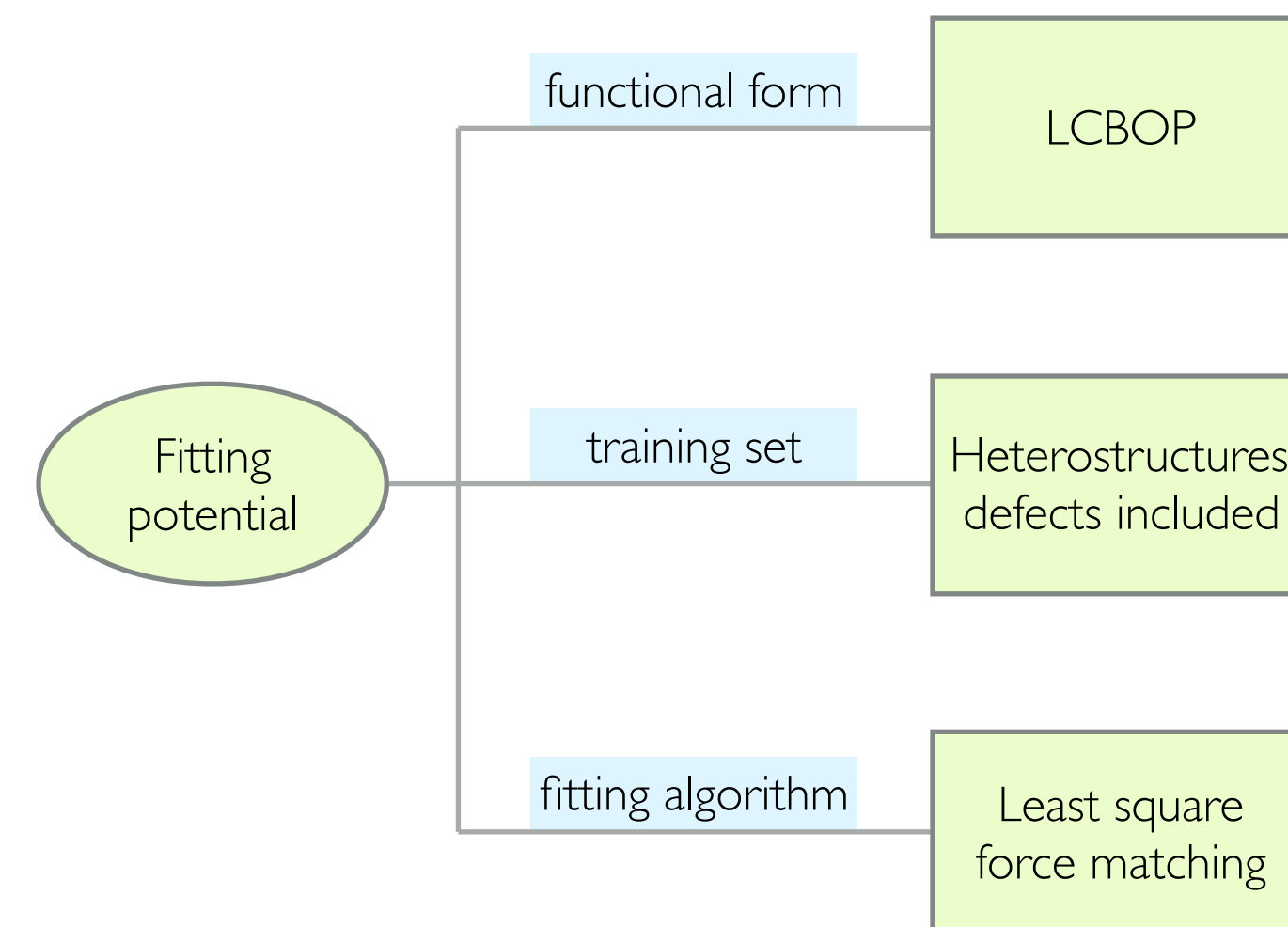


Objective:

The objective is to create a universal empirical interatomic potential for layered heterostructures of 2D materials such as graphene, hBN, MoS₂, WSe₂, and fluorographene. The potential should have the following features:

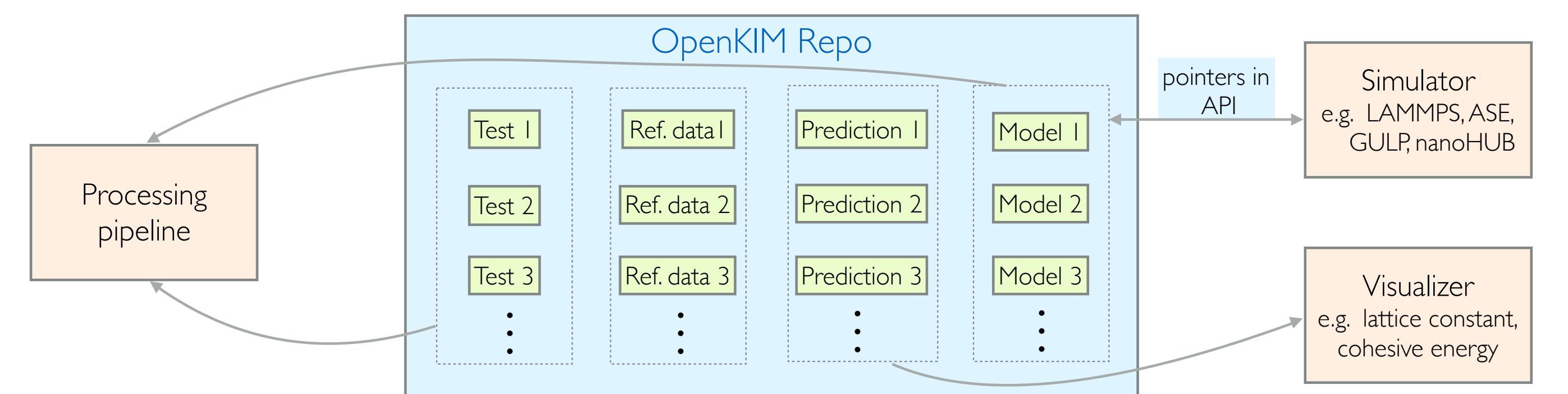
- Characterized by a single parameter set that describes the interaction of all layer materials. When the potential is extended to support a new layer material, it will be refit for all materials;
- Predict basic mechanical properties (e.g. elastic constant, phonon dispersion), and thermal properties (e.g. in-plane thermal expansion coefficient) of defects-free materials;
- Predict the defects-related properties, such as the Stone-Wales formation energy, grain boundary structure, and vacancy migration energy, and the interactions between defects both within and between layers.

Essential Parts for Potential Fitting



OpenKIM:

OpenKIM (<http://openkim.org>) is an online suite of open source tools for molecular simulations of materials. These tools help to make molecular simulations more accessible and more reliable. Within OpenKIM is an online resource for standardized testing and long-term warehousing of interatomic models and data, and an *application programming interface* (API) standard for coupling atomistic simulation codes and interatomic potential routines.



Processing pipeline (PP): An automatic system for generating property Predictions (such as elastic constant) by mating a Test (that computes that property) and a Model (interatomic potential) both stored within the OpenKIM Repository. The PP is activated whenever a new Test or Model is uploaded to the Repository.

Visualizer: An online web-based visualization script that graphically displays Predictions and helps compare different Models.

Functional Form:

Bond-order potentials, which are based on the idea that the bonding between atoms can be properly described by their local environment, have been proved successful in describing covalent systems. Tersoff (PRL, 1986) proposed the first bond-order potential for Si. Later, Brenner (PRB, 1990) adapted the Tersoff potential for C and added new terms to account for free radicals, conjugation, and dihedral angles. Stuart *et al* (J. Chem. Phys. 2000) created the AIREBO potential by adding long-range interactions to the second generation Brenner potential (J. Phys. Condens. Matter, 2002). LCBOP (Los *et al*, PRB, 2003) is also based on the Brenner potential with additional long-range interactions with the difference that short- and long-range interactions are fit simultaneously with possible improved performance. LCBOP is used as the starting potential in this work.

The LCBOP total energy is given by

$$E = \sum_i \sum_{j>i} [f_c V^{SR}(r_{ij}) + (1 - f_c) V^{LR}(r_{ij})].$$

The short-range interaction is:

$$V^{SR}(r_{ij}) = V^R(r_{ij}) - b_{ij} V^A(r_{ij}),$$

in which V^R and V^A are the repulsive and attractive radical pair potentials, and the bond order is:

$$b_{ij} = \frac{1}{2} \left[b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi} + F^{conj}(N_{ij}, N_{ji}, N_{ij}^{conj}) \right],$$

$$b_{ij}^{\sigma-\pi} = \left(1 + \sum_{k \neq i,j} f_c(r_{ik}) G(\cos \theta_{ijk}) H(\delta r_{ijk}) \right)^{-\delta}.$$

The long-range interaction is:

$$V^{LR}(r) = \theta(r_0 - r) V_1^M(r) + \theta(r - r_0) V_2^M(r).$$

In these equations, f_c is a cutoff function, F^{conj} and G are splines, H is a polynomial, θ is the Heaviside step function and V^M are Morse-type potentials.

LCBOP is chosen as the starting potential because of its relatively simple functional form compared with other bond-order potentials. In addition the fact that all the parameters are fit together simplifies the fitting procedure and makes it suitable for our aim to have a single parameter set for all material systems.

LCBOP was developed for bulk carbon and must therefore be adapted to 2D materials, which may involve adding or removing terms from the functional form. This will be explored during the fitting process.

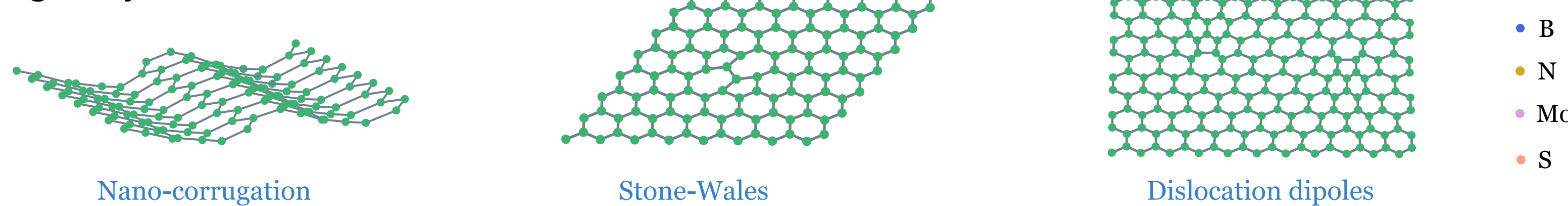
Training Set:

A key aspect of fitting a new potential involves the selection of a training set (i.e. the set of configurations deemed important for the problems to be studied to which the potential is fit). We will use a force matching algorithm (Ercolessi *et al*, Euro. Phys. Lett., 1994), which attempts to fit the forces on atoms in different configurations in addition to configuration energies, stresses and other information (e.g. phonon mode at Gamma point).

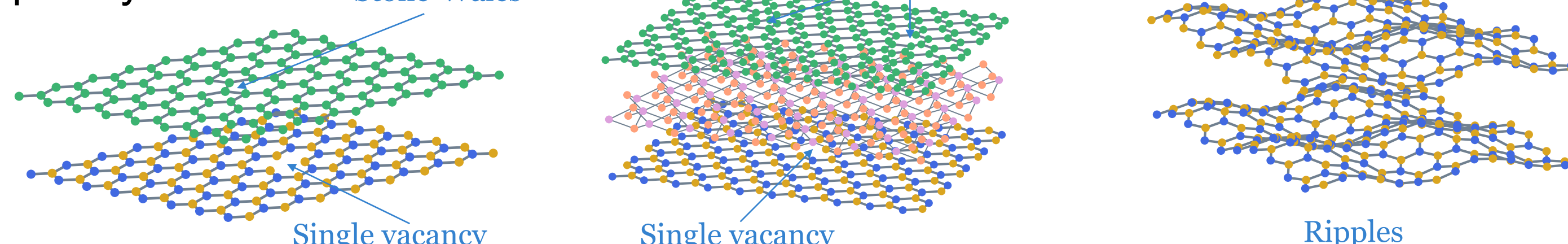
A good potential is transferable, which means that it is able to predict properties that it was not fit to reproduce. To ensure this the training set must include a wide range of information that spans the configuration space of interest. In particular, the training set for 2D materials should include configurations where the continuum mechanics predictions (based on the elastic constants and bending stiffness) break down.

Based on these ideas, we perform first principles density functional theory (DFT) calculations for the following: (1) configurations where continuum theory fails (e.g. nano-corrugation); (2) monolayer 2D systems with point and line defects (e.g. Stone-Wales and grain boundary); (3) heterostructures with defects in different layers interacting with each other (e.g. Stone-Wales in graphene interacting with single vacancy in Boron Nitride).

Single layer:



Multiple layers:



The choice of training set is an iterative process. On one hand, a particular configuration may be dropped if it provides similar information to other configurations; on the other hand, new configurations may be added if the current training set does not contain information on particular configurations of interest. The results of the DFT calculations will be stored as Reference Data in the OpenKIM Repository.

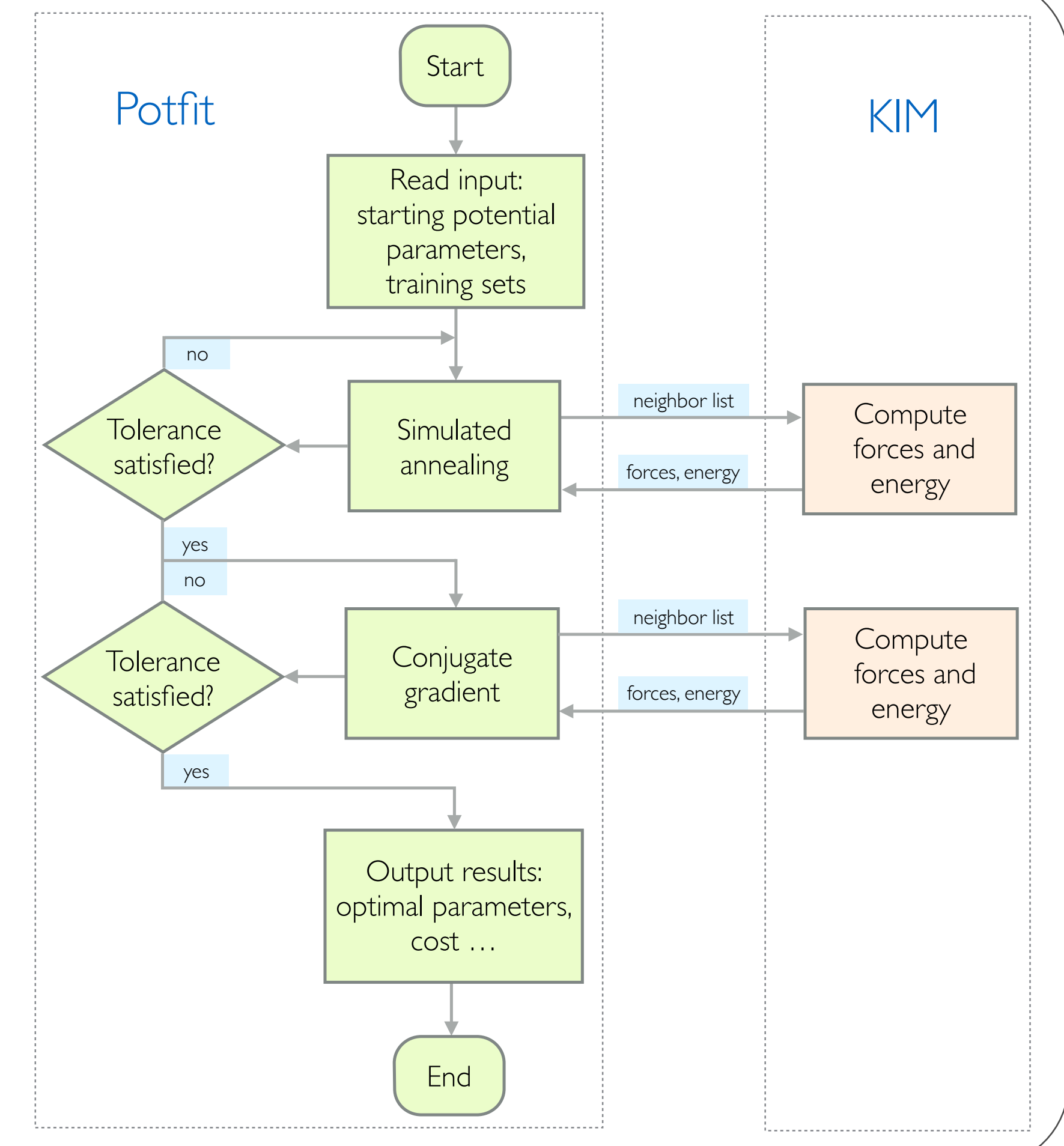
Potfit:

Potfit (Brommer *et al*, Phil. Mag., 2006) is a potential fitting program using the force matching approach. The optimal parameter set is determined through a least-squares minimization procedure using the following cost function, which includes forces and energies of training set configuration (where the 0 indicates DFT results):

$$C = w_1 \sum_{\alpha=1}^N \|f^\alpha - f^{\alpha 0}\|^2 + w_2 (E - E_0)^2.$$

- An interface between Potfit and KIM has been created, which enables KIM Models to be used seamlessly with Potfit.

- Potfit performs a global minimization (simulated annealing or differential evolution) followed by a "polish" using a conjugate gradient local minimization. The Potfit minimization algorithms have been optimized for determining potential parameters.

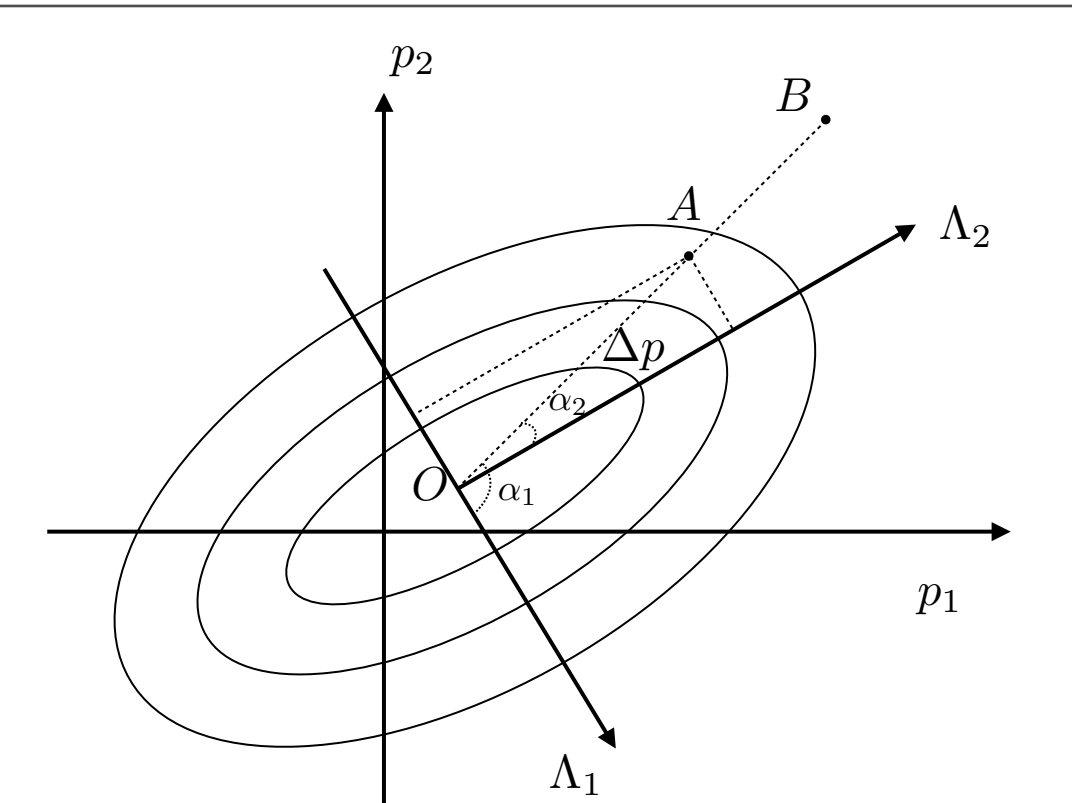


Preliminary Results:

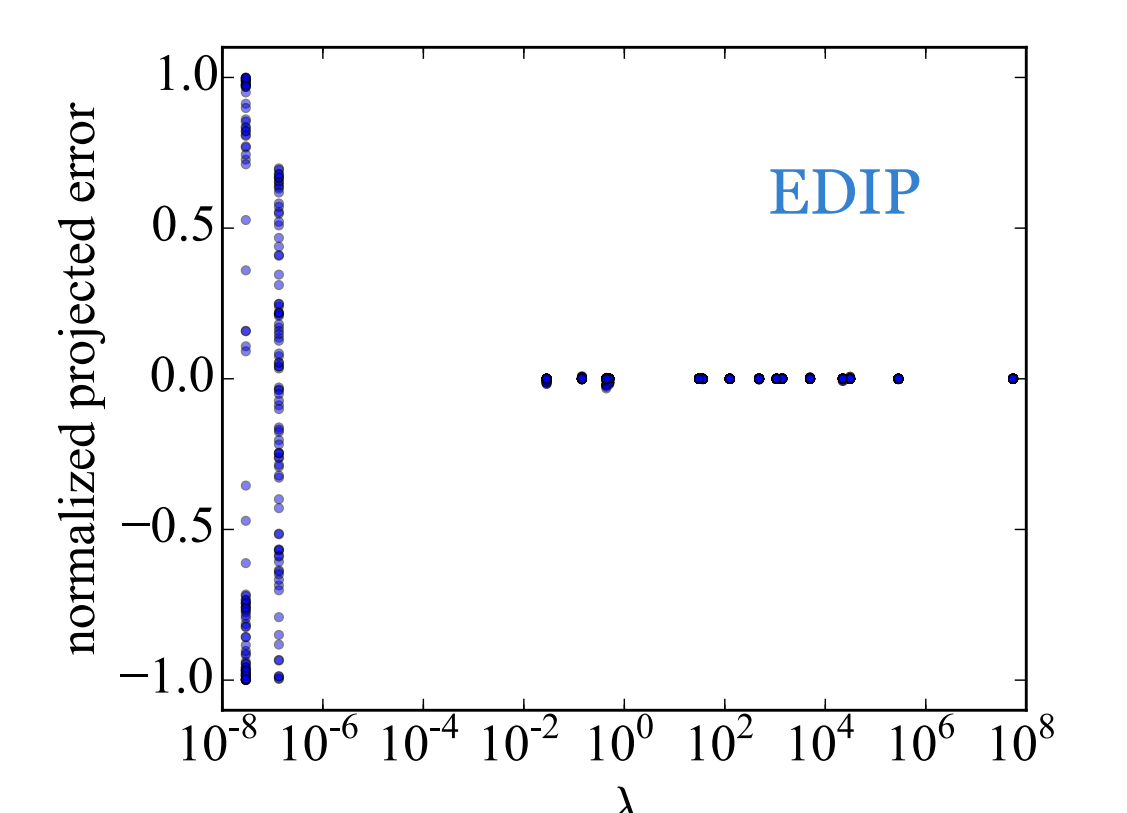
- Interatomic potentials often have the characteristic that they are largely insensitive to certain combinations of parameters. Such functions have been referred to as sloppy models (Brown *et al*, PRE, 2003). Recognizing this fact has important implications for the fitting process. To explore this behavior, we tested the Environmentally-Dependent Interatomic Potential (EDIP) for silicon (Bazant and Kaxiras, PRL, 1996). We performed a Potfit optimization starting from 100 different initial guesses for the EDIP parameters, but the final results are distributed along two "sloppy" eigendirections as anticipated. Below we plot the cosine of the angle between Δp (the difference between the parameters obtained by Potfit and the EDIP parameters) and all (17) eigendirections in parameter space, defined as

$$\cos \alpha_i = \frac{\Delta p \cdot \Lambda_i}{\|\Delta p\|}.$$

- A training set is being selected, and DFT calculations are in the process of being performed for the variety of configurations listed above.



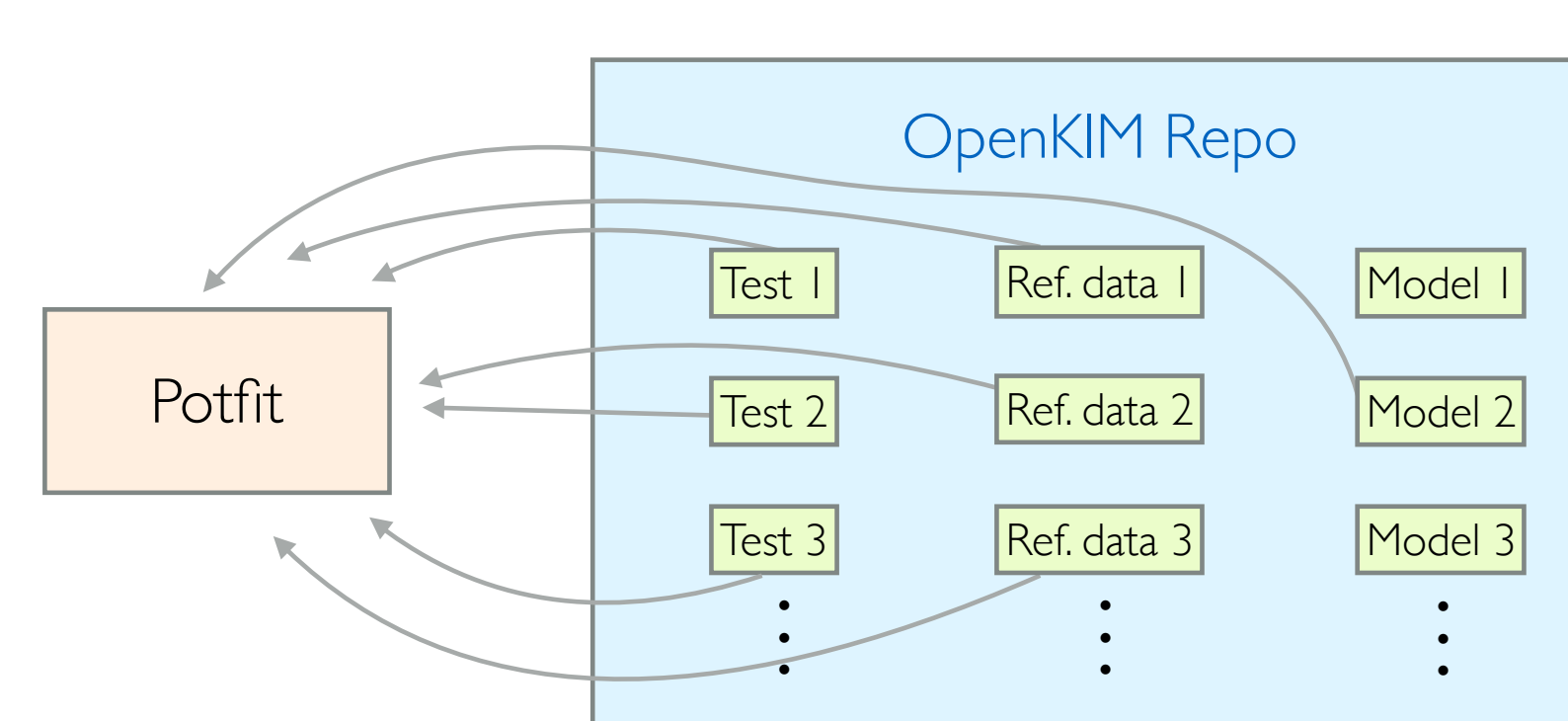
Cost contour with two parameters



Fit parameter errors projected on the eigendirections of the parameter space

Future Work:

- Select proper test set for the potential. Basically the potential needs to predict the properties listed in the "Objective" section. And other tests may also be added.
- Extend the interface between Potfit and OpenKIM, such that OpenKIM Tests and Reference Data can be incorporated in the Potfit training set in a user-friendly fashion. The training set is archived in the OpenKIM Repository, which provides comprehensive documentation and facilitates extension and reuse of the potential by the research community.



The Potfit-KIM fitting framework being developed will provide the community with a powerful platform for fitting new potentials. Users will be able to construct a training set by selecting Tests (and associated Reference Data) from OpenKIM using a user-friendly GUI. They can then interact with OpenKIM's built-in Regression Algorithm for Transferability Estimation (RATE) methodology for assessing potential transferability as part of the fitting process.