

Atomistic Simulation

1. Introduction

Atomistic simulations cover the other end of the length and time scale compared to the continuum (finite element) approach. They are used to calculate the behaviour of every single atom (or molecule), to investigate small scale problems like protein folding, crystal structures of complex alloys or crack tip propagation. This practical covers some basic atomistic applications, namely the computation of lattice and elastic constants for simple crystals at 0 K, and the simulation of bond breaking of a carbon nano-tube. The focus lies rather on the application and possible trap falls, than the numerics behind the scene. Nonetheless, an understanding of the numerics definitely helps to interpret the obtained results.

2. Basic ingredients of an atomistic simulation

For an atomistic simulation one has usually to specify three main components for the simulation. These are

1. The initial configuration for the atom placement, boundary conditions (BC) and the quantities that should be conserved (see 2.1).
2. A potential from which the forces are derived (see 2.2).
3. The numerical solver for the system, i.e. the integration rule for dynamic systems or the minimizer for static systems (see 2.3).

We discuss in this practical all these points briefly, but focus mainly on the choice and especially the verification of a proper potential.

2.1. Defining the system and boundary conditions

The initial configuration or placement of the atoms define the problem that should be solved, and is more or less straight forward. It must represent the system with its structure and the boundary conditions. The boundary conditions can be divided into

free BC: No restriction to movement or forces.

force BC: Prescription of forces at the atoms.

fixed BC: Restriction of some (or all) degrees of freedom (e.g. prescription of the movement in x-direction).

periodic BC: Atoms on the boundary interact with atoms from the other side of the boundary via periodic repetition (cf. Fig. 1).

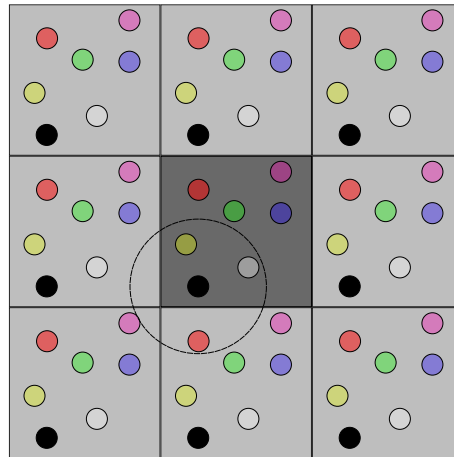


Figure 1: Sketch of periodic boundary conditions of a 2-D box (dark gray) with its periodic images (bright grey) and a possible cut-off radius (dashed circle), which defines the interaction range of the (black) atoms.

For the full description of the system we also have to define the quantities which should be preserved. This is done by the definition of the **ensemble**.

Newton's second law conserves the total energy (E), the number of atoms (N) and the volume (V) of the system. This ensemble is consequently called NVE or *microcanonical* ensemble. It is not able to preserve the kinetic energy/temperature or pressure.

By coupling the system to a heat bath the temperature can be held constant. This so-called *canonical* ensemble keeps the number of atoms (N), the volume of the system (V) and the temperature (T) constant. The most popular thermostat methods are *Nosé-Hoover*, *Langevin* and *Berendsen*.

These two ensembles are the most popular ones. But there exist other approaches, e.g. for constant pressure (P) with constant temperature and number of atoms (NPT ensemble) or constant enthalpy (H), pressure and number of atoms (NPH ensemble).

2.2. Defining the potential

The choice of a potential is one of the most critical parts of an atomistic simulation. This is especially true if an empirical or semi-empirical potential is chosen. It is important that the potential is suitable for the problem. 'Suitable' means that we have to decide on,

Accuracy: is the potential accurate enough for the specific problem?

Transferability: is the potential transferable to the specific problem?

Computational Speed: is the calculation fast enough for the specific problem?

Usually there is no ultimate answer to the problem, so that depending on the system we have to decide what is most important. For example small problems like the bonding energy of a molecule require a more accurate potential than big problems. On the other hand, bigger simulations like the propagation of a crack tip requires a potential, which can be evaluated cheaply in terms of computational costs.

Task 2.1 (Literature research): In the following tasks you should do some scientific research in papers and books. As a starting point for your research check out ScienceDirect^a, Scirus^b, GoogleScholar^c and of course the university library. The documentation and the source code of the program you use also often provide useful informations.

1. Briefly outline the main differences between the Effective-medium theory (EMT), which is a semi-empirical potential like the Embedded Atom Method (EAM), and a pair-potential (e.g. Lennard-Jones).
2. Why are pair potential not suitable for the simulation of metals (i.e. copper)? Do they have any advantage over semi-empirical potentials?
3. Compare the potentials with respect to parameter identification and parameter fitting.
4. Because we investigate only a simple copper lattice, there is no need to fit the parameters for the potential on our own. This was done already by several researchers. Figure out recommended parameters for the potentials for copper and how you can use them in ASE.

^awww.sciencedirect.com (from inside the FAU network or with vpn)

^bwww.scirus.com

^c<http://scholar.google.com>

2.3. Defining the numerical solving scheme

The main goal in an atomistic simulation is to evaluate the positions of the particles by considering all interacting forces between them. This is done by solving Newton's second law, a differential equation, by time integration. Simple integration schemes like explicit or implicit euler are not stable or do not conserve the required quantities. The most common time integration scheme in molecular dynamics is the so called velocity-verlet integration.

In *molecular static simulation* we do not have a time dependent behaviour. Instead we are comparing different configurations to find for example a minimum energy state. In general the problem, that defines the energy landscape is non-linear with multiple local minima. To minimize such a problem a non-linear optimizer is needed, which is usually a quasi-newton type solver. The most popular is the BFGS solver, which can be used with or without line-search optimization.

3. Application of a atomistic code for determination of elastic constants and verification of potentials

As a possible real life application we assume that we want to do a project with an atomistic simulation with a copper lattice. We are familiar with the atomistic program ASE, and read in the literature research (cf. Task 2.1) about the promising potential EMT. In the paper where it was presented it is suited for copper and already fitted to it*. The authors provide a fast implementation for their potential in ASAP[†], which is fully compatible with ASE.

3.1. Verification of a chosen potential

Before blindly using the potential the first step in a atomistic simulation is to verify if it is adequate for the problem. In order to do this, we have to compare simulations with experimental data. To minimize errors in the simulation it is recommended to keep the simulation as simple as possible for the verification. Hence we do a molecular statics simulation, in which we only look at different (potential) energies of the crystal lattice.

3.2. Determination of crystal structure and lattice constants

The most obvious step is to look at the lattice structure itself. The potential should give the minimum potential energy for the correct lattice. Therefore we perform different computations to find the crystal structure of copper with the lowest potential energy. We assume that we know that copper is in a cubic configuration and has the atom radius $a = 128$ pm.

*K. W. Jacobsen, P. Stoltze and J. K. Norskov: "A semi-empirical effective medium theory for metals and alloys", Surf. Sci. 366, 394 (1996)

[†]<https://wiki.fysik.dtu.dk/asap/asap>

Task 3.1: Sketch the crystal structure of face-centered cubic and body-centered cubic crystals and estimate a lattice constant l for a given atom radius a . Consider the closest packed plane in the crystal to calculate the lattice constant. For example in the simple cubic lattice, the closest packed plane coincides with the cube plane, and thus the lattice constant is twice the atom radius (cf. Fig. 2).

Task 3.2: Calculate the minimal energies W at 0 K in a Molecular Statics simulation for the three cubic crystal structures. Take your estimated lattice constants as a starting parameter and vary it to find the structure and the lattice constant l_0 with the smallest potential energy.

Plot the results in an energy-lattice constant plot, and fit the data to a second order polynomial ($W = p_0 + p_1 l + p_2 l^2$) with the coefficients p_0, p_1, p_2 . Solve the polynomial for the energy minimum, $\min\{W\} = W_0$, and give the results (l, W_0) for the three lattices. Note that the **units in ASE** are eV for the energy and Å for the length.

Compare the lattice constant of the crystal with the smallest energy with literature values.

Hint For setting up the crystal structure check the 'ase.lattice' module.

The potentials can be found in the 'ase.calculators' module or for faster computations in the ASAP3 library ^a.

ASE already provides a Equation of State module with which you can compare your results.

^a<https://wiki.fysik.dtu.dk/asap>

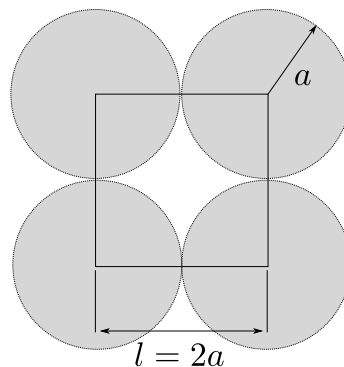


Figure 2: Sketch of the closest packed plane in a simple cubic lattice, with atoms of radius a and lattice constant l .

3.3. Computation of elastic constants

Elastic constants of crystal lattices are an important property of the material to describe the mechanical behaviour. They are also often measured experimentally, so that literature values for standard materials are available. Thus, to further verify our potential, we compute the elastic constant of copper in fcc configuration at 0 K. The elastic constants are the components of the stiffness tensor \mathbb{C} which linearly maps the second order elastic strain tensor $\boldsymbol{\varepsilon}$ to the second order elastic stress tensor $\boldsymbol{\sigma}$:

$$\boldsymbol{\sigma} = \mathbb{C} : \boldsymbol{\varepsilon}. \quad (1)$$

We assume that a strain energy density W^e exists, which acts as a potential for the stresses with respect to the strains

$$\boldsymbol{\sigma} = \frac{\partial W^e}{\partial \boldsymbol{\varepsilon}}. \quad (2)$$

Because of the linear mapping between stresses and strains (1) the strain energy density is quadratic in $\boldsymbol{\varepsilon}$

$$W^e = \frac{1}{2} \boldsymbol{\varepsilon} : \mathbb{C} : \boldsymbol{\varepsilon}. \quad (3)$$

Therefore the stiffness tensor is the second derivative of the strain energy density with respect to $\boldsymbol{\varepsilon}$,

$$\mathbb{C} = \frac{\partial^2 W^e}{\partial \boldsymbol{\varepsilon}^2}. \quad (4)$$

The elastic constants can then easily be computed through the energies and the prescribed deformation of the lattice. For example a deformation with a uni-axial strain distribution in Voigt notation (cf. Appendix B)

$$\boldsymbol{\varepsilon}^v = \begin{bmatrix} \bar{\varepsilon}_1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (5)$$

leads to the strain energy density

$$W^e = \frac{1}{2} \bar{\varepsilon}_1 C_{11} \bar{\varepsilon}_1. \quad (6)$$

By reformulation of (6) we get C_{11} as

$$C_{11} = \frac{2W^e}{\bar{\varepsilon}_1 \cdot \bar{\varepsilon}_1}. \quad (7)$$

Task 3.3: Write down the equations for the missing elastic constants and give a possible strain distribution for the calculation. Use already computed constants (i.e. C_{11}) if needed. Assume at first an isotropic material with the components of the elastic stiffness tensor in Voigt notation (cf. Appendix B)

$$C_{\text{iso}}^{\text{v}} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & (C_{11} - C_{12})/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & (C_{11} - C_{12})/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & (C_{11} - C_{12})/2 \end{bmatrix}. \quad (8)$$

Task 3.4: In the same manner write down the equations and the strain distribution for a material with cubic symmetry

$$C_{\text{ortho}}^{\text{v}} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}.$$

The evaluation of the elastic constants is similar to computation of the lattice constants. Instead of deforming the whole lattice by choosing different lattice constants, we prescribe specific deformations (e.g. in only one direction) to calculate the energies. As we saw in Tasks 3.1 and 3.2 we can derive the components of the stiffness tensor from the energies by deforming the lattice in a specific way.

In ASE the crystal structure is specified by 3 unit cell row-vectors in a 3×3 array. To deform the structure, we deform the cell by using matrix multiplication with the strain tensor. Note that we want to deform the optimal cell, so that we need to add the identity matrix to the strain. As an example the deformed cell induced by a strain in 11-direction is calculated by

$$\underbrace{\begin{bmatrix} l_0 & 0 & 0 \\ 0 & l_0 & 0 \\ 0 & 0 & l_0 \end{bmatrix}}_{\text{optimal cell}} \left(\underbrace{\begin{bmatrix} \bar{\varepsilon}_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}}_{\text{strain tensor}} + \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{\text{identity matrix}} \right) = \underbrace{\begin{bmatrix} l_0(1 + \bar{\varepsilon}_1) & 0 & 0 \\ 0 & l_0 & 0 \\ 0 & 0 & l_0 \end{bmatrix}}_{\text{deformed cell}}. \quad (9)$$

In the same way we can compute the deformations in other direction to evaluate all elastic constants.

To get a more precise result we do not take only one value for the deformation, instead we vary it starting at the relaxed minimum energy state, similar to the computation of the lattice constants (cf. Task 2.2). As we saw in (4) the stiffness is the second derivative of the strain energy density with respect to the strains. By generating a dataset with energies and strains of the same deformation direction we obtain energy-strain curves. Good practise is to fit these curves to a third order polynomial $W(\bar{\varepsilon}) = p_0 + p_1\bar{\varepsilon} + p_2\bar{\varepsilon}^2 + p_3\bar{\varepsilon}^3$ and

determine the components of the stiffness tensor at the minimum energy state via the second derivative of the energy

$$\frac{d^2W}{d\bar{\epsilon}^2} = 2p_2 + 6p_3\bar{\epsilon}_{\min}, \quad (10)$$

where $\bar{\epsilon}_{\min}$ is the strain for which the energy W has it's minimum. Each solution of (10) for a specifically deformed cell corresponds to a coefficient (or combination of coefficients) of the stiffness tensor (cf. Task 2.2 and 2.3). Note that the dimensions of the coefficients p_i are in eV/Å³.

Task 3.5: Evaluate the elastic constants of copper in the fcc configuration. Cubic crystal lattices usually have a orthotropic symmetry, so that you can use the deformation states from Task 3.3. Start with your reference cell with the optimal lattice parameter l_0 . For best results let the structure relax before you deform it to make sure that you start at the minimum energy state. With matrix multiplication you can obtain different deformed crystal structures (cf. Eqn. (9)). Now vary the same general structure with different values for the strains (similar to a tension/compression test) around the optimal cell. You should get a dataset of energies and strains, which can be fitted as described with a third order polynomial. Compare the computed results with the literature values for 0 K from Table 1. How big is the error (in percent) for each constant?

Task 3.6: We assumed a quadratic dependency of the energy density with respect to the strains. By looking at the strain energy plots give an approximate of the range around the relaxed state for which this assumption is reasonable.

T	C_{11}	C_{12}	C_{44}
0	1.7620	1.2494	0.8177
50	1.7593	1.2475	0.8149
100	1.7493	1.2437	0.8080
200	1.7192	1.2295	0.7816
300	1.6839	1.2142	0.7539

Table 1: Single-crystal elastic constants in 10¹¹ N/m² of copper at different temperatures in K [‡].

[‡]Overton, W. C. and Gaffney, John: *Temperature Variation of the Elastic Constants of Cubic Elements. I. Copper*; Phys. Rev. 98, 969-977 (1955)

4. Molecular Dynamics simulation of bond breaking of carbon-nanotubes

So far we only investigated properties in a static simulation. Often the behaviour at a non-zero temperature is of interest. Via the Boltzmann constant

$$k_B = 1.3806488 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \quad (11)$$

the temperature T is connected to the average kinetic energy $\langle E_{\text{kin}} \rangle$,

$$\langle E_{\text{kin}} \rangle = \frac{3}{2} k_B T. \quad (12)$$

As a result non-zero temperature means a (average) movement of the atoms and that static energy minimization is not suitable.

As already mentioned in Section 2 we have different possibilities to define the ensemble depending which quantities we want to conserve. Because we are interested in the bond-breaking of a carbon-nanotube (CNT) it is of interest how much energy we put into the system through mechanical work (by stretching the nanotube).

In the first step we are interested in the energy we give the system by mechanical work (deformation) for different nanotubes. A common potential that is used for CNT is the Brenner-Potential.

Task 4.1: Look up in the literature what kind of different CNT do exist. How are they specified and how does their structure look. Can you already give a rough estimation about the mechanical behaviour, by just looking at the structure (w.r.t anisotropy and pattern of the carbon atoms)? For the following tasks choose a (5,5) nanotube (armchair nanotube)^a.

Task 4.2: In a first step we would like to estimate a critical deformation rate, in which the system has not enough time to relax and therefore is unstable. Simulate a stretching of the nanotube along the longitudinal axis in a NVE ensemble. Use the velocity-verlet algorithm for the integration. Start with the relaxed state at 0 K, and incrementally deform the system.

Start with small time step (e.g. 0.1 fs) and investigate the relaxation time. How does the relaxation time changes for larger steps? Estimate the critical deformation rate for which the system becomes unstable.

For a given deformation rate is it better to have many small steps with short relaxations or a few larger steps with longer relaxation times?

Hint You can deform you CNT by scaling the system (and the positions of the atoms) in one direction similar to Task 3.5.

Task 4.3: Calculate the energy increase induced by the deformation. Plot the energy over the deformation. What is happening to the kinetic, potential and total energy at big deformations?

^aYou can use the module 'ase.structure.nanotube' to define the structure.

To investigate the mechanical behaviour at a specific temperature we couple the system to a heat bath. This will dissipate the energy gained through the mechanical work, so that we get a constant temperature.

Task 4.4: Use a NVT ensemble to perform the uniaxial deformation test from the previous tasks at constant Temperature $T = 300$ K. Compare the energies of the two systems. What can you observe w.r.t to the energies?

Task 4.5: Calculate the bond breaking energy of a CNT with the Brenner-Potential at room temperature. How can you obtain a stress-strain curve from your calculations?

Appendix A. Notations

We use the common continuum mechanical notation with bold letters. Small, bold Latin letters like \mathbf{u}, \mathbf{n} denote *vectors* if not stated otherwise. *Second order tensors* are denoted with bold Latin capitals or Greek letters, e.g. $\mathbf{A}, \boldsymbol{\sigma}, \boldsymbol{\varepsilon}$. *Tensors of order four* use the notation $\mathbb{C}, \mathbb{A}, \dots$. *Scalar values* are identified with non-bold letters (e.g. f, a, α). We make use of Einstein's summation convention which states that, when an index variable appears twice in a single term, this implies summation of that term over all values of the index. By use of a orthonormal base in 3D with basis vectors $\mathbf{e}_i (i = 1, 2, 3)$, vectors and tensors can be written as

$$\mathbf{a} = \sum_{i=1}^3 a_i \mathbf{e}_i = a_i \mathbf{e}_i, \quad (13)$$

$$\mathbf{A} = \sum_{i=1}^3 \sum_{j=1}^3 A_{ij} \mathbf{e}_i \otimes \mathbf{e}_j = A_{ij} \mathbf{e}_i \otimes \mathbf{e}_j. \quad (14)$$

For single and double contractions we use a single and a double dot, respectively

$$\mathbf{A} \cdot \mathbf{a} = A_{ij} a_j \mathbf{e}_i, \quad (15)$$

$$\mathbf{A} \cdot \mathbf{B} = A_{ik} B_{kj} \mathbf{e}_i \otimes \mathbf{e}_j, \quad (16)$$

$$\mathbf{A} : \mathbf{B} = A_{ij} B_{ij}, \quad (17)$$

$$\mathbb{C} : \mathbf{A} = C_{ijkl} A_{kl} \mathbf{e}_i \otimes \mathbf{e}_j. \quad (18)$$

Appendix B. Voigt Notation

The Voigt Notation allows to simplify computation and notation by using the symmetries of $\boldsymbol{\sigma}, \boldsymbol{\varepsilon}$ and \mathbb{C} . Instead of writing the components of the symmetric tensor $\boldsymbol{\sigma}$ in matrix notation they are written as a 6-dimensional vector

$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ & \sigma_{22} & \sigma_{23} \\ \text{sym} & & \sigma_{33} \end{bmatrix} \longrightarrow \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{13} \\ \sigma_{12} \end{bmatrix} =: \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \sigma_\alpha^v. \quad (19)$$

In the same manner the components of the strain tensor are given by

$$\varepsilon_{ij} = \begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ & \varepsilon_{22} & \varepsilon_{23} \\ \text{sym} & & \varepsilon_{33} \end{bmatrix} \longrightarrow \begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ 2\varepsilon_{23} \\ 2\varepsilon_{13} \\ 2\varepsilon_{12} \end{bmatrix} =: \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix} = \varepsilon_\alpha^v. \quad (20)$$

Note that the factor 2 in the components of the strain tensor is needed to preserve the invariance of the energy

$$\boldsymbol{\sigma} : \boldsymbol{\varepsilon} = \sigma^v \cdot \varepsilon^v = 2W^e. \quad (21)$$

The reduction of the matrix representation to vector notation for tensors second order also allows a reduction of the components of \mathbb{C} to a 6×6 matrix

$$C_{ijkl} \longrightarrow \begin{bmatrix} C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1113} & C_{1112} \\ C_{2211} & C_{2222} & C_{2233} & C_{2223} & C_{2213} & C_{2212} \\ C_{3311} & C_{3322} & C_{3333} & C_{3323} & C_{3313} & C_{3312} \\ C_{2311} & C_{2322} & C_{2333} & C_{2323} & C_{2313} & C_{2312} \\ C_{1311} & C_{1322} & C_{1333} & C_{1323} & C_{1313} & C_{1312} \\ C_{1211} & C_{1222} & C_{1233} & C_{1223} & C_{1213} & C_{1212} \end{bmatrix} =: \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} = C_{\alpha\beta}^v. \quad (22)$$

The computation in Voigt notation is equivalent to the regular computation. E.g.

$$\begin{aligned}
 \sigma_{23} &= C_{23kl}\varepsilon_{kl} \\
 &= C_{2311}\varepsilon_{11} + C_{2312}\varepsilon_{12} + C_{2313}\varepsilon_{13} + C_{2321}\varepsilon_{21} + C_{2322}\varepsilon_{22} \\
 &\quad + C_{2323}\varepsilon_{23} + C_{2331}\varepsilon_{31} + C_{2332}\varepsilon_{32} + C_{2333}\varepsilon_{33}
 \end{aligned} \quad (23)$$

\Leftrightarrow

$$\begin{aligned}
 \sigma_4^v &= C_{4\alpha}\varepsilon_{\alpha} \\
 &= C_{41}\varepsilon_1 + C_{42}\varepsilon_2 + C_{43}\varepsilon_3 + C_{44}\varepsilon_4 + C_{45}\varepsilon_5 + C_{46}\varepsilon_6
 \end{aligned} \quad (24)$$