Classical effective potentials – what to do and what to avoid

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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?

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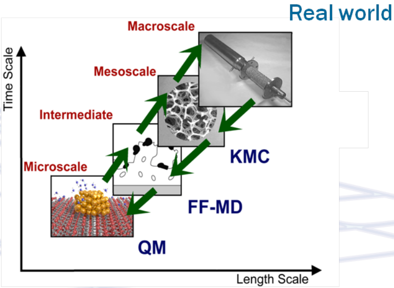
“Sequential” Multiscale Modelling

Use proper simulation tool for each scale.

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

Propagate uncertainty from one scale to the next.



essenceofescience.se/nobel-2013/

Outline

1. Standard Sequential QM/MM Multiscale Modelling
   - Density Functional Theory
   - Molecular Dynamics
   - Effective Potentials
   - Force Matching

2. Uncertainty
   - Sources
   - Testing potentials
   - Quantification
   - Example

(Plane Wave) Density Functional Theory

The briefest DFT recap

Schrödinger Equation:

$$\hat{H}\,|\psi\rangle = E\,|\psi\rangle$$

$$\hat{H} = T_N + T_e + V_{NN}(\boldsymbol{R}) + V_{ee}(\boldsymbol{r}) + V_{Ne}(\boldsymbol{r}, \boldsymbol{R})$$

Born-Oppenheimer approximation:

$$[T_e + V_{ee}(\boldsymbol{r}) + V_{Ne}(\boldsymbol{r}, \boldsymbol{R})]\,\Psi(\boldsymbol{x}, \boldsymbol{R}) = \epsilon_n(\boldsymbol{R})\Psi(\boldsymbol{x}, \boldsymbol{R})$$

$$\frac{\partial \boldsymbol{P}_I}{\partial t} = -\nabla_I(\epsilon_0(\boldsymbol{R}) + V_{NN}(\boldsymbol{R})).$$

What if we don't care about what the electrons do, only about their effects on the nuclei?

Molecular Dynamics

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

Effective Potentials

Eliminate electronic degrees of freedom

Re-write equation of motion:

$$\frac{\partial \boldsymbol{P}_I}{\partial t} = -\nabla_I(\epsilon_0(\boldsymbol{R}) + V_{NN}(\boldsymbol{R})) = \nabla_I(\tilde{V}_{\mathrm{eff}}(\boldsymbol{R}))$$

Usually, V_{eff} much simpler. Expand in manybody contributions:

$$V_{\mathrm{eff}}(\boldsymbol{R}) = \sum_i \phi_1(\boldsymbol{r}_i) + \tfrac{1}{2}\sum_{\substack{i,j\\ i\neq j}} \phi_2(\boldsymbol{r}_i, \boldsymbol{r}_j) + \tfrac{1}{6}\sum_{\substack{i,j,k\\ i\neq j\neq k\neq i}} \phi_3(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k) + \ldots$$

Even simpler: Central (homogeneous and isotropic) pair potentials:

$$V(\boldsymbol{R}) = \tfrac{1}{2}\sum_{\substack{i,j\\ i\neq j}} \phi_{ij}(r_{ij}), \qquad \text{with } r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$$

Interactions

Choice of interaction model depends on material to simulate

(different ways to truncate manybody expansion, different calculation prescriptions)

- Central pair potentials, EAM potentials for metals.
- Angular dependent potential (ADP), MEAM.
- Covalent potentials (Tersoff, Stillinger-Weber, . . .) for ceramics.
- Coulomb potential (Ewald method, Wolf summation).
- Dipolar interaction for oxides.
- Bond-order potentials, charge-optimising force fields.
- Temperature-dependent potentials (laser ablation).
- Coarse-grained potentials.
- Simulation of organic molecules: Force fields for polymer chains, water, amino acids,. . .

Example: EAM potentials

EAM potentials

(Semi-)empirical 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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Analytic vs. tabulated potentials

- Φ, F, ρ are the potential functions.
- Can be represented by analytic functions, e.g. $F = c\sqrt{\rho}$.
- Alternative: Tabulated at sampling points.

Potential Development

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- 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.

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- The material properties to be reproduced are often computed ab-initio, instead of measured experimentally.

Reference quantities

Experimental Quantities of Interest

e.g. phase diagrams, elastic properties, diffusivities. . .

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- Sampling configurational space?

Example: ReaxFF.

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Example: ReaxFF.

First-principles forces, stresses, energies

- easily calculated (1 MD step).
- sample configurational space.

Force Matching!

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

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,
- 60 citations with potentials,
- from more than ten distinct groups around the globe.

Brommer, Gähler, Model. Simul. Mater. Sci. Eng. **15**, 295 (2007).
Brommer *et al.*, Model. Simul. Mater. Sci. Eng. **23**, 074002 (2015)
`http://potfit.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.
   ⇒ more realistic configurations.
6. Test potential.

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If results are not satisfying

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

and iterate procedure.

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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).
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- Wrong

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

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Properties of force-matched potentials:

- (Generally) good representability.
- Limited transferability.

Caveat emptor! Don’t just trust any potential.

Interpolated potentials

Special case: tabulated or interpolated potential

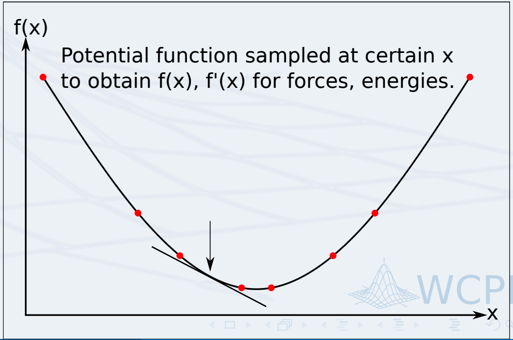
Interpolated potentials can have many parameters (>100).

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

No formal uncertainty propagation in literature.

Confidence of sampling point values

Forces: evaluate potential functions and gradients.



Potential function sampled at certain x to obtain f(x), f'(x) for forces, energies.

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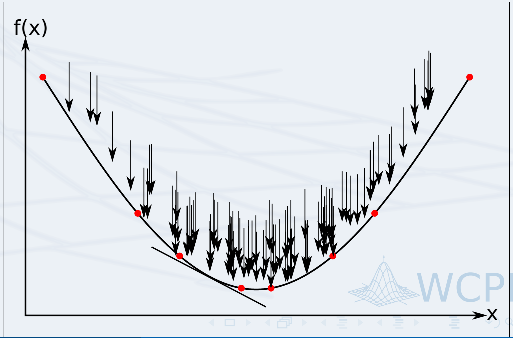
Forces: evaluate potential functions and gradients.

- Both in training and use.

Training set and application: sample similarly.



Testing potentials

. . . or why is my simulation doing freaky things

Fe monovacancy migration

Iron: Well studied system (FP6: Perfect project)

Family of EAM potentials for iron (Ackland, Mendelev, Marinica)

- Optimised to DFT energies of defects (available from 2000 onwards).

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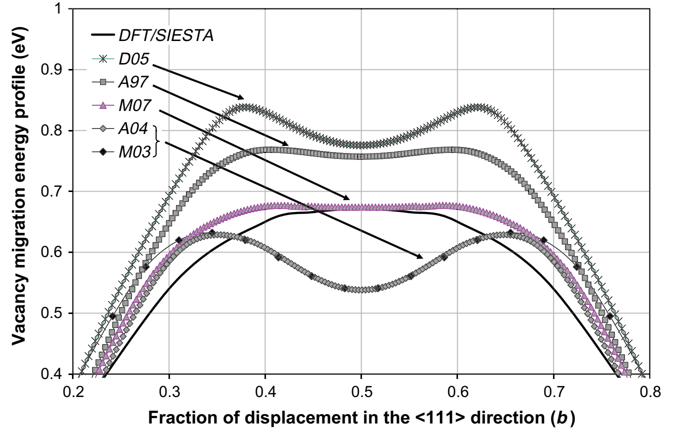

Testing potentials

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You want to do a MD/MC/. . . simulation with a potential, but you don't yet have a potential. So you

- look on Google Scholar
- ask your supervisor/colleague
- run *potfit*

But does the potential actually do what you want it to do?

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What could go wrong?

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What could go wrong?

Surprisingly much (something frustratingly trivial):

- Potential not available for your MD/MC/…tool (⇒ conversion errors).
- Differences in implementation (cutoff handling, interpolation).
- Typos in publications (!!!).
- Not optimised for your situation

Two-fold problem

Implementation problems

Potential not working as designed.

- “Unit” testing? Not always trivial.
- Ask authors for potential?
- Potential databases?[a]

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[a] e.g. `www.ctcms.nist.gov/potentials`

Potential problems

Potential not designed for use case.

- Validation of QoI.
- What are good QoI for my application?

Potential solution: OpenKIM Framework

API that provides

- Models (i.e. potentials) including implementation.
- Tests (i.e. QoI calculated from models) including reference data.
- Workflow to cross-reference (new models/tests trigger new test results).
- Interface to MD and *potfit*.

Standardised access to potentials with guaranteed results.

LAMMPS and potentials

LAMMPS comes free with a selection of potentials

There is a whole directory full of potentials.

Ag_u3 AlCu AlFe_mm AlO AlSiMgCuFe Al_jnp Al_mm Al_zhou Au_u3 BNC C CCu_v2 CH CdTe CdTeSe CdTeZnSeHgS0 CdZnTe_v1 CdZnTe_v2 CoAl Cu CuH CuNi CuTa CuTa_eam CuZr_mm Cu_mishin1 Cu_smf7 Cu_u3 Cu_u6 Cu_zhou FeCr FeP_mm Fe_mm GaAs GaN GaN_sw GaN_tersoff InP MOH Mg_mm Mo5 Ni NiAlH_jea Ni_smf7 Ni_u3 Pd_u3 Pt_u3 Si SiC SiCGe SiC_1989 SiC_1990 SiC_1994 SiC_Erhart-Albe SiO Si_1 Si_2 Ta06A Ta06A_pot Ta4 Ta6 Ti V6 VFe_mm W_zhou Zr_mm

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There is also a README (which is actually a disclaimer)

- Executive summary: Use at your own risk.

Q: How many simulations were made using those potentials just because they are there?

Formal UQ: Potential derivation as an inverse problem

Forward problem: data (e.g. forces) δ from parameters u

$$\delta = G(u)$$

- u: Parameter vector
- δ: Result vector

Well-posed problem.

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Well-posed problem.

Inverse problem: parameters u from noisy data δ

$$\delta = G(u) + \eta$$

Ill-posed. Optimisation problem:

$$\min_u \frac{1}{2}||\delta - G(u)||^2$$

Potential derivation as a Bayesian inverse problem

Interpret u, η, δ as RV/random fields

Attack problem using “standard” techniques:

- MCMC methods
- MAP estimators
- Sparse deterministic approximations

⇒ Account naturally for noisy reference data.

Computationally involved (to say the least).

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In the following:

- How has this been used so far (selection)?

The problem is two-fold:

1. Quantifying uncertainty in potential (inverse problem).
2. Propagate uncertainty to MD simulations (forward problem).

“Sloppy model” MD

Replace best-fit effective potential by ensemble

Conditional probability of parameter set u:

$$P(u|\delta, G) \propto \exp\left[-\frac{C(u)}{T}\right],$$

- cost function $C(u) = \frac{1}{2}||\delta - G(u)||^2$
- formal temperature T, with $T_0 = 2C_0/N_p$, $C_0 = \min_u C(u)$

For any observable O, calculate mean $\langle O\rangle|_{T,D,M}$, variance $\sigma_O^2|_{T,D,M}$.

Frederiksen *et al.*, PRL **93** 165501 (2004)

Sloppy model pros and cons

Advantages

- Integrates seamlessly into force matching/MD software stack:
  - Generate ensemble of potentials.
  - Run *N* independent MD simulations.
- Accounts for model & parameter errors.
- Computational cost: factor *N*.

Disadvantages

- No error propagation from DFT (DFT=truth).
- Sampling of parameter space can be tricky (anisotropic).

PhD project Sarah Wishart.

Conclusions

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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Effective potentials

(Semi-)empirical potentials have their limitations.

- Know their limits (don't guess them).
- Predictive simulations: Quantify Uncertainty,

Materials properties require materials potentials.