ETH Zurich
Department of Mechanical and Process Engineering
Statistical Mechanics of Elasticity
Exercise 10 - Summer 2007

Institute for Mechanical Systems
Center of Mechanics
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Useful Definitions

Equations of Motion in Alternate Coordinates

The linearized equations of motion for vibrations of atoms about the equilibrium positions in a lattice are given by

$$m_r \ddot{q}_\alpha \begin{pmatrix} A \\ r \end{pmatrix} = - \sum_{\beta,B,n} K_\alpha \begin{pmatrix} A \\ r \end{pmatrix}_\beta \begin{pmatrix} B \\ n \end{pmatrix} q_\beta \begin{pmatrix} B \\ n \end{pmatrix} \tag{1}$$

where $\alpha, \beta = \{1, 2, 3\}$ denote the coordinate directions, $A, B = \{1, ..., N_C\}$ the unit cell numbers out of the $N_C = N^3$ unit cells in the interior region/supercell and $r, n = \{1, ..., s\}$ the atom numbers inside the unit cell with s atoms each in total. The total degrees of freedom of the system are thus $n = 3sN_C$.

$K_\alpha \begin{pmatrix} A \\ r \end{pmatrix}_\beta \begin{pmatrix} B \\ n \end{pmatrix}$ is the stiffness matrix defined by

$$K_\alpha \begin{pmatrix} A \\ r \end{pmatrix}_\beta \begin{pmatrix} B \\ n \end{pmatrix} = \left. \frac{\partial^2 U(\mathbf{F}, \mathbf{q})}{\partial q_\alpha \begin{pmatrix} A \\ r \end{pmatrix} \partial q_\beta \begin{pmatrix} B \\ n \end{pmatrix}} \right|_{\mathbf{q}=\mathbf{0}}, \tag{2}$$

where $U(\mathbf{F}, \mathbf{q})$ is the potential energy of the (stretched) system with shifts determined by its minimization.

Complex Ansatz

To solve the equations of motion (1) taking advantage of the structure of the problem, we assume harmonic vibrations of the atoms and chose a complex wave ansatz of the form

$$q_\alpha \begin{pmatrix} A \\ r \end{pmatrix} = \mathrm{Re}\left[\hat{q}_{\alpha r}(\omega, \mathbf{k}) e^{i(\mathbf{R}_A \cdot \mathbf{k} - \omega t)} \right], \tag{3}$$

where ω is the eigenfrequency, $\mathbf{k}$ the wave vector and $\mathbf{R}_A$ the vector pointing to the local origin of unit cell A.

Unitcell and Supercell Periodicity

Unit cell periodicity and the resulting indistinguishability of lattice sites allows us to set

$$A = 1 \qquad \text{and} \qquad \mathbf{R}_A = \mathbf{0} \tag{4}$$

without loss of generality.

Super cell periodicity can be expressed by

$$q_\alpha \begin{pmatrix} N+1 \\ k \end{pmatrix} = q_\alpha \begin{pmatrix} 1 \\ k \end{pmatrix} \tag{5}$$

in each periodicity direction and yields admissible values of the wave vector $\mathbf{k}$:

$$\mathbf{k} = \left(\frac{2\pi a}{N} n_1, \frac{2\pi b}{N} n_2, \frac{2\pi c}{N} n_3 \right)^T, \tag{6}$$

where a, b, c are three of the six lattice parameters, N is the number of unit cells in each direction of the super cell and $n_1, n_2, n_3 = \{-(N-1)/2, .., 0, .., (N-1)/2\}$ (this produces $\omega(\mathbf{k})$ in the familiar Brillouin).

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Resulting Generalized Eigenvalue Problem

The resulting generalized eigenvalue problem is

$$-\omega^2 \underbrace{m_r I_{(\alpha r)(\beta n)}}_{M_{(\alpha r)(\beta n)}} \hat{q}_{\beta n} = -\sum_{\beta,n} \underbrace{\left[\sum_B K_\alpha \begin{pmatrix} 1 \\ r \end{pmatrix}_\beta \begin{pmatrix} B \\ n \end{pmatrix} e^{i\mathbf{R}_B \cdot \mathbf{k}}\right]}_{D_{(\alpha r)(\beta n)}} \hat{q}_{\beta n}, \tag{7}$$

where $M_{(\alpha r)(\beta n)}$ is the mass matrix and $D_{(\alpha r)(\beta n)}$ is the so called dynamical matrix.

For a given wave vector $\mathbf{k}$ one can thus determine the corresponding $3s$ eigenfrequencies from

$$\det\left(\mathbf{M}\omega^2 - \mathbf{D}(\mathbf{k})\right) = 0. \tag{8}$$

Dynamical Matrix for Pair Potentials

The dynamical matrix has dimensions $3s \times 3s$ and can be written in (non-overlapping) block form as

$$\mathbf{D} = \begin{bmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \cdots & \mathbf{D}_{1s} \\ \mathbf{D}_{21} & \mathbf{D}_{22} & & \\ \vdots & & \ddots & \\ \mathbf{D}_{s1} & & & \mathbf{D}_{ss} \end{bmatrix}, \tag{9}$$

where s is the number of atoms per unit cell.

If the interactions between atoms are governed by pair potentials $\phi(r)$, each individual block entry is obtained from

$$\mathbf{D}_{mp} = \sum_{D=1}^{N_C=N^3} \left\{ e^{i\mathbf{R}_D\cdot\mathbf{k}} \left[\phi'\left(\| \underbrace{\mathbf{x}_m^1 - \mathbf{x}_p^D}_{\mathbf{v}} \| \right) \left(\frac{\mathbf{v}\otimes\mathbf{v}}{\|\mathbf{v}\|^3} - \frac{\mathbf{I}}{\|\mathbf{v}\|} \right) - \phi''(\|\mathbf{v}\|) \frac{\mathbf{v}\otimes\mathbf{v}}{\|\mathbf{v}\|^2} \right] \right.$$
$$\left. + \textstyle\sum_{n=1}^{s} \delta_{mp} \left[\phi'\left(\| \underbrace{\mathbf{x}_m^1 - \mathbf{x}_n^D}_{\mathbf{w}} \| \right) \left(\frac{\mathbf{I}}{\|\mathbf{w}\|} - \frac{\mathbf{w}\otimes\mathbf{w}}{\|\mathbf{w}\|^3} \right) + \phi''(\|\mathbf{w}\|) \frac{\mathbf{w}\otimes\mathbf{w}}{\|\mathbf{w}\|^2} \right] \right\}, \tag{10}$$

where $\mathbf{x}_a^A$ is the position vector of atom a in unit cell A without thermal vibrations.

Phonon Programm Headers

- `[energy,force,stiffness] = morse(V0,a0,r0,r)`
  Returns the function value (*energy*), the first (*force*) and second derivative (*stiffness*) of the Morse potential with parameters *V0*, *a0*, *r0* at function value *r*.
- `[a,b,c,alpha,beta,gamma] = get_cell_3D(a1,a2,a3)`
  Calculates the six lattice parameters from the three (column) lattice vectors.
- `[a1,a2,a3] = get_lattice_vec_3D(a,b,c,alpha,beta,gamma)`
  Inverse of the previous function.

- `out_basis_3D(bv)`

  Prints basis vectors that are stored as columns of a $3 \times s$ matrix *bv*, where s is the number of basis vectors (and thus the number of atoms per unit cell).

- `out_cell_3D(a,b,c,alpha,beta,gamma)`

  Prints lattice parameters.

- `out_lattice_3D(a1,a2,a3)`

  Prints lattice vectors.

- `plot_lattice_3D(a1,a2,a3,bv,m,name)`

  Plots the lattice with (column) lattice vectors *a1*, *a2* and *a3* and the $3 \times s$ matrix *bv* formed by the column basis vectors where the $1 \times s$ mass vector *m* is used to scale the atom representations relative to each other. The string *name* contains the name to be displayed as header of the figure. To plot deformed lattices, pass in *Fa1*, *Fa2* and *Fa3* and the corresponding energy-minimizing *bv*.

- `[energy]=lattice_energy_3D(a1,a2,a3,bv,F,V0,a0,r0,N)`

  Returns the *energy* per unit cell of a lattice described by lattice vectors *a1*, *a2* and *a3* and the $3 \times s$ matrix *bv* formed by the column basis vectors, stretched by deformation gradient *F*, with interactions described by the $s \times s$ matrices *V0*, *r0* and *a0* using a parallelepipetic super cell with *N* unit cells in each direction. To calculate the energy of the reference configuration, simply chose $\mathbf{F} = \mathbf{I}$.

- `[a1,a2,a3,bv] = equil_lattice_3D(a1,a2,a3,bv,V0,a0,r0,N)`

  Returns (column) lattice vectors *a1*, *a2* and *a3* and the $3 \times s$ matrix *bv* formed by the column basis vectors of the closest local minimum energy configuration to the supplied guess given the $s \times s$ interaction matrices *V0*, *r0* and *a0* using a parallelepipetic super cell with *N* unit cells in each direction.

- `[bv] = affine_equil_lattice_3D(a1,a2,a3,bv,F,V0,a0,r0,N)`

  Returns the $3 \times s$ matrix *bv* formed by the column basis vectors minimized for a deformation of a reference lattice with lattice vectors *a1*, *a2* and *a3* with deformation gradient F whose interactions are described by interaction matrices *V0*, *r0* and *a0* and for which a parallelepipetic super cell with *N* unit cells in each direction is used.

- **INCOMPLETE:**

  `[Dmat,M]=dynam_3D(a1,a2,a3,bv,F,V0,a0,r0,m,k,N)`

  Returns the $3s \times 3s$ dynamic matrix *Dmat* for a given wave vector *k* and the $3s \times 3s$ mass matrix *M* for a lattice desribed by (column, reference) lattice vectors *a1*, *a2* and *a3* and the $3 \times s$ matrix *bv* formed by the (minimized!) column basis vectors, stretched by the corresponding deformation gradient *F*, interaction matrices *V0*, *r0* and *a0*, the $1 \times s$ mass vector *m* and using a parallelepipetic super cell with *N* unit cells in each direction.

- **INCOMPLETE:**

  `phonon_2lattice_3D`

  Main file giving the structure of the problem.

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Homework 1 - Dispersion in a 3D Two-Lattice

Given is a two-lattice in a three-dimensional setting with masses $m_1 = 44\text{amu}$ and $m_2 = 33\text{amu}$. Interactions are governed by Morse potentials, where the following 2×2 matrices contain all necessary interaction parameters (i.e. $[r_o]_{ij}$ is the r_o parameter for the interaction between an i and a j atom):

$$[r_o]_{ij} = \begin{pmatrix} 3.2 & 2.7 \\ 2.7 & 3.2 \end{pmatrix} \text{Å}, \qquad [V_o]_{ij} = \begin{pmatrix} 3.0 & 3.0 \\ 3.0 & 3.0 \end{pmatrix} eV, \qquad [a_o]_{ij} = \begin{pmatrix} 5.0 & 5.0 \\ 5.0 & 5.0 \end{pmatrix}. \tag{11}$$

The lattice is parametrized by six parameters (three lengths a, b, c and three angles α, β, γ, where α is the angle between $\mathbf{a}_2$ and $\mathbf{a}_3$, β is the angle between $\mathbf{a}_1$ and $\mathbf{a}_3$ and γ is the angle between $\mathbf{a}_1$ and $\mathbf{a}_2$,). The three lattice vectors relate to them by

$$\mathbf{a}_1 = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix}, \qquad \mathbf{a}_2 = \begin{pmatrix} b\cos(\gamma) \\ b\sin(\gamma) \\ 0 \end{pmatrix} \tag{12}$$

and $\mathbf{a}_3$ can be obtained from

$$\mathbf{a}_1 \cdot \mathbf{a}_3 = \cos(\beta)ac, \qquad \mathbf{a}_2 \cdot \mathbf{a}_3 = \cos(\alpha)bc, \qquad \mathbf{a}_3 \cdot \mathbf{a}_3 = c^2. \tag{13}$$

The shifts of atoms 1 and 2 in each unit cell with respect to the lattice is described using vectors b_i^1 and b_i^2, where

$$\mathbf{p}_j = b_i^j \mathbf{F} \mathbf{a}_i. \tag{14}$$

Without loss of generality, we chose $b_i^1 = 0$ and keep it fixed during all calculations.

To obtain the dispersion relation in the direction of all three lattice vectors, carry out the following steps:

a) Equilibrate the (unstretched, i.e. $\mathbf{F} = \mathbf{I}$) lattice by minimizing its ($0K$) potential energy with respect to the lattice parameters and the shift using the startig guess

$$\begin{array}{lll} a = 3.2\text{Å} & b = 3.2\text{Å} & c = 3.2\text{Å} \\ \alpha = \pi/2 & \beta = \pi/2 & \gamma = \pi/2 \\ b_1^2 = 0.5 & b_2^2 = 0.5 & b_3^2 = 0.5 \end{array} \quad . \tag{15}$$

   Plot the resulting structure, print its lattice and basis vectors and calculate its potential energy.

b) Set up a function that calculates the dynamic matrix $\mathbf{D}$ and the corresponding mass matrix $\mathbf{M}$ using $N = 11$ (i.e. five neighbors in each direction).

c) Determine all $3N$ allowable wave vectors $\mathbf{k}$ that are parallel to the lattice vectors $\mathbf{a}_i$. For each direction, calculate and plot the corresponding $6N$ eigenfrequencies $\omega(\mathbf{k})$ in dispersion plots.

d) Now subject the lattice to a homogeneous deformation described by

$$\mathbf{F} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0.95 & 0 \\ 0 & 0 & 1.05 \end{pmatrix} \tag{16}$$

   and calculate the corresponding equilibrium lattice structure by minimizing with respect to the basis vector b_i^2. Plot the resulting configuration, print the corresponding lattice and basis vectors and calculate its potential energy.

e) Now modify your function such that it calculates the dynamic matrix $\mathbf{D}$ (the mass matrix $\mathbf{M}$ remains unchanged) of the *stretched* lattice using $N = 11$ (i.e. five neighbors in each direction).

f) Determine all $3N$ allowable wave vectors $\mathbf{k}$ that are parallel to the lattice vectors $\mathbf{a}_i$. For each direction, calculate and plot the corresponding $6N$ eigenfrequencies $\omega(\mathbf{k})$ in dispersion plots.

To compute the desired quantities you may use any of the functions in *hw10.zip*, of which all but *phonon-2lattice-3D.m* and *dynam-3D.m* are complete. The descriptions of the headers and the input/output format can be found above.

Questions/Comments/Suggestions? Felix Hildebrand - CLA H23.1 - 044/632-7755 - felixhi@ethz.ch