Manual 07 for MD++

MD++ Tour with Sample Scripts

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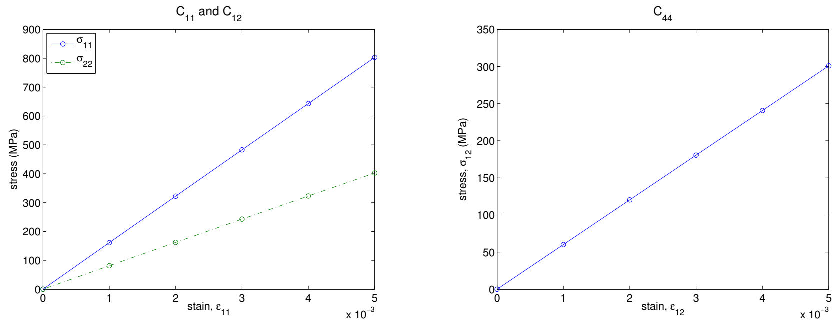
1 Calculating Elastic Constants

The cubic crystal has three independent elastic constants, C_{11}, C_{12}, and C_{44}. To calculate the elastic constants is a simple way of validating a potential model, and as a byproduct, we obtain the equlibrium lattice constant. There are two methods to obtain elastic constants: one is to monitor Virial stress and the other is to monitor strain energy as a function of the applied strain. Conceptually, the two approaches are equivalent. If stress is a linear function of strain, then the strain energy is a quadratic function of strain. In this manual, both methods will be explained for the case of bulk silicon.

1.1 Using Virial stress

If Virial stress is available, the task of computing elastic constants is relatively easy. In crystals with cubic symmetry, there are three independent elastic constants: C_{11}, C_{12}, and C_{44}. C_{11} is the proportional constant between the stress σ_{11} and the strain ε_{11}, and C_{12} is the proportional constant between the stress σ_{22} and the strain ε_{11}. We can measure C_{11} and C_{12} by exerting strain ε_{11} and monitor stresses σ_{11} and σ_{22} as in the following MD++ script.

```
# -*-shell-script-*-
# Calculate Elastic Constants of Si
# setnolog
setoverwrite
dirname = ~/Codes/MD++/runs/si_elastconst
#------------------------------------------------
#Create Perfect Lattice Configuration
crystalstructure = diamond-cubic
latticeconst = 5.430953e+00 #(A) for Si
latticesize = [     1    0    0    3
                    0    1    0    3
                    0    0    1    3 ]
makecrystal
```



(a) σ_{11} and σ_{22} vs. ε_{11}

(b) σ_{12} vs. ε_{12}

Figure 1: The elastic constants C_{11}, C_{12}, and C_{44} are determined by the linear fitting between (a) σ_{11} and ε_{11}, σ_{22} and ε_{11}, and (b) σ_{12} and ε_{12}. According to Stillinger-Weber potential, Si has C_{11} =160.6, C_{12} =80.5, and C_{44} =60.2 (GPa).

```
#------------------------------------------------------------
#Conjugate-Gradient relaxation
conj_ftol = 1e-4 conj_itmax = 1000 conj_fevalmax = 1000
conj_fixbox = 1
eval relax eval finalcnfile = relaxed.cn writecn
#------------------------------------------------------------
conj_fixbox = 1 #conj_monitor = 1 conj_summary = 1
input = [ 1 1 0.001 ] shiftbox relax eval
input = [ 1 1 9.99000999000999e-04 ] shiftbox  relax eval
input = [ 1 1 9.98003992015968e-04 ] shiftbox  relax eval
input = [ 1 1 9.97008973080758e-04 ] shiftbox  relax eval
input = [ 1 1 9.96015936254980e-04 ] shiftbox  relax eval
quit
```

The above script first generates a 3 × 3 × 3 perfect diamond cubic structure of Si. It then applies tensile strain in increments of 0.1% along [100] direction by *shiftbox*, and calculate the corresponding Virial stress at each strained state by *eval*. From the log file, the stress components σ_{11} and σ_{22} can be obtained and plotted as a function of the applied strain ε_{11}. Fig. 1(a) plots the result from running the script with Stillinger-Weber(SW) potential.

```
$ bin/sw_gpp scripts/si_elastic.script
```

The slopes of these lines give C_{11} =160.6 (GPa) and C_{12} =80.5 (GPa). To compute C_{44}, we can simply insert the following lines before *quit* in the above script.

```
incnfile = relaxed.cn readcn
input = [ 1 2 0.001 ] shiftbox relax eval
input = [ 1 2 0.001 ] shiftbox relax eval
input = [ 1 2 0.001 ] shiftbox relax eval
input = [ 1 2 0.001 ] shiftbox relax eval
input = [ 1 2 0.001 ] shiftbox relax eval
```

These commands shear the crystal in increments of ε_{12} =0.1%. Again, from the log file, the stress component σ_{12} can be obtained and plotted as a function of the applied strain. The result from SW potential is plotted in Fig. 1(b).), from which we obtain C_{44}=60.2(GPa). The values for C_{11}, C_{12}, and C_{44} obtained here are consistent with the original paper.[1]

1.2 Using the potential energy

Sometimes, the simulation code does not implement the Virial stress calculation. In *ab initio* simulations, the Virial stress is usually not very accurate. In this case, we can compute the elastic constants by monitoring the potential energy of the system. Because the strain energy density W is

$$W = \frac{1}{2}\sigma_{ij}\varepsilon_{ij} = \frac{1}{2}\varepsilon_{ij}C_{ijkl}\varepsilon_{kl}, \tag{1}$$

we have

$$\sigma_{ij} = \frac{\partial W}{\partial \varepsilon_{ij}}. \tag{2}$$

If the only nonzero strain is ε_{11}, then $W = C_{11}\varepsilon_{11}^2/2$. We can determine C_{11} by fitting $W(\varepsilon_{11})$ to a parabola as shown in Fig.2(a). The elastic constnat C_{44} can be determined in a similar way as shown in Fig.2(b). the elastic constants obtained in this way are C_{11}=160.5(GPa) and C_{44} =60.2(GPa), which are almost the same as the results obtained from Virial stress. The potential energy in the plot can be found in the log file generated by the same script file as in the previous subsection.

The elastic constant C_{12} is easily determined by the elastic relation

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \tag{3}$$

where B is the bulk modulus, which we have already calculated in the manual 03. Since the bulk modulus of silicon is 108.3(GPa) with SW potential, the elastic constant C_{12} is

$$C_{12} = \frac{1}{2}(3B - C_{11}) = 82.2\,(\text{GPa}).$$

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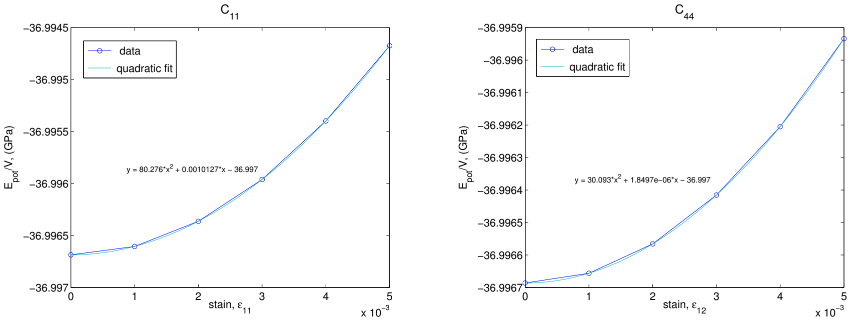
[1] According to the calculation by Balamane *et al*[1], the elastic constants C_{11}, C_{12}, and C_{44} are 161.6, 81.6, and 60.3(GPa), respectively. All our values are slightly lower than theirs, which means our strain regime(0 to 0.5%) may include part of plastic region. To avoid it, we can reduce the strain regime.



(a) $E_{pot}^{(11)}/V$ vs. ε_{11}

(b) $E_{pot}^{(12)}/V$ vs. ε_{12}

Figure 2: The elastic constants C_{11} and C_{44} can be determined by the quadratic fitting between (a) the strain ε_{11} and the energy density $E_{pot}^{(11)}$, and (b) the strain ε_{12} and the energy density $E_{pot}^{(12)}$. The superscrits in the E designate which strain component results in the strain energy change.

1.3 Finding shear elastic constant for a non-tilting simulation cell

In the previous subsections, we compute C_{44} by shearing the simulation cell. The simulation cell was rectangular before the shear, but becomes tilted after the shear. However, sometimes a simulation code only permits the use of rectangular cells. How can we find shear elastic constant C_{44} in this case?

Notice that C_{11} and C_{12} can be always obtained with rectangular cells, when the repeat vectors of the cell are aligned with the cubic axes of the crystal. With known C_{11} and C_{12}, we can determine C_{44} using the orthogonal transformation rule for the 4th order tensor. When the repeat vectors are not aligned with the cubic axes, we should be able to compute linear combination of C_{11}, C_{12}, and C_{44} while keeping the simulation cell rectangular. Remember that C_{11}, C_{12}, and C_{44} are components of a 4th order tensor which transforms as

$$C'_{ijkl} = T_{mi}T_{nj}T_{sk}T_{tl}C_{mnst} \tag{4}$$

where $T_{ij} = \mathbf{e}_i \cdot \mathbf{e}'_j$ is relation between two coordinate systems $\{\mathbf{e}_i\}$ and $\{\mathbf{e}'_j\}$. For example, if we have one coordinate system $\mathbf{e}_1 = [1\,0\,0]$, $\mathbf{e}_2 = [0\,1\,0]$, and $\mathbf{e}_3 = [0\,0\,1]$ and the new coordinate system $\mathbf{e}'_1 = [1\,1\,0]/\sqrt{2}$, $\mathbf{e}'_2 = [-1\,1\,0]/\sqrt{2}$, and $\mathbf{e}'_3 = [0\,0\,1]$, then the matrix $[T]$ is

$$[T] = \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

In particular,

$$
\begin{aligned}
C'_{1111} &= T_{m1}T_{n1}T_{s1}T_{t1}C_{mnst} \\
&= \sum_{i=1}^{3} T_{i1}T_{i1}T_{i1}T_{i1}C_{11} \\
&\quad +2(T_{11}T_{11}T_{21}T_{21}+T_{11}T_{11}T_{31}T_{31}+T_{21}T_{21}T_{31}T_{31})C_{12} \\
&\quad +4(T_{21}T_{31}T_{21}T_{31}+T_{11}T_{31}T_{11}T_{31}+T_{11}T_{21}T_{11}T_{21})C_{44} \qquad (5)
\end{aligned}
$$

Suppose we create a perfect crystal such that x, y, and z axes of the simulation cell are aligned with $\mathbf{e}'_1$, $\mathbf{e}'_2$, and $\mathbf{e}'_3$. Then by straining the crystal along x axis, we can obtain C'_{1111}=180.4 (GPa) using the SW potential. Given C_{11}=160.6, C_{12}=80.5, the matlab script below gives C_{44}=59.9(GPa) for silicon.

```
% With given C11, C12, and C1111', find C44 in cubic materials.
% C11, C12, and C44 are the elastic constants in Cartesian
% coordinate system.
% C1111' is the elastic constant in the new coordinate.

syms C11 C12 C44

C11n = 160.6; C12n = 80.5; C44n = 60.2;
C1111prime = 180.40;

xyz0 = [ 1 0 0; % original coordinate
         0 1 0;
         0 0 1];

xyz1 = [ 1  1 0; % new coordinate
         -1 1 0;
         0  0 1];

T = zeros(3,3);
for i=1:3
    for j=1:3
        T(i,j) = dot(xyz0(i,:),xyz1(j,:)/norm(xyz1(j,:)));
    end
end

p=1; q=1; r=1; s=1;
A = T(1,p)*T(1,q)*T(1,r)*T(1,s) + T(2,p)*T(2,q)*T(2,r)*T(2,s) + ...
                                  T(3,p)*T(3,q)*T(3,r)*T(3,s);
B = T(1,p)*T(1,q)*T(2,r)*T(2,s) + T(1,p)*T(1,q)*T(3,r)*T(3,s) + ...
                                  T(2,p)*T(2,q)*T(3,r)*T(3,s);
C = T(2,p)*T(3,q)*T(2,r)*T(3,s) + T(1,p)*T(3,q)*T(1,r)*T(3,s) + ...
                                  T(1,p)*T(2,q)*T(1,r)*T(2,s);
```

```
CC = A*C11 + 2*B*C12 + 4*C*C44;
cc = subs(CC, C11, C11n); cc = subs(cc, C12, C12n);
disp(sprintf('C44 = %f',double(solve(cc-C1111prime,C44))))
```

References

[1] H. Balamane, T. Halicioglu, and W. A. Tiler, PRB **46** 2250-2279