Interatomic potentials

What they can and cannot do

Functional Forms

- Must be such as to allow million atom MD
- Short-ranged (order-N calculation)

- Should describe electronic structure
- Motivated by DFT (a *sufficient* theory)
- Fitted to relevant properties

History lesson

- 1930s Pair potentials $\sum_{ij} V(r_{ij})$
- 1980s Many body potentials

$$\sum_{ij} V(r_{ij}) + F_i[\sum_j \phi(r_{ij})]$$

- 1990s Angle-dependence

$$\sum_{ij} V(r_{ij}) + F[\sum_{ij} \phi(r_{ij})] + G[\sum_{ijk} \Theta(r_{ij}, r_{jk}.\theta_{ijk})]$$

- 2000s Onsite dependence:

$$\sum_i Min_{\mu_i}[F(\mu_i, \sum_j \phi(r_{ij})) + \sum_j V_i(r_{ij}, \mu_i)]$$

History lesson

- 1930s Pair potentials $\sum_{ij} V(r_{ij})$
- 1980s Many body potentials

$$\sum_{ij} V(r_{ij}) + F_i[\sum_j \phi(r_{ij})]$$

- 1990s Angle-dependence

$$\sum_{ij} V(r_{ij}) + F[\sum_{ij} \phi(r_{ij})] + G[\sum_{ijk} \Theta(r_{ij}, r_{jk}.\theta_{ijk})]$$

- 2000s Onsite dependence:

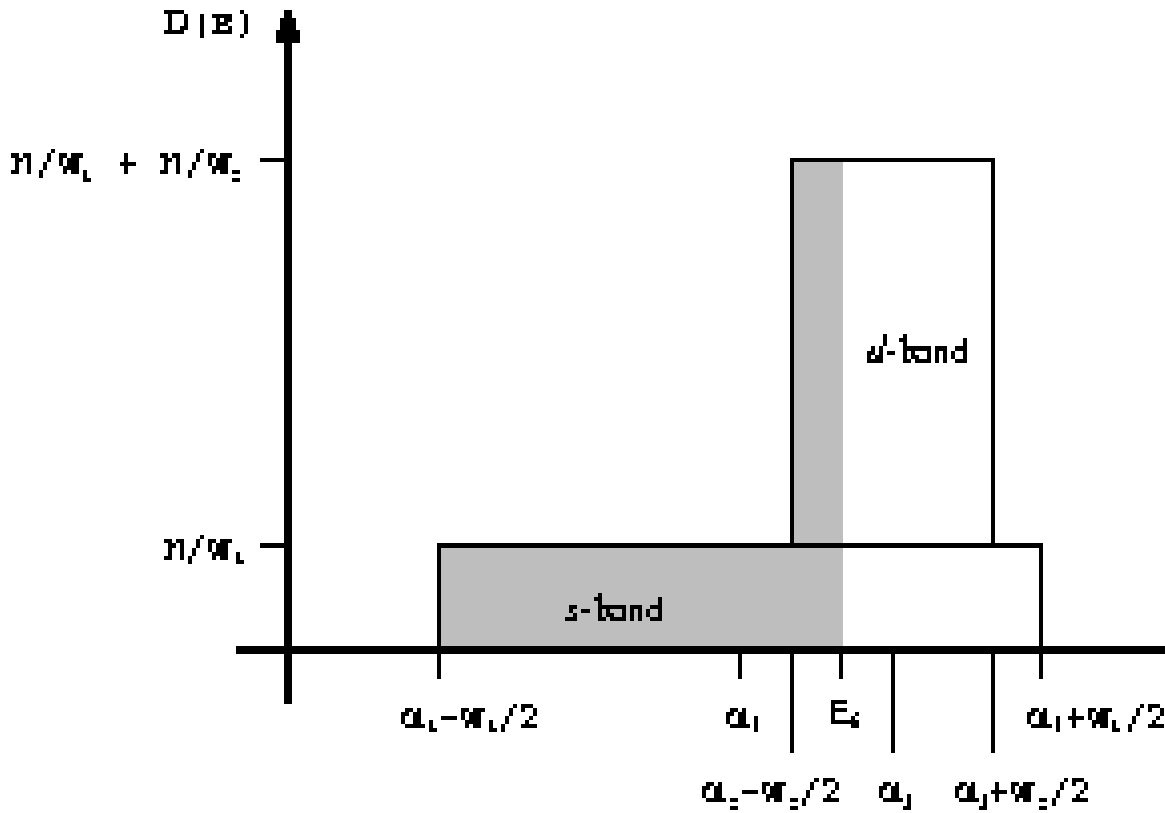
$$\sum_i Min_{\mu_i}[F(\mu_i, \sum_j \phi(r_{ij})) + \sum_j V_i(r_{ij}, \mu_i)]$$

What can empirical/MD do?

- Reproduce reliable energies – YES
- Predict reliable energies – NO
- Reproduce mechanisms and correlations – YES
- Predict unexpected mechanisms – YES

Potential developments

- Finnis-Sinclair mode
- Fill two bands
- Different widths
- Fixed offset
- Optimise wrt occupation of band locally.



Two Band Model

- Allows localised orbitals on atom to change state – e.g. s-d or ↓ ↑
- Demonstrated for s-d transfer – gives a discontinuous isostructural transition.
- Work in progress for iron
- Minimisation done analytically => still EAM-type speed not Car-Parrinello.

Cohesive term looks like Finnis-Sinclair with variable number of electrons in each band (second moment tight-binding)

$$U_{bond} = \sum_i \int_{-W_i/2}^{E_f=(\frac{n}{N}-\frac{1}{2})W_i} E \frac{N}{W_i} dE = -\sum_i \frac{W_i}{2N} n(N-n)$$

Plus extra energy associated with band centres being different

$$U_{bond} = \sum_i \frac{W_{i1}}{2N_1} n_{i1}(n_{i1}-N_1) + \frac{W_{i2}}{2N_2} n_{i2}(n_{i2}-N_2) + E_{prom}$$

Plus a pairwise potential (also dependent on occupation)

Problem: minimising *total* energy with respect to electron transfer at *each* site η_ι appears to be minimisation of N-variable function

BUT, by writing energy as sum of atomic energies, and splitting the pair potential part between atoms appropriately, determining η_ι becomes *local* and *analytic* (i.e. as fast as pair potentials) in the absence of charge transfer

$$\eta_{i_0} = \frac{N_1 N_2}{W_{i1} N_2 + W_{i2} N_1} \left[W_{i1} - W_{i2} - T\left(\frac{W_{i1}}{N_1} - \frac{W_{i2}}{N_2}\right) + 2E_0 - 2U_{i1,pair} + 2U_{i2,pair} \right]$$

W and U are sums of pair potentials E_0, N and T are constants

(band centre offset, band capacities, total number of electrons/atom)

BETTER STILL…

Force is variational in η, so can be evaluated locally (quickly) for MD. (Hellman-Feynman theorem!)

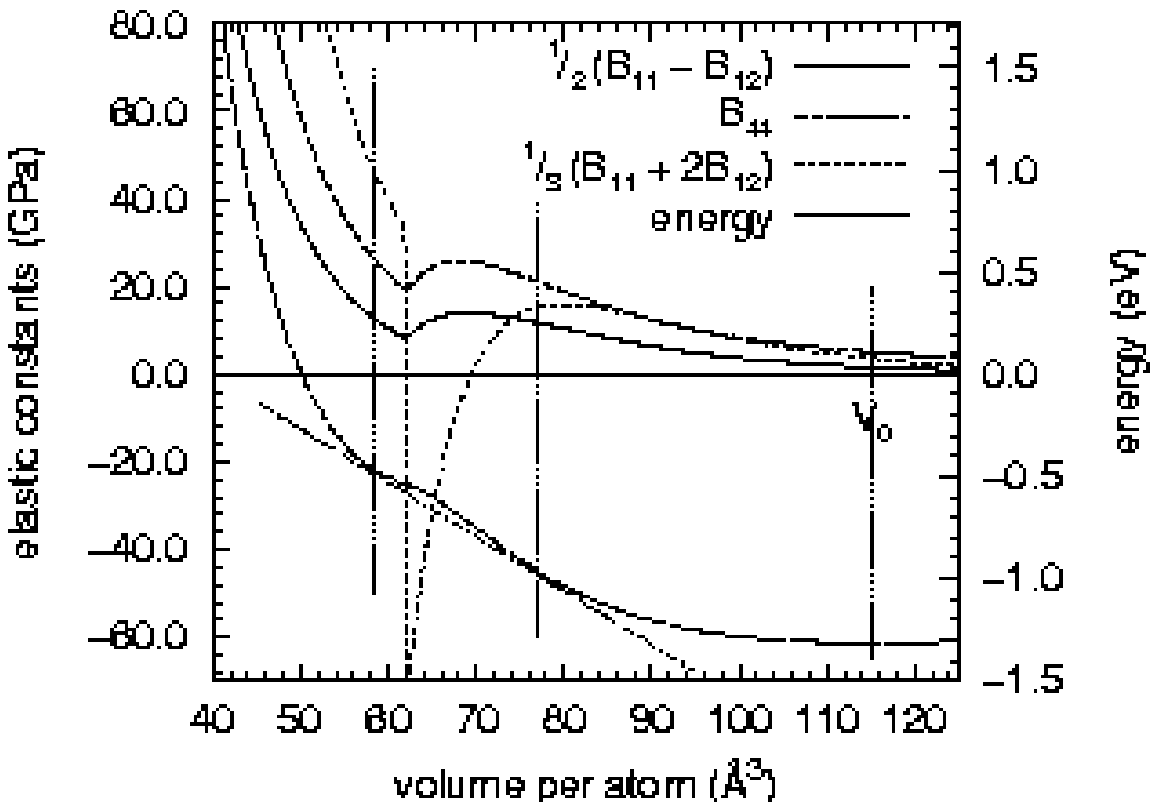
Elasticity is non-local – great flexibility in fitting.

$$\begin{aligned}
\mathbf{f}_i &= -\frac{dU_{tot}}{d\mathbf{r}_i} \\
&= -\frac{\partial U_{tot}}{\partial \mathbf{r}_i}\bigg|_{\eta} - \frac{\partial U_{tot}}{\partial \eta}\frac{\partial \eta}{d\mathbf{r}_i} \\
&= -\frac{\partial U_{tot}}{\partial \mathbf{r}_i}\bigg|_{\eta}
\end{aligned} \tag{15}$$

$$\mathbf{f_i} = \sum_j \Big[(\tilde{W_{i1}} + \tilde{W_{j1}})\phi'_1(r_{ij}) + (\tilde{W_{i2}} + \tilde{W_{j2}})\phi'_2(r_{ij}) - (n_{i1} + n_{j1})\mathbf{V'}_1(r_{ij}) - (n_{i2} + n_{j2})\mathbf{V'}_2(r_{ij}) \Big] \hat{\mathbf{r}}_{ij}$$

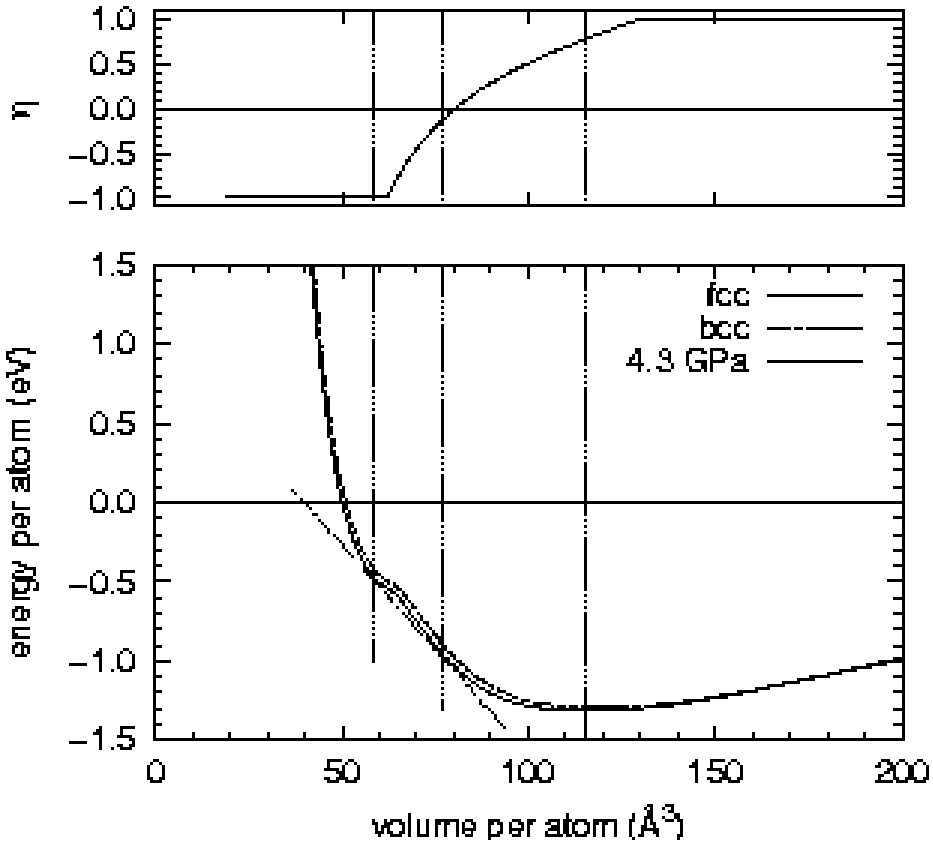
Two band model – caesium

- s-d transfer
- Isostructural phase transition
- Elastic anomalies
- d-like atom is smaller – favoured under pressure
- Correlation effect beyond DFT-GGA!



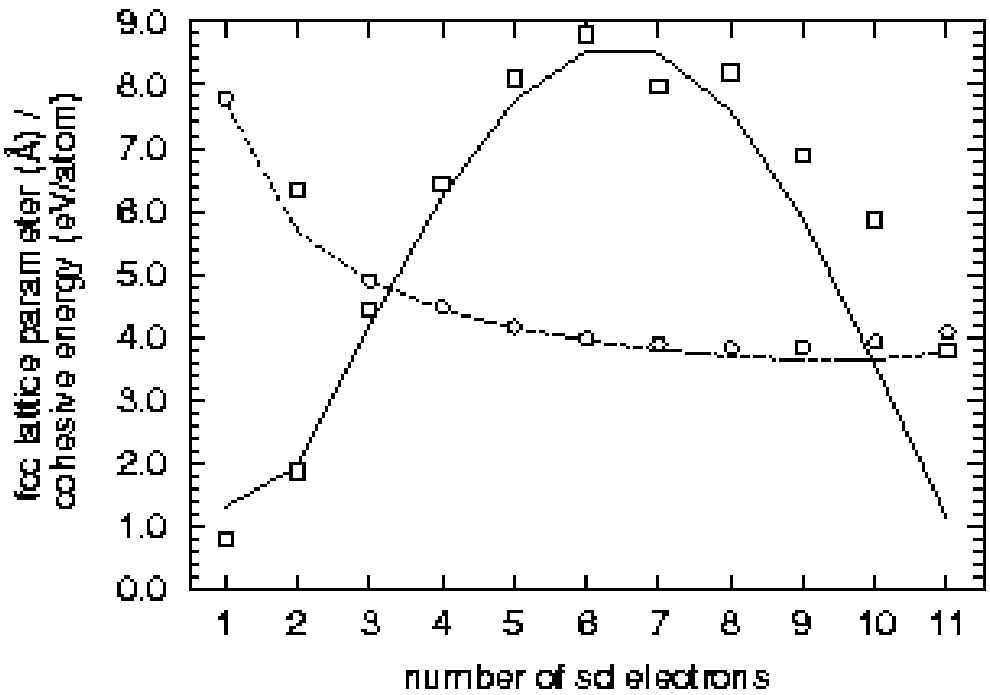
Electron transfer

- Optimise Ns-Nd
- Fit phase transition pressure, energy, volumes



Two-band model - transferability

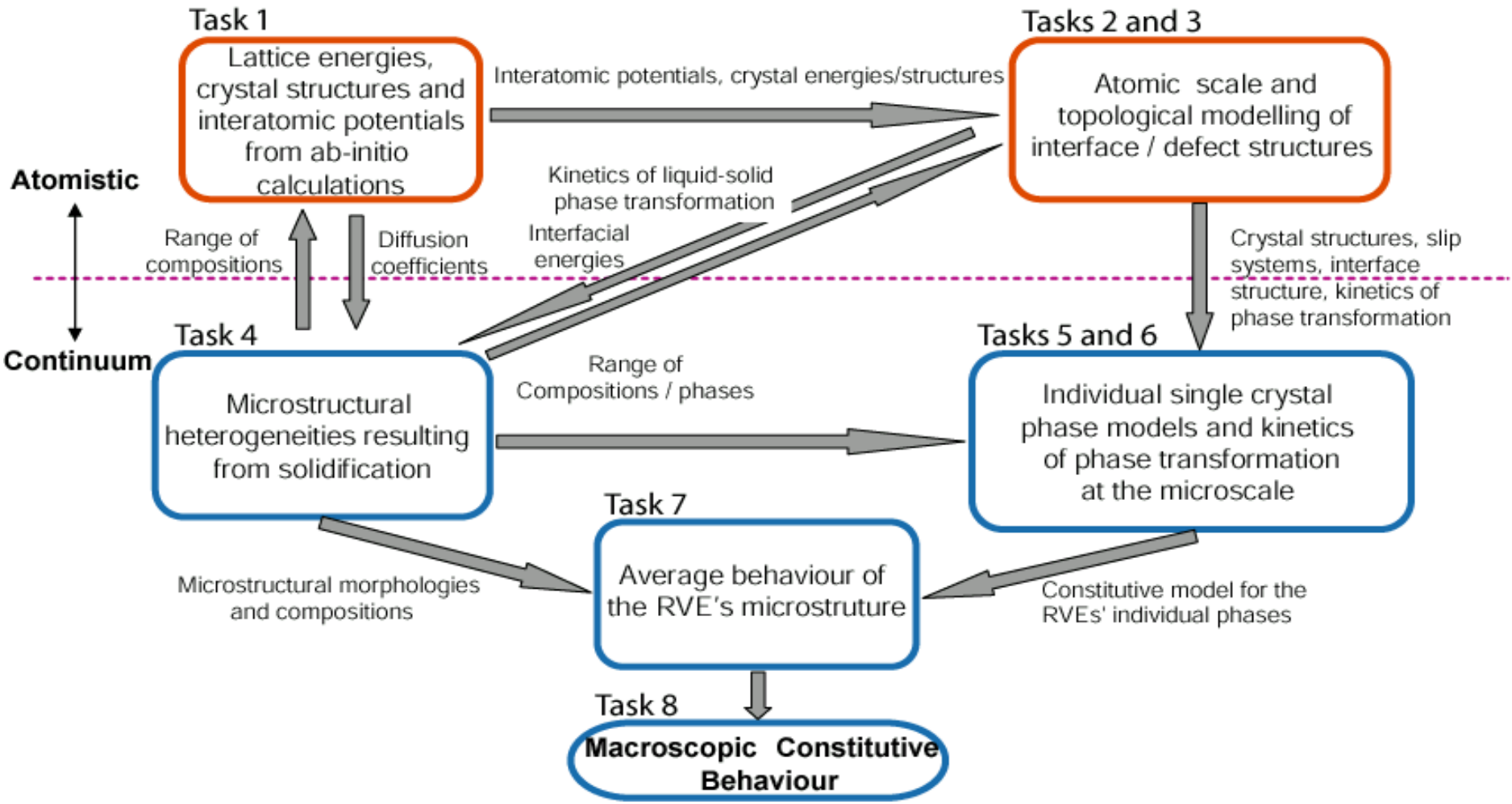
- Parameters fitted to Cs describe all 6s5d metals!
- Suggests the physics is right



Composition dependent potentials

- For alloys, properties depend on Fermi energy.
- Potentials capture only local effects (e.g. pinning), not global effects (phase stability)
- Two-band model shows that the total number of electrons can be included in fit *without* extra computational cost
- For MD, composition-dependent potentials can be generated at start of each run with no computing cost.

Links Between the Different Project Tasks and Deliverables



Role of MD in multiscale

- Identifying important processes
- Correlations
- Transformation mechanisms
- Trial defect geometries
- Key configurations for fitting to potential
- Not accurate energies from extrapolation – these come from ab initio

Crucial R&D needs

- Better understanding by modellers of the key materials problems.

- Commitment by experimentalists to think about their problems at the atomic level.