ME 697R: Computational Methods for Nanoscale Energy Transport

Chapter 5: First Principles Method
Section 5.5: Development of Empirical Interatomic Potentials using DFT

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Topics and Readings

- Readings:
Availability of Interatomic Potentials

- Reliable interatomic potentials are still rare for solids.

- For many relatively new bulk materials, interatomic potentials do not exist.

- For most interfaces such as solid-solid, solid-liquid, solid-gas interfaces, interatomic potentials are unavailable.

- New developments: machine-learning potentials.
Basics of Potential Development

- An inverse problem
  - Empirical interatomic potentials
    - Equilibrium lattice constant
    - Bulk modulus and elastic constants
    - Phonon density of states and phonon dispersion
    - Energy surfaces

- Conventional: fitting to experimental data.
  - Depends on the availability of experimental data

- Fitting to a potential energy surface
  - Depends on the accuracy of DFT calculations on total energies
Limitation of the Conventional Method

- The amount of experimental data is typically not sufficient to generate a potential of good quality.

- Most experimental data only correspond to the interatomic potentials near the equilibrium. They do not touch the region that is far from equilibrium. However, heat transfer is determined by anharmonic effects. The region away from the equilibrium is crucial.

- Ab initio calculations can touch this region conveniently.

![Parabolic Potential of Harmonic Oscillator](attachment:parabolic_potential.png)
Total Energy in DFT Calculation

- Now we have seen that empirical interatomic potentials have a quantum mechanics origin.

- Recall the total energy for the electronic part of a system is

\[
E_{el} = T[\rho] + E_{ext}[\rho] + E_{coul}[\rho] + E_{xc}[\rho]
\]

- The total energy of the system needs to take into account the coulombic energy of ion-ion interactions

\[
E_{tot} = T[\rho] + E_{ext}[\rho] + E_{coul}[\rho] + E_{xc}[\rho] + \sum_{i,j>i} \frac{Z_i Z_j e^2}{R_{ij}}
\]

where \(Z_i, Z_j\) are charges of ions, and \(R_{ij}\) is the distance between ions \(i\) and \(j\).
Total Energy in Lattice Dynamics Calculation

- In lattice dynamics, the empirical interatomic potential contains the short-range and long-range (Coulombic) components

\[ E_{tot} = \sum_{i,j>i} U_{ij,sh} + \sum_{i,j>i} \frac{Z_i Z_j e^2}{R_{ij}} \]

- Comparing DFT and LD, the Coulombic part is calculated the same way. However, DFT can only determine the total short-range potential energy of the entire system, while cannot decompose it to each atomic pair, i.e.,

\[
\{ T[\rho] + E_{ext}[\rho] + E_{coul}[\rho] + E_{xc}[\rho] \}_\text{DFT} = \left\{ \sum_{i,j>i} U_{ij,sh} \right\}_\text{LD}
\]

- Multiple unknowns in the empirical potential model: needs a multi-variable fitting process
First Step: Select Potential Forms

- Mini-review: mostly used two-body interatomic potential forms

### Lennard-Jones form
\[
\phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]

### Morse form
\[
V(r) = D_e \left( 1 - e^{-a(r-r_0)} \right)^2
\]

### Buckingham form
\[
\phi(r_{ij}) = A_{ij} \exp \left( -\frac{r_{ij}}{b_{ij}} \right) - \frac{C_{ij}}{r_{ij}^{6}}
\]

- Besides two-body, there are dozens of other potential forms describing many body interactions.
Fitting Technique and Weighting Factor

In order to perform a fit, first it is necessary to define a quantity that measures the quality of the results, known as the sum of squares;

\[ F = \sum_{i=1}^{N_{\text{obs}}} w_i \left( f_{i}^{\text{obs}} - f_{i}^{\text{calc}} \right)^2 \]

where \( N_{\text{obs}} \) is the number of observables, \( f_{i}^{\text{obs}} \) and \( f_{i}^{\text{calc}} \) are the fitted and calculated values of the observable, respectively, and \( w_i \) is the weighting factor for the given observable.

- If fitting experimental data, the weighting factor should be inversely proportional to the uncertainty in the measured value. Obviously, trusted, precise values should be given more priority than data where there are large error bars.

- The weight factor should be inversely proportional to the magnitude of the observable squared. This ensures that all values are fitted on an equal footing, regardless of units. For example, fitted vibrational frequencies in wavenumbers are typically two to three orders of magnitude larger than structural variables.
Conventional Fitting Methodology

Experimental structure is known

Varying the potential parameters

Calculate forces

Forces minimized?

Matches bulk properties?

Potential parameters obtained

N

Y

N

Y
Potential Energy Surface

Atomic configurations near equilibrium

Density Functional Theory (DFT)

Classical potentials

\[ E = f(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \]

\[ F = -\frac{dE}{dr_{ij}} \]