Monte Carlo with second order energy estimation can achieve near-uniform acceptance rates.

Thank you

Collaborators

- Tobias Neumann
- Manuel Konrad
- Simon Kaiser

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