Bridging the gap: Gaussian Approximation Potential

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Bridging the GAP

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Outline

- from QM to interatomic potentials
- potential based directly on detailed QM data
- high dimensional fit (Gaussian Processes)
- atomic neighbourhoods: bispectrum
- the first GAP for carbon
- other uses: defining the local energy
From QM...

- quantum mechanics is the 'ultimate truth'
- expensive to solve
- sequence of approximations:
  - Full CI
  - QMC
  - DFT-LDA
  - tight binding
- interatomic potentials
• energy is sum of atomic energies
• atomic energy depends on neighbouring atoms
• electronic problem is not solved

• cluster expansion of total energy

\[ V(r_1, r_2, \ldots, r_N) = V^{(0)} + \sum_i V^{(1)}(r_i) + \]
\[ \sum_{i<j} V^{(2)}(r_i, r_j) + \sum_{i<j<k} V^{(3)}(r_i, r_j, r_k) + \ldots \]

• EAM expansion

\[ V(r_1, r_2, \ldots, r_N) = \sum_i E(\rho_i) \quad \rho_i = \sum_{\text{neighbours}} \rho(r_{in}) \]
Generating potentials

- How is an interatomic potential generated?
  - empirical, analytic formula
  - choose target properties (even forces)
  - fit free parameters to reproduce properties
  - hope that the formula remains reasonably valid everywhere in the configurational space

- The GAP way:
  - no fixed formula
  - search in the space of smooth functions
  - identify target configurations
  - fit to arbitrary precision QM data
  - extend target set if needed
• energy is sum of atomic energies
• $\epsilon(r_1, r_2, r_3 \ldots)$ is not practical
• matrix $r_i \cdot r_j$ is complete but not invariant to permutations
• symmetric polynomials are also complete but not invariant to rotation
  • $\text{CH}_5^+$: all terms, chosen the rotationally invariant ones
• our solution
  • atomic energy is a functional of atomic density
  • express atomic density in rotationally invariant terms
how to choose the target configurations?

an optimal way to interpolate many-dimensional functions

$$f(x) = \sum_i w_i \exp \left( -\frac{(x - x_i)^2}{2\sigma^2} \right)$$

magic trick: finding which fitting points are optimal for reproducing a very large data set

calculate accurate forces and energies (DFT)

perform fit using sum of derivatives of $\epsilon_i$ (forces) and sum of $\epsilon_i$ (energy) as the target function
Invariant representations

- Two examples:
  - 1D periodic function
  - 2D object

- 1D: \( f(\phi) \rightarrow \hat{f}_n \)

- 2D: project on the Riemann-sphere then express it in spherical harmonics basis:

\[ f(x, y) = f(\theta, \phi) \rightarrow f_{lm} \]
Invariant representations

- Power spectrum:
  - 1D: \( g(\phi) = f(\phi + \phi_0) \) \( \hat{g}_n = \exp(i n \phi_0) \hat{f}_n \)
    \[ p_n = \hat{f}_n^* \hat{f}_n \to \hat{f}_n^* \exp(-i n \phi_0) \hat{f}_n \exp(i n \phi_0) = \hat{f}_n^* \hat{f}_n \]
  - 2D: \( f_l \to D_l f_l \)
    \[ f_l^\dagger f_l \to f_l^\dagger D_l^\dagger D_l f_l = f_l^\dagger f_l \]
  - incomplete representation, phase information lost
Invariant representations

• Bispectrum (almost complete):

  • **1D:** \( b_n = \hat{f}_{n+m}^* \hat{f}_n \hat{f}_m \rightarrow \hat{f}_{n+m}^* \exp(-i(n + m)\phi_0) \hat{f}_n \exp(in\phi_0) \hat{f}_m \exp(im\phi_0) = \hat{f}_{n+m}^* \hat{f}_n \hat{f}_m \)

  • **2D:** \( f_{l_1} \otimes f_{l_2} \rightarrow (D_{l_1} \otimes D_{l_2}) f_{l_1} \otimes f_{l_2} \)

\[
D_{l_1} \otimes D_{l_2} = C_{l_1,l_2}^{\dagger} \left[ \begin{array}{c c} \oplus_{l+|l_1-l_2|} D_l \\ l_{1}+l_{2} \end{array} \right] C_{l_1,l_2}
\]

\[
C_{l_1,l_2} f_{l_1} \otimes f_{l_2} \rightarrow \left[ \begin{array}{c c} \oplus_{l+|l_1-l_2|} D_l \\ l_{1}+l_{2} \end{array} \right] C_{l_1,l_2} f_{l_1} \otimes f_{l_2} = \bigoplus_{l=|l_1-l_2|}^{l_1+l_2} g_{l_1,l_2,l}
\]

\[ p_{l_1,l_2,l} = f_{l}^{\dagger} g_{l_1,l_2,l} \]
Invariant representations: 3D objects

- project on a 4D sphere
- $f(x, y, z) \rightarrow f(\alpha, \theta, \phi)$
- $\theta$ and $\phi$ are the same as the 3D polar coordinates
- express in 4D spherical harmonics basis: the Wigner D-matrices
- bispectrum is analogous to 3D case
- 4D CG-coefficients are direct products of 3D CG-coefficients
target function: $\sin x$
fit points between 3 and 7
random noise on fit points
expectation value and variance predicted

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Target configurations

- Hot MD of interesting systems
  - surfaces
  - interstitial
  - vacancy
  - quenched liquid
- energies and forces of configuration samples with DFT
'Baseline' potential

- GP gives 0 as an answer when unsure
- add core repulsion to correct for very close atoms
  - EAM formula
  - fitted to high pressure DFT results
- add dispersion term for long-range interactions

\[
\rho_i = \sum_{n} \rho(r_{in})
\]

\[
E_{\text{core}} = \sum_{i} E(\rho_i)
\]
GAP for carbon

- target configurations
  - bulk phases
  - transition from diamond to graphite
  - 111 and 100 surfaces
  - vacancy
  - interstitial
  - amorphous carbon
force correlation
DFT vs (REBO, GAP)

\( \sigma = 0.26 \text{ eV/A} \)

100 teaching points

2.5 Å cutoff
diamond to graphite transition along arbitrary reaction coordinate
energy from DFT, REBO and GAP
Defining local energies

- how to obtain local energy from DFT
  - surface energy
  - visualisation
- best fit potential: use local energy
- equivalent to chemical potential of an atom
  - replacing atoms to infinity
Approximate local energies

- restricted part of configurational space
  - use force and energy information only along a minimisation from 'gas' phase or
  - blow up a configuration
- use it as post-processing tool
- visualise 'hot' atoms
Summary

- interpolation in high-dimensional space via GP
- target is quantum mechanical data
- extendable method
- carbon potential that captures $sp^2$-$sp^3$ transition
- new approach in defining local energies
• more than one atom type: \[ \rho(r) = \sum_{i} c_i \delta(r - r_i) \]

• electrostatics: subtract Coulomb energy