

MASTER THESIS

Theoretical Methods for Determining Local Stress and Elastic Constants in Different Statistical Ensembles

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Declaration of Authorship

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- Where I have consulted the published work of others, this is always clearly attributed.
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Abstract

In this work, we review three methods for determining elastic constants of a system from equilibrium fluctuations, where only one of them allows the computation of elastic properties on the local scale. We combine this method with a formalism that relates fluctuations in different statistical ensembles, to derive a novel fluctuation formula, which is applicable in the isothermal-isobaric ensemble. In the first part of this thesis, we introduce the basic concepts in the theory of elasticity, including stress and strain tensors, and a generalization of Hooke's law, valid for arbitrary initial stress, that describes the linear response of a system to deformations by a set of elastic constants. In the main part, we derive three methods for the determination these elastic constants in the framework of statistical mechanics. We modify one of them, namely the stress-stress fluctuation formula, to obtain a new version that can be used in the isothermal-isobaric ensemble on global and local scale. In the last part of this work, we compare the results for both stress-stress fluctuation formulas for two systems, the ideal gas and the nearest-neighbor Lennard-Jones solid, and find accurate agreement.

Zusammenfassung

In dieser Arbeit stellen wir drei Methoden zur Bestimmung der elastischen Konstanten eines Systems mittels Gleichgewichtsfluktuationen vor, wobei nur eine die Möglichkeit bietet elastische Eigenschaften auch auf lokaler Ebene zu berechnen. Wir kombinieren diese Methode mit einem Formalismus, welcher Fluktuationen in verschiedenen statistischen Ensembles in Beziehung setzt. Dies ermöglicht es uns ein neue Fluktuationsformel herzuleiten, welche im isothermalen-isobaren Ensemble eingesetzt werden kann. Im ersten Teil der Arbeit führen wir die Grundlagen der Elastizitätstheorie ein, dazu gehören Spannungs- und Verzerrungstensoren, sowie eine allgemeine Form des Hook'schen Gesetzes, welches die lineare elastische Antwort eines System bei beliebigen Initialspannungen durch einen Satz von elastischen Konstanten beschreibt. In Hauptteil leiten wir die drei Methode zur Bestimmung dieser elastischen Konstanten im Kontext der statistischen Mechanik her. Eine dieser Methoden, die Spannungs-Spannungs-Fluktuationsformal, modifizieren wir anschließend um eine neue Formel zu erhalten, welche im isothermalen-isobaren Ensemble zur Berechnung von globalen und lokalen elastischen Konstanten anwendbar ist. Im letzten Abschnitt vergleichen wir die Resultate der beiden Spannungs-Spannungs-Fluktuationsformeln für zwei Systeme, das idealen Gas und der nächste Nachbarn Lennard-Jones Festkörper, und finden akurate Übereinstimmung.

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Chapter 1

Introduction

The determination of elastic constants on the local scale by theoretical methods has become more important than ever with rise of nanostructured materials in the recent years. Computer simulations are often used to predict, interpret or supplement experimental results for these materials [1, 2]. Another point of interest is the relation between local and bulk elastic constants in materials which are heterogeneous on microscopic scale but become isotropic on the macroscopic scales [3, 4, 5].

The theory of elasticity is a rather old discipline of physics. The roots are going back to 17th and 18th century [6], when almost every today well known scientist from that era worked on elasticity problems including Galilei, Hooke, Bernoulli, Euler, Young, Navier, Poisson and Cauchy - just to name a few. Today many physical laws and quantities used in the theory are named after these pioneers. The elastic continuum theories developed during this time were besides thermodynamics and later electrodynamics, the key concepts for engineering applications driving the industrial revolution. With the rise of classical and quantum statistical mechanics in the 20th century, which are theories based on microscopic principles, it was for the first time possible to relate the atomic structure of materials to their macroscopic elastic properties. First dealing with crystalline systems was the today well known work by Born and Huang [7] in 1954. Later Hoover, Holt and Squire reported the elastic constants for Argon computed by first principle calculations [8]. At the beginning of the 1980s Parrinello and Rahman *et al.* developed several new techniques to calculate the bulk elastic response of a classical system from fluctuations of equilibrium quantities and derived equations of motion for the relevant molecular dynamics ensembles [9, 10, 11, 12, 13, 14]. A review of this work can be found in [15]. Another important contribution was the work by Irving and Kirkwood in 1950 [16], which was later refined by Noll [17], where they used the framework of non-equilibrium statistical mechanics to establish a link between microscopic and continuum theories. This idea has been taken further by Hardy *et al.* [18], Murdoch [19] and Admal and Tadmour [20] in the recent decades. Now it was possible to calculate coarse-grained local continuum fields, like the stress tensor, by averaging over microscopic expressions in statistical ensembles. In 1988 Lutsko combined the work of Parrinello and Rahman *et al.* and the locality approach by Irving and Kirkwood, to obtain a fluctuation formula for local elastic constants in the canonical ensemble, which is applicable in molecular dynamics and Monte Carlo simulations [21, 22]. In this work we will derive a modified version of this formula, which can be used in the isothermal-isobaric ensemble.

In the first chapter we introduce the central quantities in the theory of

elasticity, these are the stress and strain tensors. The strain tensor describes the deformation of an elastic body, while the stress tensor measures the forces induced in the body by that deformation. The link between the mechanical part of the theory and thermodynamics is established at the end of the chapter. The second chapter consists of a derivation of a microscopic stress tensor, which follows the work of Lutsko. In the third chapter we derive a generalized Hooke's law, that describes the linear elastic response of a system at arbitrary initial stress through a set of elastic constants. Afterwards we discuss the influence of material symmetries on the number of elastic constants needed to describe the linear response of a system. We close the chapter by presenting a set of elastic response coefficients with special significance for experiments. The fifth chapter consists of the derivation of four fluctuation formulas for the calculation of elastic constants in molecular dynamics and Monte Carlo simulations of different statistical ensembles. Further we discuss the benefits and drawbacks of each method. In the last chapter we apply the fluctuation formula for the canonical ensemble and our newly derived version for the isothermal-isobaric ensemble to two systems and compare the result on global and local scale. The first system is the ideal gas, which can be treated analytically, and the second one is the nearest-neighbor Lennard-Jones solid, that is investigated with Monte Carlo simulations.

Chapter 2

Basic concepts in the theory of elasticity

In this chapter we introduce the basic quantities in the theory of elasticity used to describe the deformation of an elastic body. This includes a measure for the deformation of the system, namely the strain tensor, and a measure for the response to a deformation, the stress tensor. We start by a description in the context of continuum mechanics and then make use of the framework of statistical mechanics to obtain a microscopic formulation for the stress tensor. The introduction of the macroscopic strain and stress tensor is partly based on the one of Landau and Lifschitz in [23].

2.1 The strain tensor

The deformation of an elastic body can be described by a mapping $\mathbf{x}(\overset{\circ}{\mathbf{x}})$ of a material point $\overset{\circ}{\mathbf{x}}$ to its new position \mathbf{x} . This mapping transfers the initial configuration of the body, called the reference configuration, to the deformed configuration, called the current configuration. In the following we mark symbols referring to the reference configuration with a circle on top. The mapping defines a displacement field

$$\mathbf{u}(\overset{\circ}{\mathbf{x}}) = \mathbf{x}(\overset{\circ}{\mathbf{x}}) - \overset{\circ}{\mathbf{x}}. \quad (2.1)$$

It can consist of rigid body transformation (translation and rotation) and strain, where only the latter changes distances between material points. From the physical point of view, especially in the context of thermodynamics, quantities like the system's free energy \mathcal{F} are independent of translations and rotations in the absence of external fields, which is also known as *principle of material frame-indifference*. As a consequence, corresponding physical quantities are only functions of the reference coordinates and strains. In order to find a measure for the pure strains we start by looking into the length change of an infinitesimal line segment

$$dl^2 = d\overset{\circ}{x}_i d\overset{\circ}{x}_i = d\overset{\circ}{x}_i^2. \quad (2.2)$$

Here and throughout this work we make use of the Einstein summation convention, that repeated indices are summed over, unless otherwise noted.

The length after the deformation is

$$\begin{aligned} dl'^2 &= \left(d\overset{\circ}{x}_i + du_i \right)^2 \\ &= dl^2 + 2 d\overset{\circ}{x}_i du_i + du_i^2. \end{aligned} \quad (2.3)$$

With the total differential $du_i = \frac{\partial u_i}{\partial \overset{\circ}{x}_k} d\overset{\circ}{x}_k$ we obtain

$$dl'^2 - dl^2 = 2 \frac{\partial u_i}{\partial \overset{\circ}{x}_k} d\overset{\circ}{x}_i d\overset{\circ}{x}_k + \frac{\partial u_i}{\partial \overset{\circ}{x}_k} \frac{\partial u_i}{\partial \overset{\circ}{x}_l} d\overset{\circ}{x}_l d\overset{\circ}{x}_k. \quad (2.4)$$

At this point we can use the fact that dummy summation indices can be interchanged, yielding

$$\begin{aligned} dl'^2 - dl^2 &= \frac{\partial u_i}{\partial \overset{\circ}{x}_k} d\overset{\circ}{x}_i d\overset{\circ}{x}_k + \frac{\partial u_k}{\partial \overset{\circ}{x}_i} d\overset{\circ}{x}_i d\overset{\circ}{x}_k + \frac{\partial u_l}{\partial \overset{\circ}{x}_k} \frac{\partial u_l}{\partial \overset{\circ}{x}_i} d\overset{\circ}{x}_i d\overset{\circ}{x}_k \\ &= 2\eta_{ik} d\overset{\circ}{x}_i d\overset{\circ}{x}_k, \end{aligned} \quad (2.5)$$

where

$$\eta_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial \overset{\circ}{x}_k} + \frac{\partial u_k}{\partial \overset{\circ}{x}_i} + \frac{\partial u_l}{\partial \overset{\circ}{x}_k} \frac{\partial u_l}{\partial \overset{\circ}{x}_i} \right) \quad (2.6)$$

is the second rank symmetric strain tensor. In the literature, this strain measure is often called the Green-Lagrange strain tensor and is used in the theory of finite elasticity. Finite in this context means that the displacements can be arbitrarily large. We note that Eq. (2.6) can be recast to the expression

$$\eta = \frac{1}{2} (J^T J - \mathbb{I}) \quad (2.7)$$

by using the Jacobi matrix J of the mapping $\mathbf{x}(\overset{\circ}{\mathbf{x}})$, $J_{ik} = \partial x_i / \partial \overset{\circ}{x}_k$. A^T denotes the transpose of a matrix A and \mathbb{I} is the unit matrix. In this form one immediately sees that all η_{ik} are zero for rigid body transformations $\mathbf{x}(\overset{\circ}{\mathbf{x}}) = R\overset{\circ}{\mathbf{x}} + \mathbf{t}$ with an arbitrary rotation matrix ($R^T R = \mathbb{I}$) and a constant vector \mathbf{t} , which shows that η really corresponds to pure strains. Since in general η is dependent on $\overset{\circ}{\mathbf{x}}$, it can be interpreted as a measure for the local deviation of displacements from rigid body transformations.

If the displacement field is only slowly varying with $\overset{\circ}{\mathbf{x}}$, meaning that all $\partial u_i / \partial \overset{\circ}{x}_k \ll 1$, one can neglect the higher order terms in Eq. (2.6) and obtains the infinitesimal strain tensor

$$\epsilon_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial \overset{\circ}{x}_k} + \frac{\partial u_k}{\partial \overset{\circ}{x}_i} \right), \quad (2.8)$$

which is used in the linearized theory of elasticity. In terms of the Jacobi matrix it is given by

$$\epsilon = \frac{1}{2} (\mathbf{J} + \mathbf{J}^T) - \mathbb{I}, \quad (2.9)$$

showing that it is basically the symmetric part of \mathbf{J} . The antisymmetric part of the Jacobi matrix measures pure rotations and defines the infinitesimal

rotation tensor

$$\omega = \frac{1}{2} (\mathbf{J} - \mathbf{J}^T) . \quad (2.10)$$

He we point out that the condition of small partial derivatives does not mean that the displacements themselves have to be small. Imagine bending a long rod with a very small diameter all the way down to a circle. In this case the displacements are large, but vary only little between neighboring slices along the rod. Nevertheless often all displacements are small compared to the relevant length scales, typically given by the geometric lengths (linear size) of the sample under study. Then the difference between the reference and deformed configuration is negligible and one can describe a system with equations formulated in the initial configuration.

We close this section with two remarks. The first one is regarding a mathematical restriction on the possible realizations of displacements. Intuitively speaking, this constraint prohibits deformations in which neighboring volumes in the reference configuration, intersect or are torn apart in the deformed configuration. Mathematically, this means that the displacements can be obtained by integrating the strains. These compatibility equations were first given by Barré de Saint-Venant in 1864 and in the modern form they are formulated as a problem of determining allowable single-valued functions on a simply connected body [24]. Without going in the mathematical details, we state the compatibility equation to be

$$\nabla \times \mathbf{J} = 0 , \quad (2.11)$$

where $\nabla \times \mathbf{A}$ denotes the curl of a second rank tensor field \mathbf{A} . Later we will use homogeneous deformations that map every point equally to the current configuration and therefore can be described by a linear map $\mathbf{x} = \mathbf{A}\mathring{\mathbf{x}}$. Here the Jacobi matrix is a constant and the compatibility equation is obviously fulfilled.

The second remark is on the different geometric dependency of the two strain tensors. Suppose we apply on a body a homogeneous uniaxial displacement in x_1 direction, changing it's length from L_1 to $L_1 + \delta L$. This deformation is represented by a linear map $\mathbf{x} = \mathbf{A}\mathring{\mathbf{x}}$ with a stretch matrix

$$\mathbf{A} = \begin{pmatrix} (1+s) & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} , \quad (2.12)$$

where $s = \delta L/L_1$ is the relative change in length. The Jacobi matrix is simply equal to \mathbf{A} and we find

$$\eta = \frac{1}{2} \begin{pmatrix} s^2 + 2s & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2.13)$$

for the finite strain tensor and

$$\epsilon = \begin{pmatrix} s & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2.14)$$

for the infinitesimal strain tensor, in agreement with the linearization of $1/2(s^2 + 2s) = s + \mathcal{O}(\|s\|^2)$. If the calculation is repeated with a pure shear transformation, similar results are obtained. This shows that η is nonlinear dependent on geometrical changes, while ϵ has a linear dependency. The difference between both strain tensors will be important later on, when we discuss the linear response of a system to small deformations.

2.2 The stress tensor

After we introduced the strain tensor as a measure for deformations in the previous section, we now turn to the corresponding response variable, the stress tensor. We start with an undeformed body that is in thermal and mechanical equilibrium, where undeformed means that all strains are zero. From the definition of mechanical equilibrium, we know that the net forces on an arbitrary part of the body are zero. A deformation of the body from its initial state generates inner forces called stresses, which try to bring the system back to the equilibrium state. But because strains are always expressed in terms of a reference configuration, this also includes scenarios where external forces are applied to the body, sustaining the initial mechanical equilibrium. From that we distinguish between two types of reference configurations:

- *Unstrained reference configuration (URC)*: All strains vanish, but nonzero external forces may exist which produce stresses in the body even in the initial configuration.
- *Stress free reference configuration (SFRC)*: If all strains vanish and there are no external forces, then all stresses are zero and the body is called stress free. In that sense the SFRC is a special case of URC.

In order to define the stress tensor we consider the i -th component of the net force \mathbf{F} on a volume Ω

$$F_i = \int_{\Omega} f_i dV = \int_{\Omega} f_i^{(ext)} dV + \int_{\Omega} f_i^{(int)} dV, \quad (2.15)$$

where $\mathbf{f}^{(ext)}$ ($\mathbf{f}^{(int)}$) is the external (internal) force per unit volume. By Newton's third law, the forces between inner parts of the volume compensate each other, canceling the contribution of $\mathbf{f}^{(int)}$ to the net force and yielding $\mathbf{f} = \mathbf{f}^{(ext)}$. So we are left with the external forces from the environment on the volume Ω . To get insight into the properties of these forces, we think about the origin of stresses. Their sources are the inter-atomic forces between the particles which make up the body. From the macroscopic viewpoint of continuum mechanics, these interactions occur on a small length scale. This justifies the assumption that for a macroscopic small, but still microscopic large volume inside the body, the inter-atomic forces act only through the surface of that volume. But this implies that we should be able to rewrite Eq. (2.15) as an integral over the surface of Ω . In order to do that we define

$$f_i = \frac{\partial \sigma_{ik}}{\partial x_k} \quad (2.16)$$

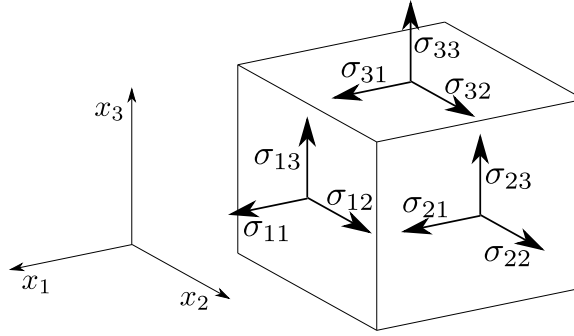


FIGURE 2.1: Graphical representation of stress tensor elements.

to be the divergence of a second rank tensor σ , called the stress tensor. Now one can apply the divergence theorem from tensor calculus and obtain

$$F_i = \int_{\Omega} f_i dV = \int_{\Omega} \frac{\partial \sigma_{ik}}{\partial x_k} dV = \oint_{\partial\Omega} \sigma_{ik} dS_k, \quad (2.17)$$

where dS_k is k -th component of the surface element $d\mathbf{S}$. From Eq. (2.17) we see that $\sigma_{ik}dS_k$ is the i -th component of the force acting on the surface element $d\mathbf{S}$. If we lay the surface elements in the planes parallel to the axis of a Cartesian coordinate system we can interpret the stress tensor elements as follows: For a plane which is orthogonal to the x_1 axis, σ_{11} is the force per unit area normal to that plane and σ_{12} , σ_{13} are the tangential forces per unit area in x_2 and x_3 direction within the plane. Figure 2.1 shows a graphical representation of the stress tensor for all elements σ_{ik} . Regarding this figure we have to add one remark about the sign of σ_{ik} . Since the forces $\mathbf{f}^{(ext)}$ in Eq. (2.15) are acting from the environment on the volume Ω , the normals of the surface elements point inwards the volume. So if we want to obtain the force applied from Ω on the environment, then because of Newton's third law, we have to reverse the sign of σ_{ik} and invert the direction of surface normals. This is the usual point of view in the literature, where the stress tensor is described in terms of surface normals pointing outwards.

We now want to discuss the symmetry properties of σ . From the stress tensor's definition, Eq. (2.16), one immediately sees that it is not unique. One can add any divergence-less quantity to the stress tensor and still obtains the same force:

$$\tilde{\sigma}_{ik} = \sigma_{ik} + \frac{\partial \Phi_{ikl}}{\partial x_l}, \quad (2.18)$$

if Φ is an arbitrary third rank tensor which is antisymmetric in the last index pair. So if σ has an antisymmetric part which we can write as

$$\sigma_{ik} - \sigma_{ki} = 2 \frac{\partial \varphi_{ikl}}{\partial x_l}, \quad (2.19)$$

where φ is an arbitrary tensor antisymmetric in the first index pair, then we could always define a transformation $\Phi_{ikl} = \varphi_{kli} + \varphi_{ilk} - \varphi_{ikl}$, that gives a the symmetric stress tensor [25]

$$\tilde{\sigma}_{ik} = \frac{1}{2} (\sigma_{ik} + \sigma_{ki}) + \frac{\partial}{\partial x_l} (\varphi_{ilk} + \varphi_{kli}). \quad (2.20)$$

But this means that we can in general assume the stress tensor to be symmetric,¹

$$\sigma_{ik} = \sigma_{ki}. \quad (2.21)$$

At last we note that in mechanical equilibrium the net force for an arbitrary volume has to vanish. If we look at Eq. (2.15) we see that this is only possible if the force density \mathbf{f} is zero everywhere. This leads to the equilibrium condition for the stress tensor:

$$\frac{\partial \sigma_{ik}}{\partial x_k} = 0. \quad (2.22)$$

Here and in the following we neglect body forces, like gravity, which act on the system as a whole because they are not relevant for this work.

2.3 Thermoelasticity

Until now we viewed the theory of elasticity from a purely mechanical perspective. At this point we want to introduce thermodynamics into our considerations. The goal is to formulate the first law of thermodynamics

$$d\mathcal{E} = \delta\mathcal{Q} - \delta\mathcal{W} \quad (2.23)$$

in terms of generalized thermodynamic forces and displacements appropriate in the context of elasticity. Here \mathcal{E} is the internal energy of the system, $\delta\mathcal{Q}$ the heat supplied to the system by the environment and $\delta\mathcal{W}$ the work done by the system on the surroundings.

The first step is to obtain an expression for the infinitesimal work done during a deformation. Instead of calculating the work directly, we start by considering the mechanical work performed on the environment per unit time, and combine this with Eq. (2.17),

$$\frac{d\mathcal{W}}{dt} = \mathbf{F} \cdot \mathbf{v} = F_i v_i = - \oint_{\partial\Omega} \sigma_{ik} v_i dS_k. \quad (2.24)$$

Now we use the divergence theorem to transform the surface integral into a volume integral

$$\begin{aligned} \frac{d\mathcal{W}}{dt} &= - \int_{\Omega} \frac{\partial(\sigma_{ik} v_i)}{\partial x_k} dV \\ &= - \int_{\Omega} \left(\frac{\partial \sigma_{ik}}{\partial x_k} v_i + \sigma_{ik} \frac{\partial v_i}{\partial x_k} \right) dV. \end{aligned} \quad (2.25)$$

Since we assume that the body is in mechanical equilibrium in the current configuration, the first term of the integrand in the second line is zero. The second term can be written in symmetric form by interchanging the dummy indices and using the symmetry of the stress tensor and we obtain

$$\frac{d\mathcal{W}}{dt} = - \int_{\Omega} \sigma_{ik} D_{ik} dV, \quad (2.26)$$

¹An exception are systems with couple stresses which can produce a non-symmetric stress tensor.

where we introduced the rate of deformation tensor \mathbf{D} as

$$D_{ik} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} \right). \quad (2.27)$$

The reason why \mathbf{D} is called the rate of deformation tensor becomes clear when we calculate the time-derivative of the strain tensor

$$\begin{aligned} \dot{\eta}_{ik} &= \frac{1}{2} \left(\dot{J}_{il}^T J_{lk} + J_{il}^T \dot{J}_{lk} \right) \\ &= \frac{1}{2} \left[\left(\frac{d}{dt} \frac{\partial x_j}{\partial \overset{\circ}{x}_i} \right) \frac{\partial x_j}{\partial \overset{\circ}{x}_k} + \frac{\partial x_j}{\partial \overset{\circ}{x}_i} \left(\frac{d}{dt} \frac{\partial x_j}{\partial \overset{\circ}{x}_k} \right) \right], \end{aligned} \quad (2.28)$$

where the dot over a variable denotes its time-derivative. The time-derivative of the Jacobi matrix can, after an exchange of differentiation order and use of the chain rule, be written as

$$\frac{d}{dt} \frac{\partial x_i}{\partial \overset{\circ}{x}_j} = \frac{\partial}{\partial \overset{\circ}{x}_j} \frac{dx_i}{dt} = \frac{\partial v_i}{\partial \overset{\circ}{x}_j} = \frac{\partial v_i}{\partial x_k} \frac{\partial x_k}{\partial \overset{\circ}{x}_j}. \quad (2.29)$$

Inserting this into Eq. (2.28) leads to

$$\begin{aligned} \dot{\eta}_{ik} &= \frac{\partial x_l}{\partial \overset{\circ}{x}_i} \frac{1}{2} \left(\frac{\partial v_j}{\partial x_l} + \frac{\partial v_l}{\partial x_j} \right) \frac{\partial x_j}{\partial \overset{\circ}{x}_k} \\ &= J_{ij}^T D_{jl} J_{lk}, \end{aligned} \quad (2.30)$$

or the inverse relationship

$$D_{ik} = J_{ij}^{-T} \dot{\eta}_{jl} J_{lk}^{-1}. \quad (2.31)$$

Here \mathbf{A}^{-T} is a shorthand for the inverse of a transposed matrix $(\mathbf{A}^T)^{-1} = (\mathbf{A}^{-1})^T$. When transforming to the reference configuration, using $dV = \det \mathbf{J} dV_0$, we thus obtain with Eq. (2.31)

$$\frac{d\mathcal{W}}{dt} = - \int_{\Omega} \sigma_{ik} J_{ij}^{-T} \dot{\eta}_{jl} J_{lk}^{-1} \det \mathbf{J} dV_0, \quad (2.32)$$

This can be written as

$$\frac{d\mathcal{W}}{dt} = - \int_{\Omega} \tau_{jl} \dot{\eta}_{jl} dV_0, \quad (2.33)$$

where we defined the thermodynamic tension tensor

$$\tau_{jl} = \det \mathbf{J} J_{ji}^{-1} \sigma_{ik} J_{kl}^{-T}. \quad (2.34)$$

In the literature this tensor is also referred to as the second Piola-Kirchhoff stress tensor. It does not have an intuitive geometrical interpretation like σ , but it is the energy conjugate to the Lagrange strain tensor and must be used if we want to express the work with respect to the reference configuration. Since σ is symmetric, τ is also symmetric. In the case of small displacements, $\mathbf{J} \simeq \mathbb{I}$, the two stress tensors can be considered as equal $\sigma \simeq \tau$.

Finally, we obtain from Eq. (2.33) for the infinitesimal work per unit volume

$$\delta W = -\tau_{ik} d\eta_{ik}. \quad (2.35)$$

Further more, if the deformation change is sufficiently slow, deformation process is thermodynamically reversible, and the heat exchange is given by

$$\delta Q = T dS. \quad (2.36)$$

This assumption explicitly excludes plasticity from our consideration. Combining Eqs. (2.23), (2.35) and (2.36), we get for the internal energy per unit mass

$$d\mathcal{E} = T dS + \tau_{ik} d\eta_{ik} \quad (2.37)$$

and for the free energy per unit mass

$$d\mathcal{F} = S dT + \tau_{ik} d\eta_{ik}, \quad (2.38)$$

where the two are related by the Legendre transformation $\mathcal{F} = \mathcal{E} - TS$. Some authors define the internal and free energy per unit volume, but we think that this is not appropriate for systems undergoing finite deformation because the volume is not a conserved quantity. On the other hand mass is conserved during deformation and the mass density ρ obeys the conservation law

$$\rho(\overset{\circ}{\mathbf{x}}) = \rho(\mathbf{x}) \det \mathbf{J}. \quad (2.39)$$

In the following we use abbreviations for the mass densities $\rho = \rho(\mathbf{x})$ in the current and $\rho_0 = \rho(\overset{\circ}{\mathbf{x}})$ in the reference configuration.

If we compute the total differentials of \mathcal{E} and \mathcal{F} respectively, we obtain for the thermodynamic tensions the relations

$$\tau_{ik} = \left(\frac{\partial \mathcal{E}}{\partial \eta_{ik}} \right)_S = \left(\frac{\partial \mathcal{F}}{\partial \eta_{ik}} \right)_T, \quad (2.40)$$

where it is implicitly understood that during differentiation all components $\eta_{jl} \neq \eta_{ik}$ of the strain tensor are held constant.

Chapter 3

The microscopic stress tensor

The derivation of the local microscopic stress tensor on the procedure developed by Lutsko in [21]. The starting point is the definition of the stress tensor, which is interpreted as a continuity equation for the local momentum flux. By introducing a pseudo momentum density, we are then able to find a microscopic expression for the local stress tensor in terms of particle positions and momenta. This *microscopic stress operator* can be averaged spatially and ensemble-wise to obtain a course grained stress field.

As we said, we start by writing Eq. (2.16) as a continuity equation for the local momentum flux:

$$\frac{d}{dt}\hat{p}_\alpha(\mathbf{x}) = \frac{\partial \hat{\sigma}_{\alpha\beta}(\mathbf{x})}{\partial x_\beta}. \quad (3.1)$$

Now we introduce the pseudo momentum density

$$\hat{\mathbf{p}}(\mathbf{x}) = \sum_a \mathbf{p}_a \delta^{(3)}(\mathbf{x} - \mathbf{q}_a), \quad (3.2)$$

which has the simple interpretation, that at the a -th particle position \mathbf{q}_a we have its momentum \mathbf{p}_a and everywhere else the momentum density is zero. Here we establish the convention that phase space functions dependent on the system particle positions and momenta are denoted by carets over them. Further Latin indices always refer to particle numbers and Greek indices to Cartesian components. Expressing $\hat{\mathbf{p}}(\mathbf{x})$ and $\hat{\sigma}(\mathbf{x})$ through their Fourier-transforms we obtain

$$\frac{d}{dt} \int \frac{d^3k}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{x}} \hat{p}_\alpha(\mathbf{k}) = \frac{\partial}{\partial x_\beta} \int \frac{d^3k}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{x}} \hat{\sigma}_{\alpha\beta}(\mathbf{k}). \quad (3.3)$$

We can evaluate the divergence on the right hand side and interchange the time-derivative with integration on the left hand side, then compare the integrands on both sides to arrive at

$$\frac{d}{dt}\hat{p}_\alpha(\mathbf{k}) = -ik_\beta \hat{\sigma}_{\alpha\beta}(\mathbf{k}). \quad (3.4)$$

Because $\hat{\mathbf{p}}(\mathbf{k})$ is easily obtained from Eq. (3.2) as

$$\hat{\mathbf{p}}(\mathbf{k}) = \int d^3x e^{i\mathbf{k}\cdot\mathbf{x}} \hat{\mathbf{p}}(\mathbf{x}) = \sum_a \mathbf{p}_a e^{i\mathbf{k}\cdot\mathbf{q}_a}, \quad (3.5)$$

we can try to express the left hand side as a divergence of a tensor field in Fourier space, which then can be identified as the yet unknown stress

tensor. Executing the time-derivative of $\hat{\mathbf{p}}(\mathbf{k})$ is straightforward and leads to

$$\frac{d}{dt}\hat{p}_\alpha = \sum_a (\dot{p}_{a,\alpha} e^{i\mathbf{k}\cdot\mathbf{q}_a} + ik_\beta \dot{q}_{a,\beta} p_{a,\alpha} e^{i\mathbf{k}\cdot\mathbf{q}_a}). \quad (3.6)$$

Using Newton's laws $\dot{\mathbf{p}}_a = \mathbf{F}_a$ and $\dot{\mathbf{q}}_a = \mathbf{p}_a/m$, where m is the particles mass which is equal for all particles, we obtain

$$\frac{d}{dt}\hat{p}_\alpha = \sum_a (F_{a,\alpha} e^{i\mathbf{k}\cdot\mathbf{q}_a} + ik_\beta \frac{p_{a,\beta} p_{a,\alpha}}{m} e^{i\mathbf{k}\cdot\mathbf{q}_a}). \quad (3.7)$$

Now we identify the product $p_{a,\beta} p_{a,\alpha}$ in the second term on the RHS as the dyadic product of \mathbf{p}_a with itself which is denoted as $\mathbf{p}_a \otimes \mathbf{p}_a$ where

$$(\mathbf{p}_a \otimes \mathbf{p}_a)_{\beta\alpha} = p_{a,\beta} p_{a,\alpha}. \quad (3.8)$$

Thus, the second term on the RHS is already in the shape of Eq. (3.4) and is called the kinetic part of the stress tensor. The first term on the RHS of Eq. (3.7) has to be manipulated further:

$$\sum_a F_{a,\alpha} e^{i\mathbf{k}\cdot\mathbf{q}_a} = \sum_a \sum_{b,b \neq a} F_{ab,\alpha} e^{i\mathbf{k}\cdot\mathbf{q}_a} \quad (3.9)$$

$$= \frac{1}{2} \left[\sum_a \sum_{b,b \neq a} F_{ab,\alpha} e^{i\mathbf{k}\cdot\mathbf{q}_a} + \sum_b \sum_{a,a \neq b} F_{ba,\alpha} e^{i\mathbf{k}\cdot\mathbf{q}_b} \right], \quad (3.10)$$

where \mathbf{F}_{ab} is the inter-particle force between the particles a and b . Here we used the expression for \mathbf{F}_a known from Newtonian mechanics, that the total force on a particle in absence of external forces is equal to the sum of inter-particle forces, and simply added the double sum again with interchanged dummy indices b, a . Using Newton's third law, $\mathbf{F}_{ab} = -\mathbf{F}_{ba}$ we get

$$\frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} F_{ab,\alpha} [e^{i\mathbf{k}\cdot\mathbf{q}_a} - e^{i\mathbf{k}\cdot\mathbf{q}_b}] = \frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} F_{ab,\alpha} \frac{[e^{i\mathbf{k}\cdot\mathbf{q}_a} - e^{i\mathbf{k}\cdot\mathbf{q}_b}]}{i\mathbf{k} \cdot \mathbf{v}_{ab}} ik_\beta v_{ab,\beta}, \quad (3.11)$$

where on the RHS the fraction was extended with $i\mathbf{k} \cdot \mathbf{v}_{ab}$. If the force between the particles a and b is only dependent on the distance between them, we can insert the usual expression for the force

$$F_{ab,\alpha} = -\frac{\partial U}{\partial q_{ab}} \frac{q_{ab,\alpha}}{q_{ab}} \quad (3.12)$$

where $\mathbf{q}_{ab} = \mathbf{q}_a - \mathbf{q}_b$, $q_{ab} = |\mathbf{q}_{ab}|$ and $U(\{\mathbf{q}_a\})$ is the potential energy. After some simple algebra we arrive at

$$ik_\beta \left[-\frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} \left(\frac{\partial U}{\partial q_{ab}} q_{ab} \right) \frac{v_{ab,\beta} q_{ab,\alpha}}{q_{ab}^2} \frac{[e^{i\mathbf{k}\cdot\mathbf{q}_a} - e^{i\mathbf{k}\cdot\mathbf{q}_b}]}{i\mathbf{k} \cdot \mathbf{v}_{ab}} \right]. \quad (3.13)$$

We can again identify the product $v_{ab,\beta} q_{ab,\alpha}$ as a component of a dyadic product $\mathbf{v}_{ab} \otimes \mathbf{q}_{ab}$. At this stage the vector \mathbf{v}_{ab} is arbitrary. It can be fixed by the additional requirement that the stress tensor is symmetric (cf. chapter

2) $\hat{\sigma}_{\alpha\beta} = \hat{\sigma}_{\beta\alpha}$. This implies the constrain

$$v_{ab,\alpha} q_{ab,\beta} \stackrel{!}{=} v_{ab,\beta} q_{ab,\alpha} \quad (3.14)$$

which can be satisfied by $v_{ab,\mu} = c_{ab} q_{ab,\mu}$, where c_{ab} is an arbitrary real constant which is in the following taken to be one. Combining Eqns. (3.4), (3.7), (3.13) and setting $v_{ab,\mu} = q_{ab,\mu}$, we arrive at the final expression for the stress tensor in Fourier-space:

$$\hat{\sigma}(\mathbf{k}) = - \sum_a \frac{\mathbf{P}_a \otimes \mathbf{P}_a}{m} e^{i\mathbf{k} \cdot \mathbf{q}_a} + \frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} \left(\frac{\partial U}{\partial q_{ab}} q_{ab} \right) \frac{\mathbf{q}_{ab} \otimes \mathbf{q}_{ab}}{q_{ab}^2} \cdot \frac{[e^{i\mathbf{k} \cdot \mathbf{q}_a} - e^{i\mathbf{k} \cdot \mathbf{q}_b}]}{i\mathbf{k} \cdot \mathbf{q}_{ab}}. \quad (3.15)$$

The next step is to transform this expression back to real space. The kinetic term is easily calculated to be

$$- \sum_a \frac{\mathbf{P}_a \otimes \mathbf{P}_a}{m} \delta^{(3)}(\mathbf{x} - \mathbf{q}_a). \quad (3.16)$$

For the potential part we are left to carry out the integral

$$\begin{aligned} & \int \frac{d^3 k}{(2\pi)^3} \frac{[e^{i\mathbf{k} \cdot \mathbf{q}_a} - e^{i\mathbf{k} \cdot \mathbf{q}_b}]}{i\mathbf{k} \cdot (\mathbf{q}_a - \mathbf{q}_b)} e^{-i\mathbf{k} \cdot \mathbf{x}} \\ &= \int \frac{d^3 k}{(2\pi)^3} \frac{[e^{i\mathbf{k} \cdot \mathbf{q}_{ab}/2} - e^{-i\mathbf{k} \cdot \mathbf{q}_{ab}/2}]}{i\mathbf{k} \cdot \mathbf{q}_{ab}} e^{i\mathbf{k} \cdot (\mathbf{Q} - \mathbf{x})} \end{aligned} \quad (3.17)$$

where on the RHS we introduced the center of mass coordinate $\mathbf{Q} = \frac{1}{2}(\mathbf{q}_a + \mathbf{q}_b)$ and used $\mathbf{q}_a = \mathbf{Q} + \frac{1}{2}\mathbf{q}_{ab}$, $\mathbf{q}_b = \mathbf{Q} - \frac{1}{2}\mathbf{q}_{ab}$. With the abbreviation $\mathbf{q}' = \frac{1}{2}\mathbf{q}_{ab}$ we obtain

$$\int \frac{d^3 k}{(2\pi)^3} \frac{\sin(\mathbf{k} \cdot \mathbf{q}')}{\mathbf{k} \cdot \mathbf{q}'} e^{i\mathbf{k} \cdot (\mathbf{Q} - \mathbf{x})}. \quad (3.18)$$

The fraction containing the sine function can be expressed in the following way

$$\frac{\sin(\mathbf{k} \cdot \mathbf{q}')}{\mathbf{k} \cdot \mathbf{q}'} = \frac{1}{2i\mathbf{k} \cdot \mathbf{q}'} \left(e^{i\mathbf{k} \cdot \mathbf{q}'} - e^{-i\mathbf{k} \cdot \mathbf{q}'} \right) = \frac{1}{2} \int_{-1}^1 d\lambda e^{i\mathbf{k} \cdot \mathbf{q}' \lambda}. \quad (3.19)$$

Inserting this into Eq. (3.18) and interchanging the order of integration leads to

$$\frac{1}{2} \int_{-1}^1 d\lambda \int \frac{d^3 k}{(2\pi)^3} e^{i\mathbf{k} \cdot (\mathbf{Q} - \mathbf{x} + \lambda \mathbf{q}')} = \frac{1}{2} \int_{-1}^1 d\lambda \delta^{(3)}(\mathbf{Q} - \mathbf{x} + \lambda \mathbf{q}') \quad (3.20)$$

$$= \frac{1}{2} w(\mathbf{q}_a, \mathbf{q}_b, \mathbf{x}), \quad (3.21)$$

where we defined the weighting function w , which is only non-zero for

$$\mathbf{x} \in \left\{ \mathbf{y} \mid \mathbf{y} = \mathbf{Q} + \frac{\mu}{2} \mathbf{q}_{ab} \wedge \mu \in [-1, 1] \right\}. \quad (3.22)$$

This shows that w is singular on the line segment joining the coordinates of particle a and b . With this definition of w we arrive at the final expression

for the microscopic stress tensor in real space

$$\hat{\sigma}(\mathbf{x}) = - \sum_a \frac{\mathbf{p}_a \otimes \mathbf{p}_a}{m} \delta^{(3)}(\mathbf{x} - \mathbf{q}_a) + \frac{1}{4} \sum_{\substack{a,b \\ a \neq b}} \frac{\partial U}{\partial q_{ab}} \frac{\mathbf{q}_{ab} \otimes \mathbf{q}_{ab}}{q_{ab}^2} w(\mathbf{q}_a, \mathbf{q}_b, \mathbf{x}). \quad (3.23)$$

To illustrate the usage of this expression, we suppose to have a system with a total volume V_0 . If we want to calculate the stress tensor for a sub-volume $\Omega \subseteq V_0$, we spatially average $\hat{\sigma}$ over this volume:

$$\begin{aligned} \hat{\sigma}^\Omega &= \frac{1}{\Omega} \int_\Omega dV \hat{\sigma}(\mathbf{x}) \\ &= \frac{1}{\Omega} \left(- \sum_{a \in \Omega} \frac{\mathbf{p}_a \otimes \mathbf{p}_a}{m} + \frac{1}{4} \sum_{\substack{a,b \\ a \neq b}} \frac{\partial U}{\partial q_{ab}} \frac{\mathbf{q}_{ab} \otimes \mathbf{q}_{ab}}{q_{ab}} \frac{w_{ab}}{q_{ab}} \right). \end{aligned} \quad (3.24)$$

Now only momenta of particles contained in Ω contribute to the kinetic part and the w_{ab} in the potential part stands for the length of the line segment between a and b located in Ω . There are three distinct constellations of the particles a and b , that contribute to the potential part of the stress tensor, which are shown in figure 3.1. At first it seems unintuitive, that even when both particles are outside of Ω the weighting function w can produce a non-zero contribution if the line segment crosses through Ω , but this fact can be understood in the sense of a coarse-grained continuum field. If we set $\Omega = V_0$, every particle momenta contributes to the kinetic part, and all line segments are fully contained in V_0 , meaning that $w_{ab} = q_{ab}$ for all particle pairs. From this we obtain the microscopic stress tensor of the bulk system

$$\hat{\sigma}^B = \frac{1}{V_0} \left(- \sum_a \frac{\mathbf{p}_a \otimes \mathbf{p}_a}{m} + \frac{1}{4} \sum_{\substack{a,b \\ a \neq b}} \frac{\partial U}{\partial q_{ab}} \frac{\mathbf{q}_{ab} \otimes \mathbf{q}_{ab}}{q_{ab}} \right). \quad (3.25)$$

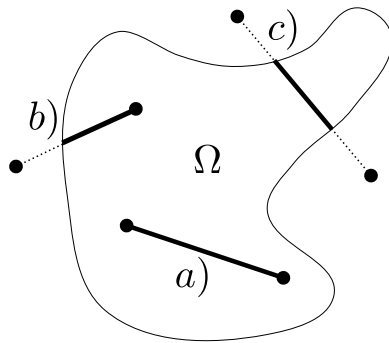


FIGURE 3.1: Illustration of the three different constellations that contribute to the potential part of the microscopic stress tensor spatially averaged over a volume Ω : a) Both particles are located in Ω , b) only one particle is contained in Ω , c) both particles are outside of Ω . The part of the line segment that contributes through the weighting function w is represented by thick solid lines.

Chapter 4

Elastic constants

This chapter describes the linear elastic response of a system. We start by deriving Hooke's law, that connects resulting stresses to applied strains by a linear map, called the stiffness tensor. Afterwards we discuss a compact notation for the stiffness tensor and the influence of underlying material symmetries on its structure. The chapter is closed by a description of elastic moduli that are commonly measured in experiments and their relation to the stiffness tensor elements.

4.1 Linear elastic response: Hooke's law

In this section we introduce the linear elastic response of a system to small deformations. We do this by deriving a generalized form of Hooke's law, valid for bodies under arbitrary initial stress [26]. For anisotropic three dimensional solids, Hooke's law is given by

$$\sigma_{ij} = \sigma_{ij}^0 + c_{ijkl}\epsilon_{kl}, \quad (4.1)$$

where σ^0 is the stress tensor in the reference configuration. It relates stresses σ in the current configuration to infinitesimal strains ϵ via the elastic stiffness tensor c . According to Eq. (4.1) the stiffness tensor is the first order coefficient of the Taylor expansion of stress around the reference configuration:

$$c_{ijkl} = \left(\frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}} \right)_{\epsilon=0}. \quad (4.2)$$

The main steps in the derivation of the generalized Hooke's law, are the use of thermodynamic tensions and their relation to the thermodynamic potentials to express the derivative of stress with respect to infinitesimal strain and then apply a Taylor expansion of the potentials to relate the expansion coefficients to the stiffness tensor elements. In the following we will focus on isothermal deformations, but we note that all calculations can be analogously done for adiabatic deformations by replacing the free energy with the internal energy and the isothermal expansion coefficients with the adiabatic ones.

We start the derivation with the inversion of Eq. (2.34),

$$\sigma_{ij} = \frac{1}{\det \mathbf{J}} J_{ik} J_{jl} \left(\frac{\partial \mathcal{F}}{\partial \eta_{kl}} \right)_T, \quad (4.3)$$

where we used Eq. (2.40) to express the thermodynamic tensions as derivatives of the free energy. As we mentioned in section 2.1, we can require the free energy to be rotationally invariant, meaning that it is only dependent

one the relative positions of material particles¹. But because the relative positions in the current configuration are fully specified by the positions in the reference configuration and the strain tensor η [7], we can expand the free energy at constant temperature around the reference configuration in terms of η . For small but not necessarily infinitesimal strains we can write

$$\mathcal{F}(\eta, T) = \mathcal{F}(0, T) + C_{ij}^T \eta_{ij} + \frac{1}{2} C_{ijkl}^T \eta_{ij} \eta_{kl} + \mathcal{O}(\eta^3), \quad (4.4)$$

where the expansion coefficients are

$$C_{ij}^T = \left(\frac{\partial \mathcal{F}}{\partial \eta_{ij}} \right)_{\eta=0}, \quad (4.5)$$

$$C_{ijkl}^T = \left(\frac{\partial^2 \mathcal{F}}{\partial \eta_{ij} \partial \eta_{kl}} \right)_{\eta=0}. \quad (4.6)$$

If we insert Eq. (4.4) into Eq. (4.3) and neglect higher order terms, we obtain

$$\sigma_{ij} = \frac{1}{\det \mathbf{J}} J_{ik} J_{jl} (C_{kl}^T + C_{klmn}^T \eta_{mn}). \quad (4.7)$$

At this point we have to take the derivative with respect to infinitesimal strains ϵ_{rs} . Since η and ϵ can both be expressed through \mathbf{J} , we can apply the chain rule which leads to

$$\left(\frac{\partial \sigma_{ij}}{\partial \epsilon_{rs}} \right)_{\epsilon=0} = \left(\frac{\partial \sigma_{ij}}{\partial J_{pq}} \right)_{\mathbf{J}=\mathbb{I}} \frac{\partial J_{pq}}{\partial \epsilon_{rs}}. \quad (4.8)$$

We first calculate the derivative with respect to J_{pq} from Eq. (4.7), which becomes a quite lengthy expression, but reduces in the zero strain limit to

$$\left(\frac{\partial \sigma_{ij}}{\partial J_{pq}} \right)_{\mathbf{J}=\mathbb{I}} = (\sigma_{iq}^0 \delta_{jp} + \sigma_{jq}^0 \delta_{ip} - \sigma_{ij}^0 \delta_{pq}) + C_{ijpq}^T. \quad (4.9)$$

Here we have used the fact that in the reference configuration the thermodynamic tension and stress tensors are identical. So we can, through Eq. (2.40), identify the C_{ij}^T as the stresses in the reference configuration: $C_{ij}^T = \sigma_{ij}^0$. The second order expansion coefficients C_{ijkl}^T are in following simply called isothermal elastic constants.

The derivative of \mathbf{J} with respect to ϵ can be computed as follows: If we combine Eq. (2.9) and (2.10), we can solve for \mathbf{J} . This gives

$$J_{pq} = \frac{1}{2} (\epsilon_{pq} + \epsilon_{qp} + \omega_{pq} - \omega_{qp}) + \delta_{pq}, \quad (4.10)$$

where we explicitly expressed the symmetries of ϵ and ω . For the derivative with respect to ϵ we then obtain

$$\frac{\partial J_{pq}}{\partial \epsilon_{rs}} = \frac{1}{2} (\delta_{pr} \delta_{qs} + \delta_{ps} \delta_{qr}). \quad (4.11)$$

¹The term particles here has to be understood in the sense of a continuum mechanics.

Our final result for the stiffness tensor in Eq. (4.1) is obtained after inserting Eq. (4.9) and (4.11) in (4.8):

$$c_{ijkl} = C_{ijkl}^T + \frac{1}{2} (\sigma_{ik}^0 \delta_{jl} + \sigma_{il}^0 \delta_{jk} + \sigma_{jk}^0 \delta_{il} + \sigma_{jl}^0 \delta_{ik} - 2\sigma_{ij}^0 \delta_{kl}). \quad (4.12)$$

From Eq. (4.12) we see that the stiffness tensor and the isothermal elastic constants are only equal for a stress-free reference configuration. For a general initial configuration they deviate by a term which is dependent on the stress in the reference configuration. This influences the symmetry properties of the stiffness tensor as discussed in the next section.

If we know the applied stresses and are interested in the resulting strains, it is also possible to invert Hooke's law. With the inverse of the stiffness tensor, $s = c^{-1}$, which is called the compliance tensor, Hooke's law takes the form

$$\epsilon_{ij} = s_{ijkl} \sigma_{kl}. \quad (4.13)$$

Because the stiffness and compliance tensors are inverse to each other, both contain the complete information about the linear elastic response of system.

4.2 Voigt notation

A fourth rank tensor has in general $3^4 = 81$ components. Owing to the symmetry of η , we conclude from Eq. (4.4) that the elastic constants are symmetric with respect to interchanges in the first and second index pair,

$$C_{ijkl}^T = C_{jikl}^T = C_{ijlk}^T = C_{jilk}^T \quad (4.14)$$

and also with respect to interchanges of the index pairs themselves,

$$C_{ijkl}^T = C_{klij}^T. \quad (4.15)$$

This reduces the number of independent components to 21.

Knowing these general symmetry properties of the tensor of elastic constants, the symmetry properties for the elastic stiffness tensor can be deduced from Eq. (4.12). The tensor is still symmetric with respect to an exchange of first and second index and an exchange of the third and fourth index. But it loses its symmetry with respect to the interchange of the index pairs. Only in special cases, for example for a stress free reference configuration or for a system exposed to an initial isotropic pressure, this symmetry is present.

Both the stiffness tensor and the isothermal elastic constants obey in general enough symmetry to be written as a 6x6 matrix. This is done by mapping the first and second index pair to a single index according to the following mapping:

$$\begin{aligned} 11 &\rightarrow 1, & 23 \text{ and } 32 &\rightarrow 4, \\ 22 &\rightarrow 2, & 13 \text{ and } 31 &\rightarrow 5, \\ 33 &\rightarrow 3, & 12 \text{ and } 21 &\rightarrow 6. \end{aligned}$$

This mapping is named after Woldemar Voigt as the Voigt notation. For example, c_{1132} becomes \tilde{c}_{14} in the Voigt notation. We can apply the same transformation to convert the stress and strain tensors to the six-dimensional

vectors

$$\tilde{\sigma} = (\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{23}, \sigma_{13}, \sigma_{12}), \quad (4.16a)$$

$$\tilde{\epsilon} = (\epsilon_{11}, \epsilon_{22}, \epsilon_{33}, 2\epsilon_{23}, 2\epsilon_{13}, 2\epsilon_{12}), \quad (4.16b)$$

with the addition that ϵ_{12} , ϵ_{13} and ϵ_{23} are multiplied by 2. This is necessary to preserve the scalar invariance of the strain energy from Hooke's law

$$U = \sigma_{ij}\epsilon_{ij} = \tilde{\sigma}_k\tilde{\epsilon}_k. \quad (4.17)$$

Then we can write Hooke's law in Voigt notation simply as

$$\tilde{\sigma}_i = \tilde{c}_{ij}\tilde{\epsilon}_j. \quad (4.18)$$

Because of the different general symmetry properties with respect to interchange of index pairs, the isothermal elastic constants in Voigt notation are always represented by a symmetric matrix, while the stiffness tensor is generally not.

At last we remark that the mapping to Voigt notation does not preserve the transformation properties of tensors. This means that care has to be taken with coordinate transformations in Voigt notation. There are other notations, which preserve the transformation properties of tensors [27], for example the Mandel-Kelvin-Notation. However these alter the values of the stiffness tensor components and this makes a comparison with literature values, given mostly in Voigt notation, more difficult.

4.3 Material symmetries

The number of independent components in the stiffness tensor is in general 36 and 21 in the case of isotropic pressure.² This number becomes further reduced if material symmetries are present in the system. The connection between the underlying symmetries and the tensor properties of the system is given by Neumann's principle [28]:

The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal [29].

A systematic way to derive the interdependency between the components of the stiffness tensor (or elastic constants) consists of the following steps:

1. Represent the n symmetry operations of the point group of the crystal as matrices $\mathbf{A}^{(n)}$.
2. Transform the elastic constants with the symmetry operations according to the tensor transformation law

$$c_{ijkl}^{(n)} = A_{ir}^{(n)} A_{js}^{(n)} A_{kp}^{(n)} A_{lq}^{(n)} c_{rspq}. \quad (4.19)$$

²This includes also the stress free state, where the pressure is zero.

3. Equate the former tensor elements with the transformed ones

$$c_{ijkl} = c_{ijkl}^{(n)}. \quad (4.20)$$

From that we obtain several equations, relating the different components. For example, two components can be equal, a component is zero or a component is given by a combination of other tensor elements. The calculations are straightforward, but often result in plenty of equations, many of them being mutually dependent. It is therefore convenient to automate this task with a computer algebra system like Mathematica [30]. An example Mathematica Notebook calculating the structure of the stiffness tensor for a cubic crystal is given in Appendix B. We note that Neumann's principle applies in the same way to the compliance tensor, therefore it always has the same symmetry as the stiffness tensor.

In this work we need the reduced stiffness tensor for two systems, a cubic crystal and a completely isotropic system. The number of independent elements in the cubic system is three and the stiffness tensor in Voigt notation is

$$\begin{pmatrix} \tilde{c}_{11} & \tilde{c}_{12} & \tilde{c}_{12} & 0 & 0 & 0 \\ \tilde{c}_{12} & \tilde{c}_{11} & \tilde{c}_{12} & 0 & 0 & 0 \\ \tilde{c}_{12} & \tilde{c}_{12} & \tilde{c}_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \tilde{c}_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \tilde{c}_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \tilde{c}_{44} \end{pmatrix}. \quad (4.21)$$

The stiffness tensor for a isotropic material is described by two independent elements:

$$\begin{pmatrix} \tilde{c}_{11} & \tilde{c}_{12} & \tilde{c}_{12} & 0 & 0 & 0 \\ \tilde{c}_{12} & \tilde{c}_{11} & \tilde{c}_{12} & 0 & 0 & 0 \\ \tilde{c}_{12} & \tilde{c}_{12} & \tilde{c}_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}(\tilde{c}_{11} - \tilde{c}_{12}) & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}(\tilde{c}_{11} - \tilde{c}_{12}) & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(\tilde{c}_{11} - \tilde{c}_{12}) \end{pmatrix}. \quad (4.22)$$

The form of the stiffness tensors for other crystal symmetry classes can be found in [29].

4.4 Elastic moduli

There is a set of elastic parameters that characterize the response of a material to common experimental setups. These have specific geometrical interpretations and are called the elastic moduli. We want to discuss four of them here, namely the Young's, shear, axial and bulk modulus. For simplicity we suppose a stress free reference configuration, so that σ^0 in Eq. (4.1) vanishes. In this section we use the notational convention that we have no summation over uppercase latin indices in index notation.

4.4.1 Young's modulus

The Young's modulus measures the change in length along the x_i axis, when an uniaxial stress is applied in the same direction. Figure 4.1 shows

an example where a tensile stress $\sigma_{11} = F/A$ is applied in the x_1 direction. This results in a stretch strain ϵ_{11} given by the relative change of length: $\epsilon_{11} = \Delta L/L$.

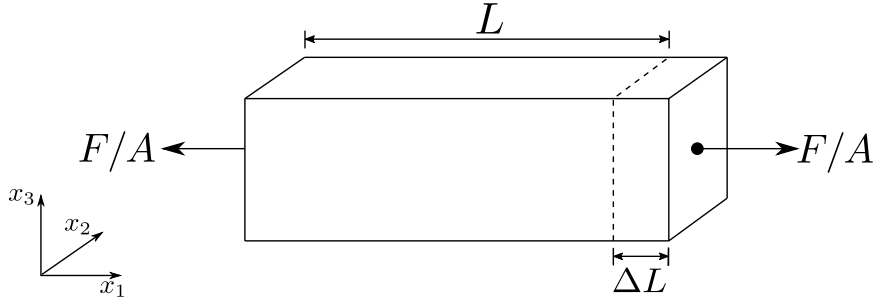


FIGURE 4.1: Illustration of an experiment to measure Young's modulus. The dashed lines show length before the deformation.

Then Young's modulus along the x_1 direction is defined as

$$E_1 = \frac{\sigma_{11}}{\epsilon_{11}}. \quad (4.23)$$

For an anisotropic solid Young's modulus can be different along each principal axis, so we define for the general case

$$E_K = \frac{\sigma_{KK}}{\epsilon_{KK}}. \quad (4.24)$$

The Young's modulus can be related to the compliance tensor as follows. For a uniaxial load σ_{KK} in the x_K direction, the stress tensor becomes

$$\sigma_{ij} = \sigma_{KK} \delta_{Ki} \delta_{Kj}. \quad (4.25)$$

Then the strain ϵ_{KK} is given by Eq. (4.13) as

$$\epsilon_{KK} = s_{KKij} \sigma_{KK} \delta_{Ki} \delta_{Kj} = s_{KKKK} \sigma_{KK}. \quad (4.26)$$

Together with Eq. (4.24), we then obtain

$$E_K = \frac{1}{s_{KKKK}}. \quad (4.27)$$

4.4.2 Shear modulus

The shear modulus is the ratio of shear stress to shear strain for a situation where only shear stress is applied to a body:

$$G_{KL} = \frac{\sigma_{KL}}{\epsilon_{KL}}, \quad L \neq K. \quad (4.28)$$

An example is shown in FIG. 4.2. A force F is applied in the x_1 direction on an area which is normal to the x_3 direction. This results in a shear stress $\sigma_{13} = F/A$. Under this load, the material elements in the area A are displaced by Δx_1 , giving the shear strain $\epsilon_{13} = 2\Delta x_1/L_3$.

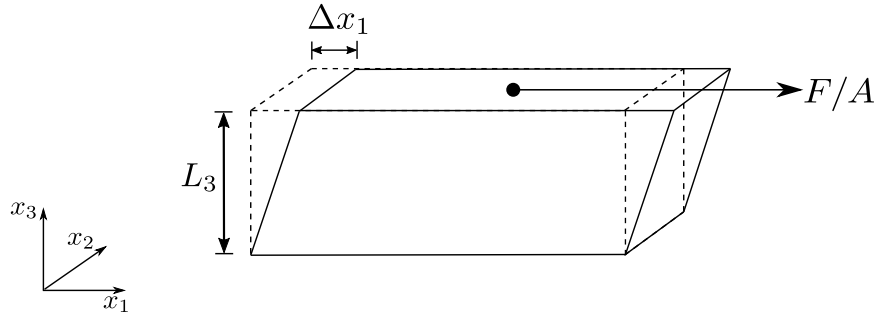


FIGURE 4.2: Illustration of an experiment to measure the shear modulus.

Again we can calculate G_{KL} from the compliance tensor. A pure shear stress in Eq. (4.13) gives the relation

$$2G_{KL} = \frac{1}{s_{KLKL}}, \quad L \neq K. \quad (4.29)$$

4.4.3 Axial modulus

The axial modulus is also known as Poisson's ratio, because it is related to the Poisson effect. This effect describes behavior of many materials, that if they are subject to a tensile or compressive load, they shrink or enlarge in the dimensions perpendicular to the load direction. This is illustrated in FIG. 4.3. The force F is applied parallel to the x_1 axis to the area A , which causes length changes along the x_2 and x_3 axes due to the Poisson effect.

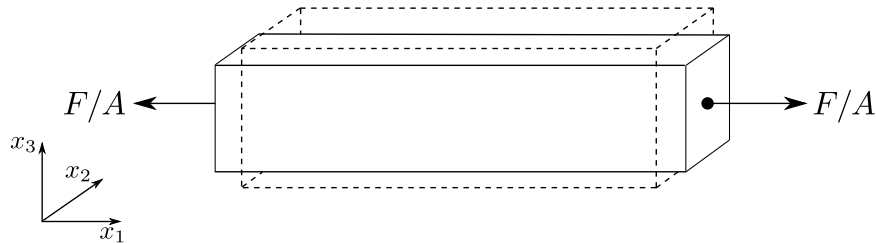


FIGURE 4.3: Illustration of the Poisson effect. The body is shown before (dashed lines) and after the deformation (solid lines).

The axial modulus is defined as the negative of the ratio of strain in load direction ϵ_{KK} and strain perpendicular to it ϵ_{LL} under an uniaxial stress σ_{KK} :

$$\nu_{KL} = -\frac{\epsilon_{KK}}{\epsilon_{LL}}, \quad L \neq K. \quad (4.30)$$

In terms of the compliance tensor, the axial modulus is given by

$$\nu_{KL} = -\frac{s_{KLKL}}{s_{LLLL}}, \quad L \neq K. \quad (4.31)$$

4.4.4 Bulk modulus

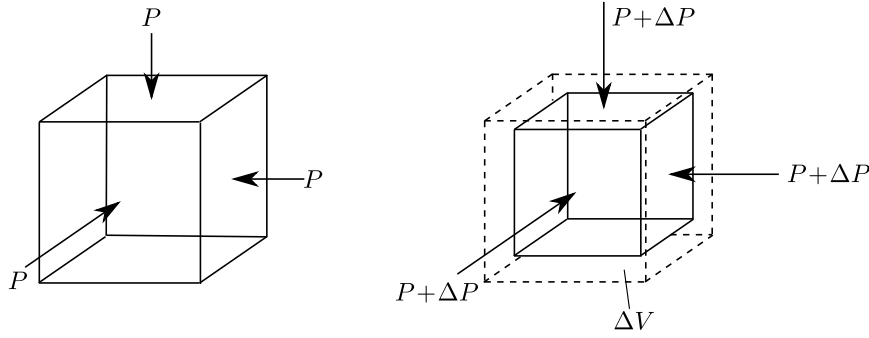


FIGURE 4.4: Illustration of an experiment to measure the bulk modulus.

If a body is under hydrostatic pressure $\sigma_{ij} = -P\delta_{ij}$ and the pressure is increased from P to $P + \Delta P$, its volume will change from V to $V - \Delta V$. Then the bulk modulus is defined as

$$B = -V \frac{\Delta P}{\Delta V}. \quad (4.32)$$

Again using Hooke's law, we can express the bulk modulus in terms of c or s :

$$B = \frac{1}{9} \sum_{i,j} c_{iijj} = \frac{1}{\sum_{i,j} s_{iijj}}. \quad (4.33)$$

4.4.5 Lamé parameters

We already mentioned in the previous section that the elastic response of a homogeneous isotropic material is fully specified by two stiffness or compliance components. This not only means that the elastic moduli for different directions are the same, but also that they are interrelated. This drastically simplifies Eq. (4.1), which can then be written as

$$\sigma_{ij} = \lambda_L \epsilon_{kk} \delta_{ij} + 2\mu_L \epsilon_{ij}, \quad (4.34)$$

where λ_L and μ_L are called Lamé parameters. The derivation of this equation can be found in almost every book on elasticity, see for example Ref. [31]. The Lamé parameters can be expressed in terms of E and ν . For the first parameter one obtains,

$$\lambda_L = \frac{\nu E}{(1 + \nu)(1 - 2\nu)} \quad (4.35)$$

and for the second parameter

$$\mu_L = G = \frac{E}{2(1 + \nu)}. \quad (4.36)$$

We can also express the bulk modulus in terms of the other moduli:

$$B = \lambda_L + \frac{2}{3}\mu_L = \frac{E}{3(1 - 2\nu)}. \quad (4.37)$$

By combining Eq. (4.35), (4.36) and (4.37), it is possible to obtain many more relations between the elastic moduli in an isotropic material. We state here only additional equations if needed and refer the interested reader to [31] for a complete summary.

Chapter 5

Determination of elastic constants in simulations

In this chapter we present several methods for calculating the isothermal elastic constants $C_{\kappa\lambda\mu\nu}$ in Monte Carlo (MC) and Molecular Dynamics (MD) simulations of different statistical ensembles. All methods have in common that the elastic constants are expressed by equilibrium ensemble averages of fluctuations, namely stress-stress, strain-strain and stress-strain fluctuations. Each method has its own advantages and disadvantages, which are discussed in the respective sections and summarized in table 5.1.

5.1 The stress-stress fluctuation formula

The stress-stress fluctuation formula can be used in simulation of the canonical (NVT) ensemble. It consists of three parts. A non-affine part which is proportional to the stress fluctuations and originates from internal relaxations of the particles in the simulation cell. An affine part that is given by the Born-Term known from [7] corresponding to affine deformation of the system without internal relaxation and a kinetic part representing the ideal gas contribution.

The derivation presented here is based on the work of Lutsko in [21]. The main idea is to use a canonical transformation to construct a formalism of evaluating the strain derivatives of ensemble averaged phase space functions. Applying that formalism to the definition of isothermal elastic constants then results in an expression consisting only of equilibrium averages in the canonical ensemble. The first step in this derivation is to shift the implicit size and shape dependence of the phase space volume to an explicit one of phase space functions. Then the second step is to find an expression for evaluating derivatives of the transformed phase space functions with respect to strain, which in the last step can be used to construct a formalism for the strain derivatives of ensemble averaged phase space functions.

We start with the introduction of a canonical transformation to make the phase space volume independent of the size and shape of the simulation box [12]. Starting from the Hamiltonian

$$\hat{H}(\{\mathbf{p}_i, \mathbf{q}_i\}) = \sum_i \frac{\mathbf{p}_i^2}{2m} + U(\{\mathbf{q}_i\}), \quad (5.1)$$

where the caret denotes phase space functions of the particle momenta and coordinates $\{\mathbf{p}_i, \mathbf{q}_i\}$ and U is the system's potential energy. Then the free energy \mathcal{F} is given by

$$\mathcal{F} = -k_B T \ln Z, \quad (5.2)$$

where

$$Z = \int d\mathbf{p}^{3N} d\mathbf{q}^{3N} e^{-\beta \hat{H}(\{\mathbf{p}_i, \mathbf{q}_i\})} \quad (5.3)$$

is the canonical partition function. Now we represent the geometry of the simulation cell, which we restrict to be a parallelepiped, by a matrix $\mathbf{h} = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ where \mathbf{a} , \mathbf{b} and \mathbf{c} are the vectors along the cell edges meeting at the origin. The scaled momenta $\tilde{\mathbf{p}}_i$ and coordinates $\tilde{\mathbf{q}}_i$ are then defined by

$$q_{i,\alpha} = h_{\alpha\beta} \tilde{q}_{i,\beta} \quad \Leftrightarrow \quad \tilde{q}_{i,\alpha} = h_{\alpha\beta}^{-1} q_{i,\beta}, \quad (5.4a)$$

$$p_{i,\alpha} = h_{\alpha\beta}^{-T} \tilde{p}_{i,\beta} \quad \Leftrightarrow \quad \tilde{p}_{i,\alpha} = h_{\alpha\beta}^T p_{i,\beta}, \quad (5.4b)$$

with the following identities (see Appendix A)

$$\frac{\partial q_\alpha}{\partial h_{\nu\xi}} = \delta_{\alpha\nu} h_{\xi\gamma}^{-1} q_\gamma, \quad (5.5a)$$

$$\frac{\partial p_\alpha}{\partial h_{\nu\xi}} = -h_{\xi\alpha}^{-1} p_\nu. \quad (5.5b)$$

This transformation maps the particle coordinates to a unit cube centered at the origin so that $-0.5 \leq \tilde{q}_{i,\alpha} \leq 0.5 \forall i, \alpha$. That removes the shape dependence from the integration borders in Eq. (5.3), which now appears explicitly via the \mathbf{h} dependence of phase space functions, like \hat{H} , on $\{\mathbf{h}^{-T} \tilde{\mathbf{p}}_i, \mathbf{h} \tilde{\mathbf{q}}_i\}$. The new partition function reads

$$Z = \int d\tilde{\mathbf{p}}^{3N} d\tilde{\mathbf{q}}^{3N} e^{-\beta \hat{H}}, \quad (5.6)$$

where the scaled coordinates $\tilde{q}_{i,\alpha}$ are integrated over $[-0.5, +0.5]$.

Having shifted the \mathbf{h} dependence to the phase space functions, our next task is to find an expression for their strain derivatives in terms of derivatives with respect to \mathbf{h} . We do this by calculating the total differential of a phase space function at constant position and momenta.

If the simulation cell is deformed by an infinitesimal homogeneous strain, \mathbf{h} changes from its initial value of \mathbf{h}_0 to $\mathbf{h} = \mathbf{h}_0 + d\mathbf{h}$, which maps a particle coordinate $\mathbf{q}_i = \mathbf{h}_0 \tilde{\mathbf{q}}_i$ in the reference configuration to $\mathbf{q}'_i = \mathbf{h} \tilde{\mathbf{q}}_i = \mathbf{h} \mathbf{h}_0^{-1} \mathbf{q}_i$ in the deformed configuration. Using the definition of the Green-Lagrange strain tensor introduced in section 2.1 we get

$$\eta = \frac{1}{2} \left(\mathbf{h}_0^{-T} \mathbf{h}^T \mathbf{h} \mathbf{h}_0^{-1} - \mathbb{I} \right) \quad (5.7)$$

for the imposed strain and

$$d\eta = \frac{1}{2} \left(\mathbf{h}_0^{-T} d\mathbf{h}^T \mathbf{h} \mathbf{h}_0^{-1} + \mathbf{h}_0^{-T} \mathbf{h}^T d\mathbf{h} \mathbf{h}_0^{-1} \right) \quad (5.8)$$

for an infinitesimal displacement. As discussed in section 2.1 the strain

tensor is symmetric and therefore has only six independent components. But the right hand side of Eq. (5.8) has nine independent components, since some changes of \mathbf{h} correspond to rigid rotations. To account for this fact, we have to subtract the antisymmetric part

$$d\omega = \frac{1}{2} \left(\mathbf{h}_0^{-T} d\mathbf{h}^T \mathbf{h} \mathbf{h}_0^{-1} - \mathbf{h}_0^{-T} \mathbf{h}^T d\mathbf{h} \mathbf{h}_0^{-1} \right) \quad (5.9)$$

of $d\eta$ from Eq. (5.8), leading to the relation

$$\mathbf{h}_0^{-T} d\mathbf{h}^T \mathbf{h} \mathbf{h}_0^{-1} = d\eta + d\omega. \quad (5.10)$$

From matrix calculus we find that for a general function $f(\mathbf{h})$ the total differential is given by

$$\begin{aligned} df &= \text{Tr} \left[\frac{\partial f}{\partial \mathbf{h}} d\mathbf{h}^T \right] \\ &= \text{Tr} \left[\frac{\partial f}{\partial \mathbf{h}} \mathbf{h}_0^T \left(\mathbf{h}_0^{-T} d\mathbf{h}^T \mathbf{h} \mathbf{h}_0^{-1} \right) \mathbf{h}_0 \mathbf{h}^{-1} \right] \\ &= \text{Tr} \left[\mathbf{h}_0 \mathbf{h}^{-1} \frac{\partial f}{\partial \mathbf{h}} \mathbf{h}_0^T (d\eta + d\omega) \right]. \end{aligned} \quad (5.11)$$

Here we inserted in the second line three times the unit matrix

$$\mathbb{I} = \mathbf{h}_0^T \mathbf{h}_0^{-T} = \mathbf{h}_0^{-1} \mathbf{h}_0 = \mathbf{h} \mathbf{h}^{-1} \quad (5.12)$$

and used Eq. (5.10) in the third line. From this follows directly the already symmetrized strain derivative

$$\frac{\partial f}{\partial \eta} = \frac{1}{2} \left[\mathbf{h}_0 \mathbf{h}^{-1} \left(\frac{\partial f}{\partial \mathbf{h}} \right) \mathbf{h}_0^T + \mathbf{h}_0 \left(\frac{\partial f}{\partial \mathbf{h}^T} \right) \mathbf{h}^{-T} \mathbf{h}_0^T \right]. \quad (5.13)$$

If f is a phase space function \hat{A} the derivatives with respect to \mathbf{h} can be evaluated by the chain rule together with Eq. (5.5)

$$\begin{aligned} \frac{\partial \hat{A}}{\partial h_{\alpha\beta}} &= \frac{\partial \hat{A}}{\partial q_{i,\gamma}} \frac{\partial q_{i,\gamma}}{\partial h_{\alpha\beta}} + \frac{\partial \hat{A}}{\partial p_{i,\gamma}} \frac{\partial p_{i,\gamma}}{\partial h_{\alpha\beta}} \\ &= \frac{\partial \hat{A}}{\partial q_{i,\alpha}} h_{\beta\xi}^{-1} q_{i,\xi} - \frac{\partial \hat{A}}{\partial p_{i,\gamma}} h_{\beta\gamma}^{-1} p_{i,\alpha}, \end{aligned} \quad (5.14)$$

which leads to the strain derivative of a phase space function \hat{A}

$$\frac{\partial \hat{A}}{\partial \eta} = \mathbf{h}_0 \mathbf{h} (\mathbf{D}\hat{A}) \mathbf{h}^{-T} \mathbf{h}_0^T, \quad (5.15)$$

where we introduced the matrix valued differential operator

$$D_{\alpha\beta} \hat{A} = \left(q_{i,\alpha} \frac{\partial}{\partial q_{i,\beta}} + q_{i,\beta} \frac{\partial}{\partial q_{i,\alpha}} - p_{i,\alpha} \frac{\partial}{\partial p_{i,\beta}} - p_{i,\beta} \frac{\partial}{\partial p_{i,\alpha}} \right) \hat{A}. \quad (5.16)$$

We are now able to proceed with the next step, the construction of an expression for the strain derivatives of the ensemble average over an arbitrary

phase space function

$$\langle \hat{A} \rangle = \frac{1}{Z} \int d\mathbf{p}^{3N} d\mathbf{q}^{3N} \hat{A} \exp\left(-\frac{\hat{H}}{k_B T}\right). \quad (5.17)$$

We start by calculating the derivative of $\langle \hat{A} \rangle$ with respect to \mathbf{h} :

$$\frac{\partial \langle \hat{A} \rangle}{\partial h_{\alpha\beta}} = \frac{\partial}{\partial h_{\alpha\beta}} \left[\frac{1}{Z} \int d\mathbf{p}^{3N} d\mathbf{q}^{3N} \hat{A} \exp\left(-\frac{\hat{H}}{k_B T}\right) \right]. \quad (5.18)$$

Utilizing the canonical transformation the derivative can be brought inside the integral which leads

$$\frac{\partial \langle \hat{A} \rangle}{\partial h_{\alpha\beta}} = \left\langle \frac{\partial \hat{A}}{\partial h_{\alpha\beta}} \right\rangle - \frac{1}{k_B T} \left[\left\langle \hat{A} \frac{\partial \hat{H}}{\partial h_{\alpha\beta}} \right\rangle - \langle \hat{A} \rangle \left\langle \frac{\partial \hat{H}}{\partial h_{\alpha\beta}} \right\rangle \right], \quad (5.19)$$

where the derivatives with respect to h are given by Eq. (5.14). Combining this result with Eq. (5.13) we obtain

$$\frac{\partial \langle \hat{A} \rangle}{\partial \eta} = \mathbf{h}_0 \mathbf{h}^{-1} \left[\langle \mathbf{D} \hat{A} \rangle - \frac{1}{k_B T} \left(\langle \hat{A} \mathbf{D} \hat{H} \rangle - \langle \hat{A} \rangle \langle \mathbf{D} \hat{H} \rangle \right) \right] \mathbf{h}^{-T} \mathbf{h}_0^T. \quad (5.20)$$

In order to understand the meaning of $D_{\alpha\beta} \hat{H}$, we consider the definition of the thermodynamic tension $\tau_{\alpha\beta}$:

$$V \tau_{\alpha\beta} = \frac{\partial \mathcal{F}}{\partial \eta_{\alpha\beta}} = -k_B T \frac{1}{Z} \frac{\partial Z}{\partial \eta_{\alpha\beta}} \quad (5.21)$$

Again we can make use of the formalism developed in the previous paragraph to evaluate the strain derivative of the partition function which gives

$$\begin{aligned} \tau_{\alpha\beta} &= \frac{1}{V} \left\langle \frac{\partial \hat{H}}{\partial \eta_{\alpha\beta}} \right\rangle \\ &= \frac{1}{V} [\mathbf{h}_0 \mathbf{h}^{-1}]_{\alpha\nu} \langle D_{\nu\xi} \hat{H} \rangle [\mathbf{h}^{-T} \mathbf{h}_0^T]_{\xi\beta} \\ &= \langle \hat{\tau}_{\alpha\beta} \rangle. \end{aligned} \quad (5.22)$$

By evaluating $D_{\nu\xi} \hat{H}$ according to Eq. (5.16) we find that

$$\frac{1}{V} D_{\alpha\beta} \hat{H} = \frac{1}{V} \left(- \sum_i \frac{p_{i,\alpha} p_{i,\beta}}{m} + \sum_i \left[q_{i,\alpha} \frac{\partial U}{\partial q_{i,\beta}} + q_{i,\beta} \frac{\partial U}{\partial q_{i,\alpha}} \right] \right), \quad (5.23)$$

is identical with the bulk microscopic stress tensor $\hat{\sigma}^B$ derived in chapter 3. In the zero strain limit $\mathbf{h} = \mathbf{h}_0$, it follows that $\hat{\tau} = \hat{\sigma}^B$. Combining Eqns. (5.20) and (5.23) leads to the final result of this paragraph

$$\frac{\partial \langle \hat{A} \rangle}{\partial \eta_{\alpha\beta}} = \langle D'_{\alpha\beta} \hat{A} \rangle + \frac{1}{k_B T} V_0 \left(\langle \hat{A} \hat{\tau}_{\alpha\beta} \rangle - \langle \hat{A} \rangle \langle \hat{\tau}_{\alpha\beta} \rangle \right), \quad (5.24)$$

where

$$D'_{\alpha\beta} = [h_0^T h^{-T}]_{\alpha\nu} D_{\nu\xi} [h^{-1} h_0]_{\xi\beta}. \quad (5.25)$$

The elastic constants are defined as

$$C_{\alpha\beta\nu\xi} = \left. \frac{\partial \tau_{\alpha\beta}}{\partial \eta_{\nu\xi}} \right|_{\eta=0} = \left. \frac{\partial \langle \hat{\tau}_{\alpha\beta} \rangle}{\partial \eta_{\nu\xi}} \right|_{\eta=0}. \quad (5.26)$$

Applying the developed formalism of strain derivatives to Eq. (5.23) results in the zero strain limit in

$$\begin{aligned} C_{\alpha\beta\nu\xi} = & -\frac{V_0}{k_B T} (\langle \hat{\sigma}_{\alpha\beta}^B \hat{\sigma}_{\nu\xi}^B \rangle - \langle \hat{\sigma}_{\alpha\beta}^B \rangle \langle \hat{\sigma}_{\nu\xi}^B \rangle) + \langle D_{\nu\xi} \hat{\sigma}_{\alpha\beta}^B \rangle \\ & + \frac{1}{2} (\delta_{\beta\xi} \langle \hat{\sigma}_{\alpha\nu}^B \rangle + \delta_{\alpha\xi} \langle \hat{\sigma}_{\beta\nu}^B \rangle + \delta_{\beta\nu} \langle \hat{\sigma}_{\alpha\xi}^B \rangle + \delta_{\alpha\nu} \langle \hat{\sigma}_{\beta\xi}^B \rangle), \end{aligned} \quad (5.27)$$

where the explicit stress terms are due to the dependence of thermodynamic tensions $\hat{\tau}$ on the scaling matrix \mathbf{h} . This expression can be written in a different form by introducing the so called Born term

$$\hat{B}_{\kappa\lambda\mu\nu} = \frac{1}{4} (B'_{\kappa\lambda\mu\nu} + B'_{\lambda\kappa\mu\nu} + B'_{\kappa\lambda\nu\mu} + B'_{\lambda\kappa\nu\mu}), \quad (5.28)$$

where

$$\begin{aligned} \hat{B}'_{\kappa\lambda\mu\nu} = & \frac{1}{V} \sum_{i,j} \left(q_{i,\lambda} q_{j,\nu} \frac{\partial U}{\partial q_{j,\mu} \partial q_{i,\kappa}} + \delta_{\lambda\nu} \delta_{ij} q_{i,\mu} \frac{\partial U}{\partial q_{i,\kappa}} \right) \\ & + 2\delta_{\lambda\nu} \hat{\sigma}_{\kappa\mu}^B. \end{aligned} \quad (5.29)$$

This leads to a more compact expression of Eq. (5.27):

$$\begin{aligned} C_{\alpha\beta\nu\xi} = & 2k_B T \rho (\delta_{\alpha\nu} \delta_{\beta\xi} + \delta_{\alpha\xi} \delta_{\beta\nu}) \\ & - \frac{V_0}{k_B T} \langle \Delta \hat{\sigma}_{\alpha\beta}^B \Delta \hat{\sigma}_{\nu\xi}^B \rangle \\ & + \langle \hat{B}_{\alpha\beta\nu\xi} \rangle, \end{aligned} \quad (5.30)$$

where $\rho = N/V$ is the number density and $\Delta \hat{\sigma}_{\alpha\beta}^B = \hat{\sigma}_{\alpha\beta}^B - \langle \hat{\sigma}_{\alpha\beta}^B \rangle$.

5.1.1 Local elastic constants

In chapter 3 we obtained a local form of the microscopic stress tensor. This can be used to derive a local version of the stress-stress fluctuation formula [21]. Again we restrict ourselves to homogeneous deformations and describe the simulation by the same scaling matrix as in the previous sections, where a point \mathbf{r} in the initial configuration is mapped to a point \mathbf{r}' by $\mathbf{r}' = \mathbf{h}\mathbf{h}_0^{-1}\mathbf{r}$. The strain is again given by Eq. (5.7). But this time the local elastic constants are defined as

$$C_{\kappa\lambda\mu\nu}(\mathbf{r}) = \left. \frac{\partial \tau_{\kappa\lambda}(\mathbf{r}')}{\partial \eta_{\mu\nu}} \right|_{\mathbf{r}' = \mathbf{h}\mathbf{h}_0^{-1}\mathbf{r}}, \quad (5.31)$$

where the local thermodynamic tensions are given by

$$\tau_{\kappa\lambda}(\mathbf{r}) = |\det \mathbf{J}| J_{\kappa\mu}^{-1} \langle \hat{\sigma}_{\mu\nu}(\mathbf{r}) \rangle J_{\mu\lambda}^{-T}. \quad (5.32)$$

Here the derivative is taken at constant \mathbf{r} so that variation due to inhomogeneity of the material do not enter into $C_{\kappa\lambda\mu\nu}(\mathbf{r})$. To execute the strain derivative we can again employ the formalism developed earlier in this chapter. Then the final result, a fluctuation formula for the local elastic constants, follows to be

$$\begin{aligned}
C_{\kappa\lambda\mu\nu}(\mathbf{r}) = & 2k_{\text{B}}T \langle \hat{\rho}(\mathbf{r}) \rangle \left(\delta_{\kappa\mu}\delta_{\lambda\nu} + \delta_{\kappa\nu}\delta_{\lambda\mu} \right) \\
& - \frac{V_0}{k_{\text{B}}T} \left(\langle \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \hat{\sigma}_{\mu\nu}^{\text{B}} \rangle - \langle \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \rangle \langle \hat{\sigma}_{\mu\nu}^{\text{B}} \rangle \right) \\
& + \left\langle \sum_{i<j} \left(\frac{\partial^2 U}{\partial q_{ij}^2} - \frac{1}{q_{ij}} \frac{\partial U}{\partial q_{ij}} \right) \frac{q_{ij,\kappa} q_{ij,\lambda} q_{ij,\mu} q_{ij,\nu}}{q_{ij}^2} w(\mathbf{q}_i, \mathbf{q}_j, \mathbf{r}) \right\rangle,
\end{aligned} \tag{5.33}$$

where $w(\mathbf{q}_i, \mathbf{q}_j, \mathbf{r})$ the weighting function from Eq. (3.20) and $\hat{\rho}(\mathbf{r})$ is the local number density defined as

$$\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{q}_i). \tag{5.34}$$

We note that because of the restriction to two-body forces in the derivation of the local stress tensor in chapter 3, the last term in Eq. (5.33) is the local version of the Born term defined in Eq. (5.28) for the special case of pairwise interactions.

5.1.2 Transforming to the isothermal-isobaric ensemble

The motivation to apply the stress-stress fluctuation formula in simulations of the isothermal-isobaric TPN ensemble is that it corresponds more to a usual experimental set up. Often it is even not feasible to do experiments at strictly fixed volume. On the other hand, if we want to investigate the pressure dependence of the elastic constants, we would first have to determine the volume (or density) corresponding to a given pressure in the TPN ensemble, and then do an additional simulation in the TVN ensemble to calculate the elastic constants. This step can be skipped, if we could employ the stress-stress fluctuation formula in the TPN ensemble directly. But using the stress-stress fluctuation formula in this ensemble is not straightforward. The reason for this is, that fluctuations in different ensembles are not the same, even in the thermodynamic limit as has been shown by Lebowitz, Percus and Verlet in [32]. Hence we derive here the necessary correction term, which will turn out to be proportional to the bulk modulus. We do not introduce the theoretical background for the general formalism of transforming between ensembles here, instead we apply it directly to a transformation from the canonical to the isothermal-isobaric ensemble. For an introduction to the general formalism we refer the reader to [33].

If we transform from an ensemble where the intensive variable G is fixed, to an ensemble where the energetically conjugated intensive variable g is constant, then the covariances of two variables \hat{A} and \hat{B} in the different ensembles are related by [32]

$$\langle \Delta \hat{A} \Delta \hat{B} \rangle_G = \langle \Delta \hat{A} \Delta \hat{B} \rangle_g + \left(\frac{\partial g}{\partial G} \right) \left(\frac{\partial}{\partial g} \langle \hat{A} \rangle_g \right) \left(\frac{\partial}{\partial g} \langle \hat{B} \rangle_g \right), \tag{5.35}$$

where the subscript of the ensemble average denotes the fixed quantity. The ensemble dependence of fluctuations explicitly affects the stress-stress covariance in Eq. (5.27), but not the Born and kinetic term since they are behaving well enough (cf. Eq. (1.6) in [32]). The conjugate pair for a switch from canonical to isothermal-isobaric ensemble is $(V, \beta P)$. where $\beta = 1/k_B T$ is the inverse temperature and P the pressure. Applying Eq. (5.35) with $(V, \beta P)$ to the stress-stress covariance in Eq. (5.27) leads to

$$\begin{aligned} \langle \Delta \hat{\sigma}_{\kappa\lambda}^B \Delta \hat{\sigma}_{\mu\nu}^B \rangle_V &= \langle \Delta \hat{\sigma}_{\kappa\lambda}^B \Delta \hat{\sigma}_{\mu\nu}^B \rangle_P \\ &+ \frac{1}{\beta} \left(\frac{\partial P}{\partial V} \right) \\ &\times \left(\frac{\partial}{\partial P} \langle \hat{\sigma}_{\kappa\lambda}^B \rangle_P \right) \\ &\times \left(\frac{\partial}{\partial P} \langle \hat{\sigma}_{\mu\nu}^B \rangle_P \right), \end{aligned} \quad (5.36)$$

We are now left with the calculation of the three factors in the second term on the right hand side. The first factor is related to the bulk modulus K by

$$\frac{\partial P}{\partial V} = -\frac{K}{V}. \quad (5.37)$$

Since we are interested in the determination of elastic constants in simulations, we need a way to compute the bulk modulus in the TPN ensemble. For this we start with the inverse relationship of Eq. (5.37) and replace the volume by its ensemble average:

$$\frac{1}{K} = -\frac{1}{\langle V \rangle_P} \frac{\partial \langle V \rangle_P}{\partial P}. \quad (5.38)$$

Here the isothermal-isobaric ensemble average of a quantity \hat{A} is given by

$$\langle \hat{A} \rangle_P = \frac{1}{\tilde{Z}} \int_0^\infty dV \int dp^{3N} dq^{3N} e^{-\beta(PV + \hat{H})} \hat{A}, \quad (5.39)$$

where the partition functions \tilde{Z} and Z of the TPN and TVN ensemble are related by the Laplace transformation

$$\tilde{Z}(T, P, N) = \int_0^\infty dV e^{-\beta PV} Z(T, V, N). \quad (5.40)$$

Now we can directly take the derivative with respect to P , invert the expression again and obtain

$$K = \frac{1}{\beta} \frac{\langle V \rangle_P}{\langle V^2 \rangle_P - \langle V \rangle_P^2} = \frac{1}{\beta} \frac{\langle V \rangle_P}{\langle (\Delta V)^2 \rangle_P}. \quad (5.41)$$

Now we have to deal with the second and third factor in Eq. (5.36). Using the relation between thermodynamic tensions and the stress tensor Eq. (2.34) in combination with Eq. (5.22) leads to

$$\hat{\sigma}_{\kappa\lambda}^B = \frac{1}{\det \mathbf{J}} J_{\kappa\gamma} J_{\xi\lambda}^T \frac{1}{V_0} \left\langle \frac{\partial \hat{H}}{\partial \eta_{\gamma\xi}} \right\rangle_V, \quad (5.42)$$

where, like in the previous section, we assume that the simulation box is described by a scaling matrix \mathbf{h} and the Jacobi matrix is $J_{\kappa\lambda} = h_{\kappa\nu} h_{0,\nu\lambda}^{-1}$. The isothermal-isobaric ensemble average of $\hat{\sigma}^B$ is given by

$$\langle \hat{\sigma}_{\kappa\lambda}^B \rangle_P = \frac{1}{\bar{Z}} \int_0^\infty dV e^{-\beta PV} \int dp^{3N} dq^{3N} e^{-\beta \hat{H}} \frac{\partial \hat{H}}{\partial \eta_{\gamma\xi}} \frac{1}{V_0 \det \mathbf{J}} J_{\kappa\gamma} J_{\xi\lambda}^T. \quad (5.43)$$

By writing the inner integrand as

$$e^{-\beta \hat{H}} \frac{\partial \hat{H}}{\partial \eta_{\kappa\lambda}} = -\frac{1}{\beta} \frac{\partial}{\partial \eta_{\kappa\lambda}} e^{-\beta \hat{H}}, \quad (5.44)$$

we can pull the derivative out the inner integral and identify the remaining integral as the canonical partition function:

$$\langle \hat{\sigma}_{\kappa\lambda}^B \rangle_P = -\frac{1}{\bar{Z}} \int_0^\infty dV e^{-\beta PV} \frac{1}{\beta} \frac{1}{V_0 \det \mathbf{J}} J_{\kappa\gamma} J_{\xi\lambda}^T \frac{\partial}{\partial \eta_{\gamma\xi}} Z(T, V, N). \quad (5.45)$$

The canonical partition function is dependent on the strain tensor through the volume V . So we can apply the chain rule

$$\frac{\partial Z(T, V, N)}{\partial V} \frac{\partial V}{\partial \eta_{\gamma\xi}} = \frac{\partial Z(T, V, N)}{\partial V} V_0 \det \mathbf{J} J_{\gamma\mu}^{-1} J_{\mu\xi}^{-T}, \quad (5.46)$$

where we used the fact that $V = V_0 \det \mathbf{J}$ and $J_{\kappa\lambda} = h_{\kappa\nu} h_{0,\nu\lambda}^{-1}$ in combination with Eq. (5.14). Inserting Eq. (5.46) in (5.45) then leads to

$$\langle \hat{\sigma}_{\kappa\lambda}^B \rangle_P = -\frac{1}{\bar{Z}} \int_0^\infty dV e^{-\beta PV} \frac{1}{\beta} \frac{\partial Z(T, V, N)}{\partial V} \delta_{\kappa\lambda}. \quad (5.47)$$

If we integrate by parts we obtain

$$\begin{aligned} \langle \hat{\sigma}_{\kappa\lambda}^B \rangle_P &= -\delta_{\kappa\lambda} \left(\frac{1}{\bar{Z}} \left[\frac{1}{\beta} e^{-\beta PV} Z(T, V, N) \right]_0^\infty \right. \\ &\quad \left. - \frac{1}{\bar{Z}} \int_0^\infty dV Z(T, V, N) \frac{1}{\beta} \frac{\partial}{\partial V} e^{-\beta PV} \right), \end{aligned} \quad (5.48)$$

where the first term in the brackets is zero and after executing the derivative, the integral in the second term becomes $P\bar{Z}$. Finally we obtain for the ensemble average of the stress tensor

$$\langle \hat{\sigma}_{\kappa\lambda}^B \rangle_P = -P\delta_{\kappa\lambda}. \quad (5.49)$$

Combining this result with Eqns. (5.36) and (5.37), the relation between the stress-stress covariance in the TVN and TPN ensemble is given by

$$\langle \Delta \hat{\sigma}_{\kappa\lambda}^B \Delta \hat{\sigma}_{\mu\nu}^B \rangle_V = \langle \Delta \hat{\sigma}_{\kappa\lambda}^B \Delta \hat{\sigma}_{\mu\nu}^B \rangle_P - \frac{k_B T}{\langle V \rangle_P} K \delta_{\kappa\lambda} \delta_{\mu\nu}, \quad (5.50)$$

where the bulk modulus K can be calculated from the volume fluctuations of the simulation box by Eq. (5.41). Additionally we have to substitute in Eq. (5.30) the reference volume V_0 and number density ρ by the average volume $\langle V \rangle_P$ and average number density $\langle \rho \rangle_P$, so get in total for the bulk

elastic constants

$$\begin{aligned}
C_{\kappa\lambda\mu\nu} &= 2k_{\text{B}}T \langle \hat{\rho} \rangle_P (\delta_{\kappa\mu}\delta_{\lambda\nu} + \delta_{\kappa\nu}\delta_{\lambda\mu}) \\
&\quad - \frac{\langle V \rangle_P}{k_{\text{B}}T} \langle \Delta \hat{\sigma}_{\kappa\lambda}^{\text{B}} \Delta \hat{\sigma}_{\mu\nu}^{\text{B}} \rangle_P \\
&\quad + \langle \hat{B}_{\kappa\lambda\mu\nu} \rangle_P + K \delta_{\kappa\lambda} \delta_{\mu\nu}.
\end{aligned} \tag{5.51}$$

If we want to determine local elastic constants, we have to use Eq. (5.33) and thus have to calculate the correction term for the covariance between local and bulk stresses:

$$\begin{aligned}
\langle \Delta \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \Delta \hat{\sigma}_{\mu\nu}^{\text{B}} \rangle_V &= \langle \Delta \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \Delta \hat{\sigma}_{\mu\nu}^{\text{B}} \rangle_P \\
&\quad + \frac{1}{\beta} \left(\frac{\partial P}{\partial V} \right) \\
&\quad \times \left(\frac{\partial}{\partial P} \langle \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \rangle_P \right) \\
&\quad \times \left(\frac{\partial}{\partial P} \langle \hat{\sigma}_{\mu\nu}^{\text{B}} \rangle_P \right).
\end{aligned} \tag{5.52}$$

Two of the factors in Eqns. (5.36) and (5.52) are the same. So we only have to compute

$$\frac{\partial}{\partial P} \langle \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \rangle_P, \tag{5.53}$$

which can be done with Eq. (5.39) in straightforward way, because $\hat{\sigma}_{\kappa\lambda}(\mathbf{r})$ is only a function of particle coordinates and momenta and not explicitly dependent on P :

$$\begin{aligned}
\frac{\partial}{\partial P} \langle \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \rangle_P &= \frac{\partial}{\partial P} \left(\frac{1}{\tilde{Z}} \int_0^\infty dV \int dp^{3N} dq^{3N} e^{-\beta(PV+\hat{H})} \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \right) \\
&= -\frac{1}{\tilde{Z}} \frac{\partial \tilde{Z}}{\partial P} \frac{1}{\tilde{Z}} \int_0^\infty dV \int dp^{3N} dq^{3N} e^{-\beta(PV+\hat{H})} \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \\
&\quad + \frac{1}{\tilde{Z}} \int_0^\infty dV \int dp^{3N} dq^{3N} e^{-\beta(PV+\hat{H})} \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) (-\beta V) \\
&= -\frac{1}{\tilde{Z}} \frac{\partial \tilde{Z}}{\partial P} \langle \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \rangle_P - \beta \langle \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) V \rangle_P.
\end{aligned} \tag{5.54}$$

Together with $\partial \tilde{Z} / \partial P = -\beta \tilde{Z} \langle V \rangle_P$ we obtain

$$\frac{\partial}{\partial P} \langle \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \rangle_P = -\beta (\langle \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) V \rangle_P - \langle \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \rangle_P \langle V \rangle_P), \tag{5.55}$$

which is the correlation between the local stress tensor and the bulk volume of the system and leads in combination with Eqns. (5.49) and (5.37) to the local ensemble transformation correction term

$$\langle \Delta \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \Delta \hat{\sigma}_{\mu\nu}^{\text{B}} \rangle_V = \langle \Delta \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \Delta \hat{\sigma}_{\mu\nu}^{\text{B}} \rangle_P - \frac{K}{V} \delta_{\mu\nu} \langle \Delta \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \Delta V \rangle_P. \tag{5.56}$$

Incorporating this term in the local stress-stress fluctuation formula in Eq. (5.33) gives the final result for the local elastic constants in the TPN ensemble:

$$\begin{aligned}
C_{\kappa\lambda\mu\nu}(\mathbf{r}) = & 2k_{\text{B}}T \langle \hat{\rho}(\mathbf{r}) \rangle \left(\delta_{\kappa\mu} \delta_{\lambda\nu} + \delta_{\kappa\nu} \delta_{\lambda\mu} \right) \\
& - \frac{\langle V \rangle}{k_{\text{B}}T} \left\langle \Delta \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \Delta \hat{\sigma}_{\mu\nu}^{\text{B}} \right\rangle + \frac{K}{k_{\text{B}}T} \delta_{\mu\nu} \left\langle \Delta \hat{\sigma}_{\kappa\lambda}(\mathbf{r}) \Delta V \right\rangle \\
& + \left\langle \sum_{i < j} \left(\frac{\partial^2 U}{\partial q_{ij}^2} - \frac{1}{q_{ij}} \frac{\partial U}{\partial q_{ij}} \right) \frac{q_{ij,\kappa} q_{ij,\lambda} q_{ij,\mu} q_{ij,\nu}}{q_{ij}^2} w(\mathbf{q}_i, \mathbf{q}_j, \mathbf{r}) \right\rangle \quad (5.57)
\end{aligned}$$

5.2 The strain-strain fluctuation formula

The strain-strain fluctuation formula [11] can be used in the $T\tau N$ (isothermal elastic constants) or in the $\mathcal{H}\tau N$ (adiabatic elastic constants). It can be derived directly from the Fluctuation-Dissipation-Theorem [34]:

$$k_{\text{B}}T \chi_{AB} = \langle \Delta A \Delta B \rangle, \quad (5.58)$$

where χ_{AB} is the response function of a observable quantity A with respect to some perturbation, whose conjugated variable is B . $\Delta A = A - \langle A \rangle$ and $\Delta B = B - \langle B \rangle$ are the deviation of A and B from their average values and $\langle \dots \rangle$ denotes the equilibrium ensemble average. Since we are interested in the change of strain with respect to small applied stresses, the response function is taken to be

$$\chi_{AB} = \frac{\partial \eta_{ij}}{\partial \tau_{kl}} = s_{ijkl}. \quad (5.59)$$

Our observable of interest is $A = \eta_{ij}$ and from the analysis of the corresponding thermodynamic potential (enthalpy for the adiabatic compliances and Gibbs free energy for the isothermal compliances), we find that the conjugated observable to τ_{kl} is $V \eta_{kl}$, where V is the volume of the system. Putting it all together we obtain the strain-strain fluctuation formula:

$$s_{ijkl} = \frac{k_{\text{B}}T}{\langle V \rangle} \langle \eta_{ij} \eta_{kl} \rangle. \quad (5.60)$$

Here we assumed a strain free reference configuration and replaced the macroscopic volume by its ensemble average. If we express the size and shape of the simulation box like in the previous sections with a matrix \mathbf{h} , the strain tensor in a variable shape ensemble is given by

$$\eta_{ik} = \frac{1}{2} \left(h_{nl} \langle h \rangle_{lk}^{-1} h_{np} \langle h \rangle_{pi}^{-1} - \delta_{ik} \right), \quad (5.61)$$

where $\langle h \rangle$ is the ensemble average of the scaling matrix \mathbf{h} . By tensor inversion we get the equivalent form for the stiffness tensor

$$c_{ijkl} = \frac{k_{\text{B}}T}{\langle V \rangle} \langle \eta_{ij} \eta_{kl} \rangle^{-1}. \quad (5.62)$$

So it is possible to calculate the stiffnesses from the size and shape fluctuations of the simulation box, without putting in any information about

the particle interactions in the system. This is in contrast to the stress-stress fluctuation formula, which is based on the knowledge of the first and second derivative of the potential energy. Thus it can be an advantage to use the strain-strain fluctuation formula for example in Monte Carlo simulations with tabulated pseudo-potentials obtained from *ab initio* calculation, where a numerical differentiation of the potential is infeasible. On the downside this simplicity comes at the cost of much poorer convergence properties [35].

5.3 The stress-strain fluctuation formula

The stress-strain fluctuation formula [35] is applicable in the same ensembles as the strain-strain fluctuation formula. It is an attempt to improve the convergence properties by the use of the first order derivatives of the potential (forces) through the stress tensor, since in MD simulation the forces are usually known. This works especially well in the low temperature regime [36].

We start by applying the generalized equipartition theorem [37] to the strain tensor

$$\left\langle \eta_{\alpha\beta} \frac{\partial \hat{H}}{\partial \eta_{\nu\xi}} \right\rangle = k_{\text{B}} T \delta_{\alpha\nu} \delta_{\beta\xi}, \quad (5.63)$$

that holds in the canonical ensemble and is an $\mathcal{O}(1/N)$ approximation in any ensemble. The Hamiltonian \hat{H} has the form

$$\hat{H} = \sum_i \frac{p_i^2}{2m_i} + U(\{q_{ab}\}). \quad (5.64)$$

where the potential energy U is assumed to depend only on the relative distances q_{ab} between the particles a and b . We now have to derive \hat{H} with respect to η . To do this, we restrict the deformations to be homogeneous. Then Eq. (2.4) does not only hold for infinitesimal line elements, but also for finite line elements, leading to

$$l'^2 = l^2 + 2\eta_{\alpha\beta} \overset{\circ}{x}_\alpha \overset{\circ}{x}_\beta, \quad (5.65)$$

where $\overset{\circ}{x}_i$ are the components of the line element l in the reference configuration. If we differentiate both sites with respect to η_{ij} , we obtain

$$\frac{\partial l'}{\partial \eta_{\alpha\beta}} = \frac{\overset{\circ}{x}_\alpha \overset{\circ}{x}_\beta}{l'}. \quad (5.66)$$

Since coordinates under a homogeneous deformation, with an instant scaling matrix \mathbf{h} from a reference configuration with average scaling matrix $\mathbf{h}_0 = \langle \mathbf{h} \rangle$, are related by $\overset{\circ}{x}_\alpha = h_{0,\alpha\beta} h_{\beta\gamma}^{-1} x_\gamma$, we arrive after combining Eqs. (5.63),

(5.64) and (5.66) at:

$$\begin{aligned}
& \left\langle \eta_{\alpha\beta} \left(\sum_a \frac{h_{0,\nu\gamma} h_{\gamma\sigma}^{-1} p_{a,\sigma} h_{0,\xi\mu} h_{\mu\lambda}^{-1} p_{a,\lambda}}{m_a} \right. \right. \\
& \quad \left. \left. + \sum_{a>b} \frac{\partial U}{\partial q_{ab}} \frac{h_{0,\nu\gamma} h_{\gamma\sigma}^{-1} q_{ab,\sigma} h_{0,\xi\mu} h_{\mu\lambda}^{-1} q_{ab,\lambda}}{q_{ab}} \right) \right\rangle \\
& = \frac{1}{2} k_B T (\delta_{\alpha\nu} \delta_{\beta\xi} + \delta_{\alpha\xi} \delta_{\beta\nu}). \tag{5.67}
\end{aligned}$$

Inserting Eq. (5.67) in (5.62) then leads to the stress-strain fluctuation formula:

$$c_{\alpha\beta\nu\xi} = \langle \eta_{\alpha\beta} \hat{\tau}_{\gamma\mu} \rangle \langle \eta_{\gamma\mu} \eta_{\nu\xi} \rangle^{-1}. \tag{5.68}$$

Here we identified $h_{0,\alpha\beta} h_{\beta\gamma}^{-1}$ in Eq. (5.67) as the inverse of the Jacobi matrix $J_{\alpha\gamma}^{-1}$, compared with the definitions of thermodynamic tensions and the microscopic stress tensor and so obtained the compact form of Eq. (5.68).

The reason why the stress-strain fluctuation formula has better convergence properties than the strain-strain fluctuation formula is the correlation of stresses and strains. This is most obvious in the low temperature regime, where the entropic contributions are negligible and the instantaneous stresses and strains are directly related by Hooke's law [35]. Additionally one can benefit from the use of Eq. (5.67) as a convergence criterion [36].

5.4 Summary of fluctuation formulas

Here we briefly summarize in table 5.1 the important points of the different fluctuation formulas outlined in this chapter.

Stress-stress fluctuation formula	
Ensemble for adiabatic EC	EVN
Ensemble for isothermal EC	TVN, TPN
Advantages:	<ul style="list-style-type: none"> • Good convergence • Local elastic constants
Disadvantages:	<ul style="list-style-type: none"> • First and second derivative of the potential needed • Computationally expensive
Strain-strain fluctuation formula	
Ensemble for adiabatic EC	$\mathcal{H}\tau N$
Ensemble for isothermal EC	$T\tau N$
Advantages:	<ul style="list-style-type: none"> • No information of the potential needed • Computationally cheap
Disadvantages:	<ul style="list-style-type: none"> • Poor convergence compared to stress-stress fluctuation formula
Stress-strain fluctuation formula	
Ensemble for adiabatic EC	$\mathcal{H}\tau N$
Ensemble for isothermal EC	$T\tau N$
Advantages:	<ul style="list-style-type: none"> • Better convergence than strain-strain fluctuation formula at low temperatures • Convergence criterion
Disadvantages:	<ul style="list-style-type: none"> • Poor convergence compared to stress-stress fluctuation formula

TABLE 5.1: Summary of the different fluctuation formulas.

Chapter 6

Example applications

In this chapter we apply the stress-stress fluctuation formula to two systems and compare the results in the TVN and TPN ensemble. The first system is the ideal gas, which can be treated analytically. The second system is a nearest-neighbor Lennard-Jones FCC crystal, that is investigated with Monte Carlo simulations and has been heavily studied in the literature [8, 38, 39, 13, 35, 40]. For later reference we divide the stress-stress fluctuation formula in Eq. (5.27) in three terms:

$$C_{\kappa\lambda\mu\nu} = C_{\kappa\lambda\mu\nu}^{\text{B}} - C_{\kappa\lambda\mu\nu}^{\text{N}} + C_{\kappa\lambda\mu\nu}^{\text{K}} \quad (6.1)$$

where

$$\begin{aligned} C_{\kappa\lambda\mu\nu}^{\text{B}} &= \langle \hat{B}_{\kappa\lambda\mu\nu} \rangle, \\ C_{\kappa\lambda\mu\nu}^{\text{N}} &= \frac{V}{k_{\text{B}}T} \left(\langle \hat{\Sigma}_{\kappa\lambda} \hat{\Sigma}_{\mu\nu} \rangle - \langle \hat{\Sigma}_{\kappa\lambda} \rangle \langle \hat{\Sigma}_{\mu\nu} \rangle \right), \\ C_{\kappa\lambda\mu\nu}^{\text{K}} &= 2k_{\text{B}}T\rho (\delta_{\kappa\mu}\delta_{\lambda\nu} + \delta_{\kappa\nu}\delta_{\lambda\mu}). \end{aligned} \quad (6.2)$$

6.1 The ideal gas

The ideal gas is the typical textbook example that can be found in almost every book on statistical mechanics. The reason for this is, that the partition function can be calculated analytically and hence all thermodynamic observables. At first glance it seems unusual to examine a gas in the context of elasticity, but we point out that a gas has an important elastic property, namely its compressibility, which is the inverse of the bulk modulus. One can determine the structure of the stiffness tensor for a gas with the following argumentation. A gas can be considered as an isotropic body without a shear modulus $\mu_{\text{L}} = 0$, then the simplified version of Hooke's law in Eq. (4.34) reduces further to:

$$\sigma_{\kappa\lambda} = \lambda_{\text{L}}\epsilon_{\nu\nu}\delta_{\kappa\lambda} = \lambda_{\text{L}}\delta_{\kappa\lambda}\delta_{\mu\nu}\epsilon_{\mu\nu}. \quad (6.3)$$

The stress tensor of a gas is simply $\sigma_{\lambda\kappa} = -\Delta P\delta_{\kappa\lambda}$, where ΔP measures the pressure deviation from a pressure P_0 in an reference configuration with volume V_0 . Additionally we know that for a strain measured from the same reference configuration we have $\epsilon_{\nu\nu} = \Delta V/V_0$. If we substitute this in Eq. (6.3) and rearrange the factors, we obtain

$$\lambda_{\text{L}} = -V_0 \frac{\Delta P}{\Delta V}, \quad (6.4)$$

which is the definition of the bulk modulus, so we have $\lambda_L = K$. Finally by comparison with the general form of Hooke's law we can deduce the stiffness tensor for a gas

$$c_{\kappa\lambda\mu\nu} = K\delta_{\kappa\lambda}\delta_{\mu\nu}, \quad (6.5)$$

that can be compared with the results obtained by the microscopic theory.

Before we start with the calculations of stress-stress fluctuation formula, we quickly review some properties of the ideal gas. The Hamiltonian is given by

$$\hat{H} = \sum_i \frac{p_{i,\alpha} p_{i,\alpha}}{2m}, \quad (6.6)$$

where the N gas particles with mass m are confined in a cubic box with edge length L . Then the canonical partition function is

$$Z = \int dp^{3N} dq^{3N} e^{-\beta\hat{H}} = V^N \lambda_{\text{th}}^{3N}, \quad (6.7)$$

where $V = L^3$ is the volume of the box and $\lambda_{\text{th}} = \sqrt{2\pi m k_B T}$ is the thermal de Broglie wavelength. Here we omitted the prefactor which renders the partition function dimensionless and accounts for quantum corrections, since it will not contribute to the final outcome. The partition function \tilde{Z} in the isothermal-isobaric ensemble can be calculated by Eq. (5.40):

$$\tilde{Z} = \lambda_{\text{th}}^{3N} \int_0^\infty dV e^{-\beta PV} V^N = \lambda_{\text{th}}^{3N} (\beta P)^{-(N+1)} N!, \quad (6.8)$$

where we used the fact that for all positive integers N the gamma function $\Gamma(N+1) = N!$. The equation of state (ideal gas law) can be derived by differentiating the free energy, which is given through the canonical partition function by $\mathcal{F} = -k_B T \ln Z$, with respect to volume:

$$P = -\frac{\partial \mathcal{F}}{\partial V} = k_B T \frac{\partial \ln Z}{\partial V} = \frac{k_B T N}{V}. \quad (6.9)$$

From the ideal gas law, we can compute the bulk modulus by its definition from macroscopic thermodynamics

$$K = -V \left(\frac{\partial P}{\partial V} \right)_T = \frac{k_B T N}{V} = P. \quad (6.10)$$

Now we want to calculate the stiffness tensor with the stress-stress fluctuation formula first in the TVN ensemble. Since there is no interaction between the ideal gas particles the Born term in Eq. (6.1) is obviously zero. Thus we only have to calculate $C_{\kappa\lambda\mu\nu}^N$. For the ideal gas the microscopic bulk stress tensor is given by

$$\hat{\sigma}_{\kappa\lambda}^B = -\frac{1}{V} \sum_i \frac{p_{i,\kappa} p_{i,\lambda}}{m}, \quad (6.11)$$

and its ensemble average is

$$\begin{aligned}\langle \hat{\sigma}_{\kappa\lambda}^B \rangle &= -\frac{1}{Z} \int dp^{3N} dq^{3N} e^{-\beta \hat{H}} \frac{p_{i,\kappa} p_{i,\lambda}}{Vm} \\ &= -\frac{Nk_B T}{V} \delta_{\kappa\lambda} = -k_B T \rho \delta_{\kappa\lambda},\end{aligned}\quad (6.12)$$

where we used the definition of the number density $\rho = N/V$. The stress-stress correlation is given by

$$\begin{aligned}\langle \hat{\sigma}_{\kappa\lambda}^B \hat{\sigma}_{\mu\nu}^B \rangle &= \frac{1}{Z} \int dp^{3N} dq^{3N} e^{-\beta \hat{H}} \frac{p_{i,\kappa} p_{i,\lambda} p_{j,\mu} p_{j,\nu}}{V^2 m^2} \\ &= \frac{1}{\lambda_{\text{th}}^{3N}} \int dp^{3N} e^{-\beta \hat{H}} \frac{p_{i,\kappa} p_{i,\lambda} p_{j,\mu} p_{j,\nu}}{V^2 m^2},\end{aligned}\quad (6.13)$$

where in the second line we have integrated over the particle coordinates \mathbf{q}_n and used Eq. (6.7). The statistics for the momenta \mathbf{p}_n is a multivariate Gaussian and so we can apply a classical version of Wick's theorem [41] to decompose the four point correlations as a sum of products of two point correlations:

$$\begin{aligned}\langle p_{i,\kappa} p_{i,\lambda} p_{j,\mu} p_{j,\nu} \rangle_{\mathbf{p}_n} &= \langle p_{i,\kappa} p_{i,\lambda} \rangle_{\mathbf{p}_n} \langle p_{j,\mu} p_{j,\nu} \rangle_{\mathbf{p}_n} \\ &\quad + \langle p_{i,\kappa} p_{j,\mu} \rangle_{\mathbf{p}_n} \langle p_{i,\lambda} p_{j,\nu} \rangle_{\mathbf{p}_n} \\ &\quad + \langle p_{i,\kappa} p_{j,\nu} \rangle_{\mathbf{p}_n} \langle p_{j,\mu} p_{i,\lambda} \rangle_{\mathbf{p}_n}.\end{aligned}\quad (6.14)$$

Here $\langle \dots \rangle_{\mathbf{p}_n}$ stands for the average only over the momenta \mathbf{p}_n . Together with $\langle p_{i,\kappa} p_{j,\lambda} \rangle_{\mathbf{p}_n} = mk_B T \delta_{ij} \delta_{\kappa\lambda}$ we then obtain for the stress-stress correlation

$$\langle \hat{\sigma}_{\kappa\lambda}^B \hat{\sigma}_{\mu\nu}^B \rangle = \frac{(k_B T)^2}{V^2} (N^2 \delta_{\kappa\lambda} \delta_{\mu\nu} + N \delta_{\kappa\mu} \delta_{\lambda\nu} + N \delta_{\kappa\nu} \delta_{\lambda\mu}).\quad (6.15)$$

From this follows the complete non-affine contribution $C_{\kappa\lambda\mu\nu}^N$ as

$$\begin{aligned}C_{\kappa\lambda\mu\nu}^N &= \frac{k_B T N}{V} (\delta_{\kappa\mu} \delta_{\lambda\nu} + \delta_{\kappa\nu} \delta_{\lambda\mu}) \\ &= k_B T \rho (\delta_{\kappa\mu} \delta_{\lambda\nu} + \delta_{\kappa\nu} \delta_{\lambda\mu}).\end{aligned}\quad (6.16)$$

Combining this result with the kinetic contribution $C_{\kappa\lambda\mu\nu}^K$, the isothermal elastic constants of the ideal gas are given by

$$C_{\kappa\lambda\mu\nu} = k_B T \rho (\delta_{\kappa\mu} \delta_{\lambda\nu} + \delta_{\kappa\nu} \delta_{\lambda\mu}).\quad (6.17)$$

As we discussed in chapter 4 these elastic constants are only equal to the stiffnesses in Hooke's law in a stress free reference configuration, but if the ideal gas is contained in a box at finite volume V and at pressure P this is not a SFRC. So we have to incorporate the correction term in Eq. (4.12) where we set $\sigma_{\kappa\lambda}^0 = -P \delta_{\kappa\lambda}$:

$$\begin{aligned}c_{\kappa\lambda\mu\nu} &= C_{\kappa\lambda\mu\nu} - P (\delta_{\kappa\mu} \delta_{\lambda\nu} + \delta_{\kappa\nu} \delta_{\lambda\mu} - \delta_{\kappa\lambda} \delta_{\mu\nu}) \\ &= K \delta_{\kappa\lambda} \delta_{\mu\nu},\end{aligned}\quad (6.18)$$

where we used the fact that for the ideal gas $K = P = k_B T \rho$. This result is

in agreement with our expectations stated earlier. The shear modulus G for the ideal gas is zero, which it should be for any gas or fluid and Eq. (4.33) for the bulk modulus is also fulfilled.

Next we want to compute the stiffness tensor in the isothermal-isobaric ensemble to check the validity of the correction term in Eq. (5.50). As we already showed in section 5.1.2 the TPN ensemble average of the microscopic stress tensor is

$$\langle \hat{\sigma}_{\kappa\lambda}^B \rangle = -P\delta_{\kappa\lambda}. \quad (6.19)$$

The stress-stress correlation in the isothermal-isobaric ensemble is given by

$$\begin{aligned} \langle \hat{\sigma}_{\kappa\lambda}^B \hat{\sigma}_{\mu\nu}^B \rangle &= \frac{1}{\bar{Z}} \int_0^\infty dV e^{-\beta PV} \int dp^{3N} dq^{3N} e^{-\beta \hat{H}} \frac{p_{i,\kappa} p_{i,\lambda} p_{j,\mu} p_{j,\nu}}{V^2 m^2} \\ &= \frac{1}{\bar{Z}} \int_0^\infty dV e^{-\beta PV} V^{N-2} \int dp^{3N} e^{-\beta \hat{H}} \frac{p_{i,\kappa} p_{i,\lambda} p_{j,\mu} p_{j,\nu}}{m^2} \\ &= \frac{\lambda_{\text{th}}^{3N}}{\beta^2 \bar{Z}} \int_0^\infty dV e^{-\beta PV} V^{N-2} \\ &\quad \times (N^2 \delta_{\kappa\lambda} \delta_{\mu\nu} + N \delta_{\kappa\mu} \delta_{\lambda\nu} + N \delta_{\kappa\nu} \delta_{\lambda\mu}). \end{aligned}$$

Here we used again Wick's theorem in the second line. Carrying out the remaining volume integral and using the partition function \bar{Z} in Eq. (6.8) we arrive at

$$\langle \hat{\sigma}_{\kappa\lambda}^B \hat{\sigma}_{\mu\nu}^B \rangle = \frac{P^2}{N(N-1)} \left(N^2 \delta_{\kappa\lambda} \delta_{\mu\nu} + N \delta_{\kappa\mu} \delta_{\lambda\nu} + N \delta_{\kappa\nu} \delta_{\lambda\mu} \right). \quad (6.20)$$

Now we can approximate the fractions containing the particle number for large $N \gg 1$ as:

$$\begin{aligned} \frac{N^2}{N^2 - N} &\approx 1 + \frac{1}{N}, \\ \frac{N}{N^2 - N} &\approx \frac{1}{N}. \end{aligned} \quad (6.21)$$

This leads together with the ideal gas law to the $\mathcal{O}(1/N)$ approximation

$$\begin{aligned} \langle \hat{\sigma}_{\kappa\lambda}^B \hat{\sigma}_{\mu\nu}^B \rangle &= \frac{(k_B T)^2}{\langle V \rangle^2} (N^2 \delta_{\kappa\lambda} \delta_{\mu\nu} + N \delta_{\kappa\mu} \delta_{\lambda\nu} + N \delta_{\kappa\nu} \delta_{\lambda\mu}) \\ &\quad + \frac{k_B T}{\langle V \rangle} P \delta_{\kappa\lambda} \delta_{\mu\nu}, \end{aligned} \quad (6.22)$$

which is consistent with the correction term in Eq. (5.50), since the starting point, Eq. (5.35) which relates the fluctuations in different ensembles, is already an $\mathcal{O}(1/N)$ approximation. After taking into account the correction terms for the non stress free reference configuration and the ensemble transformation, we obtain the same stiffness coefficients as in the canonical ensemble:

$$c_{\kappa\lambda\mu\nu} = K \delta_{\kappa\lambda} \delta_{\mu\nu}. \quad (6.23)$$

6.2 The nearest-neighbor Lennard-Jones solid

In this section we investigate a nearest-neighbor Lennard-Jones (NNLJ) solid. We compare the isothermal elastic stiffnesses calculated with the stress-stress fluctuation formula in the canonical and isothermal-isobaric ensemble on the global and local scale, investigate the influence of the ensemble transformation correction for stress-stress fluctuations on the convergence, and compare the elastic moduli on the global and local scale.

The NNLJ solid is a simplified model for the description of crystals formed by noble gases like Argon. These noble gases form at low temperatures face centered cubic crystals (see figure 6.1), which is also the case for the NNLJ solid. The Hamiltonian of the system is given by

$$\hat{H} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{(i,j)} U_{\text{LJ}}(q_{ij}), \quad (6.24)$$

where the notation (i, j) indicates that the particles i and j are nearest-neighbors and $q_{ij} = |\mathbf{q}_i - \mathbf{q}_j|$ is the distance between them. The Lennard-Jones potential is shown in figure 6.1 and given by

$$U_{\text{LJ}}(r) = 4\varepsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right]. \quad (6.25)$$

For this system it is suitable to introduce the dimensionless Lennard-Jones units

$$\begin{aligned} T^* &= k_{\text{B}}T/\varepsilon, \\ \mathbf{q}_i^* &= \mathbf{q}_i/r_0. \end{aligned} \quad (6.26)$$

All results in the following analysis are given in these units.

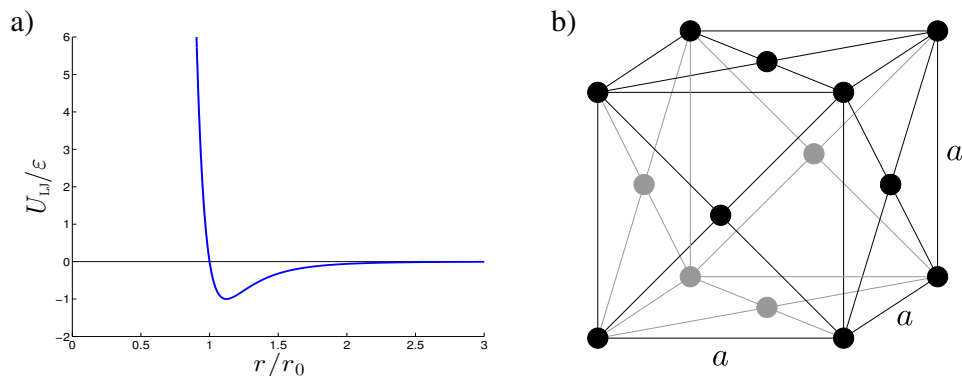


FIGURE 6.1: a) Plot of the Lennard-Jones potential. It has a minimum of $U_{\text{LJ}}(r_m) = -\varepsilon$ at $r_m = \sqrt[6]{2}r_0$. b) Bravais lattice of a face centered cubic crystal with lattice constant a .

6.2.1 Monte Carlo simulation method

To obtain the ensemble averages in the stress-stress fluctuation formula for the NNLJ solid we performed Monte Carlo simulations in the canonical and isothermal-isobaric ensemble. The initial configuration is generated as a perfect FCC structure with lattice constant a in a cubic box with volume $V = (n_c a)^3$, where n_c is the number of unit cells along each dimension. The total number of particles in the box is then $N = 4n_c^3$. Afterwards a Metropolis Monte Carlo algorithm was used to sample the configuration space, which performs trial moves by randomly changing one degree of freedom (DOF) of the system and accepting that move with a probability p_{acc} . In the following one Monte Carlo step (MCS) refers to a set of trial moves where each DOF is changed once on average.

The acceptance probability p_{acc} is dependent on the ensemble which has to be simulated. For the canonical ensemble an acceptance probability given by

$$p_{\text{acc}} = \min \left\{ 1, e^{-\beta(U_n - U_{n-1})} \right\}, \quad (6.27)$$

was used¹, where U_{n-1} and U_n is the potential energy of the system before and after the n -th trial move. The DOF in the canonical ensemble are the $3N$ particle coordinates and one trial move consisted of a change of the coordinates of a randomly picked particle i by

$$\mathbf{q}_n^{(i)} = \mathbf{q}_{n-1}^{(i)} + \Delta q_{\text{max}}(\mathbf{r}_u - 0.5), \quad (6.28)$$

where \mathbf{r}_u is a vector which components are uniformly distributed random number on the interval $[0, 1]$.

In the isothermal-isobaric ensemble we have an additional DOF, namely the volume of the simulation box, and the acceptance probability is given by

$$p_{\text{acc}} = \min \left\{ 1, e^{-\beta\Delta\mathcal{H}} \right\}, \quad (6.29)$$

where $\Delta\mathcal{H}$ is the change of enthalpy between trail moves:

$$\Delta\mathcal{H} = (U_n - U_{n-1}) + P(V_n - V_{n-1}) - k_B T N \ln(V_n/V_{n-1}). \quad (6.30)$$

Additionally to the trial moves changing the particle coordinates according to Eq. (6.28), the trial move for a volume change consists of a random change in volume

$$V_n = V_{n-1} + \Delta V_{\text{max}}(r_u - 0.5), \quad (6.31)$$

where r_u is a uniform random number on the interval $[0, 1]$, and then rescaling all particle coordinates by

$$\mathbf{q}_n^{(i)} = \sqrt[3]{V_n/V_{n-1}} \mathbf{q}_{n-1}^{(i)}. \quad (6.32)$$

The values of Δq_{max} and ΔV_{max} where adjusted, so that the ratio of the accepted and total number of trail moves is around 50%.

¹The acceptance probability is not unique. Alternatively every transition probability that fulfills the detailed balance condition and produces the same stationary distribution could be used [42].

In the first part of the simulation the system was equilibrated, which we checked by making sure that the total energy and the virial pressure fluctuate around a constant value. In the second part configuration samples were taken every tenth MCS to minimize correlations between sampled configurations. Afterwards the elastic constants were calculated from this samples. To compare the values for the elastic constants in both ensembles, we first simulated the isothermal-isobaric ensemble at a given pressure and calculated the corresponding mean volume of the system. Then the canonical ensemble was simulated, where the volume was set to the previously determined mean value. Here we checked, that the mean virial pressure in the *TVN* ensemble is in agreement with the specified pressure from the *TPN* simulation. To avoid translational drift, the center of mass of one crystal layer was held fixed at $z = V^{1/3}/2$ in both ensembles.

All results in the following are calculated in a system with $n_c = 3$ and consisting of $N = 108$ particles at a temperature of $T^* = 0.3$ and a pressure of $P^* = 0$. As discussed in chapter 4 the elastic constants and stiffnesses are equal in the case of zero pressure, so it is sufficient to analyze only the elastic constants. For completeness the non-zero stress correction term has been included in the calculations, but was always found to be negligible.

6.2.2 Bulk and local elastic constants

We first compare the values for the bulk elastic constants of the>NNLJ solid in the canonical and isothermal-isobaric ensemble. For notational convenience all quantities are listed in Voigt notation in the following. The results are listed in table 6.1 and agree well in both ensembles, and also with the given literature values. This confirms the validity of the ensemble transformation correction term in Eq. (5.50). Secondly we compared the local elastic constants to check the validity of Eq. (5.57) on the local scale. For this we divided the simulation box in 100 layers of thickness $3a/100$ perpendicular to the z axis and averaged over $2 \cdot 10^6$ configurations. Because the symmetries of the bulk elastic constants derived from the Neumann principle do not persist on local scale, we now have more than three independent components. All 12 non-zero local elastic constants as a function of z are shown in figure 6.3. For comparison the local density in the layers is shown in figure 6.2. One immediately sees that the periodicity in the local elastic constants corresponds to the periodicity in the local density. This behavior was also observed in [40].

If we compare the curves for the canonical and isothermal-isobaric ensemble, one can often not distinguish between the two. This shows that Eq. (5.57) gives the correct local elastic constants in TPN ensemble. The only clearly visible difference can be observed in the components C_{31} and C_{32} . We investigated this discrepancy and found that with increasing sample size the two curves become more and more similar, which allows the conclusion that the deviation stems from the fact that these elements are not totally converged within $2 \cdot 10^6$ samples.

	<i>TVN</i> ensemble	<i>TPN</i> ensemble	Ref. [38]
C_{11}	44.86	44.87	44.01
C_{12}	19.58	19.59	19.41
C_{44}	23.39	23.43	23.03

TABLE 6.1: Bulk elastic constants (in Voigt notation) of the Nearest-Neighbor Lennard-Jones solid at zero pressure and reduced temperature $T^* = 0.3$ in dimensionless Lennard-Jones units. The listed values are symmetry averaged quantities calculated from 10^6 configurations. The *TVN* simulation was done with a volume of $V^* = 115.6$.

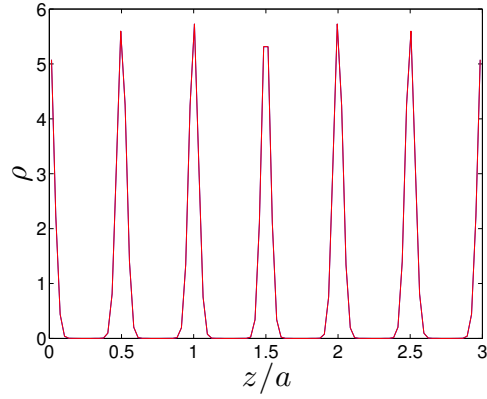


FIGURE 6.2: Local density in the NNLJ solid as a function of z in the *TVN* (blue line) and *TPN* (red line) ensemble. The lattice constant was $a^* = 1.6238$.

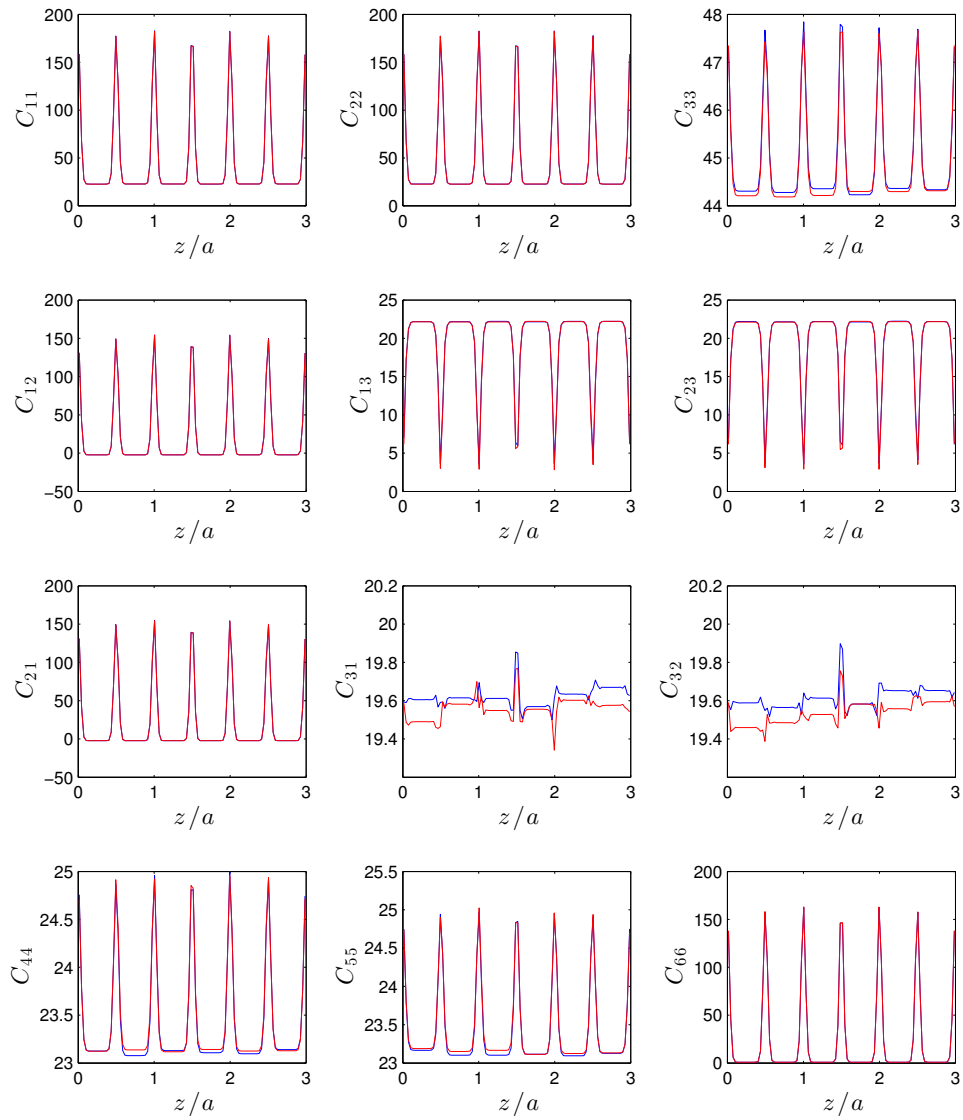


FIGURE 6.3: Local elastic constants (in Voigt notation) in the NNLJ solid as a function of z in the *TVN* (blue lines) and *TPN* (red lines) ensemble calculated over $2 \cdot 10^6$ samples. The lattice constant is $a^* = 1.6238$.

6.2.3 Convergence of bulk elastic constants

Next we investigate the influence of the ensemble transformation correction term in the TPN ensemble on the convergence of the bulk elastic constants. For this we calculated the relative error after averaging over n configurations, which for a quantity X is given by

$$\Delta_{\text{rel}}(X(n)) = \left| \frac{X(n) - X^\infty}{X^\infty} \right|, \quad (6.33)$$

where X^∞ is the value of X for $n \rightarrow \infty$. The relative error for C_{11} , C_{12} and C_{44} in both ensembles is shown in figure 6.4, together with the bulk modulus calculated from Eq. (5.41) in the TPN ensemble. The influence of the bulk modulus is clearly noticed in the region $n < 4 \cdot 10^5$ for the elements C_{11} and C_{12} . We can observe how the peak region in the relative error of the bulk modulus between $n = 2 \cdot 10^5$ and $n = 4 \cdot 10^5$ propagates to the relative error of C_{11} and C_{12} respectively. But after the error of the bulk modulus drops permanently below 0.1 % the relative error of C_{11} and C_{12} in both ensembles is of comparable size. The C_{44} does not show this behavior, since it is untouched by the correction term and already after $2 \cdot 10^5$ samples the relative error in both ensembles is of equal magnitude.

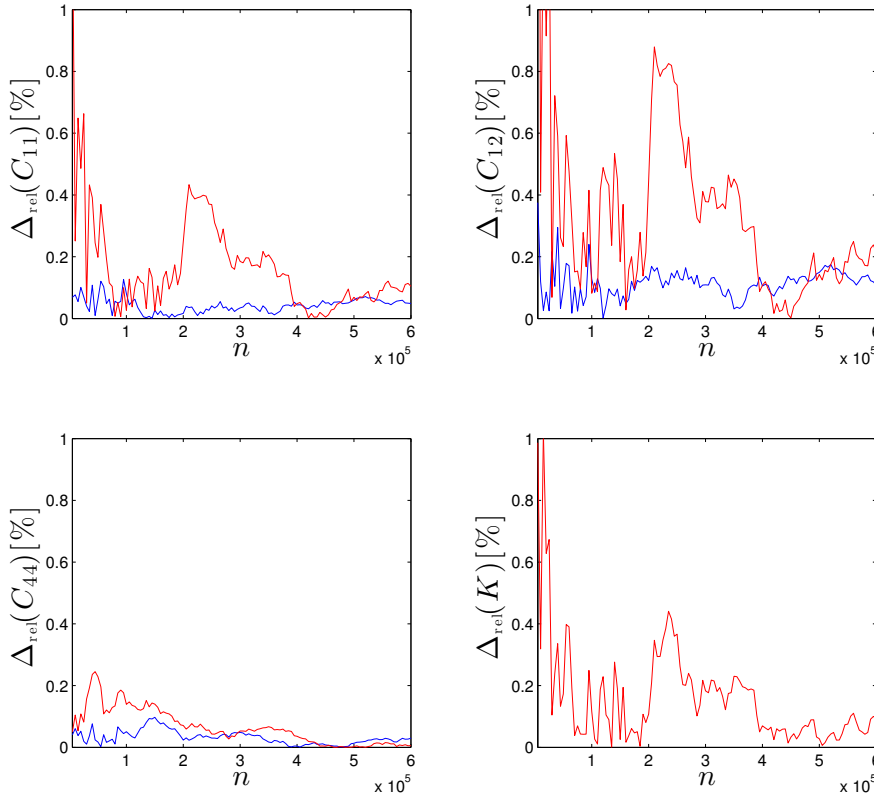


FIGURE 6.4: Relative error in the calculation of elastic constants in dependence of the number of samples n in the TVN (blue line) and TPN (red line) ensemble. The reference values for C_{ik}^∞ and K^∞ were estimated by the value of the respective quantity averaged over 10^6 samples.

Altogether we can state that the convergence of the stress-stress fluctuation formula is definitely influenced by the convergence of the ensemble transformation correction term, but since we are considering differences in the relative error of less than 1 %, we can conclude that the overall convergence in both ensembles is of comparable magnitude.

6.2.4 Bulk and local elastic moduli

At last we analyze the bulk and local elastic moduli in the NNLJ solid. Because the results are identical for the canonical and isothermal-isobaric ensemble, we only discuss the elastic moduli obtained in the first one. The Young, shear, axial and bulk moduli were calculated from the same dataset used for figure 6.3, according to the definitions given in section 4.4. Owing to the cubic crystal symmetry, we have only four independent elastic moduli for the bulk system. The results are listed in table 6.2. Again on the local scale the crystal symmetry is broken and Young, shear and axial moduli along the various principal axis are different. The elastic moduli as a function of z are shown in figure 6.5. These were calculated in the same layers as the local elastic constants in the previous section. Once more we can observe the periodicity corresponding to the different atomic layers. The three Young moduli are all quantitatively very similar, with the tendency of E_2 to have slightly higher peaks at the atomic layers. The shear modulus G_3 shows high peaks at regions of high density, while going to zero in between. On the other hand G_1 and G_2 are always equal on the local scale, remaining close to their bulk value throughout the solid. For the axial modulus we observe three pairs of equal values: $\nu_{13} = \nu_{23}$, $\nu_{31} = \nu_{32}$ and $\nu_{12} = \nu_{21}$. While ν_{13} , ν_{23} , ν_{31} and ν_{32} are at their maximum values in between atomic layers, ν_{12} and ν_{21} show opposite behavior. The bulk modulus K has a maximum of ≈ 80 where the density is also at maximum, and decreases to a constant value in between atomic sheets, which is lower than its corresponding bulk value.

E	32.96
G	11.70
ν	0.30
K	28.00

TABLE 6.2: Bulk elastic moduli of the Nearest-Neighbor Lennard-Jones solid at zero pressure and reduced temperature $T^* = 0.3$ in dimensionless Lennard-Jones units. The listed values are symmetry averaged quantities calculated from 10^6 configurations in the TVN ensemble with a volume of $V^* = 115.6$.

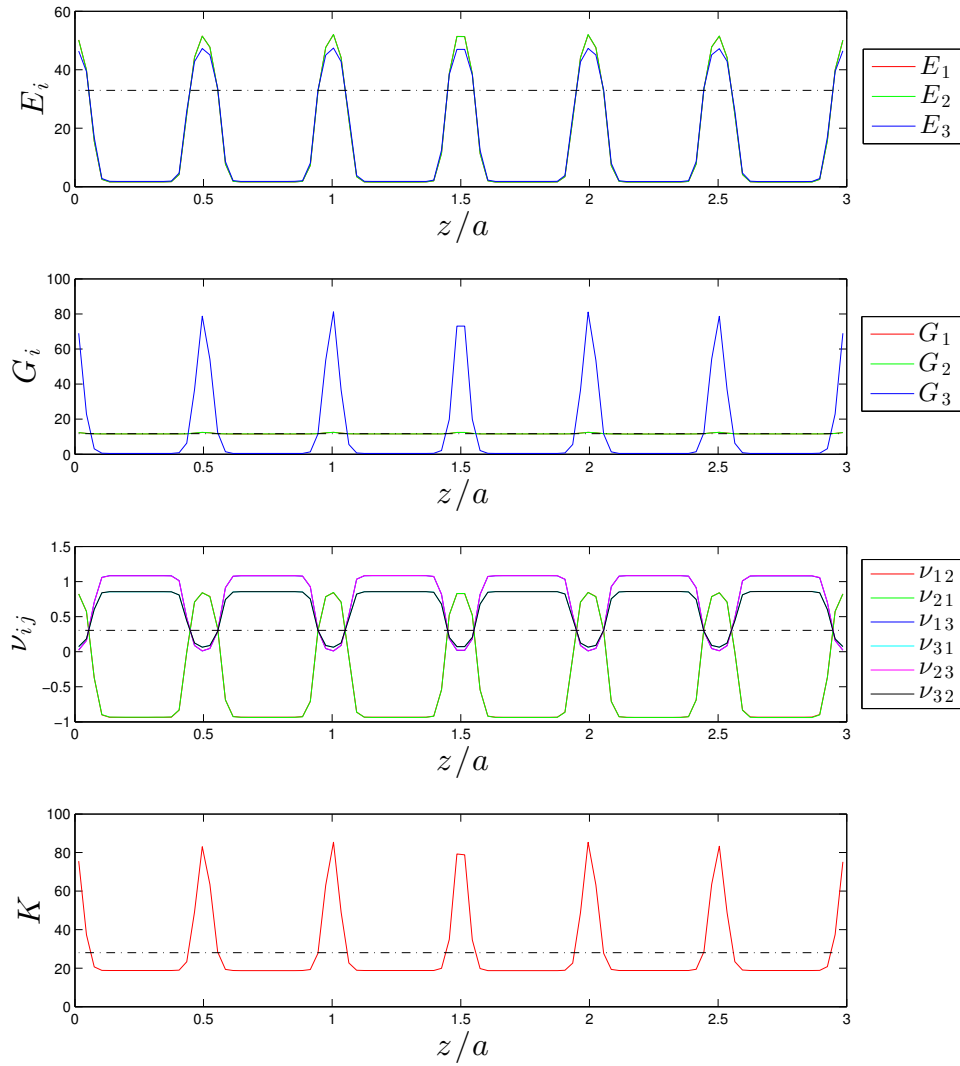


FIGURE 6.5: Local elastic moduli in the NNLJ solid as a function of z in the TVN ensemble and their respective bulk values (dashed dotted black lines) calculated over $2 \cdot 10^6$ samples. The lattice constant is $a^* = 1.6238$.

Chapter 7

Conclusion

We reviewed the established methods of determining elastic constants in computer simulations of equilibrium systems and the formalism behind them. Further we pointed out their respective advantages and disadvantages. These methods are namely the strain-strain, the stress-strain and the stress-stress fluctuation formulas, where only the later allows the calculation of elastic stiffnesses on the local scale. We then used a formalism that relates fluctuations in different ensembles, to derive for the first time a stress-stress fluctuation formula for the isothermal-isobaric ensemble. This formula has the advantage to be directly applicable in a statistical ensemble, which corresponds to a more natural experimental setup. This means that if one wants to investigate the pressure dependence of the elastic constants, it is no longer necessary to first compute equilibrium quantities like the mean volume at a given pressure in the isothermal-isobaric ensemble and then use these as an input to a simulation of the canonical ensemble that calculates the elastic constants. This can shorten the computational time needed to obtain elastic stiffnesses drastically. We have tested the validity of the derived correction term for the bulk elastic constants for the ideal gas analytically and for the nearest-neighbor Lennard-Jones solid by the use of Monte Carlo simulations. For the later system we also computed the local elastic constants in the canonical and isothermal-isobaric ensemble and found accurate agreement.

Regarding future research it will be interesting to apply the isothermal-isobaric stress-stress fluctuation formula to determine local elastic constants in soft-matter system like lipid bilayers, which are naturally embedded in an aqueous solution at non-zero pressure. For this it will be necessary to generalize the microscopic stress tensor to many-body forces, but there are already attempts in the literature considering this problem [43]. Other use cases could be the investigation of elastic constants on the local scale in amorphous solid or in carbon nanotubes.

Appendix A

Mathematical supplement

This appendix provides brief derivations of identities needed for the derivation of the stress-stress fluctuation formula in chapter 5.

Derivative of the inverse of a matrix

$$\begin{aligned}
 0 &= \frac{\partial}{\partial x} \mathbb{I} = \frac{\partial}{\partial x} X X^{-1} = \left(\frac{\partial}{\partial x} X \right) X^{-1} + X \left(\frac{\partial}{\partial x} X^{-1} \right) \\
 \Leftrightarrow \frac{\partial}{\partial x} X^{-1} &= -X^{-1} \frac{\partial X}{\partial x} X^{-1}
 \end{aligned} \tag{A.1}$$

Total differential of a scalar function depending of matrix valued variable

$$\begin{aligned}
 dy(X) &= \frac{\partial y}{\partial X_{\alpha\beta}} dX_{\alpha\beta} = \frac{\partial y}{\partial X_{\alpha\beta}} dX_{\beta\alpha}^T \\
 &= \text{Tr} \left[\frac{\partial y}{\partial X} dX^T \right]
 \end{aligned} \tag{A.2}$$

Derivative of particle coordinates and momenta with respect to the scaling matrix

$$\begin{aligned}
 \frac{\partial q_\alpha}{\partial h_{\nu\xi}} &= \frac{\partial}{\partial h_{\nu\xi}} (h_{\alpha\beta} \tilde{q}_\beta) = \delta_{\alpha\nu} \delta_{\beta\xi} \tilde{q}_\beta = \delta_{\alpha\nu} \delta_{\beta\xi} h_{\beta\gamma}^{-1} q_\gamma \\
 &= \delta_{\alpha\nu} h_{\xi\gamma}^{-1} q_\gamma
 \end{aligned} \tag{A.3}$$

$$\begin{aligned}
 \frac{\partial p_\alpha}{\partial h_{\nu\xi}} &= \frac{\partial}{\partial h_{\nu\xi}} (h_{\beta\alpha}^{-1} \tilde{p}_\beta) = -h_{\beta\nu}^{-1} h_{\xi\alpha}^{-1} \tilde{p}_\beta = -h_{\beta\nu}^{-1} h_{\xi\alpha}^{-1} h_{\gamma\beta} p_\gamma \\
 &= -\delta_{\gamma\nu} h_{\xi\alpha}^{-1} p_\gamma = -h_{\xi\alpha}^{-1} p_\nu
 \end{aligned} \tag{A.4}$$

Appendix B

Stiffness tensor for a cubic system

This appendix provides a notebook file for the computer algebra system Mathematica [30], which calculates the reduced stiffness tensor in Voigt notation for a system with cubic crystal symmetry. The conversion of the transformation matrices representing the symmetry operations to Voigt notation is done according to [44].

```

1  (* Define rotation matrix around a vector n about a degrees *)
2  RotMatrix[n_, a_] := Module[{R},
3    R = {{
4      n[[1]]^2 * (1 - Cos[a]) + Cos[a],
5      n[[1]]*n[[2]]*(1 - Cos[a]) - n[[3]] * Sin[a],
6      n[[1]]*n[[3]]*(1 - Cos[a]) + n[[2]]*Sin[a]
7    }, {
8      n[[2]]*n[[1]] * (1 - Cos[a]) + n[[3]]* Sin[a],
9      n[[2]]^2*(1 - Cos[a]) + Cos[a],
10     n[[2]]*n[[3]]*(1 - Cos[a]) - n[[1]]*Sin[a]
11   }, {
12     n[[3]]*n[[1]] * (1 - Cos[a]) - n[[2]]* Sin[a],
13     n[[3]]*n[[2]]*(1 - Cos[a]) + n[[1]]*Sin[a],
14     n[[3]]^2*(1 - Cos[a]) + Cos[a]
15   }};
16  R ];
17
18  (* Conversion of a symmetry operation matrix to Voigt notation
19     *)
20  ToVoigt[A_] := Module[{Av},
21  Av = {{
22    A[[1, 1]]^2, A[[1, 2]]^2, A[[1, 3]]^2,
23    A[[1, 2]]*A[[1, 3]], A[[1, 1]]*A[[1, 3]], A[[1, 1]]*A[[1,
24      2]]
25  }, {
26    A[[2, 1]]^2, A[[2, 2]]^2, A[[2, 3]]^2,
27    A[[2, 2]]*A[[2, 3]], A[[2, 1]]*A[[2, 3]], A[[2, 1]]*A[[2,
28      2]]
29  }, {
30    A[[3, 1]]^2, A[[3, 2]]^2, A[[3, 3]]^2,
31    A[[3, 2]]*A[[3, 3]], A[[3, 1]]*A[[3, 3]], A[[3, 1]]*A[[3,
32      2]]
33  }, {
34    2*A[[2, 1]]*A[[3, 1]], 2*A[[2, 2]]*A[[3, 2]],
35    2*A[[2, 3]]*A[[3, 3]],
36    A[[2, 2]]*A[[3, 3]] + A[[2, 3]]*A[[3, 2]],
37    A[[2, 1]]*A[[3, 3]] + A[[2, 3]]*A[[3, 1]],
38    A[[2, 1]]*A[[3, 2]] + A[[2, 2]]*A[[3, 1]]
39  }, {
40    2*A[[1, 1]]*A[[3, 1]], 2*A[[1, 2]]*A[[3, 2]],

```

```

38     2*A[[1, 3]]*A[[3, 3]],
39     A[[1, 2]]*A[[3, 3]] + A[[1, 3]]*A[[3, 2]],
40     A[[1, 1]]*A[[3, 3]] + A[[1, 3]]*A[[3, 1]],
41     A[[1, 1]]*A[[3, 2]] + A[[1, 2]]*A[[3, 1]]
42   }, {
43     2*A[[1, 1]]*A[[2, 1]], 2*A[[1, 2]]*A[[2, 2]],
44     2*A[[1, 3]]*A[[2, 3]],
45     A[[1, 2]]*A[[2, 3]] + A[[1, 3]]*A[[2, 2]],
46     A[[1, 1]]*A[[2, 3]] + A[[1, 3]]*A[[2, 1]],
47     A[[1, 1]]*A[[2, 2]] + A[[1, 2]]*A[[2, 1]]
48   }
49 Av ];
50
51 (* Definition of the symmetry operations for a cubic crystal *)
52 (* Reflection at the yz-plane *)
53 A1 = {
54   {-1, 0, 0},
55   {0, 1, 0},
56   {0, 0, 1}
57 };
58 (* Reflection at the xz-plane *)
59 A2 = {
60   {1, 0, 0},
61   {0, -1, 0},
62   {0, 0, 1}
63 };
64 (* Reflection at the xy-plane *)
65 A3 = {
66   {1, 0, 0},
67   {0, 1, 0},
68   {0, 0, -1}
69 };
70 (* Rotation about 90 degree around the z-axis *)
71 A4 = RotMatrix[{0, 0, 1}, Pi/2];
72 (* Rotation around a vector (1, 1, 1) about 120 degrees *)
73 A5 = RotMatrix[{1/Sqrt[3], 1/Sqrt[3], 1/Sqrt[3]}, 2*Pi / 3];
74 (* Rotation around face diagonal about 180 degrees *)
75 A6 = RotMatrix[{1/Sqrt[2], 1/Sqrt[2], 0}, Pi];
76 (* Mirrorsymmetry to the face diagonal *)
77 A7 = RotMatrix[{0, 0, 1}, Pi/4].A2.RotMatrix[{0, 0, 1}, -Pi/4];
78
79 (* Define the general matrix of elastic constants *)
80 Cv = {
81   {C11, C12, C13, C14, C15, C16},
82   {C12, C22, C23, C24, C25, C26},
83   {C13, C23, C33, C34, C35, C36},
84   {C14, C24, C34, C44, C45, C46},
85   {C15, C25, C35, C45, C55, C56},
86   {C16, C26, C36, C46, C56, C66}
87 };
88 (* Solve all equations simultaneously *)
89 sol = Solve[{
90   Cv == Transpose[ToVoigt[A1]].(Cv.ToVoigt[A1]),
91   Cv == Transpose[ToVoigt[A2]].(Cv.ToVoigt[A2]),
92   Cv == Transpose[ToVoigt[A3]].(Cv.ToVoigt[A3]),
93   Cv == Transpose[ToVoigt[A4]].(Cv.ToVoigt[A4]),
94   Cv == Transpose[ToVoigt[A5]].(Cv.ToVoigt[A5]),
95   Cv == Transpose[ToVoigt[A6]].(Cv.ToVoigt[A6]),
96   Cv == Transpose[ToVoigt[A7]].(Cv.ToVoigt[A7])},
97   {
98     C11, C12, C13, C14, C15, C16,
99     C22, C23, C24, C25, C26,
100    C33, C34, C35, C36,

```



```
101 |      C44, C45, C46,  
102 |      C55, C56,  
103 |      C66  
104 |    }  
105 | ];  
106 | (* Apply solution to the general matrix *)  
107 | CvCubic = Cv /. Flatten[sol];  
108 | (* Show the result *)  
109 | MatrixForm[Cv]  
110 | MatrixForm[CvCubic]
```


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