Sequential multiscale simulations with *potfit*: First principles data for classical MD

Peter Brommer

Warwick Centre for Predictive Modelling
School of Engineering, University of Warwick

JSC Workshop: From atoms to materials

http://www.warwick.ac.uk/wcpm

Motivation

Quantum theory of electrons and nuclei

QM (QED) is a theory with enormous predictive power:

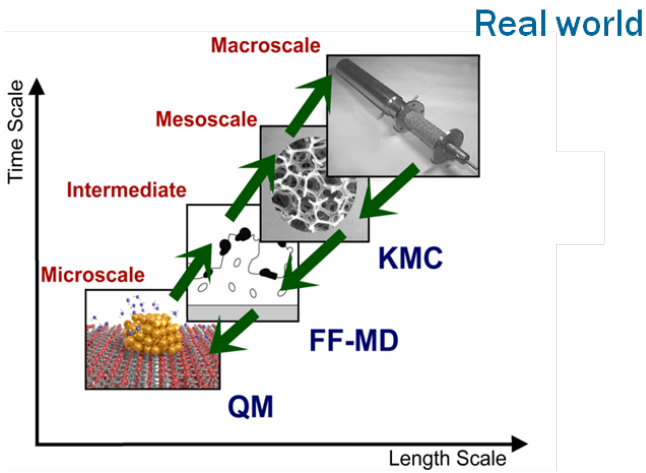
- Energy levels of hydrogen atom to a few ppm.

Solution to all our modelling needs? . . . No.

"Sequential" Multiscale Modelling

Use proper simulation tool for each scale.

- Parameterise from small to large.
- No direct coupling between models.



essenceofescience.se/nobel-2013/

Outline

1. The Fundament
   - Density Functional Theory
   - Molecular Dynamics
   - Force Matching
   - Target Function Optimisation
   - Force Calculation

2. Force matching beyond pair/EAM
   - Angular dependent potentials for clathrates
   - Tangney-Scandolo potentials for oxides
   - Electron temperature dependent potentials

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(Plane Wave) Density Functional Theory

A sequence of approximations

Solve Schrödinger (Dirac) equation of electrons and nuclei

- for stationary nuclei (Born-Oppenheimer approximation),
- mapping the many-electron problem to many one-body problems,
- which use approximative functionals to represent XC,
- while core electrons are treated by pseudopotentials;
- wave functions are represented using plane wave basis set,
- cut off at finite energy and sampled on a finite grid;
- the problem is then solved by iteration to self-consistency.

Depending on some of the choices, further corrections are necessary.

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Molecular Dynamics

What is Molecular Dynamics?

Equations of motion of a system of interacting particles are integrated numerically.

- Direct simulation of the basic laws of physics: Newton's (or Hamilton's) equations.

Needed

- Initial condition: structure model
- Equation of motion: model of the interactions

Big systems or long simulation times are feasible only with classical effective potentials.

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Interactions

Choice of interaction model depends on material to simulate

- Central pair potentials, EAM potentials for metals.
- Angular dependent potential (ADP), MEAM.
- Covalent potentials (Tersoff, Stillinger-Weber, . . .).
- Potentials for nematic liquid crystals.
- Coulomb potential (Ewald method, Wolf summation).
- Dipolar interaction for oxides.
- Simulation of organic molecules: Force fields for polymer chains, water, amino acids,. . .

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Potential Development

How to obtain effective potentials?

Potential serves to determine energies and forces
→ determines the physics of the system!

- Depending on the system (metal, oxide, etc.), a suitable potential type must be chosen.
- Within such a potential family, the potential parameters determine the physical properties a particular material.
- The parameters are chosen such that the desired material properties are correctly reproduced.
- The material properties to be reproduced are often computed ab-initio, instead of measured experimentally.

⇒ Force Matching!

Ercolessi & Adams, Europhys. Lett. **26**, 583 (1994)

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Force Matching with *potfit*

Open source force matching code ***potfit***

- Flexible and modular.
- Supports pair, (M)EAM, ADP potentials (metals).
- Oxide potentials.
- Electron-temperature dependent potentials (laser ablation).
- Interfaces to DFT and MD codes.

Widely used code

- 40 downloads/month,
- 50 citations with potentials,
- from more than ten distinct groups around the globe.

Brommer, Gähler, Model. Simul. Mater. Sci. Eng. **15**, 295 (2007).

`http://potfit.sourceforge.net/`

Potential Generation

1. Select potential model, starting potential.
2. Select reference structures (100–200 atoms, MD simulation at various temperatures, strained structures).
3. Calculate forces, stresses, energies with ab-initio code.
4. Optimize starting potential with *potfit*.
5. Generate reference structures with new potential.
   $\Rightarrow$ more realistic configurations.
6. Test potential.

If results are not satisfying

- use more/different reference configurations,
- replace insufficient potential model.

and iterate procedure.

Uncertainties

Sources of uncertainty for force-matched potentials

Generic errors:

- "Imported" uncertainty: cannot beat DFT.
- Algorithmic uncertainty: global optimum?

Force Matching specific (structural & parameter) uncertainties:

- Bad reference data selection (parameter uncertainty).
- Wrong functional form (model bias).
- Overfitting (parameter uncertainty).
- Wrong potential model (model bias).

Properties of force-matched potentials:

- (Generally) good representability.
- Limited transferability.

Caveat emptor! (US$2M NSF CDI grant, cf. https://openkim.org/).

Uncertainties

Sources of uncertainty for force-matched potentials

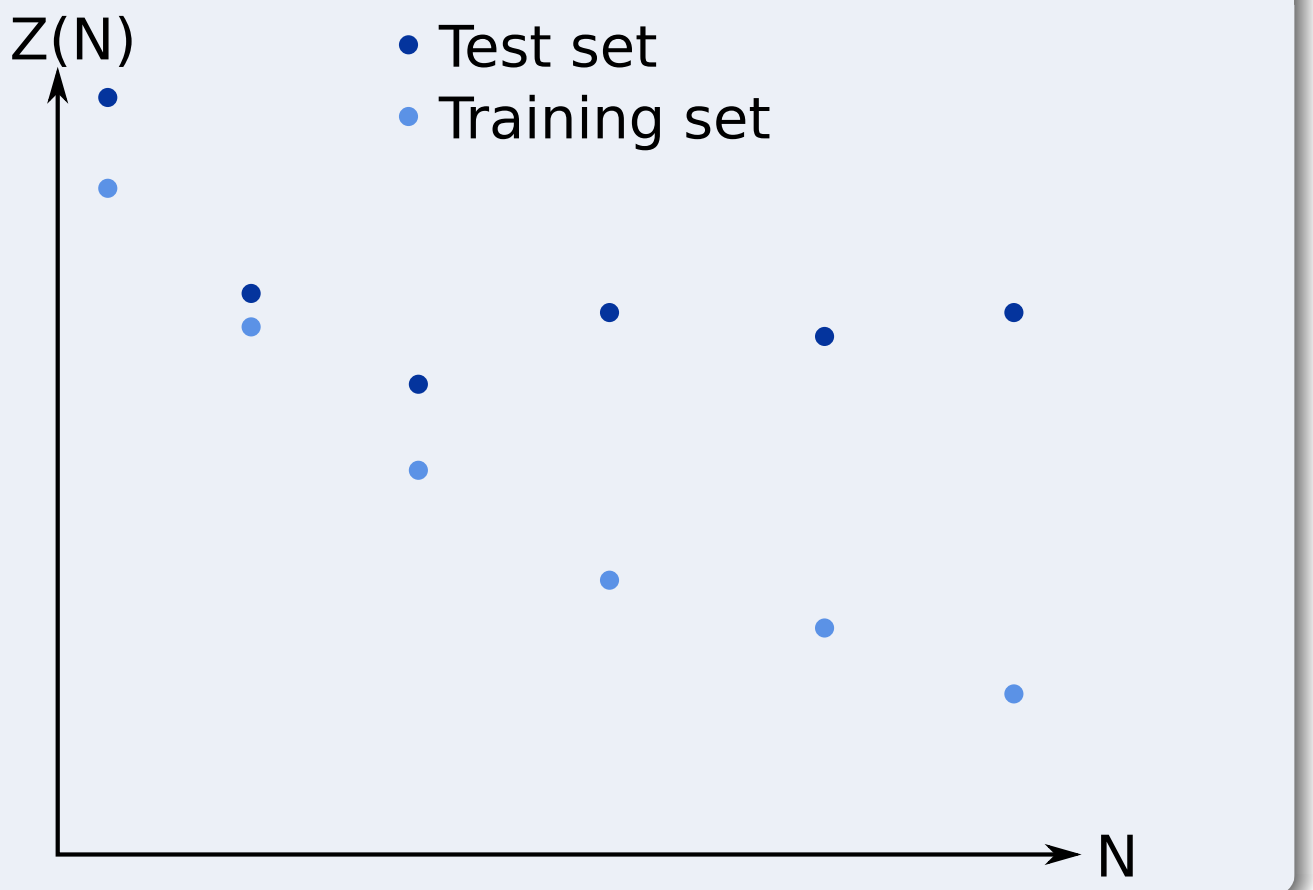
Generic errors:

- "Imp
- Algo

Force M

- Bac
- Wrc
- Ove
- Wrc

Target function $Z(N)$, N parameters in model



Propert

- (Ge
- Lim

Caveat emptor! (US$2M NSF CDI grant, cf. https://openkim.org/).

Force Matching: Optimisation problem

Find best parameter set for parameters α

Best?

- Minimise squared deviations compared to reference data (for each energy, force component, stress tensor component).
- Additional constraints? Add as sum of squares.
- Target function Z:

$$Z(\alpha) = Z_D(\alpha) + Z_C(\alpha), \tag{1}$$

$$\text{with} \quad Z_D(\alpha) = \sum_{i=0}^{m} u_k (S_k(\alpha) - S_k^0)^2 \tag{2}$$

$$\text{and} \quad Z_C(\alpha) = \sum_{r=0}^{N_c} w_r (A_r(\alpha) - A_r^0)^2. \tag{3}$$

- Z: Highly nonlinear function, expensive to calculate.

Minimisation

Target function Z

Rough potential surface:

- Many competing minima.
- Varying importance of parameters.
- No analytical gradient.

How to find the optimum?

Local optimisation

Powell's algorithm

- Conjugate Gradient-like
- Effective in number of force calculations.
- Descent into *local* minimum.

Global optimisation

Simulated annealing

- Monte-Carlo inspired.

Differential evolution

- Inherently parallel.

Both: many calculations.

Force calculation

Force calculation separated from optimisation

Forces calculated from tabulated interpolate of potentials.

- FC does not know about “parameters”.
- Optimisation does not know about details of FC.

$\Rightarrow$ Separation of force calculation and optimisation.

Easy to add optimiser or potential model.

Efficient force calculations

MD: Atoms move, potentials fixed.
FM: Atoms fixed, potentials change.

- Use neighbour lists (initialised once).
- Pre-calculate spline point and interval (once).
- Update potential as needed.

Interpolated potentials

Special case: tabulated or interpolated potential

Interpolated potentials can have many parameters (>100).

- No bias from particular functional form.
- Parameters have no meaning.

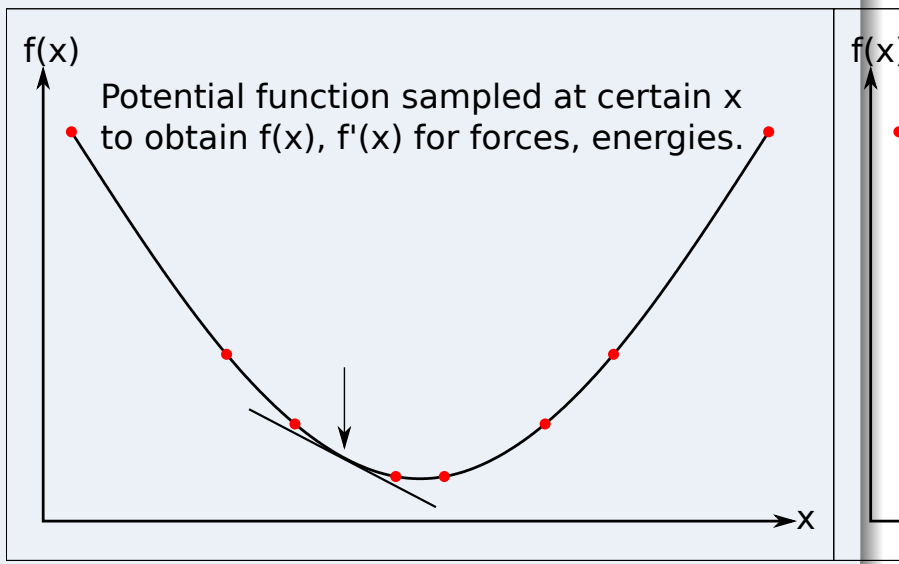
Monitor sampling points.

Confidence of sampling point values

Forces: evaluate potential functions and gradients.

- Both in training and use.

Training set and application: sample similarly.



On the selection of reference configurations

Golden rule of force matching

Your potential will do what it is trained to do.

- Elastic constants: use strained structures.
- Surfaces: use surfaces.
- Low-T structure optimisation: . . . few higher T.
- . . .

Potentials for MD

Realistic sampling of configurations essential:

- Ab-initio MD.
- Iteratively improved MD.

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For Metals: EAM potentials

Pair potentials in metals

Insufficient description:

- Elastic constants (Cauchy pressure).
- Vacancy formation energy.
- Surface relaxation.

EAM potentials

$$E = \sum_{ij} \Phi_{ij}(r_{ij}) + \sum_{i} F_i(\rho_i), \quad \text{where} \quad \rho_i = \sum_{j} \Psi_j(r_{ij})$$

Bond strength depends on environment –
better suited to describe vacancies and other defects.

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Angular dependent potentials

Directional dependence in pairwise sums

Additional contributions to energy:

$$E_{\mathrm{ADP}} = E_{\mathrm{EAM}} + \frac{1}{2}\sum_{i,\alpha}(\mu_i^\alpha)^2 + \frac{1}{2}\sum_{i,\alpha,\beta}(\lambda_i^{\alpha\beta})^2 - \frac{1}{6}\sum_i \nu_i^2 \quad (4)$$

$$\mu_i^\alpha = \sum_{j\neq i} u_{ij}(r_{ij}) r_{ij}^\alpha, \quad \lambda_i^{\alpha\beta} = \sum_{j\neq i} w_{ij}(r_{ij}) r_{ij}^\alpha r_{ij}^\beta, \quad \nu_i = \sum_\alpha \lambda_i^{\alpha\alpha}. \quad (5)$$

Multipole expansion for “charge” distribution
(dipole and quadrupole terms).
Application: Ge and Si cage compounds (Clathrates) – with and without Ba filling.

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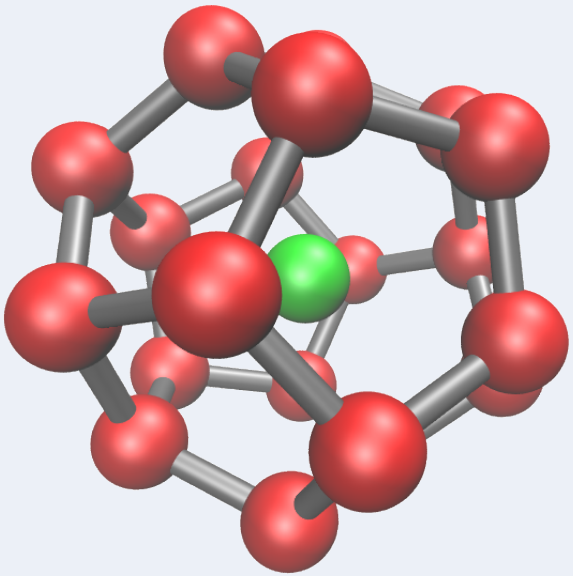
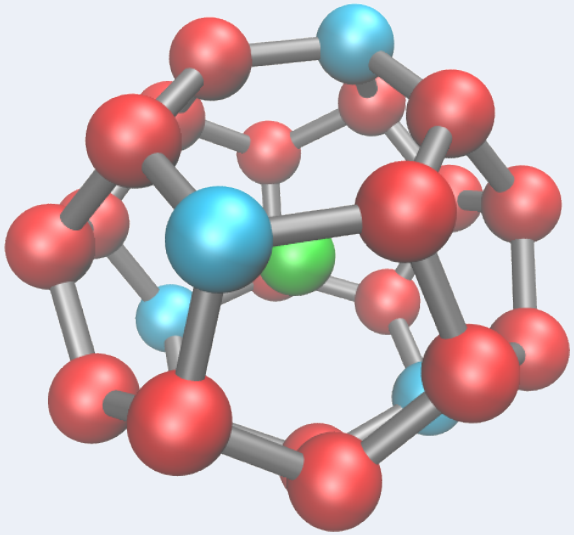
Type-I clathrates

Cage-like structure

Structure elements:



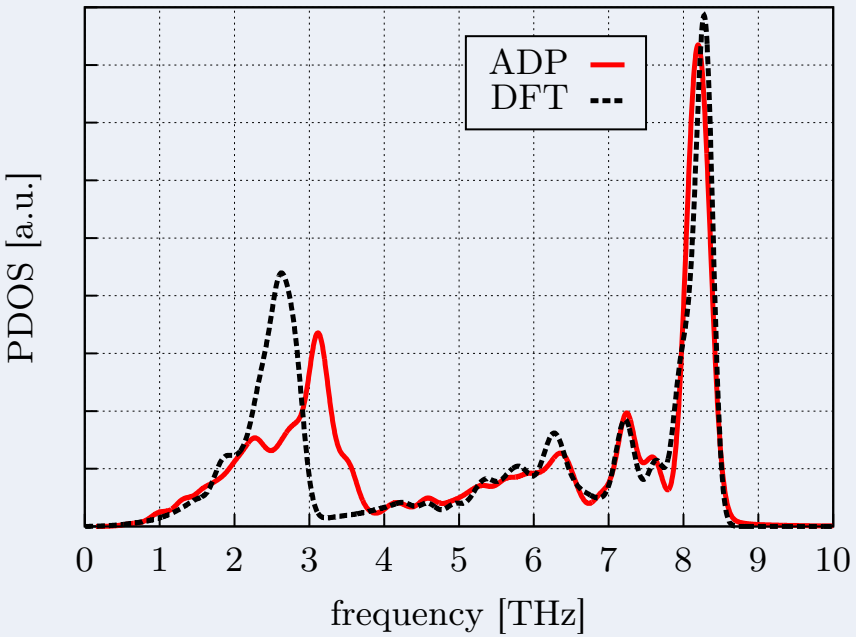


Icosahedral (20) or tetrakaidecahedral (24) cage filled with heavy rattling atom.

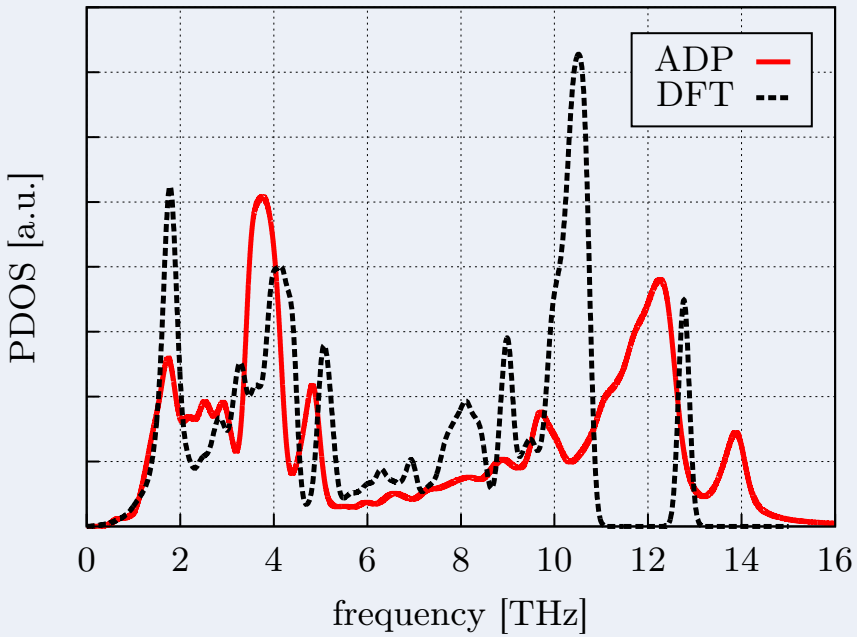
Schopf, Euchner, Trebin, *Phys. Rev. B*, **89**, 214306 (2014)

Phonon density of states for Ge and Si/Ba

PDOS *ab-initio* and with ADP potential



Ge_{46}



$Si_{46}Ba_6$

Tangney-Scandolo polarisable oxide model

Oxides not adequately described by point charges

Tangney-Scandolo model

- Coulomb interactions
- short-range repulsion (Morse-Stretch)
- polarisable oxygen (+short-range corrections)

Solve dipole moments self-consistently.

Wolf Summation

Linear scaling summation method for long-range interactions

- Use Ewald summation trick.
- Ignore reciprocal space part.

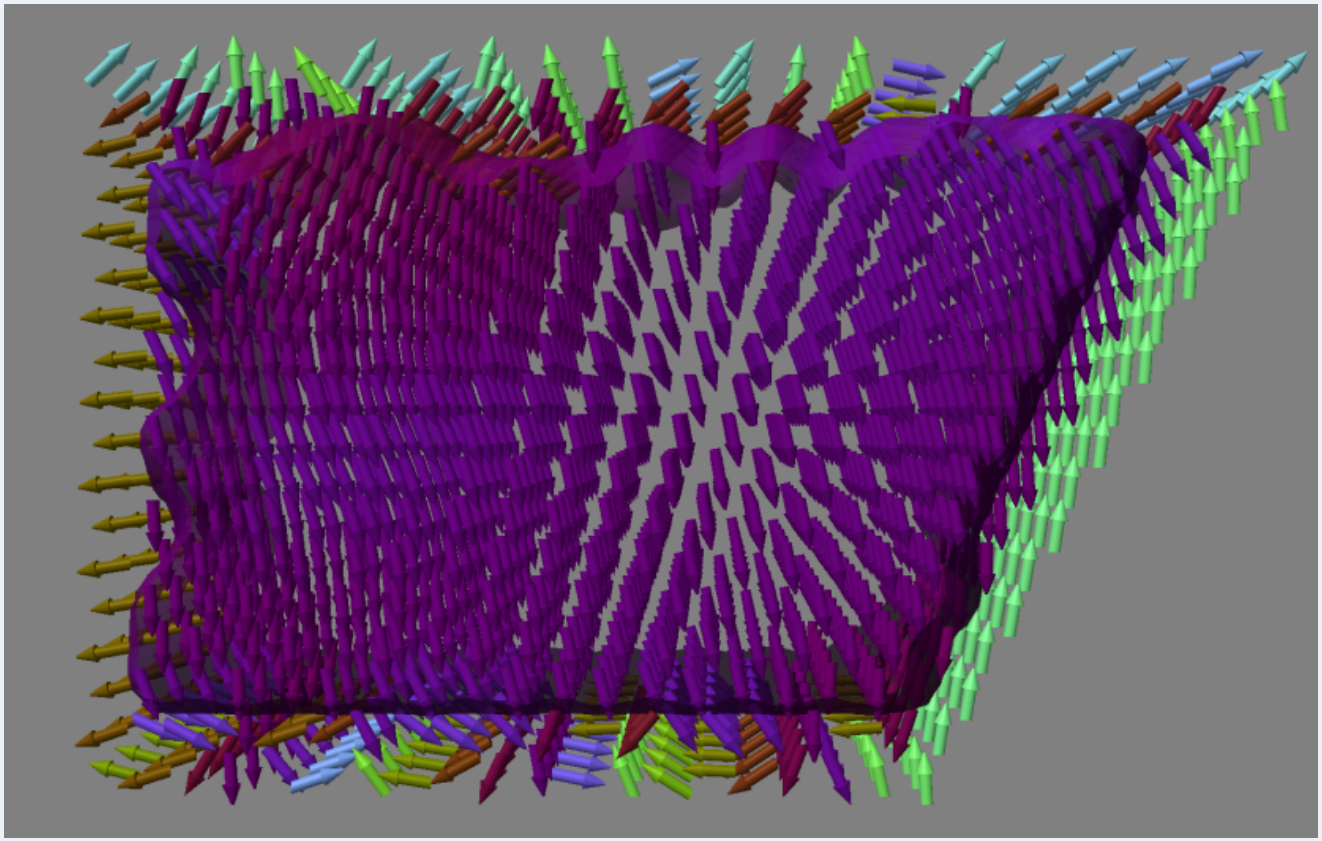
Works also for TS potential.

Brommer *et al.*, *J. Chem. Phys* **132** 194109 (2010)
Beck *et al.*, *J. Chem. Phys* **135** 485401 (2011)

Flexoelectricity in periclase (MgO)

Inversion symmetry excludes piezoelectricity

Flexoelectricity: $P_i = \mu_{ijkl} \partial_j \epsilon_{kl}$ needs inhomogeneous strain.



Roth *et al.*, in *HPC in Science and Engineering '13*, ed. Nagel *et al.*

Electron-temperature dependent potentials

Lasers and covalently bound materials

Laser excites valence band electrons.

- Non-thermal occupation of bands.
- After thermalisation: band occupation corresponding to $T_e \gg T_l$.
- Interaction between atoms dependent on T_e.

$\Rightarrow$ Two-temperature model.

$\Rightarrow$ Electron-temperature dependent potentials.

ETD potentials

ETD modified Tersoff potential for Si

Modified Tersoff potential:

$$V = \frac{1}{2}\sum_{i\neq j} f_C(r_{ij})\left[V_R(r_{ij}) - b_{ij}V_A(r_{ij})\right]$$

$$V_R(r_{ij}) = A\exp(-\lambda r_{ij}), \quad V_A(r_{ij}) = B\exp(-\mu r_{ij}), \quad b_{ij} = \left(1 + (\zeta_{ij})\eta\right)^{-\delta}$$

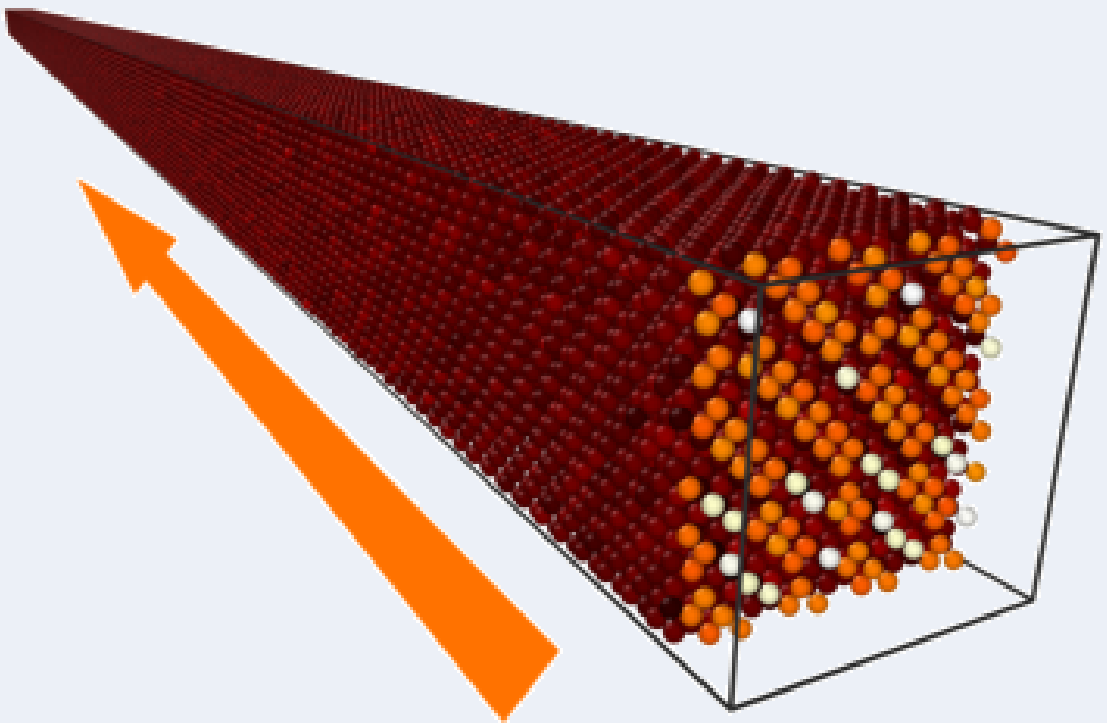
$$\zeta_{ij} = \sum_{k\neq i,j} f_C(r_{ij})g(\cos\theta)\exp(\alpha(r_{ij} - r_{ik})\beta).$$

with angular dependent term $g(\cos\theta)$ and cut-off function $f_C(r)$.
Make certain parameters explicitly temperature dependent, e.g.

$$A = A(T_e) = \sum_{n=0}^{6} a_n(k_B T_e)^n$$

Ablation of 1 µ Si film

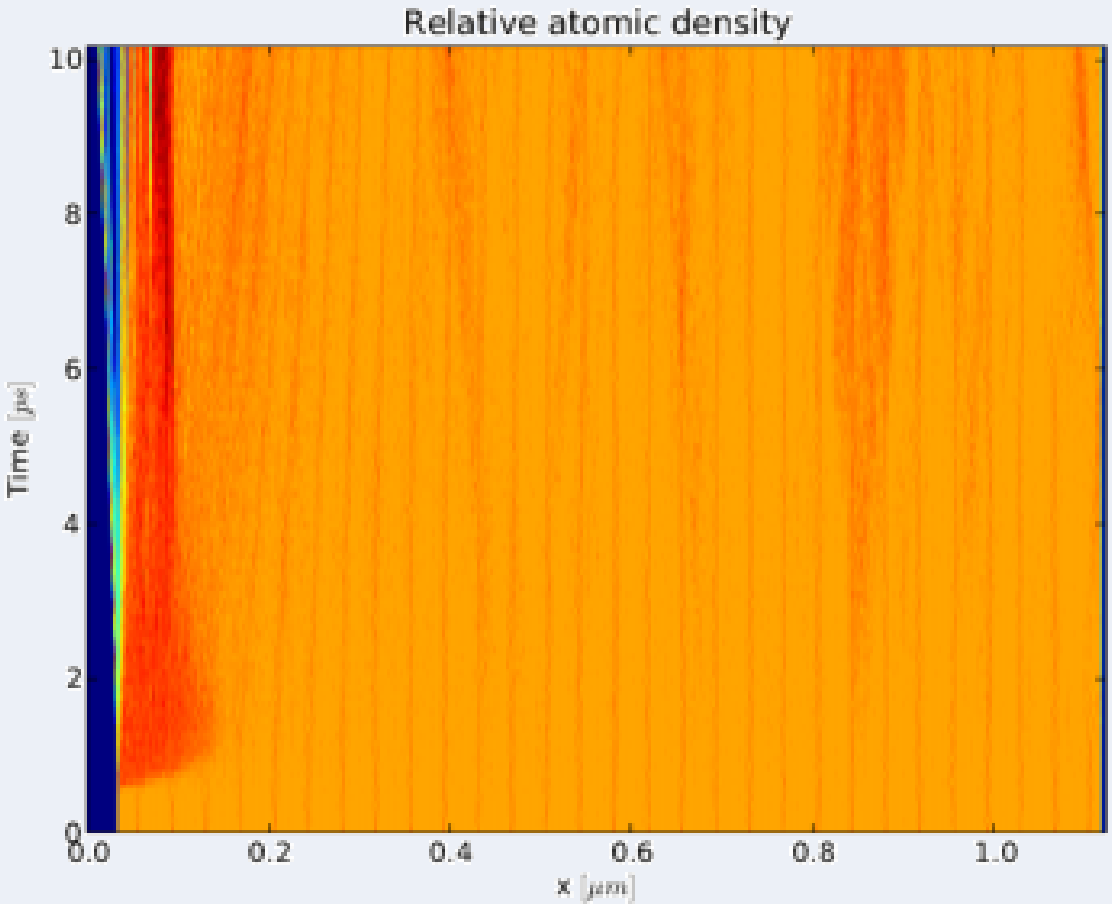
Setup



- $1124 \times 4.34 \times 4.34\ \mathrm{nm}^3$
- 1 024 000 atoms
- 750 finite difference cells.

Ablation

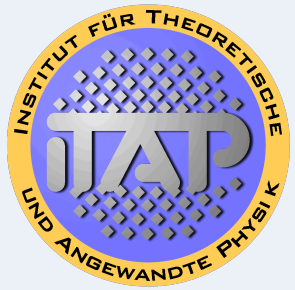
Laser fluence 0.12 J/cm^2



People & Funding

U Stuttgart: Institut für Theoretische und Angewandte Physik †

- Hans-Rainer Trebin
- Franz Gähler (now U Bielefeld)
- Johannes Roth (IMD)
- Daniel Schopf (potfit, Ph.D.)
- Alexander Kiselev (Ph.D.)



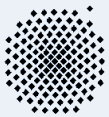
Open source

potfit home at `http://potfit.sourceforge.net`

- Wiki, Download, Mailing List

Funding

DFG SFB 384, 716

SFB  **716**

Conclusions

Sequential multiscale modelling

Build large-scale models bottom-up.

- Algorithmically straightforward (no coupling).
- Standard interfaces to standard simulation codes.
- Uncertainty propagation through the scales.

Force Matching

Extending atomistic simulations to new materials:

- Preserve DFT precision to larger systems, longer times.
- Foundation for other atomistic and meso-scale problems.

Essential part of multi-scale modelling stack.

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