Forceconstant Calculator

The force constant calculator `FCCalculator` implements properties derived from a harmonic model for the potential-energy surface,

$$H(\mathbf{U}) = \frac{1}{2} \sum_{IJ,\alpha\beta} \Phi_{IJ}^{\alpha\beta} U_I^\alpha U_J^\beta \,, \tag{1}$$

where $\Phi_{IJ}^{\alpha\beta}$ denote the force constant matrix elements

$$\Phi_{IJ}^{\alpha\beta} = \left. \frac{\partial^2 E}{\partial R_I^\alpha \partial R_J^\beta} \right|_{\mathbf{R}^0} \,, \tag{2}$$

i.e., the second-order derivative of the potential energy E w.r.t. to the atomic positions $\mathbf{R} = \{R_I^\alpha\}$ at a given configuration $\mathbf{R}^0$. Here, I, J are the atom labels and α, β denote Cartesian components. $\mathbf{U} = \{U_I^\alpha\}$ denotes the atomic displacements w.r.t. to the reference position $\mathbf{R}^0$, i.e.,

$$\mathbf{U} = \mathbf{R} - \mathbf{R}^0 \,. \tag{3}$$

Properties derived from the harmonic model

Forces

Forces are given as a derivative of the potential energy and can therefore be obtained analytically from Eq. (1):

$$F_I^\alpha = -\frac{\partial H}{\partial R_I^\alpha} = -\sum_{J,\beta} \Phi_{IJ}^{\alpha\beta} U_J^\beta \,. \tag{4}$$

This equations can be written as a matrix-vector product

$$\mathbf{F} = -P\mathbf{U} \,, \tag{5}$$

where $\mathbf{F}$ and $\mathbf{U}$ are the $3N \times 1$ vectors representing atomic forces and displacements, and P is the $3N \times 3N$ forceconstant matrix, where N is the number of atoms in the simulation. In python, this is achieved by

```
forces = -(fc @ displacements.flatten()).reshape(displacements.shape)
```

Potential energy

The energy is given by computing the displacements $\mathbf{U}$ according to Eq. (3), and performing the matrix product given by Eq. (1), i.e., by scalar multiplication of the displacements $\mathbf{U}$ with the forces $\mathbf{F}$,

$$E^{\text{pot}} = -\frac{1}{2} \mathbf{F} \cdot \mathbf{U} \,. \tag{6}$$

In python:

```
# energies: [N, 3] * [N, 3] -> [N]
energies = -(displacements * forces).sum(axis=1) / 2
# energy: [N] -> [1]
energy = energies.sum()
```

As a byproduct, atomic energy contributions (`energies`) are computed, given by

$$E_I^{\mathrm{pot}} = \frac{1}{2} \sum_{J,\alpha\beta} \Phi_{IJ}^{\alpha\beta} U_I^\alpha U_J^\beta \,. \tag{7}$$

Stress

Stress is given in terms of a strain derivative of the potential energy

$$\sigma^{\alpha\beta} = \frac{1}{V} \frac{\partial H}{\partial \epsilon^{\alpha\beta}} \,, \tag{8}$$

where $\epsilon^{\alpha\beta}$ describes a rotation-free, homogeneous straining of the atomic positions. The strain derivatives of the atomic displacements read [Knuth2015]

$$\frac{\partial U_I^\gamma}{\partial \epsilon^{\alpha\beta}} = \delta^{\alpha\gamma} U_I^\beta \,. \tag{9}$$

In turn, the harmonic stress tensor reads

$$\sigma^{\alpha\beta} = \frac{1}{V} \frac{\partial H}{\partial \epsilon^{\alpha\beta}} = \underbrace{\frac{1}{V} \sum_{IJ,\gamma} \Phi_{IJ}^{\alpha\gamma} U_I^\beta U_J^\gamma}_{\sigma_{\mathrm{HA}}^{\alpha\beta}} + \sigma_{\mathrm{QHA}}^{\alpha\beta} \,, \tag{10}$$

where the purely harmonic contribution is given by

$$\sigma_{\mathrm{HA}}^{\alpha\beta} = \frac{1}{V} \sum_{IJ,\gamma} \Phi_{IJ}^{\alpha\gamma} U_I^\beta U_J^\gamma \,, \tag{11}$$

and the the *quasiharmonic* contribution $\sigma_{\mathrm{QHA}}^{\alpha\beta}$ stems from the strain derivative of the force constants. The quasiharmonic contribution can be approximated by

$$\frac{1}{V} \frac{\partial H}{\partial \epsilon^{\alpha\beta}} \approx 3 \left(\frac{\partial H}{\partial V} \right)^{\alpha\beta} \,, \tag{12}$$

which is strictly true only in cubic systems. By denoting the quasiharmonic force constants, i.e., the volume derivative $\partial \Phi / \partial V$ as Φ', we have

$$\sigma_{\mathrm{QHA}}^{\alpha\beta} = \frac{3}{2} \sum_{IJ,\gamma} \Phi_{IJ}^{\prime\alpha\gamma} U_I^\beta U_J^\gamma \,. \tag{13}$$

Virial stress

The virial stress in periodic systems is given by [Louwerse2006]

$$\sigma_{\mathrm{vir}}^{\alpha\beta} = -\frac{1}{2V} \sum_{IJ} (R_I^\alpha - R_J^\alpha) F_{IJ}^\beta \,, \tag{14}$$

where F_{IJ}^β denotes the pairwise force between atom I and J fulfilling Newton's 3rd law,

$$F_{IJ}^\alpha = -F_{JI}^\beta \,, \tag{15}$$

and sums to the atomic force F_I^β,

$$F_I^\beta = \sum_J F_{IJ}^\beta \ . \tag{16}$$

This pairwise force is given in the harmonic approximation as

$$F_{IJ}^\beta = -\Phi_{IJ}^{\beta\gamma} U_J^\gamma + \Phi_{JI}^{\beta\gamma} U_I^\gamma \ , \tag{17}$$

where summing over repeated indices is implied. This definition complies with both Eq. (15) and (16), by using the acoustic sum rule $\sum_J \Phi_{IJ}^{\alpha\beta} = 0$. Using this pairwise force in the definition of virial stress, Eq. (14), we have

$$\begin{aligned} \sigma_{\text{vir}}^{\alpha\beta} &= -\frac{1}{V} \sum_{IJ} (R_I^\alpha - R_J^\alpha)\, \Phi_{IJ}^{\beta\gamma} U_J^\gamma & (18) \\ &= -\frac{1}{V} \sum_{IJ} (R_I^{0\alpha} - R_J^{0\alpha})\, \Phi_{IJ}^{\beta\gamma} U_J^\gamma \\ &\quad -\frac{1}{V} \sum_{IJ} (U_I^\alpha - U_J^\alpha)\, \Phi_{IJ}^{\beta\gamma} U_J^\gamma \ , & (19) \end{aligned}$$

where in the second row $\mathbf{R} = \mathbf{R}^0 + \mathbf{U}$ was written out. However, the first contribution can be written as

$$V\sigma_{\text{vir},0}^{\alpha\beta} = -\sum_{IJ} (R_I^{0\alpha} - R_J^{0\alpha})\, \Phi_{IJ}^{\beta\gamma} U_J^\gamma = \underbrace{\cancel{\sum_{IJ} R_J^{0\alpha}\, \Phi_{IJ}^{\beta\gamma} U_J^\gamma}}_{\text{acoustic sum rule}} - \sum_{IJ} R_I^{0\alpha}\, \Phi_{IJ}^{\beta\gamma} U_J^\gamma \equiv \sum_I R_I^{0\alpha} F_I^\beta \ , \tag{20}$$

which does not contribute to thermal averages because $\langle F \rangle = 0$.

Remark on finite supercells

In finite supercells, care must be taken when computing the pair distance $\mathbf{R}_I - \mathbf{R}_J$. They should obey a minimum image convention (MIC). Since MIC is a non-continuous map as it involves wrapping of atoms by finite displacements, continuity of the map must be ensured, e.g., by averaging over MIC-equivalent pairs of atoms.

Atomic virials

The harmonic virial stress can be decomposed into atomic contributions by writing

$$\sigma_{\text{vir}}^{\alpha\beta} = \sum_I \sigma_{\text{vir},I}^{\alpha\beta} \ , \tag{21}$$

with

$$\sigma_{\text{vir},I}^{\alpha\beta} = -\frac{1}{V} \sum_{IJ} (R_I^\alpha - R_J^\alpha)\, \Phi_{IJ}^{\beta\gamma} U_J^\gamma \ . \tag{22}$$

This quantity is related to the *virial heat flux* $\mathbf{J}_{\text{vir}}$ by multiplying with the atomic velocities $\dot{\mathbf{U}}$,

$$\mathbf{J}_{\text{vir}}^\alpha = \sum_{I,\gamma} \sigma_{\text{vir},I}^{\alpha\gamma} \dot{U}_I^\gamma \ . \tag{23}$$

Literature

- `Knuth2015`: F. Knuth, C. Carbogno, V. Atalla, V. Blum, and M. Scheffler, Comput. Phys. Commun. **190**, 33 (2015).
- `Louwerse2006`: M. J. Louwerse and E. J. Baerends, Chem. Phys. Lett. **421**, 138 (2006).