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Realistic frozen phonons: thermal diffuse scattering from first principles

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Abstract

Anisotropic atomic vibrations define directional thermal transport, mechanical properties and structural stability, making them critical to the understanding of nanostructured materials. Recent breakthroughs in STEM have made it possible to measure these directional vibrations at the atomic scale. In this thesis, simulations are performed to identify the specific thermal regimes and electron scattering detection schemes that allow the anisotropy of the vibrations to be measured in practice. To ensure comparability, the root-mean-square displacements of the commonly used isotropic model were matched to the thermal displacements of a phonon-based anisotropic model derived from the GAP-20 machine learning potential. 4D-STEM measurements were simulated for both models and a static reference cell, and both Annular Dark-Field (ADF) and Integrated Centre of Mass (iCOM) images were reconstructed. Realistic noise was incorporated to simulate experimental conditions and the results compared. The research confirms that incorporating anisotropic atomic displacements can be relevant for accurate STEM simulations, as traditional isotropic models fail to capture critical directional asymmetries. The results demonstrate that iCOM imaging at temperatures between 300 K and 1000 K can successfully detect these vibrations, provided specific convergence parameters are met and electron doses exceed 10^7 electrons per square Ångström.

Abstract

Anisotrope Atomschwingungen bestimmen den richtungsabhängigen Wärmetransport, die mechanischen Eigenschaften sowie die strukturelle Stabilität und sind daher entscheidend für das Verständnis nanostrukturierter Materialien. Jüngste Durchbrüche auf dem Gebiet der Rastertransmissionselektronenmikroskopie (STEM) ermöglichen es, diese richtungsabhängigen Schwingungen auf atomarer Ebene messtechnisch zu erfassen. Im Rahmen dieser Masterarbeit werden Simulationen durchgeführt, um jene spezifischen thermischen Regimes und Detektionsverfahren für die Elektronenstreuung zu identifizieren, die eine Quantifizierung der Anisotropie dieser Schwingungen in der Praxis erlauben. Zur Gewährleistung der Vergleichbarkeit wurden die mittleren quadratischen Auslenkungen des etablierten isotropen Modells an die phononenbasierten thermischen Verschiebungen eines anisotropen Modells angepasst, welches aus dem machine learning Potenzial GAP-20 abgeleitet wurde. Für beide Modelle sowie für eine statische Referenzzelle wurden 4D-STEM-Messungen simuliert und sowohl „Annular Dark-Field“ (ADF) als auch „Integrated Centre of Mass“ (iCOM) Bilder rekonstruiert. Um reale experimentelle Bedingungen zu simulieren, wurde ein realistisches Rauschen implementiert und die Resultate verglichen. Die vorliegende Arbeit bestätigt, dass die Berücksichtigung anisotroper atomarer Auslenkungen für präzise STEM-Simulationen unerlässlich ist, da traditionelle isotrope Modelle kritische richtungsabhängige Asymmetrien nicht adäquat mit einbeziehen. Die Ergebnisse belegen, dass die iCOM-Bilder bei Temperaturen zwischen 300 K und 1000 K diese Schwingungen erfolgreich detektieren können, sofern spezifische Konvergenzparameter eingehalten werden und die Elektronendosis einen Wert von 10^7 Elektronen pro $\text{\AA}^2$ überschreitet.

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Chapter 1

Introduction

1.1 Background and Motivation

In nanomaterial physics, scanning transmission electron microscopy (STEM) has become an indispensable tool for mapping atomic structures and analysing local electronic properties down to the atomic level. Characterising lattice vibrations, or phonons, is essential to the understanding of thermal conductivity and energy transport. Recent instrumental breakthroughs in energy resolution and fast pixelated detectors have unlocked the direct detection and mapping of vibrational excitations in a material. In particular, vibrational electron energy-loss spectroscopy (EELS) has emerged as a major driving force [1] to map phonon dispersion relations across specific energy and momentum ranges. Recent experimental setups have pushed limits further, successfully demonstrating real-space, column-by-column imaging of atomic rattling modes [2] as well as the precise mapping of moiré phasons down to the picometer scale using ultrahigh-resolution electron ptychography [3].

Standard STEM simulations typically rely on isotropic Debye-Waller factors, which assume atomic thermal vibrations are uniform in all spatial directions. While computationally convenient, the isotropic assumption fails especially for low-dimensional nanomaterials. In graphene, a two-dimensional monolayer honeycomb lattice, atomic displacements are highly directional. The covalent in-plane σ -bonds, formed by the head-on overlap of the carbon orbitals, strongly resist displacement along the bond axes, while vibrations perpendicular to these bonds within the sheet are less limited. Traditional simulation models using isotropic frameworks fail to capture these directional asymmetries, potentially leading to discrepancies between simulated images

and experimental data. To accurately characterise thermal properties of graphene via electron microscopy, simulations must incorporate realistic anisotropic atomic displacements.

The primary objective of this thesis is to address this modelling limitation by identifying thermal regimes, electron detection schemes and electron dose thresholds required to resolve the in-plane atomic vibrational anisotropy in monolayer graphene using 4D-STEM simulations. To achieve this an anisotropic model is generated using displacements derived from the GAP-20 machine-learning potential [4]. An isotropic model is then constructed using the built-in frozen-phonon displacement functions in *ab*TEM [5]. To ensure direct comparability between the two models the isotropic thermal displacement parameter σ is optimised by matching the displacement distribution histogram of the isotropic model to the anisotropic data. As out-of-plane flexural vibrations in monolayer graphene feature large spatial amplitudes, out-of-plane (z -direction) atomic displacements are omitted used to generate these.

Multislice 4D-STEM simulations, utilising a pixelated detector to record the full 4D dataset, are performed for the isotropic model, the anisotropic model and a static reference cell to isolate the specific signature of directional thermal motion. The resulting simulated scattering data is reconstructed using Annular Dark-Field (ADF) and Integrated Centre of Mass (iCOM) algorithms under both noised and ideal conditions, to identify the minimum electron dose required for the detection of anisotropy in the atomic vibrations. Robustness of the used parameters within the simulation framework is established via convergence testing across potential sampling, the number of frozen phonon configurations, and the supercell dimensions.

1.2 Outline

Following this introduction, the thesis is organised into four main chapters. Chapter 2 establishes the theoretical background, starting with phonon models and electron scattering mechanisms, including thermal diffuse scattering. It introduces Transmission Electron Microscopy (TEM) before outlining the multislice scattering algorithm and the force-constant potential used in this work. The simulation methodology implemented in this thesis is described in chapter 3. It details the integration of the GAP-20 machine learning potential for phonon-based displacements, the creation of the cell, potential projection, and matching of the isotropic sigma. It covers the 4D-STEM simulations, the application of Poisson noise, ADF and iCOM measurement reconstruction, and concludes with convergence verification testing. Chapter 4 presents and discusses the research results. It compares how effectively ADF and iCOM imaging resolve anisotropy across a 0 K to 1800 K thermal window. It evaluates the impact of varying electron doses to determine the minimum threshold required to prevent anisotropic vibration signals from being obscured by noise. The chapter also justifies the chosen simulation parameters by analysing grid sampling, number of used atomic configurations, and supercell dimensions, ending with limitations and future work. Finally, chapter 5 concludes the thesis with a summary of the primary findings regarding the measurement of anisotropic thermal vibrations. Supplementary data and the implemented code are available in the Appendix.

Chapter 2

Theory

2.1 Phonons

When a crystal vibrates, not all constituent atoms vibrate at the same frequency, amplitude or energy. Over time, the vibrational energy of a specific atom will also vary. Vibrational motions of atoms are influenced by temperature-dependent thermal occupation as well as zero-point energy. Vibrations of adjacent atoms are coupled due to atomic bonding which results in the formation of travelling lattice waves (elastic waves) propagating through the crystalline structure. At the atomic scale, quantum phenomena dictate only certain energy values are allowed: the resulting quanta of the atomic displacement field are called phonons. They are quasiparticles, representing collective motion of atoms around their equilibrium position, that travel within the crystal with particle-like properties and any vibratory motion of the solid can be expressed as the superposition of its normal modes. Due to their wave-particle duality, phonons can be treated as either waves (classical mechanics) or particles (quantum mechanics) with

$$\vec{p} = \hbar \vec{q} \quad \text{and} \quad E = \hbar \omega, \quad (2.1)$$

where $\vec{p}$ is the momentum, E is the energy, $\hbar$ is the reduced Planck constant ($h/2\pi$), q is the wave vector and ω is the angular frequency.

Solid-state physics distinguishes between two types of phonons, characterised by their frequency, which relates to the energy of the vibrational modes of the atoms in a material. The lower-frequency vibrations, where neighbouring atoms in a unit cell move in-phase, are responsible for sound propagation and are hence called acoustic phonons. In a 3D crystal, there are three acoustic branches: one longitudinal and two transverse. The higher-frequency vibrations, where

atoms within the unit cell move out-of-phase, interact with electromagnetic radiation and are hence called optical phonons. For a cell with p atoms, there are $3p - 3$ optical branches. As a simple analytic model, the dispersion relation for a diatomic chain is given by

$$\omega^2(\vec{k}) = C \left(\frac{1}{M} + \frac{1}{m} \right) \pm C \sqrt{\left(\frac{1}{M} + \frac{1}{m} \right)^2 - \frac{4 \sin^2(ka/2)}{Mm}}, \quad (2.2)$$

where $\omega(\vec{k})$ is the angular frequency as a function of wave vector k , C is the force constant, M, m are the atomic masses, and a is their spacing. The negative sign gives the lower acoustic branch, and the positive sign the higher optical branch.

The phonon band structure of graphene can be seen in figure 2.1 along with the corresponding density of states. The red line denotes the in-plane modes, while the out-of-plane modes, which occur in 1D and 2D materials, can have a quadratic dispersion relation near the zone centre and are shown in blue. Their dispersion is

$$\omega_{ZA}(k) \approx \alpha k^2, \quad (2.3)$$

where ω_{ZA} is the frequency of the out-of-plane acoustic branch, α is a constant denoting the bending stiffness of the 2D sheet and k is the magnitude of the in plane wave vector.

Phonons play a critical role in a material's physical properties including thermal and electrical conductivity, heat capacity, and superconductivity. The frequency of phonons does not directly translate to the temperature but rather corresponds to the vibrational modes of the lattice in a material. Since phonons are bosons, for a phonon with frequency f at temperature T , the Bose-Einstein distribution is

$$\langle n \rangle = \frac{1}{e^{hf/k_B T} - 1}, \quad (2.4)$$

where $\langle n \rangle$ is the average number of phonons, h is the Planck constant, f is the phonon frequency, k_B is the Boltzmann constant, and T is the absolute temperature (K).

Due to thermal excitation, the population of phonons increases at higher temperatures, as more phonons can exist at higher energies than at lower ones. Although there is no change of the frequencies of specific phonon modes with temperature, they can shift slightly. Temperature changes may also cause a thermal expansion of the lattice and alter interatomic distances. At high temperatures, phonon softening can occur where the frequency of certain optical phonons decreases due to anharmonic interactions. As the lattice becomes more thermally excited it allows for larger displacements of atoms. Though both types of phonons contribute, acoustic phonons are the main heat carriers in semiconductors and insulators, as optical phonons are much less

efficient. At higher temperatures more vibrational modes are excited and the contribution of both phonon modes to the specific heat of a material increases. Understanding phonons and their interactions is essential for predicting the properties of materials.

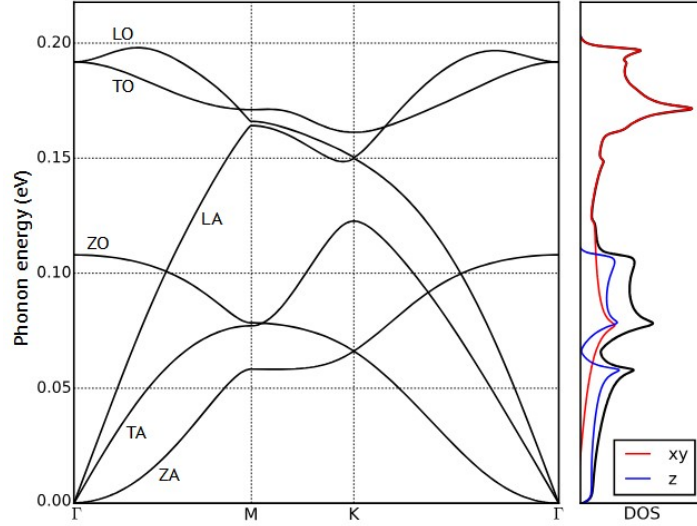


Figure 2.1: Left: phonon band structure of graphene as a function of frequency. Lower three lines are the acoustic branches, higher three the optical branches starting at the centre of the Brillouin zone. Right: density of states (DOS) of graphene. Red curve shows in-plane acoustic and optical branches, blue curve the flexural branches, and black curve is the total DOS. Image from [6].

2.1.1 Einstein model

In transmission electron microscopy, phonons affect images and diffraction patterns via thermal diffuse scattering, which due to the fast electrons can be modelled by taking thermal averages over frozen vibrational configurations of the lattice (frozen phonons [5]). Within the framework of the Einstein model, the displacements are assumed to be isotropic and uncorrelated. All atoms are regarded as independent quantum harmonic oscillators with a single characteristic frequency (Einstein frequency). The energy of a single oscillator can be calculated with

$$E_n = \left(n + \frac{3}{2} \right) \hbar \omega_E, \quad (2.5)$$

where E_n is the total energy of the oscillator, n is the principal quantum number, $\hbar$ is the reduced Planck constant, ω_E is the Einstein frequency, and $\frac{3}{2}\hbar\omega$ is the zero-point energy in three dimensions. This means the model fails to consider the interactions between neighbouring atoms and does not account for collective lattice waves. The Einstein temperature (θ_E) is a characteristic constant, which can be derived from the Bose–Einstein distribution (see 2.4) and defines the

temperature scale for a specific material:

$$\theta_E = \frac{\hbar\omega_E}{k_B}, \quad (2.6)$$

where θ_E is the Einstein temperature (K), $\hbar$ is the reduced Planck constant, and k_B is the Boltzmann constant. A higher θ_E means a higher vibration frequency. As N atoms have a total of $3N$ degrees of freedom, the total internal energy of the system can be calculated with

$$U = 3Nk_B\theta_E \left(\frac{1}{2} + \frac{1}{e^{\theta_E/T} - 1} \right), \quad (2.7)$$

where U is the total internal energy of the system, N is the total number of atoms, T is the absolute temperature, and $\frac{3}{2}Nk_B\theta_E$ is the total zero-point energy of the system.

Applying Planck's quantisation of energy to lattice vibrations means the energy levels of each oscillator are discrete. If the available thermal energy ($k_B T$) is smaller than the gap between levels ($\hbar\omega_E$), the oscillator stays in its ground state as an atom can only absorb heat in discrete packets. This results in the "freezing out" of degrees of freedom, which causes the heat capacity to drop to zero at low temperatures. The specific heat can be derived, using the Bose–Einstein distribution (see 2.4) to determine the number of phonons at a specific single frequency:

$$C_V = 3Nk_B \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}, \quad (2.8)$$

where C_V is the molar heat capacity at constant volume, and N is the number of atoms.

However, the model fails to accurately describe the specific heat at very low temperatures as it ignores low-frequency phonons which have very small energy gaps. This leads to an exponential drop of the heat capacity as the temperature approaches zero, whereas in a real crystal a T^3 dependence is observed. Another limitation is the assumption of independent oscillators with a single oscillating frequency. While this makes it mathematically easier to calculate the total internal energy, it also oversimplifies the collective nature of lattice vibrations. In addition, the model does not account for the wide range of vibrational frequencies present in real crystals. The Einstein model is still used in research to describe specific types of vibrational modes, such as localised "rattling" modes in cage-like crystal structures or optical phonons, which are nearly dispersionless [7]. However the advancement of imaging technologies such as differential phase contrast, 4D-STEM, and ptychography [3] are making it possible to visualise atomic vibrations directly. More accurate phonon models are therefore needed.

2.1.2 Phonon eigenmodes

Eigenmodes of a 3D lattice consist of the collective vibrations of atoms in a crystal. The Hamiltonian treats each normal mode of a crystal lattice as an independent quantum harmonic oscillator. With coordinates and momenta that satisfy the canonical commutation relations, the Hamiltonian of a monoatomic harmonic lattice with mass M is given by

$$H = \sum_i^N \frac{P_i^2}{2M} + \frac{1}{2} \sum_{\substack{i,j \\ \alpha,\beta}} \Phi_{\alpha\beta}(\vec{R}_i^0, \vec{R}_j^0) \vec{u}_{i\alpha} \vec{u}_{j\beta}, \quad (2.9)$$

where H is the total energy of the system. The first term represents the kinetic energy of the system with N being the total number of atoms and P_i the momentum of the i -th atom. The second term is the potential energy of the system with α, β representing Cartesian coordinates. $\Phi_{\alpha\beta}(\vec{R}_i^0, \vec{R}_j^0)$ is the force-constant matrix and $\vec{R}_i^0, \vec{R}_j^0$ and $\vec{u}_{i\alpha}, \vec{u}_{j\beta}$ the equilibrium position and displacements of atoms i and j respectively.

Using periodic boundary conditions, a Fourier transform can be used on the force-constant matrix leading to

$$D_{\alpha\beta}(\vec{k}) = \sum_i \Phi_{\alpha\beta}(\vec{R}_i^0) \exp(i\vec{k} \cdot \vec{R}_i^0). \quad (2.10)$$

The diagonalised force-constant matrix can be written as

$$\sum_{\beta} D_{\alpha\beta}(\vec{k}) e_{\nu\beta}(\vec{k}) = D_{\nu}(\vec{k}) e_{\nu\alpha}(\vec{k}), \quad (2.11)$$

where $D_{\nu}(\vec{k})$ are the eigenvalues with $\nu = 1, 2, 3$ corresponding to the two transverse and one longitudinal mode of the acoustic branches of a 3D lattice, and $e_{\nu}(\vec{k})$ are the eigenvectors. The dispersion relation, which relates the angular frequency ω to the wavevector $\vec{k}$ is obtained from the eigenvalues $D_{\nu}(\vec{k})$ as

$$\omega_{\nu}(\vec{k}) = \sqrt{\frac{D_{\nu}(\vec{k})}{M}}, \quad (2.12)$$

where M is the atomic mass. This relation describes the set of all phonon eigenmodes, which determines a material's density of states (DOS).

The Bose–Einstein distribution (2.4) determines the population of each eigenmode at a specific temperature. Acoustic modes have a linear dispersion and relatively low DOS and contribute primarily at lower temperatures, while optical modes have a narrow dispersion and high DOS and dominate at high temperatures. The difference between material types (isotropic or anisotropic) lies in the symmetry of the force-constant matrix $\Phi_{\alpha\beta}$ and the resulting dynamical matrix $D(\vec{k})$.

As the interatomic force constants in an isotropic material are rotation-invariant, the eigenvalues and phonon frequency ω depend only on the magnitude $|k|$ and the eigenvectors are purely longitudinal or purely transverse. However, phonons travel faster along atomic chains, meaning the force constants vary based on direction in anisotropic materials, as do the eigenvalues and the phonon frequency, and the eigenvectors are a combination of longitudinal and transverse modes.

2.2 Electron scattering

Electrons, which pass through the sample and scatter from its atoms, form the basis of transmission electron microscopy, providing information on the specimen structure and chemical composition. There are two main types of scattering. Elastically scattered electrons maintain their incident energy and only their momentum vector is changed as they are deflected by the Coulomb potential of the atoms' nuclei. They can be used to determine the spatial charge density distribution and thus the atomic structure of materials. Inelastically scattered electrons lose a part of their kinetic energy, which is transferred to the sample by interacting with a shell electron of the specimen or exciting plasmons or phonons. These provide information about electronic structure and other excitations. When a shell electron is knocked out, an electron from a higher shell drops down to fill the hole in the lower shell, possibly via a radiative transition. This releases energy in the form of an X-ray. These have a characteristic energy, depending only on the element and can thus be used for elemental analysis.

Some specimen-beam interactions are depicted in figure 2.2, where beam electrons (yellow) are generated by the microscope's electron gun. Heavier atoms have a stronger positive nuclear charge and deflect elastically scattered electrons more strongly, resulting in more backscattered electrons (red), which is used to show compositional contrast in scanning electron microscopy (SEM). Specimen electrons (black) originally belonging to the outer shells of the atoms of the sample can be ionized and subsequently ejected from the specimen. Secondary electrons that have been displaced from their shell by the incident beam through inelastic scattering (pink) are low-energy electrons that can only escape from the surface of a sample. These are used for topography imaging in SEM.

While inelastically scattered electrons retain no phase relationship, elastic scattering up to an angle of 10° remains mostly coherent. The probability of an electron being scattered as it passes near an atom is described by the cross section σ_{atom} [8]. In an elastic scattering event this is di-

rectly related to form factors, which are the Fourier transform of the charge-density distribution.

The total cross section

$$\sigma_{tot} = \frac{N_0 \sigma_{atom} \rho}{A}, \quad (2.13)$$

multiplied by the specimen thickness, represents the total probability of scattering. N_0 is Avogadro's number, ρ is the mass density of the specimen and A is the atomic weight. $(N_0 \rho)/A$ equals the number of atoms per unit volume, and σ_{atom} is the cross section of a single atom derived by integrating the square of the form factor over all scattering angles.

The average distance traveled between two scattering events is given by the mean-free path

$$\lambda = \frac{1}{\sigma_{tot}} = \frac{A}{N_0 \sigma_{atom} \rho}. \quad (2.14)$$

A higher atomic number (Z) thus leads to larger scattering angles and a higher cross section and consequently to a shorter mean-free path, whereas a higher beam voltage leads to a lower cross section and a longer mean-free path as the increased electron velocity reduces the interaction time with the atomic potential.

Scattering of the electron wave occurs because the sample acts as a three-dimensional electrostatic potential that modulates the incident wave. To account for the short wavelength of the highly accelerated electrons used in TEM, the electrostatic potential $V(\vec{r})$ is inserted into the relativistically corrected time-independent Schrödinger equation, to solve for the electron wave function $\psi(\vec{r})$ [9]:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \right) \psi(\vec{r}) = E \psi(\vec{r}), \quad (2.15)$$

where $m = \gamma m_0$ is the relativistic mass, m_0 being the rest mass and $\gamma = (1 - \frac{v^2}{c^2})^{-\frac{1}{2}}$ the Lorentz factor. E represents the relativistically corrected kinetic energy $E = eU(1 + \frac{eU}{2m_0 c^2})$, with U being the accelerating voltage. The screened Coulomb potential $V(\vec{r})$ represents the electrostatic potential of the atoms in the specimen, which drives elastic scattering.

For high-energy electrons and thin samples, the weak phase object approximation (WPOA) can be used, which simplifies the solution by assuming the wave travels along the z -direction and only experiences a phase change that can be described by the projected potential. The exit wave can then be expressed as

$$\psi_{exit}(x, y) = \psi_0 \exp \left[i\sigma \int V(x, y, z) dz \right], \quad (2.16)$$

where ψ_0 is the incoming electron wave and the interaction parameter σ [10] is defined as

$$\sigma = \frac{2\pi m e \lambda}{h^2}, \quad (2.17)$$

with the relativistically corrected wavelength $\lambda = \frac{h}{\sqrt{2m_0E}}$. The resulting exit wave is the complex wave function at the time it leaves the sample, where the phase term $\exp[i\sigma \int V(x, y, z)dz]$ is responsible for the lattice images and diffraction spots. As the electron wave passes through the potential, it causes a local phase shift of the electron wave relative to its path in a vacuum, leading to interference between the scattered and unscattered waves at the image plane. Because the phase object approximation assumes a purely phase-shifting specimen without beam depletion, it is highly suited for very thin materials. As monolayer graphene was used as a sample it can be treated as a nearly ideal phase object due to its single-atom thickness. Despite this, dynamical scattering was accounted for via the multislice method (see section 2.4) [11].

The electrostatic potential $V(\vec{r})$ arises from the atom's heavy nucleus and its surrounding electron shells. The nucleus acts as a strong, point-like positive Coulomb potential, which is highly localised and responsible for deflecting the incident beam electrons. However, this positive charge is screened by the atom's electron cloud, which reduces the effective range of the potential field. In the context of the WPOA, the three-dimensional screened potential is integrated along the beam propagation direction (z -direction). This results in a two-dimensional projected potential, where the sharp peaks indicate the positions of the atomic nuclei, while the broader features are shaped by the screening effect of the surrounding electrons.

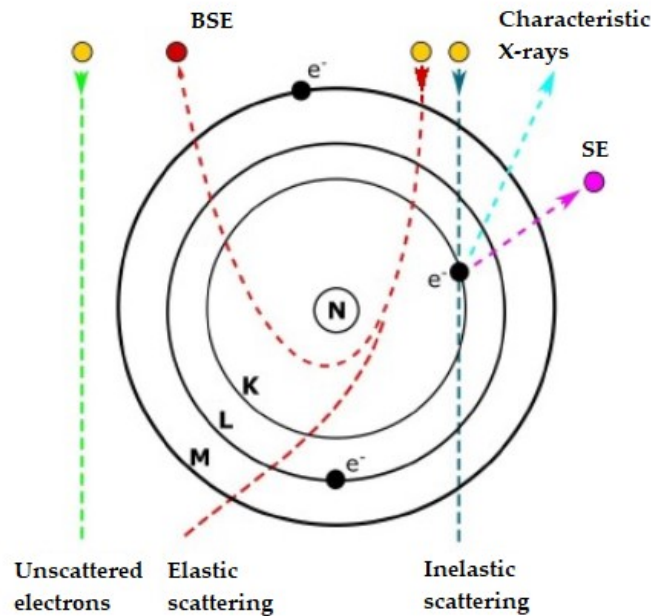


Figure 2.2: Specimen scattering: beam-electrons (yellow) undergo elastic scattering and get deflected or backscattered (red) by the nucleus. Low energy secondary electrons (pink) are emitted after interacting with specimen electrons (black), which generates characteristic X-rays. Image adapted from [12].

2.2.1 Thermal diffuse scattering

Electron-phonon scattering, called thermal diffuse scattering (TDS) in the context of TEM, can be categorised as quasi-elastic, as energy losses are smaller than a few hundred meV. Due to atoms in a crystal oscillating around their equilibrium positions, scattered waves lose their perfect coherence, which results in a diffuse, continuous intensity in diffraction patterns, between the sharp Bragg reflections of the equilibrium lattice. With the intensity highest near the Bragg reflections and extending to high angles of scattering, it ultimately results from the material's phonon dispersion. As atomic vibrations get stronger with rising temperature, the diffuse intensity increases, while the intensity of the Bragg peaks decreases. This reduction is described by the Debye–Waller factor

$$M = 8\pi^2 \langle u^2 \rangle \frac{\sin^2(\theta)}{\lambda^2} = B \frac{\sin^2(\theta)}{\lambda^2}, \quad (2.18)$$

where $\langle u^2 \rangle$ is the mean-square displacement of the atoms, the Debye–Waller parameter $B = 8\pi^2 \langle u^2 \rangle$, θ is the Bragg angle and λ the wavelength of the incident electrons. Though mostly incoherent, phonon-scattered electrons can retain some coherence and contribute significantly to image contrast as well as form interference patterns such as Kikuchi lines, which appear when scattered electrons satisfy the Bragg condition as they travel through the sample.

The Einstein model offers the simplest way to model TDS, as it assumes atoms as uncorrelated oscillators, vibrating independently of each other (see section 2.1.1). A more accurate method to generate these atomic displacements is based on realistically correlated vibrations using the force-constant potential (see section 2.5). To determine the vectors and frequencies of the displacements of the atoms in these atomic configurations, the dynamical matrix $D(\vec{k})$ is used for the transformation between real-space force constants and the reciprocal-space vibrational properties. Diagonalising it defines the phonon modes used to generate the configurations. These are then used in the phonon displacement operator

$$u_l = \sqrt{\frac{1}{NM}} \sum_{q,j} Q_{q,j} e_{q,j}^{iq \cdot R_l}, \quad (2.19)$$

which expresses the displacement of each atom as a linear combination of these modes weighted by their respective thermal amplitudes. Here u_l is the displacement vector of the l -th atom, N is the number of unit cells in the crystal, M mass of the atom. $Q_{q,j}$ is the normal coordinate for a phonon with wavevector q and branch j and $e_{q,j}$ its eigenvector, while R_l is the vector of the equilibrium position of the l -th atom. The amplitudes $Q_{q,j}$ follow the Bose-Einstein distribution (see 2.4), ensuring the model accurately represents how thermal vibrations scale with temperature.

Regardless of how these displacements are generated, the configurations can be used in the frozen-phonon method for multislice simulations [5]. By generating static snapshots and averaging their intensities, the simulation should ideally recover the thermal diffuse scattering observed in experiments. This approach is more robust than analytical models because it inherently includes all higher-order multi-phonon processes without needing extra approximations. This approach is based on the adiabatic approximation

$$\langle I(\vec{k}) \rangle \approx \frac{1}{N} \sum_{n=1}^N I_n(\vec{k}), \quad (2.20)$$

with $I_n(\vec{k})$ representing the intensity from a single snapshot of atomic displacements $\vec{u}_l$ and N being the number of frozen phonon configurations. This assumes that the incident electron travels through the sample fast enough to regard the atoms of the configuration effectively as frozen, and the averaging accounts for the loss of coherence caused by thermal vibrations.

2.3 TEM

Transmission electron microscopy (TEM) is an indispensable imaging technique to study the composition and properties of materials down to the atomic level. Operating on similar basic principles as a visible-light microscope, it uses a beam of electrons instead of light and electromagnetic lenses (usually consisting of a series of individual lenses) are used to focus and manipulate the beam. Electrons have a much smaller de Broglie wavelength

$$\lambda = \frac{hc}{\sqrt{K^2 + 2Km_0c^2}}, \quad (2.21)$$

where h is Planck's constant, c is the speed of light in a vacuum, K is the (relativistic) kinetic energy of the electron, and m_0 is the electron rest mass. The smaller wavelength compared to photons of the visible spectrum results in a significantly higher resolution of around 0.2 nm and, with the integration of correctors into the microscope, can even reach a few tens of pm.

A field-emission electron gun (FEG) at the top of the column serves as an emission source as seen in figure 2.3, which uses a single-crystal tungsten wire as a cathode with a tip radius of 100-200 nm. A strong electrostatic field is applied to the cathode surface, which lowers the potential barrier and results in quantum-mechanical tunnelling of electrons out of the metal at room temperature. Two types of anodes are used, one to pull electrons from the tip and one to accelerate them. At typical voltages of around 60 to 300 kV, this produces a stream of relativistic electrons

which is then focused and manipulated by a series of electromagnetic lenses further down the column.

The condensor lenses control the beam formation and intensity by focusing the electrons emitted from the source into a thin, coherent beam and varying the lens excitation to regulate the amount of current hitting the specimen, as a small point source is essential for high-resolution imaging and also reduces the irradiation of the specimen outside the field of view. A condensor aperture blocks high-angle electrons and reduces aberrations, as condensor stigmators correct for beam astigmatism caused by lens imperfections or contamination of the microscope's internal components. Condensor lenses also control the incident angle at which electrons hit the specimen, which allows for either parallel (TEM) or convergent-beam illumination (STEM and Convergent Beam Electron Diffraction [CBED]).

The electron beam then hits the specimen, which sits on a sample grid that is held by the specimen stage. The specimen needs to be thin (around 100 nm or less) to be electron-transparent and allow the beam to be transmitted through. The grid is a 3.05 mm diameter mesh-like disc usually made of copper or gold to avoid magnetic interference and acts as a support for the specimen. The specimen stage in turn allows for tilting, which is used to align crystal axes with the electron beam, and movement in x - and y -directions, in order to find specific areas of the sample. It is designed to minimize vibration and thermal drift.

Some electrons pass through the sample unhindered, others interact primarily through Coulomb forces with the nuclei of the atoms, which results in elastic scattering. Both are used for TEM, though there is a wide variety of other signals generated from the electron-specimen interaction. The number of electrons reaching the detector depends on local density and composition: the denser the area of the sample, the more scattering (or to higher angles).

The objective lens forms the first real, magnified image in the image plane and a diffraction pattern in the back focal plane. The main factors in limiting the spatial resolution of the TEM are spherical and chromatic aberrations of the objective lens. To mitigate these, spherical aberration correctors are commonly installed between the condensor system and the objective lens. Changing the focal length is achieved by varying the electrical current of the objective lens' windings. The objective aperture is positioned in the back focal plane and is used to block all rays outside a maximum distance of the optical axis of the electron beam. This enhances the contrast and can be used to create bright-field and dark-field images. In bright-field images, the direct beam, which does not interact with the sample is primarily detected, therefore strongly scattering areas

appear dark and weakly scattering areas appear bright. Conversely, in dark-field images only the scattered electrons get detected, so that weakly scattering areas appear dark, and strongly scattering areas bright.

The radius in the aperture corresponds to spatial frequency in the image. To maximize phase contrast for high-resolution imaging, the objective aperture is set to the Scherzer defocus

$$\Delta f_{Sch} = -1.2\sqrt{C_s\lambda}, \quad (2.22)$$

where C_s is the spherical aberration coefficient of the objective lens, and λ is the relativistic de Broglie wavelength of the electron. This sets the maximum cut-off to coincide with the first zero crossing of the transfer function, which allows for a broader band of spatial frequencies to be transferred with consistent contrast. In imaging mode, the objective lens introduces phase shifts due to aberrations and defocus, described by the Contrast Transfer Function (CTF):

$$\Psi_{im}(\vec{k}) = \Psi_{exit}(\vec{k}) \cdot e^{-i\chi(\vec{k})}, \quad (2.23)$$

where $\Psi_{im}(\vec{k})$ is the Fourier transform of the image wavefunction, $\Psi_{exit}(\vec{k})$ represents the Fourier transform of the exit-surface wavefunction, $e^{-i\chi(\vec{k})}$ is the phase transfer function and $\chi(\vec{k})$ is the phase aberration function. The CTF acts as a filter in reciprocal space, and determines how the exit-wave information is transferred into the final image contrast.

The objective aperture is optionally followed by a selected-area diffraction aperture (SAD aperture), a metallic plate with various-sized holes, which allows electrons that only pass through a specific region of the sample. The intermediate lens is used to select between imaging and diffraction modes, by varying the strength of this lens. It magnifies the first intermediate image or the diffraction pattern produced by the objective lens and projects it onto the projector lens. For imaging mode the lens is focused on the image plane, for diffraction mode on the back focal plane of the objective lens. A set of electromagnetic coils, the stigmators, are used to correct astigmatism, which ensures the magnetic field is perfectly symmetrical and the resulting image is sharp. The projector lens in turn expands the beam, providing the final magnification of the image and projects it onto the detector, either a fluorescent screen for real-time viewing or a digital CCD/CMOS camera for recording, which forms the final two-dimensional image. Because electrons in a magnetic field follow a spiral trajectory, changing the strength of a lens results in a rotation of the final image on the detector screen. The entire beam path, from source to detection, takes place in a high vacuum, to prevent electron scattering from air molecules. Due to the high magnification, the depth of focus of the projector system is very large, ensuring the final image remains sharp over the entire detector.

In scanning transmission electron microscopy (STEM), the optical configuration is reversed compared to TEM. Instead of illuminating the entire field of view simultaneously, the condensor lenses and a dedicated probe-forming objective lens focus the electron beam into a highly demagnified, sub-nanometer probe. Using electromagnetic deflection coils, this probe is raster-scanned across a designated region of the specimen, and the intensity of the transmitted and scattered electrons is recorded sequentially at each probe position by single-element or pixelated detectors. By recording the full two-dimensional scattering distribution at every scan position, a pixelated detector yields a four-dimensional dataset from which various imaging modes can be computationally reconstructed. As the image is reconstructed serially from the raster path, the spatial resolution in STEM is governed by the size and profile of the focused electron probe, rather than the aberrations of post-specimen lenses.

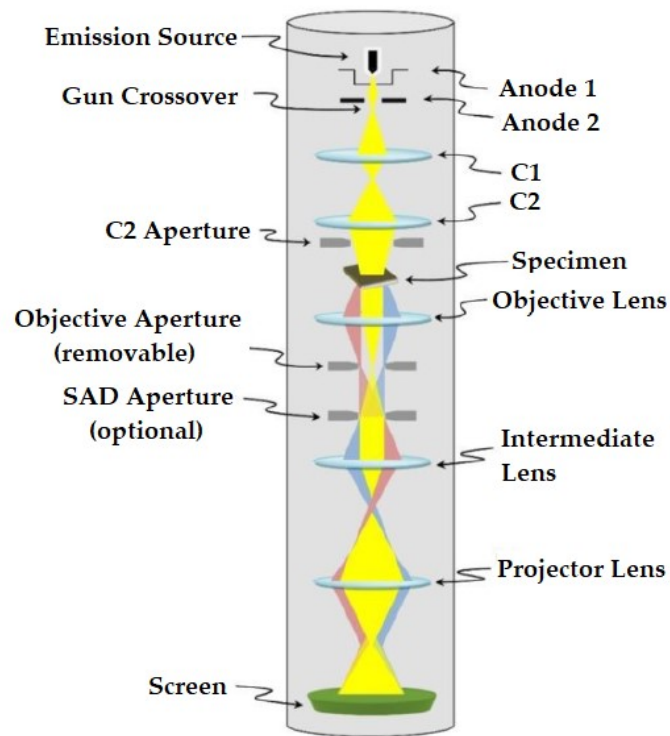


Figure 2.3: Setup of a transmission electron microscope. The beam travels from the electron source and anode assembly at the top, passing through the condensor system to the specimen. The transmitted beam is then focused by the objective lens, filtered via apertures and magnified by image forming lenses onto the viewing screen at the base of the column. Image adapted from [13].

2.4 Multislice simulation

The multislice algorithm, implemented in *abTEM* [5], is used to simulate electron scattering by numerically integrating the time-independent Schrödinger equation. It accounts for multiple scattering effects and provides a more accurate method than simpler models (see section 2.1.1). For high-energy electrons, this is simplified to a first-order differential equation in the beam direction (z) [10]

$$\frac{\partial \psi(\vec{r})}{\partial z} = \left[\frac{i}{4\pi k} \nabla_{xy}^2 + i\sigma V(\vec{r}) \right] \psi(\vec{r}), \quad (2.24)$$

where k is the electron wavevector. Instead of treating the sample as a continuous three-dimensional body, its potential $V(\vec{r})$ is divided into thin slices of thickness Δz , perpendicular to the incident beam, which must be sufficiently thin so that the potential of one slice can be collapsed into a two-dimensional projected potential

$$V(x, y) = \int_z^{z+\Delta z} V(x, y, z) dz. \quad (2.25)$$

To simulate scanning transmission electron microscopy (STEM), the initial wave function $\psi_0(x, y)$ is defined as a focused electron probe. This probe is formed by focusing a coherent beam of high-energy electrons through a condensor lens and an objective aperture, which converges the plane wave into an Ångström sized spot on the sample, whose shape is modified by the contrast transfer function (see 2.23).

The incident electron wave ψ interacts with the slice potential via the transmission function t , undergoing a phase shift, which equals a multiplication in real space (phase object approximation, POA)

$$t(x, y) = \exp(i\sigma V(x, y)), \quad (2.26)$$

where σ is the interaction constant, which depends on the electron wavelength λ . After each slice, the wave propagates through vacuum to the subsequent slice using the Fresnel propagator

$$p(x, y, \Delta z) = \frac{1}{i\lambda\Delta z} \exp\left(\frac{i\pi}{\lambda\Delta z}(x^2 + y^2)\right). \quad (2.27)$$

The multislice method alternates between transmission and Fresnel propagation. The wave is scattered from the potential in one slice, propagates through the space between the slices, then gets scattered by the next potential slice. This iterates through all slices, determining the wave function at the exit plane of the sample. The wave function at each next slice, $\psi_{z+\Delta z}$, is calculated through a convolution (*)

$$\psi_{z+\Delta z}(x, y) = p(x, y, \Delta z) * [\psi_z(x, y)t(x, y)]. \quad (2.28)$$

In *ab*TEM, Fast Fourier Transforms (FFTs) are used to compute the propagation, making the convolution a simple multiplication and meaning the wave function can be rapidly alternated between real space, for the interaction of the electron with the potential slice, and reciprocal space, for the propagation

$$\psi_{z+\Delta z}(x, y) = \mathcal{F}^{-1}\{P(k_x, k_y, \Delta z)\mathcal{F}[t(x, y)\psi_z(x, y)]\}, \quad (2.29)$$

where P is the Fourier transform of the Fresnel propagator. To ensure convergence within *ab*TEM, the slice thickness (Δz) was set to 0.5 Å, while the spatial sampling was set to one fourth of the Nyquist limit. This anti-aliasing filter was applied to both transmission and propagation.

Unlike plane-wave imaging, a STEM image is formed serially. The multislice propagation is repeated for each probe position as the focused beam is raster-scanned across the sample. The final image is captured by a pixelated detector, which records the two-dimensional intensity distribution of the exit-wave function in reciprocal space at every probe position, allowing for various imaging modes to be reconstructed from the 4D-dataset.

2.5 Force-constant potential

To accurately simulate lattice dynamics, it is necessary to determine the force constants that define the system's phonon modes. A Gaussian approximation potential (GAP) is used here to extract the force constants necessary for the subsequent phonon calculations (see 3.2).

The force constants, which define the strength of the bond between atoms, can then be extracted from a Taylor expansion of the potential around an equilibrium position. The Taylor expansion of the energy H , where u_i gives the displacement from the equilibrium positions, is

$$H = H_0 + \Phi_i^\alpha u_i^\alpha + \frac{1}{2}\Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{6}\Phi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \dots, \quad (2.30)$$

where the zero-order term H_0 represents the energy of the static lattice, the first-order term Φ_i^α the forces of a structure at equilibrium, the second-order term $\Phi_{ij}^{\alpha\beta}$ represents the harmonic force constants, and third- and higher-order are the anharmonic terms. The energy of the static lattice is minimised at equilibrium, as is the first-order term of the potential, leaving only the second- and higher-order terms.

Comparing the second-order term with the potential energy H of a system given by

$$H = \frac{1}{2}kx^2, \quad (2.31)$$

where x is the displacement from the equilibrium position $u_i^\alpha u_j^\beta$, and k being the force constant, shows the force constants are the second-order derivatives of the energy, making the force-constant potential a local approximation of the potential. This is computationally faster and accurate for small displacements around the equilibrium, though less so for larger displacements. Rattled structures are generated and the forces calculated using the potential. The utilized hiPhive package [14] uses linear regression to subsequently fit the force constants to these forces. The resulting symmetry-consistent force constants follow the potential's behaviour near equilibrium and provide a comparatively fast way to model the vibrational properties of a system.

Chapter 3

Simulation methodology

This section outlines the computational workflow used to model graphene and analyse the effect of its vibrational anisotropy on imaging at different temperatures. The process integrates ASE [15] for structure handling, hiPhive [14] for configuration sampling, and *ab*TEM [5] for simulations of 4D-STEM data from first principles. The scripts of the implemented code are provided in the appendix.

3.1 Unit cell creation

Using the Atomic Simulation Environment (ASE), a primitive graphene monolayer structure was created with 4 Å of vacuum on each side in the z -direction perpendicular to the created graphene sheet. Periodic boundary conditions were enabled, thus the x and y -directions could be treated as part of an infinitely repeating structure to avoid edge effects, while the vacuum prevents interactions with periodic images in the z -direction.

To store these properties, a single-point calculator was attached to an instance of the ASE *Atoms* class. For a given atomic configuration, this allowed the storage of computed potential energy and atomic forces as a single point of a potential energy surface, which was retrieved using existing methods of the class.

3.2 Machine-learning potential

The used machine learning potential was sourced from [4]. This is a Gaussian approximation potential (GAP) trained for carbon and presents an accurate and transferable model capable of predicting the behaviour of carbon in various configurations. The model utilises Gaussian process regression (GPR), which is a non-parametric method that predicts energy by measuring the similarity between atomic configurations to learn the complete potential energy surface and forces. The GAP defines how the potential behaves based on the chosen atomic configuration, using the smooth overlay of atomic positions (SOAP) descriptor to represent the local atomic environments. This descriptor expands the neighbour density into a series of basis functions to encode the local geometry, ensuring invariance to rotation and translation. This model provides high numerical accuracy, including configurations far from equilibrium.

The resulting calculation object holds this potential information and the specified parameters. By linking this calculator to the atomic structure, all calculations on the created primitive graphene cell used the defined potential.

3.3 Force-constant potential

A graphene supercell was created by tiling the primitive cell to dimensions six times that of the primitive cell in both the x and y -dimensions, while remaining a single layer in the z -direction. A Monte Carlo algorithm was used to generate ten different rattled configurations for the passed supercell. The standard deviation for the random displacements applied to the atoms in the supercell was set to $1 \cdot 10^{-4}$, though this does not directly translate to the final displacement of the atoms. Additionally, the minimum interatomic distance parameter was set to 1.3 Å. However, this does not completely prevent atom from coming too close to each other, though the likelihood of such a move being accepted by the Monte Carlo algorithm is low.

Iterating over each of the ten rattled structures, force calculations were performed. The resulting potential energy and forces from the atomic structures were stored by applying the previously defined single-point calculator function to each instance. This iterative process was monitored in real time using a progress bar utility to provide feedback, and the calculated structures were stored for later use.

A hiPhive *ClusterSpace* object was then defined by assigning the graphene supercell along with

a cut-off parameter, which defines the spatial limits for interactions of clusters of atoms. This parameter was set to 6.0 Å meaning it included second-order terms up to that distance. By computing the displacements and forces relative to the ideal supercell, a list of prepared structures and their associated properties was generated. A structure container was initialized using the defined *ClusterSpace* and then sequentially populated by adding the prepared structures.

The fitting data for the structures was retrieved from the *StructureContainer* and passed to an optimizer constructor. The train method then split the fit data, defaulting to 90% for the training set and 10% for the test set since no explicit size was specified. The optimizer fitted the training set and used the results to generate predictions for the test set, after which both the actual and predicted results were stored in a *Model* instance.

Born-Huang and Huang rotational sum rules [16] were enforced on the parameters retrieved from the optimizer. This ensured rotational and translational invariance in the results. A force-constant potential was then created using the *ClusterSpace* and the parameters adjusted by these rotational sum rules. This was written to disk for convenience, and in subsequent initialisations of the code read from the file.

A dedicated plotting function utilized phonopy [17] and ASE to calculate and plot the phonon-dispersion relations for the graphene unit cell based on the force-constant potential. To this end, a *PhonopyAtoms* object representing the atomic structure was created using the chemical symbols, cell parameters, and scaled positions of the primitive cell. After this, a supercell was constructed based on the previously specified dimensions of six times the primitive cell in the x - and y -directions, and a single layer in the z -direction. The primitive matrix was determined automatically by phonopy, and a conversion factor was defined to convert units to THz.

3.4 Rattled supercells

In a corresponding setup function, supercells of arbitrary size can be created by repeating the primitive cell across the lateral dimensions. The harmonic terms (as anharmonic terms were not needed here) for this supercell were retrieved from the force-constant potential in a format compatible with ASE. The function then returned both the generated supercell and its corresponding array of second-order force constants.

HiPhive's *generate_phonon_rattled_structures* function was used to create a specified number

of rattled configurations at a specific temperature. This generated structures based on a superposition of normal modes, ensuring that the atomic positions represent a physically accurate harmonic crystal by accounting for the collective vibrations of the lattice rather than treating each atom as an independent oscillator (see 2.1.1).

To make the rattled structures compatible with *abTEM*'s required orthogonality, the primitive graphene cell was orthogonalised before it was passed to the setup function. along with the corresponding force-constant potential, desired temperature and the chosen dimensions of the supercell to be created, which were defined as ten, six, and one for the x , y and z dimensions, respectively. To compare the accurate anisotropically rattled structures to the isotropic Einstein model, snapshots were also generated with the existing functionality of *abTEM*.

3.5 Matching the isotropic displacement magnitude

To make the results of the isotropic and the anisotropic model more comparable, the magnitude of the isotropic displacement amplitude was matched by finding a value at each temperature that generates a similar distribution of interatomic distances. For this, a code block from hiPhive was utilized, though slightly adapted. First, the bins for the displacement histograms were set up, with a range of 0.0 to 0.7 divided into 200 intervals. A histogram function then computed the normalized histogram of the displacement data, where setting the density parameter to true scaled the data appropriately. The bin centres were calculated by averaging the edges of each bin, returning the specific counts of data points along with the corresponding edges of each bin interval.

The *get_projected_distributions* function first initialized an empty list to store the displacements, then iterated through the list of atomic structures. A copy was created of each configuration, and the z -coordinate of each atom within it was set to zero. This projection was performed to avoid disproportionately large values of displacements in the z -direction due to the essentially two-dimensional nature of the material and its low-energy out-of-plane phonon modes. The displacements of each of the now-projected atoms were then calculated with regard to a reference position by computing the vector norm across the x and y coordinates. A dictionary to store the histogram data for the displacements was created, populated and returned.

A function was defined to return the lognormal probability density function of the passed data based on the amplitude, μ , and σ parameters. Following this, the *fit_lognormal_distributions*

function calculated the area under the displacement curves for both the isotropic and anisotropic distributions using the trapezoidal rule, then normalized these distributions by dividing the data by its respective calculated area.

Masks were generated to filter out zero values in the normalized distributions, as these would pose a mathematical problem for the lognormal fit. The filtered data was stored in arrays which were then fitted to the previously defined lognormal probability density function using a curve-fitting algorithm. An initial guess array containing values of 1.0, 0.5, and 0.5 was passed to initialize the optimizer. The fitted values were then calculated using the optimized parameters, returning the final fitted data and the resulting lognormal distributions for each respective model.

The *generate_atoms* function generated a number of atom ensembles at a set temperature, using the *abTEM FrozenPhonons* class for the isotropic model and the previously defined phonon rattling function for the anisotropic model. Both models were based on the already created graphene supercell, while only the anisotropic model uses the calculated force constants. Note here the factor $\sqrt{3}$ stemming from the definition of the isotropic sigma in the frozen-phonons class. These generated atom ensembles were passed to a plotting function, which first called the projected distributions function using the positions of the original supercell as the reference positions, then passed the returned distributions on to the fit lognormal distribution function. The returned coordinate values were plotted, and the value of the isotropic sigma parameter passed to the generate atoms function was adjusted until the fitted distribution curves for the isotropic and the anisotropic model overlapped. This was done for four different temperatures—0, 300, 1000, and 1800 K—and their suitable corresponding sigmas were determined. The built-in ensemble mean calculation was disabled, and the averaging process performed manually in the subsequent functions.

3.6 Projecting the potentials

To project the potentials of the respective ensembles and the reference supercell, they were passed to the project function of the *abTEM potentials* class, where the electrostatic potential of each configuration was calculated and subsequently meaned. The spatial sampling was defined based on the dimensions of the primitive unit cell, dividing the first lattice vector by 64 and the second vector by 52 to establish the grid spacing. Accepting the trade-off of longer computation times for a more precise result, the projection was set to finite and thus calculated over a limited, specific

slice of space using numerical methods. The static potential along with the two mean potentials were then projected, stacked for convenience, and returned with the sampling parameter.

3.6.1 Interpolated lines of projected potentials

Interpolated lines were calculated over the projected and mean potentials using the *ab*TEM interpolation framework. Starting at the coordinates of a specific centre atom within the supercell, the lines were interpolated outwards along the three main symmetry directions spaced exactly 120° apart, at angles of 90° , 210° , and 330° , to an extent of $4.5 \text{ \AA}$. The calculations used an interpolation sampling step calculated by dividing the mean of the spatial sampling parameters by 16. These too, were then stacked for convenience and returned.

3.7 Simulating 4D-STEM

For the STEM simulations a pixelated detector was selected as this allows for the reconstruction of results of all other detector models from the 4D data cube. It was set to record the intensity of the diffraction patterns up to 200 mrad . To accommodate as large a number of phonon modes as possible, a relatively large supercell of dimensions $10 \times 6 \times 1$ was used. The dimensions of the orthogonalised unit cell were set along with a small offset for the later definition of the scan area see figure (3.1). A potential based on the previously created supercell was calculated, with the sampling set to $0.04 \text{ \AA}$. A probe was defined with an energy of 60 keV and a semi-angle cutoff of the aperture of 35 mrad . A grid scan was defined over the potential of the supercell, using the previously defined dimensions of the unit cell (with offset) as the start and end points. The scan area was chosen in the middle of the supercell to mitigate edge effects and ensure the results are representative of the bulk properties material. The sampling of the grid scan was set to a quarter of the Nyquist sampling rate to avoid aliasing. The calculate function was given the supercell and the already generated atoms ensembles for both the isotropic and the anisotropic model. The electrostatic potentials of each of the models was calculated along with the potential of the supercell used as a reference. A grid scan was then performed over the static, the isotropic and the anisotropic potential using the already defined probe and pixelated detector parameters, and the measurements of the different configurations were subsequently meaned. The measurements were stacked for convenience and the stack returned.

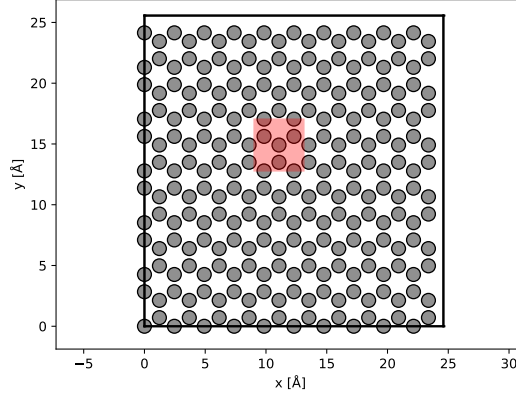


Figure 3.1: Top view of the graphene supercell (xy -plane) with the area of the grid scan marked in red.

3.7.1 Adding Poisson noise

To emulate typical shot noise in STEM data, five different doses of Poisson noise were added to the grids can stack, from the lowest dose of 10^4 to the highest of 10^8 electrons per square Ångström.

3.7.2 ADF measurements

To simulate annular dark field (ADF) measurements, the ideal (un-noised) stack of grids can diffraction patterns was integrated radially, between an inner integration limit of 37 mrad and an outer limit of 150 mrad. The same was done with the noised stack of STEM measurements. The relative differences were taken and plotted between the static cell and both the isotropic and the anisotropic model as well as between the two models themselves, of both the noised and ideal stacks.

3.7.3 Integrated centre of mass (iCOM)

The integrated centre of mass was calculated from the ideal diffraction patterns as well as the noised ones, where the centre of mass vector field was integrated via its gradient to return the phase of the complex images. As was already done with the projected potentials, interpolated lines were calculated over the ideal integrated centre of mass measurements of all four temperatures, starting at the central atom position and differing by 120° over a distance of 4.5 Å. The relative differences were taken and plotted for both noised and non-noised images.

3.8 Verifying convergence

Convergence was verified with regard to the potential sampling, number of atomic configurations in the atoms ensemble and the size of the supercell, to ensure accurate results. As the sampling rate directly impacts the resolution and insufficient sampling can lead to aliasing, an anisotropic ensemble, containing 20 configurations of the monolayer supercell of dimension ten by six unit cells, at a temperature of 300 K was created. A gridscale was performed over it at nine different sampling rates respectively, ranging from 0.02 to 0.10 Å/px, after which the results of each individual sampling rate were meaned. To calculate the convergence, first the mean-square error, computed as the sum of squared differences divided by the total number of pixels, and then the structural similarity index measure (SSIM) and relative mean-squared error (MSE) was calculated between the integrated centre of mass images of the 0.02 sampling rate results and the iCOM images of the other sampling rates and subsequently plotted. The relative MSE was normalized by dividing the raw mean-square error by the mean squared intensity of the reference image. The number of frozen phonon images was varied by generating an ensemble of 50 configurations and performing gridscales over the potentials of 14 subsets, ranging from just one configuration to all 50, after which the results of each individual subset were meaned. The chosen sampling rate was 0.04. Again the SSIM and relative MSE was calculated between the results of the subset containing all 50 configurations of the original ensemble and the subsets containing fewer. The SSIM and relative MSEs were then plotted. To vary the size of the supercell, new force constants corresponding to the new dimensions of the used supercell were generated for each individual cell size. The sampling rate was again set to 0.04 and the chosen number of configurations was 20. The dimensions of the supercell ranged from five by three to eleven by six unit cells and custom grid scans were defined for each to keep the area of the scan in the centre of the supercell. The iCOM images of the resulting measurements were once more meaned and compared via SSIM and relative MSE to the iCOM image of the eleven by six supercell and subsequently plotted.

Chapter 4

Results and Discussion

The primary goal of these simulations was to test the simple Einstein model against the computationally more demanding correlated-phonon displacements when it comes to measuring anisotropic vibrations. To achieve this, 4D STEM was simulated, and subsequently ADF and iCOM images were reconstructed for both the isotropic (Einstein) and anisotropic model as well as the static reference structure. The following subsections show the findings, beginning with the results of matching the isotropic sigma to ensure a consistent comparison between the two models.

4.1 Interpretation of results

4.1.1 Isotropic sigmas

For comparability of the isotropic and anisotropic model, displacement histograms were generated for both supercells at four different temperatures: 0, 300, 1000 and 1800 K. The displacements of the atoms in each configuration were three-dimensional, and as monolayer graphene is an essentially two-dimensional material, this led to large displacements in the z -direction which caused the anisotropic curve to be skewed. Figure 4.1 shows top and side views of both supercells at 1800 K above the corresponding displacement histogram. The solid lines in the left graph show the original displacement data, which was normalised. The solid lines in the right graph show the lognormal fit of the normalized data. With the normalised curves and their lognormal fits cutting off in the x -direction where the original curves reached zero, the curves of the anisotropic model

exhibit a notably long tail. To correct for this, the locations of the atoms were projected before the displacements were calculated. Figure 4.2 shows the histogram curves for both models at 300 K without the z -direction taken into account. (For the histogram curves of the models at the other temperatures see figure A1 in the appendix.) All displacements used for the calculations are based on second-order force-harmonics, which are assumed to be accurate for the lower temperatures, but especially the 1800 K results should be taken as approximate at best. The lognormal fits of the displacement curves of the two models were matched by adjusting the isotropic sigma until the isotropic and anisotropic curves overlapped. The sigmas for the isotropic model from lowest to highest temperature were 0.0678, 0.074, 0.105 and 0.137 Å respectively.

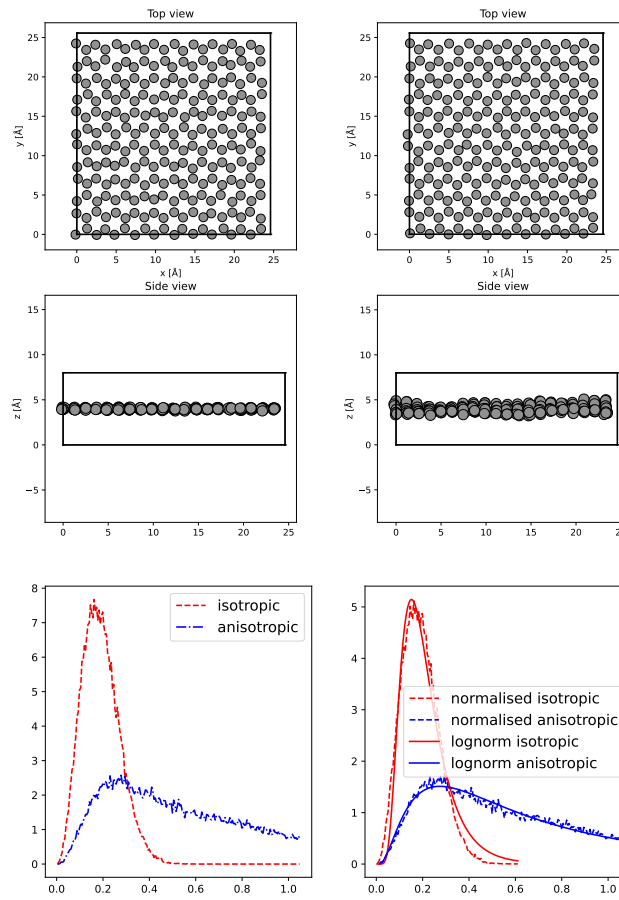


Figure 4.1: Top row left: top and side view of the isotropic supercell at 1800 K. Top row right: top and side view of the anisotropic supercell at 1800 K. Bottom row: corresponding displacement histograms of isotropic and anisotropic model at 1800 K with z -direction taken into account.

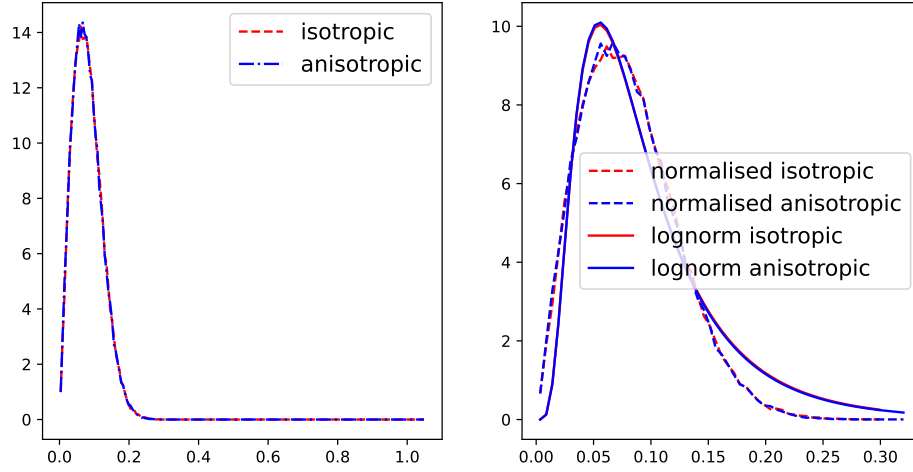


Figure 4.2: Histogram of isotropic and anisotropic models for at 300 K, without z -direction taken into account, allowing the two distributions to be precisely matched.

4.1.2 Projected potentials

Ensembles consisting of 250 configurations each were generated for both displacement models for the four different temperatures, followed by the creation of a potential for each configuration. The potentials of each ensemble were meaned, and additionally, a potential for a static reference supercell was established. All potentials were then projected. Figure 4.3 shows the relative differences to the static reference of the projected potentials of the isotropic model as a function of temperature, while figure 4.4 shows the same for the anisotropic model. The relative difference between the projected potentials of the two models can be seen in figure 4.5. The projected potentials of both models and the reference supercell were further interpolated along a line in three different directions, differing by 120° , see figure 4.6 for the lineprofiles at 300 K. (The lineprofiles at the remaining temperatures are available in the appendix, see figure A2). Figure 4.7 shows the relative differences in the lineprofiles of the two models compared to the static reference cell and to each other. The small differences in peak height are due to discretization of the potential grid with respect to the interpolated line. A slight broadening of the peaks can be seen with temperature, due to thermal displacements of the nuclei. Finally, figure 4.8 shows the relative differences in the lineprofiles of the models at each temperature compared to 0 K.

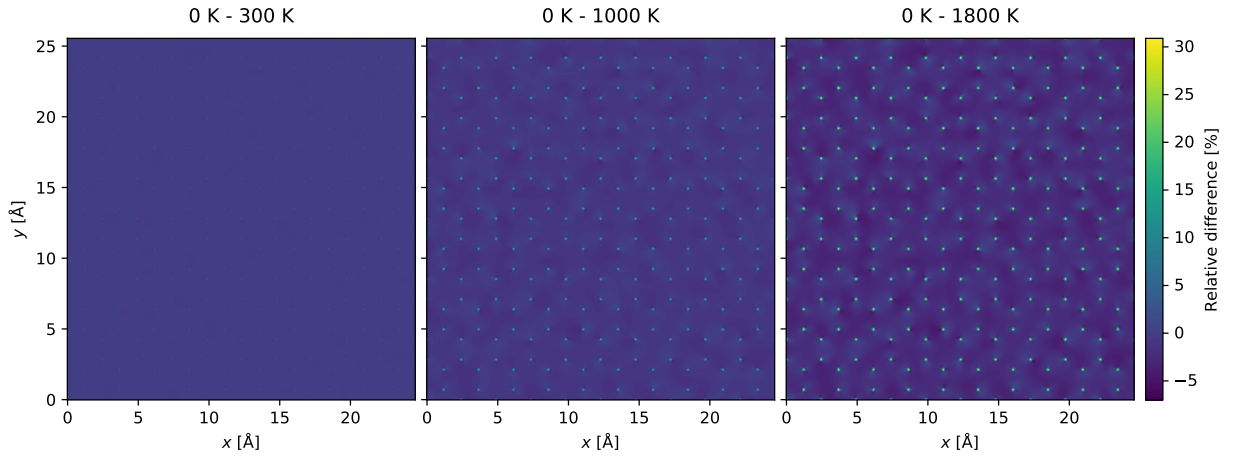


Figure 4.3: Relative differences by temperature of the isotropic projected potential compared to the static one.

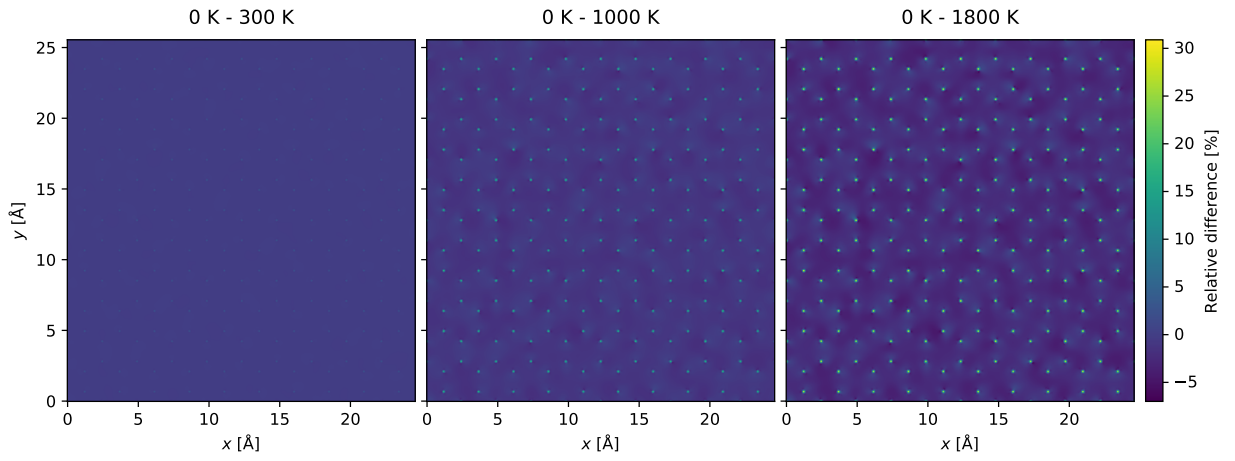


Figure 4.4: Relative difference by temperature of the anisotropic projected potential compared to the static one.

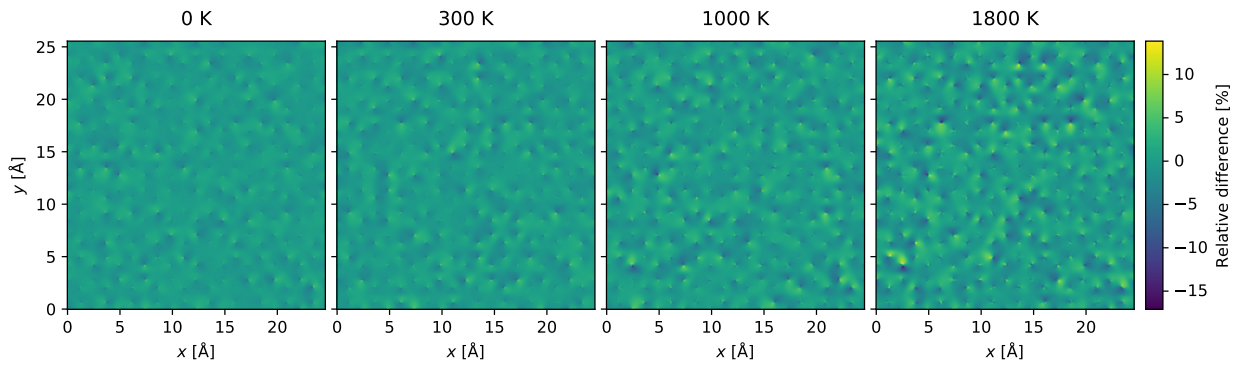


Figure 4.5: Relative differences between the projected potentials of the isotropic and the anisotropic model.

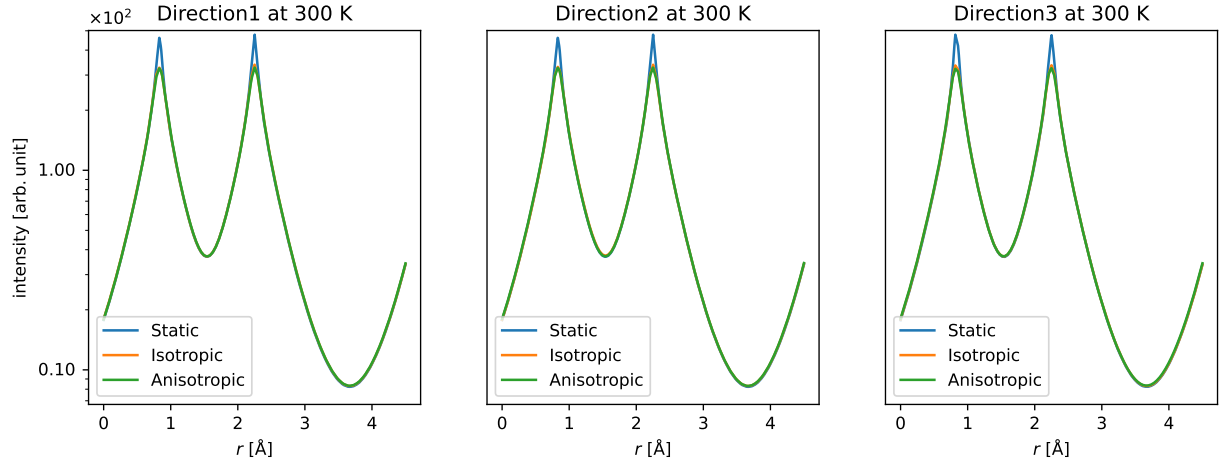


Figure 4.6: Lineprofiles of both models and the reference cell's projected potentials at 300 K.

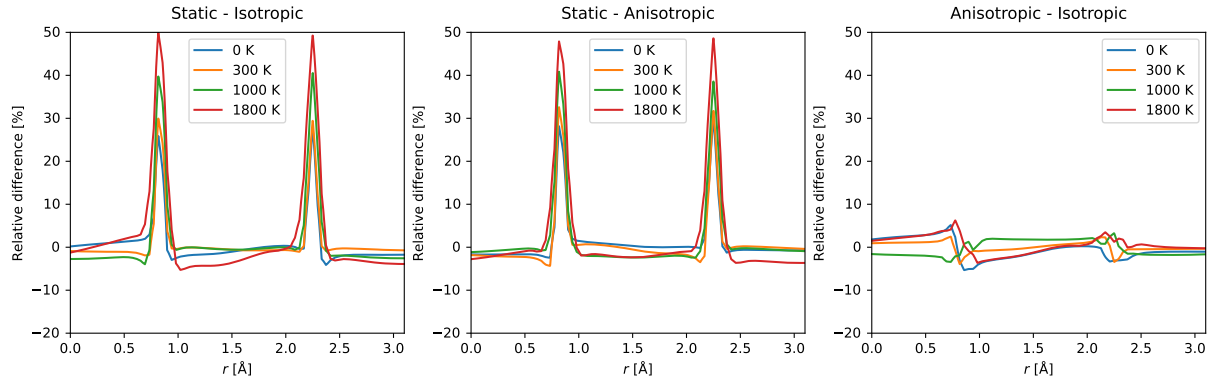


Figure 4.7: Relative differences of lineprofiles of the respective models at four temperatures. Lines interpolated along the main symmetry direction over one unit cell.

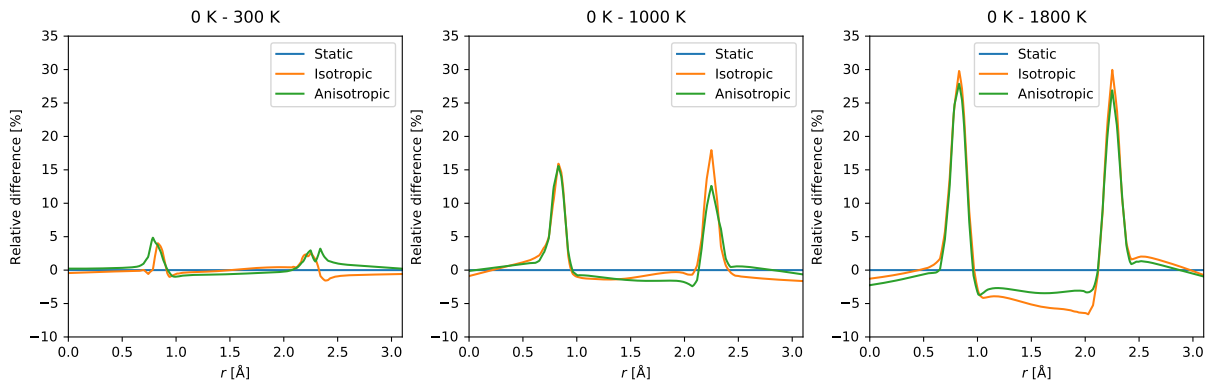


Figure 4.8: Relative differences of lineprofiles of the four different temperatures for the respective models. Lines interpolated along the main symmetry direction over one unit cell.

4.1.3 Simulating 4D STEM

Gridscans over an area of one unit cell of the created supercell were performed for the isotropic and the anisotropic model at each of the four given temperatures, as well as the static reference cell. Figure 4.9 shows the position-averaged CBED (convergent beam electron diffraction) pattern. Most of the signal is the forward beam, with only weak scattering because of the monolayer material.

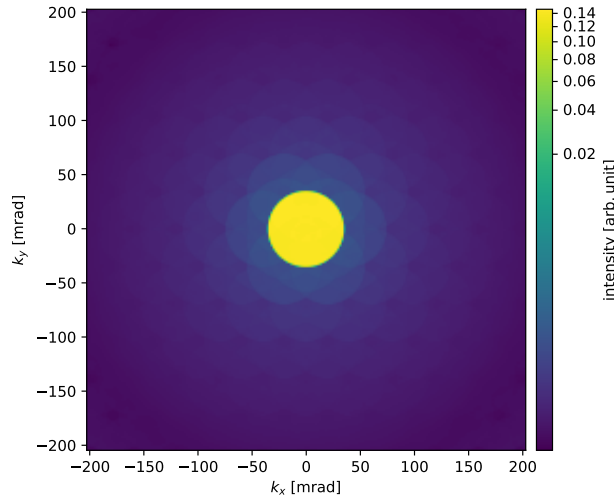


Figure 4.9: Position-averaged CBED pattern.

4.1.4 ADF measurements

Annular dark-field images were reconstructed from the 4D data as seen in figure 4.10. Figure 4.11 shows the relative difference between the ADF images of the models at different temperatures. However, for modeling realistic conditions under which experiments would be conducted, determining how noise can effect data interpretation and assessing limitations of detection and analysis methods, different doses of Poisson noise were applied to the simulated 4D data. The doses applied were 10^4 , 10^5 , 10^6 , 10^7 and 10^8 electrons per square Ångström. The diffraction patterns were then integrated radially between an inner radius of 37 mrad and an outer of 150 mrad, resulting in optimal ADF measurements since all scattered electrons are included. As seen in figure 4.12, at a dose of 10^7 differences start to emerge between the different models, becoming clearly visible at 10^8 (figure 4.13).

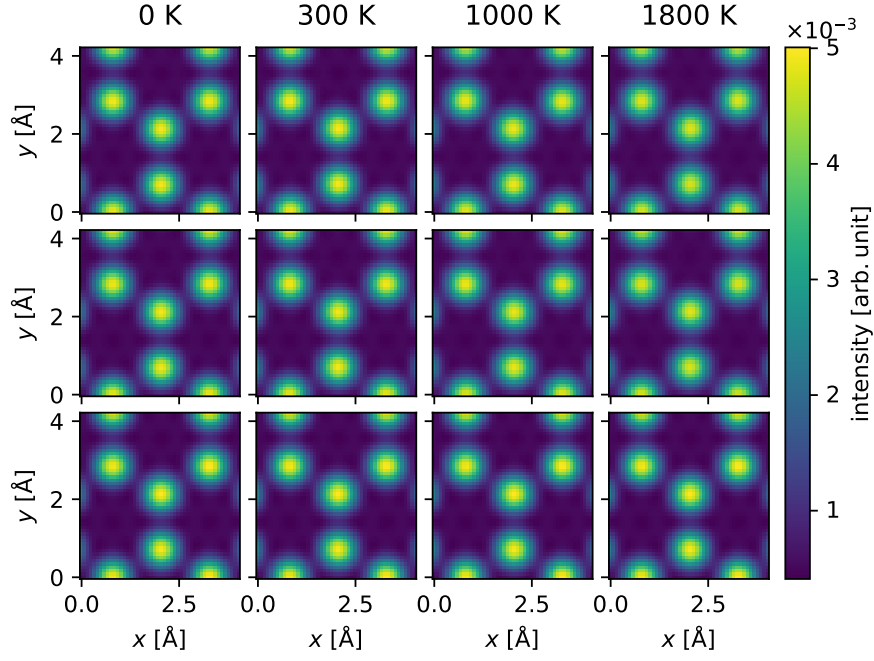


Figure 4.10: Annular dark-field images at four temperatures. Top row: anisotropic model, middle row: isotropic model and bottom row: the static reference cell.

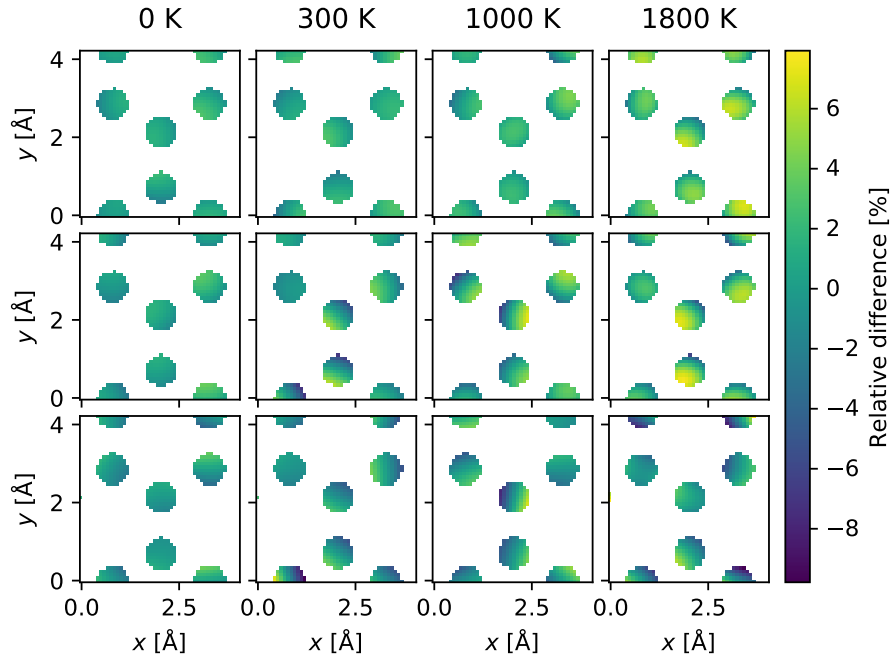


Figure 4.11: Relative differences between the annular dark field images of the respective models. Cropped to exclude numerical artifact regions. Top: static-isotropic, middle: static-anisotropic and bottom: isotropic-anisotropic.

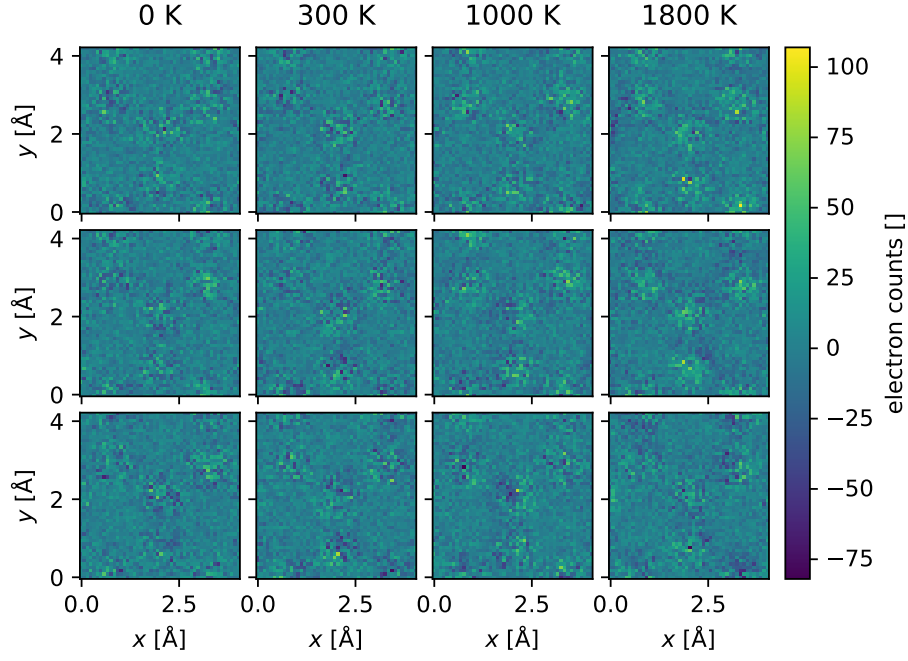


Figure 4.12: Differences of the ADF images at a dose of $10^7 \text{ e}^-/\text{\AA}^2$. Top: static-isotropic, middle: static-anisotropic and bottom: isotropic-anisotropic.

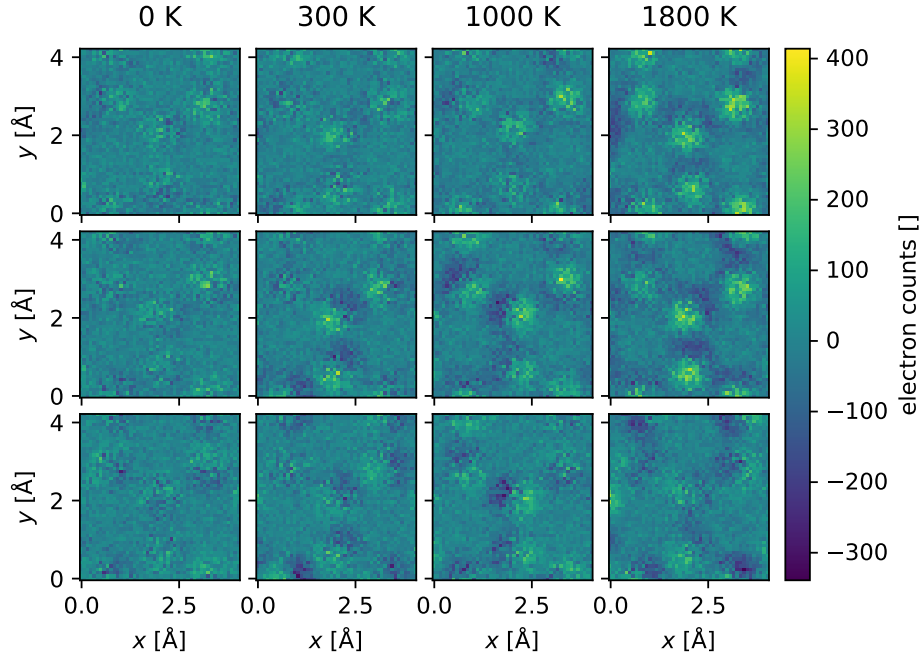


Figure 4.13: Differences of the ADF at a dose of $10^8 \text{ e}^-/\text{\AA}^2$. Top: static-isotropic, middle: static-anisotropic and bottom: isotropic-anisotropic.

4.1.5 Integrated centre of mass

As the ADF measurements are noisy and have a weak signal, integrated centre of mass (iCOM) images were reconstructed. Intensity profiles from 4D data are integrated over a defined region to obtain a weighted average position. Figure 4.14 shows the relative difference between the iCOM images of the models at different temperatures. Again the potential of both models and the reference cell for all four temperatures were interpolated along the three symmetry directions. The differences are depicted in figure 4.15. Different doses of Poisson noise were applied, ranging from 10^4 to 10^8 , and the relative differences taken again. For an electron dose of 10^7 , differences between the models start to emerge, see figure 4.16. At a dose of 10^8 , features are becoming more distinct, see figure 4.17.

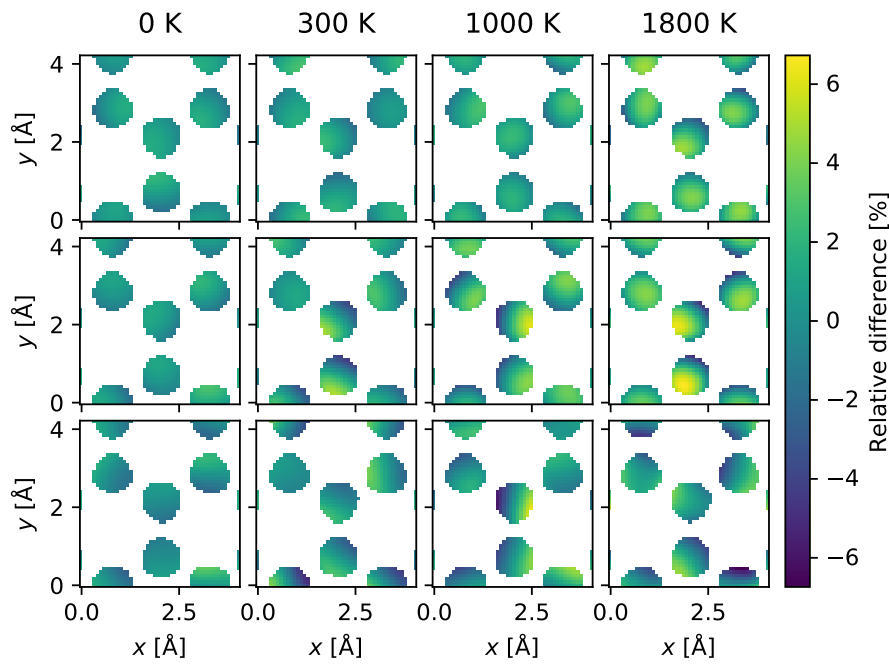


Figure 4.14: Relative differences between the iCOM images of the models at four temperatures over one unit cell. Cropped to exclude numerical artifact regions. Top: static–isotropic, middle: static–anisotropic and bottom: isotropic–anisotropic.

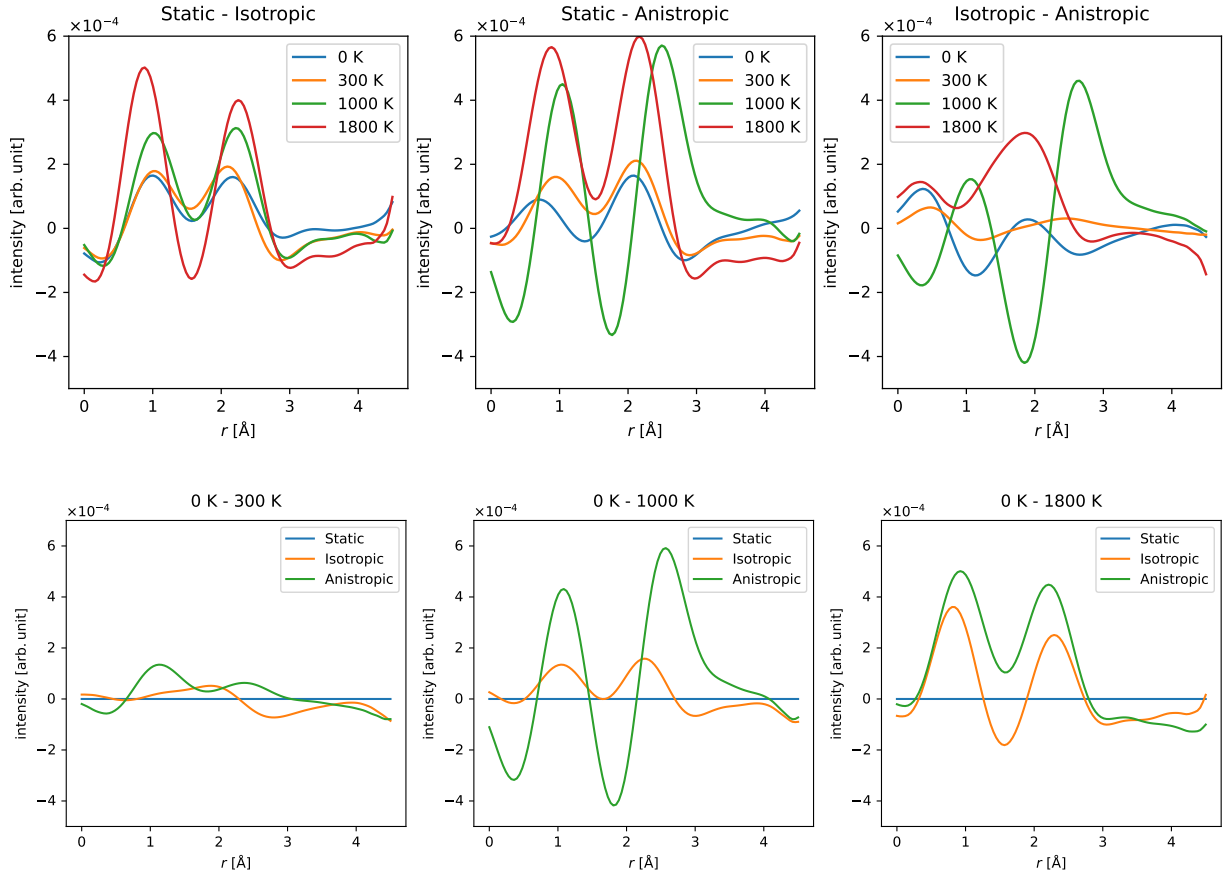


Figure 4.15: Top: differences between the models for the four temperatures. Bottom: differences between the temperatures for the three models.

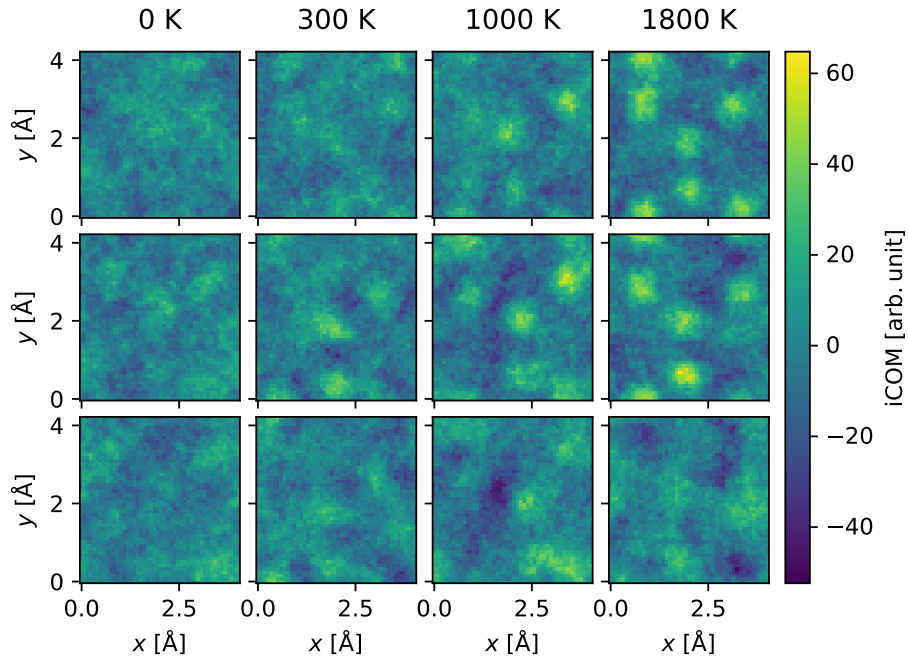


Figure 4.16: Differences between the models with a dose of 10^7 . Top: static-isotropic, middle: static-anisotropic and bottom: isotropic-anisotropic.

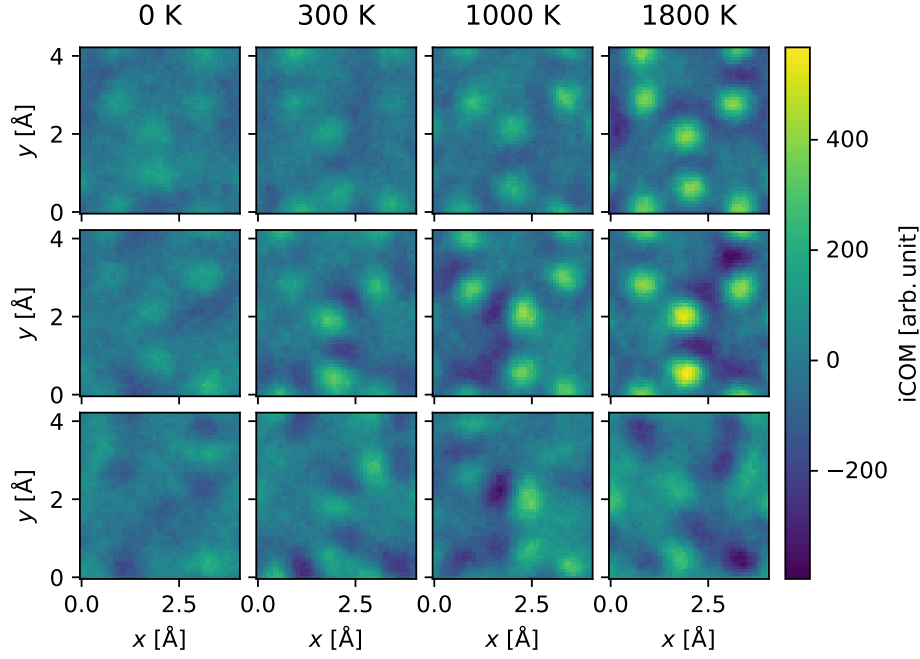


Figure 4.17: Differences between the models with a dose of noise of 10^8 , Top: static-isotropic, middle: static-anisotropic and bottom: isotropic-anisotropic.

4.1.6 Validation of the computational framework

To ensure that the parameters set in the above measurements are valid, convergence was examined in relation to the potential sampling, the number of atomic configurations used and the size of the simulated supercell. To this end, ensembles of the anisotropic model were created for a temperature of 300 K and the corresponding potentials were generated. The same pixelated detector and probe as above were chosen and grids over the area of one unit cell were performed. The resulting measurements were subsequently meaned and the integrated centre of mass calculated and compared via SSIM (structural similarity index measure) and relative MSE (mean square error).

Sampling of the potential

To examine the effect of different potential sampling, the ensembles created consisted of 20 configurations and the size of the supercell was $10 \times 6 \times 1$. The sampling of the anisotropic potential was varied between 0.02 and 0.10 Å, in steps of 0.01. Figure 4.18 illustrates the convergence of image quality in relation to the potential sampling. A value of 0.04 Å showed good consistency

and was therefore used for the simulations.

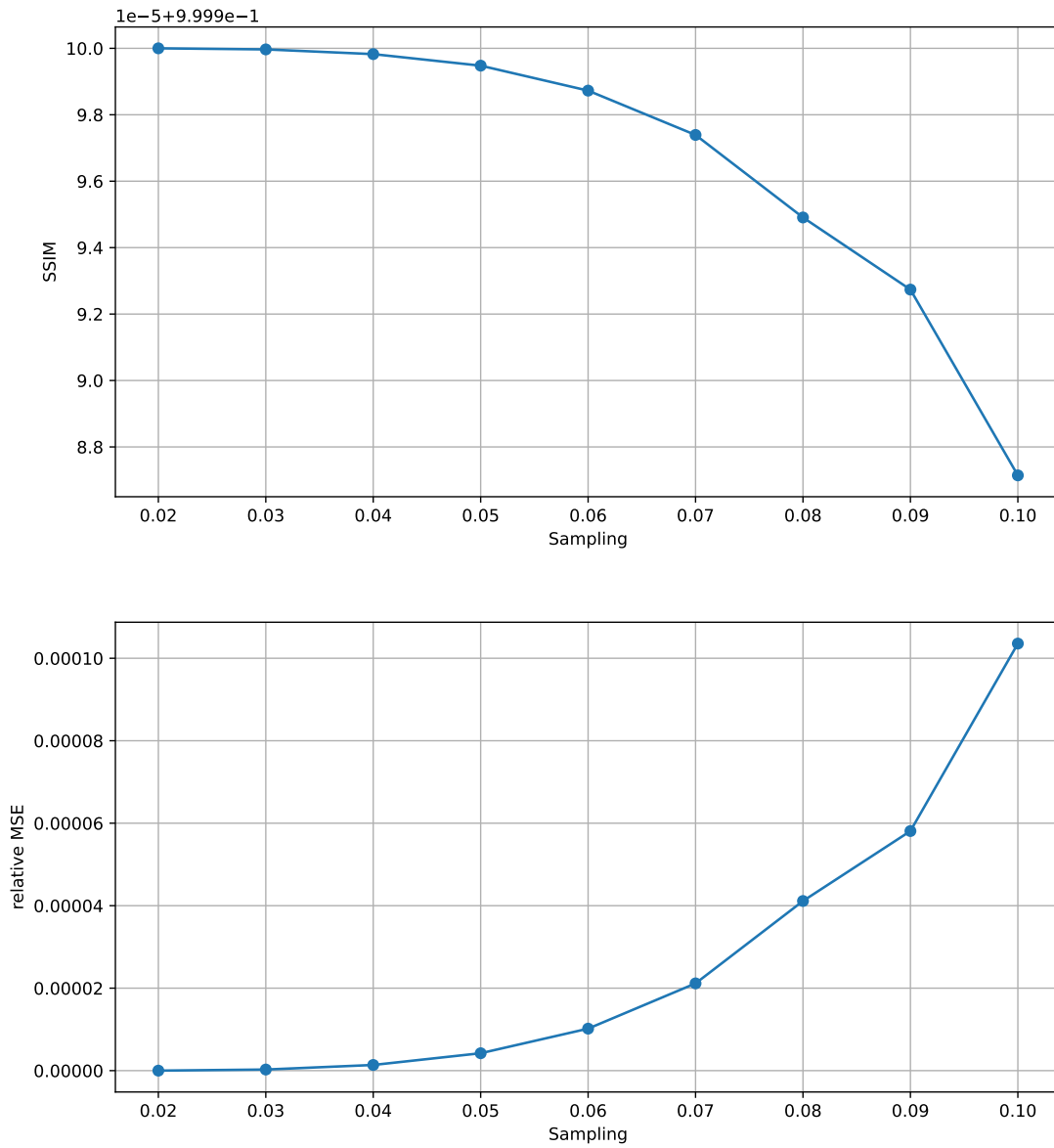


Figure 4.18: Top row: structural similarity index measure (SSIM), bottom row: relative mean square error (MSE) of increasing potential sampling.

Number of frozen-phonon images

To determine an effective number of configurations, the same supercell was used as above and the number of configurations used of the created ensemble was varied between 1 and 50, which was increased by one up to 10 configurations, then by five up to 50. Figure 4.19 illustrates the convergence in relation to the number of atomic configurations used. 20 configurations per ensemble showed acceptable convergence.

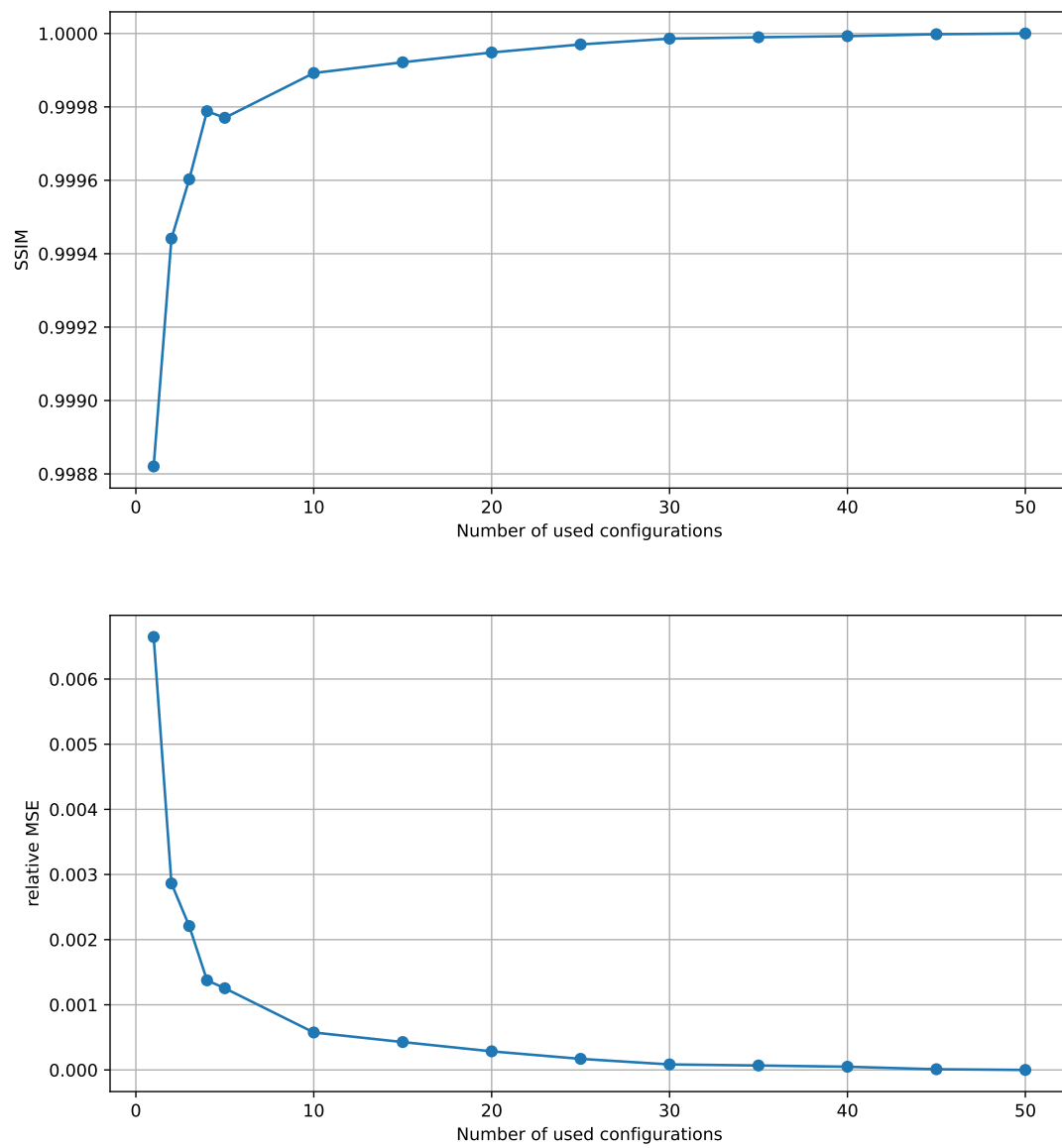


Figure 4.19: Top row: structural similarity index measure (SSIM), bottom row: relative mean square error (MSE) of increasing number of configurations per ensemble.

Cell size considerations

To assess the effect of different sizes of the simulated supercell, measurements were done on supercells with dimensions $5 \times 3 \times 1$, $6 \times 4 \times 1$, $7 \times 4 \times 1$, $8 \times 5 \times 1$, $9 \times 5 \times 1$, $10 \times 6 \times 1$ and $11 \times 6 \times 1$. While the resulting curves in Figure 4.20 does not show a clean convergence, the differences are relatively small and a supercell of size $10 \times 6 \times 1$, as used in the above STEM simulations was deemed robust.

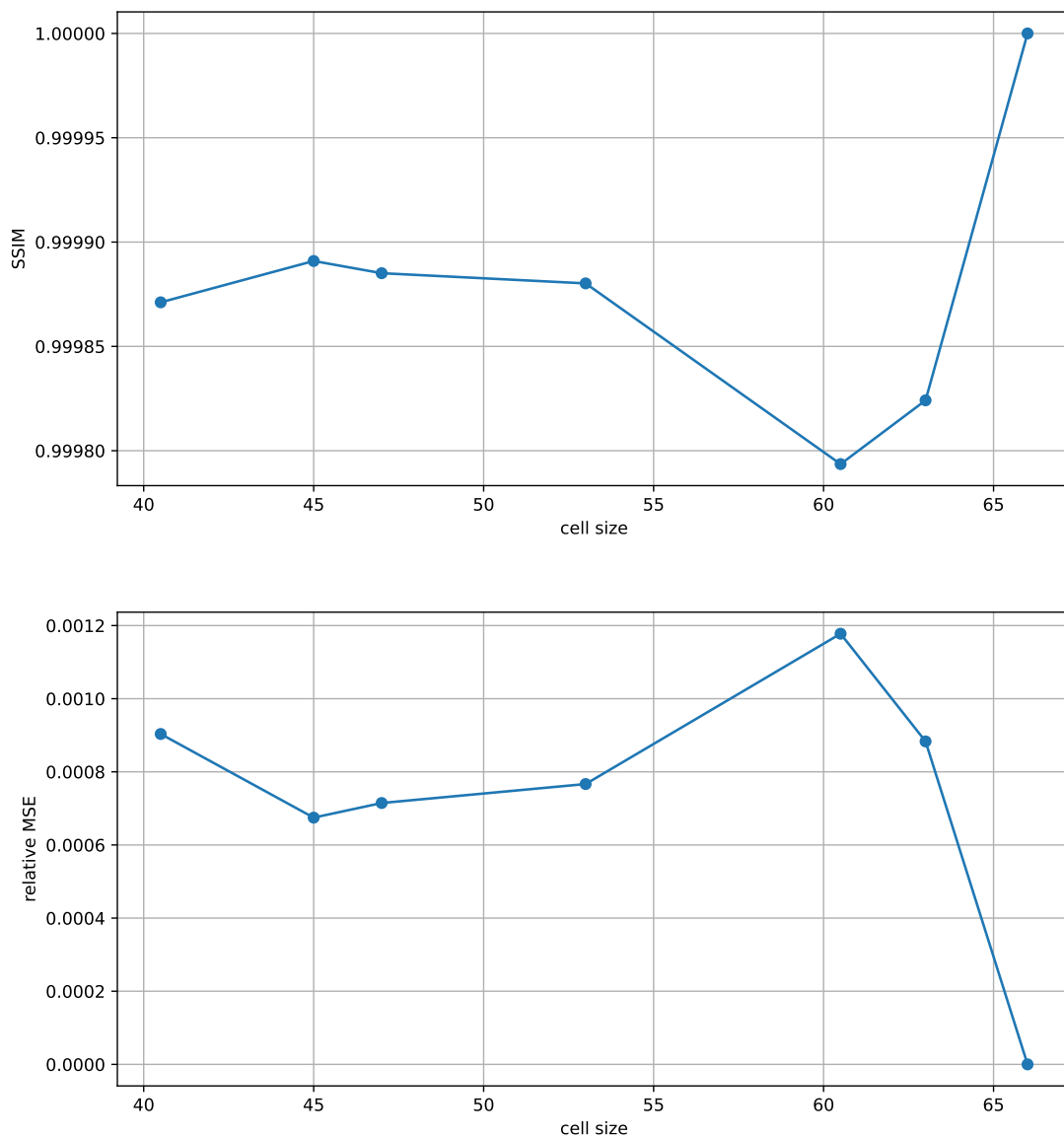


Figure 4.20: Top row: structural similarity index measure, bottom row: relative mean square error of increasing cell size.

4.2 Limitations and future work

This research involves several limitations regarding the idealised nature of the simulations. The model assumes perfect beam conditions, whereas realistic scattering includes aberrations and partial coherence. While the simulation uses an ideal point source with a single wavelength, real sources have a finite bandwidth and spatial extent. Additionally, the detection model is idealised. Real detectors have finite detection efficiencies, meaning not all scattered electrons are captured, while the simulations assume perfect collection. Also, while shot noise is being accounted for, thermal noise from a real detector is not. Finally, the simulated atomic specimen does not account for sample contamination or structural defects. Unlike the perfect lattices used in these simulations, real monolayers typically contain absorbed molecules and irregularities that affect the resulting scattering patterns.

Future research will need to integrate more sophisticated simulation models that include realistic probe aberrations, partial coherence and finite source bandwidth to accurately represent experimental conditions. Further research could also incorporate sample-specific parameters such as surface contamination and lattice defects, for a more realistic monolayer specimen. Additionally, the anisotropic rattle could be integrated into *ab*TEM to allow for more accurate frozen-phonon simulations of thermal diffuse scattering. Finally, the ultimate objective is to measure scattering anisotropy in practice.

Chapter 5

Conclusions

This study investigated whether incorporating realistic, anisotropic atomic displacements via hiPhive and GAP-20 produces quantitative differences in STEM simulations over the standard isotropic Einstein model. The primary objective was to define the specific imaging modes, temperatures, and shot noise thresholds required to resolve directional vibration patterns and to establish whether these asymmetries are detectable or lost to experimental noise. Asymmetries in projected potentials were observed from 0 K upwards, with iCOM imaging demonstrating higher sensitivity to these directional displacements than ADF. Analysis of noise influence showed that anisotropic signatures are obscured when shot noise corresponds to a dose below 10^7 electrons per $\text{\AA}^2$, but remain resolvable at temperatures of 300 K and are even more distinct at 1000 K with a dose of 10^8 electrons per $\text{\AA}^2$ or higher. Convergence tests confirmed using 20 configurations, 0.04 $\text{\AA}$ potential sampling, and a supercell of $10 \times 6 \times 1$ dimensions ensured the numerical stability of the results and provide a framework for modeling the effect of anisotropy of atomic vibrations in graphene.

Appendices

The preliminary setup of the machine learning potential, in preparation of the actual training.

```
1 prim_gra = ase.build.graphene(vacuum=4.0)
2 prim_gra.pbc = True
3
4 def _properties_to_spc(atoms: Atoms) -> Atoms:
5     atoms.calc = SinglePointCalculator(atoms, energy=atoms.get_potential_energy(),
6     forces=atoms.get_forces())
7     return atoms
8
9 from quippy.potential import Potential
10 calc_gra_gra = Potential('xml_label=GAP_2021_4_21_0_21_17_24_635',
11 param_filename='GAP/Carbon_GAP_V10_2_LDIter1_kptconsistent_grr6_2b_3b_soap_n1214_sp9k
12 _delta-2-0.05-0.1.xml', calc_args='local_gap_variance')
13
14 calc_gra = calc_gra_gra
15 prim_gra.calc = calc_gra
```

A1: Setting up the machine learning potential (MLP) calculator.

The training of the force-constant potential (FCP), which was written to disk and read from the file in subsequent initialisations.

```
1 supercell_gra = prim_gra.repeat(SUPERCELL_DIM)
2 rattled_structures_gra = generate_mc_rattled_structures(
3     supercell_gra, N_STRUCTURES, RATTLE_STD, MINIMUM_DISTANCE)
4
5 for atoms in tqdm(rattled_structures_gra):
6     atoms.calc = calc_gra
7     atoms.get_forces()
8     _properties_to_spc(atoms)
9
10 cs_gra = ClusterSpace(prim_gra, CUTOFFS)
11 structures_gra = prepare_structures(rattled_structures_gra, supercell_gra)
12 sc_gra = StructureContainer(cs_gra)
13 for structure in structures_gra:
14     sc_gra.add_structure(structure)
15
16 opt_gra = Optimizer(sc_gra.get_fit_data())
```

```

17 opt_gra.train()
18
19 parameters_bornhuang_gra = enforce_rotational_sum_rules(
20     cs_gra, opt_gra.parameters, ['Huang', 'Born-Huang'])
21 fcp_bornhuang_gra = ForceConstantPotential(cs_gra, parameters_bornhuang_gra)
22
23 def setuprattle(prim, fcp, nx, ny, nz):
24     sc = prim.repeat((nx,ny,nz))
25     fc2sc = fcp.get_force_constants(sc).get_fc_array(order=2, format='ase')
26     return sc, fc2sc
27
28 def hiphiverattlesc(sc, fc2sc, N=1, T=300, QM_statistics=True, show_atoms=False, plane='xy'):
29     from hiphive.structure_generation import generate_phonon_rattled_structures
30     rattled = generate_phonon_rattled_structures(sc, fc2sc, N, T, QM_statistics=QM_statistics)
31     return rattled
32
33 orth_gra = abtem.orthogonalize_cell(prim_gra)
34 sc, fc2sc = setuprattle(orth_gra, fcp_gra, 10, 6, 1)

```

A2: Training of the FCP and creation of the supercell.

The histogram curves of the isotropic and anisotropic models were plotted, visually compared and the isotropic sigma adjusted until the two curves overlapped.

```

1 bins = {'displacement': np.linspace(0.0, 0.7, 200)}
2 def get_histogram_data(data, bins=100):
3     counts, bins = np.histogram(data, bins=bins, density=True)
4     bin_centers = [bins[i+1]+bins[i]/2.0 for i in range(len(bins)-1)]
5     return bin_centers, counts
6
7 def get_projected_distributions(structure_list, ref_pos):
8     displacements = []
9     for atoms in structure_list:
10         atoms_flat = atoms.copy()
11         atoms_flat.positions[:,2] = 0.0
12         displacements.extend(np.linalg.norm(atoms_flat.positions[:, :2]-ref_pos[:, :2], axis=1))
13     distributions = {}
14     distributions['displacement'] = get_histogram_data(displacements, bins['displacement'])
15     return distributions
16
17 def lognormal(x, amp, mu, sigma):
18     return amp/(np.sqrt(2*np.pi)*sigma*x)*np.exp(-((np.log(x)-mu)**2)/(2*sigma**2))
19
20 def fit_lognormal_distributions(distributions_isotropic, distributions_anisotropic):
21     area_iso = np.trapz(distributions_isotropic['displacement'][1],
22         distributions_isotropic['displacement'][0])
23     area_anis = np.trapz(distributions_anisotropic['displacement'][1],
24         distributions_anisotropic['displacement'][0])
25     normalized_distr_iso = distributions_isotropic['displacement'][1]/area_iso
26     normalized_distr_anis = distributions_anisotropic['displacement'][1]/area_anis
27

```

```

28 mask_iso = normalized_distr_iso > 0
29 mask_anis = normalized_distr_anis > 0
30 x_fit_iso = np.array(distributions_isotropic['displacement'][0])[mask_iso]
31 y_fit_iso = normalized_distr_iso[mask_iso]
32 x_fit_anis = np.array(distributions_anisotropic['displacement'][0])[mask_anis]
33 y_fit_anis = normalized_distr_anis[mask_anis]
34
35 initial_guess = [1.0, 0.5, 0.5]
36 params_iso, covariance_iso = curve_fit(lognormal, x_fit_iso, y_fit_iso, p0=initial_guess)
37 params_anis, covariance_anis = curve_fit(lognormal, x_fit_anis, y_fit_anis, p0=initial_guess)
38 y2_fit_iso = lognormal(x_fit_iso, *params_iso)
39 y2_fit_anis = lognormal(x_fit_anis, *params_anis)
40 return x_fit_iso, y_fit_iso, x_fit_anis, y_fit_anis, y2_fit_iso, y2_fit_anis,
41
42 def generate_atoms(sc, fc2sc, num_configs, T, sigmas):
43     isotropic = abtem.FrozenPhonons(sc, num_configs=num_configs, sigmas=sigmas/np.sqrt(3),
44     ensemble_mean=False)
45     snapshots = hiphiverattle(sc, fc2sc, num_configs, T=T, show_atoms = False)
46     anisotropic = abtem.AtomsEnsemble(snapshots, ensemble_mean=False)
47     return sc, isotropic, anisotropic, snapshots[0]

```

A3: Matching the isotropic sigma.

Potentials of the two models and static reference cell were created and subsequently projected.

```

1 def project_potentials(sc, isotropic, anisotropic):
2     uc = prim_gra.cell
3     sx = uc[0,0] / 64
4     sy = uc[1,1] / 52
5     sampling = (sx, sy)
6
7     potential_static = abtem.Potential(static, sampling=sampling,
8     projection='finite').build(lazy=True).compute()
9     potentials_isotropic = abtem.Potential(isotropic, sampling=sampling,
10    projection='finite').build(lazy=True).mean(axis=0).compute()
11    potentials_anisotropic = abtem.Potential(anisotropic, sampling=sampling,
12    projection='finite').build(lazy=True).mean(axis=0).compute()
13
14    projected_potential_static = potential_static.project().compute()
15    projected_potentials_isotropic = potentials_isotropic.project().compute()
16    projected_potentials_anisotropic = potentials_anisotropic.project().compute()
17    projstack = abtem.stack([projected_potential_static, projected_potentials_isotropic,
18    projected_potentials_anisotropic], ("Static", "Isotropic", "Anisotropic"))
19    return projstack, sampling

```

A4: Projecting the potentials.

The projected potentials were interpolated along a line.

```
1 def calculate_interpolated_lines(projstack, sampling, temp):
2     centx = sc[111].position[0]
3     centy = sc[111].position[1]
4     sam = np.array(sampling).mean()
5     dir1 = projstack.interpolate_line_at_position(center=(centx, centy),
6         angle=330, extent=4.5, sampling=sam/16, order=1)
7     dir2 = projstack.interpolate_line_at_position(center=(centx, centy),
8         angle=210, extent=4.5, sampling=sam/16, order=1)
9     dir3 = projstack.interpolate_line_at_position(center=(centx, centy),
10        angle=90, extent=4.5, sampling=sam/16, order=1)
11     stack_all_dir = abtem.stack([dir1, dir2, dir3], ("Direction1", "Direction2", "Direction3"))
12     return stack_all_dir
```

A5: Interpolating lines of projected potentials.

The simulation of 4D STEM was setup and grid scans were performed.

```
1 pixelated_detector = abtem.PixelatedDetector(max_angle=200)
2 a = orth_gra.cell[0,0]
3 b = orth_gra.cell[1,1]
4 off = a/12
5 potential = abtem.Potential(sc, sampling=0.04)
6 probe = abtem.Probe(energy=60e3, semiangle_cutoff=35)
7 sampling = probe.aperture.nyquist_sampling
8 grid_scan = abtem.GridScan(
9     start=[4*a-off*4, 3*b],
10    end=[5*a+off*4, 4*b],
11    sampling=sampling/4,
12    fractional=False,
13    potential=potential)
14
15 def calculate(sc, isotropic, anisotropic):
16     static = sc.copy()
17     potential_static = abtem.Potential(static, sampling=0.04, projection='finite')
18     .build(lazy=True).compute()
19     potentials_isotropic = abtem.Potential(isotropic, sampling=0.04, projection='finite')
20     .build(lazy=True).compute()
21     potentials_anisotropic = abtem.Potential(anisotropic, sampling=0.04, projection='finite')
22     .build(lazy=True).compute()
23     static_meas = probe.scan(potential=potential_static, scan=grid_scan,
24        detectors=pixelated_detector)
25     isotropic_meas = probe.scan(potential=potentials_isotropic, scan=grid_scan,
26        detectors=pixelated_detector).mean(axis=0)
27     anisotropic_meas = probe.scan(potential=potentials_anisotropic, scan=grid_scan,
28        detectors=pixelated_detector).mean(axis=0)
29     stack = abtem.stack([static_meas, isotropic_meas, anisotropic_meas],
30        ("Static", "Isotropic", "Anisotropic"))
31     return stack
```

A6: Simulating 4D STEM.

Poisson noise was applied in different doses (here $1 \cdot 10^4$ electrons per Angström).

```
1 stack_pn_1e4 = stack.poisson_noise(1e4)
```

A7: Adding Poisson noise.

ADF images were reconstructed from the 4D data.

```
1 ADF_measurements = stack.integrate_radial(37, 150)
```

A8: Reconstruction of ADF images.

ICOM images were reconstructed from the 4D data.

```
1 comstack = stack.center_of_mass(units="1/A")
2 icom = comstack.integrate_gradient()
```

A9: Integrating center of mass (iCOM).

Convergence testing results were compared via relative MSE and SSIM.

```
1 def get_mse(img1, img2):
2     err = np.sum((img1 - img2)**2)
3     err/= float(img1.shape[0] * img2.shape[1])
4     return err
5
6 mses = []
7 rel_mses = []
8 img1, sampl1 = images[len(images)-1]
9
10 for i in range(len(images)):
11     img2, sampl2 = images[i]
12     mse = get_mse(img1, img2)
13     mses.append((mse, sampl1, sampl2))
14     mean_sq_or = np.mean(img1 ** 2)
15     rel_mse = mse/mean_sq_or if mean_sq_or !=0 else float('inf')
16     rel_mses.append((rel_mse, sampl1, sampl2))
```

A10: Verifying convergence.

The histogram curves for the remaining three temperatures are very similar. A slight lowering and widening of the peak can be seen with increasing temperature.

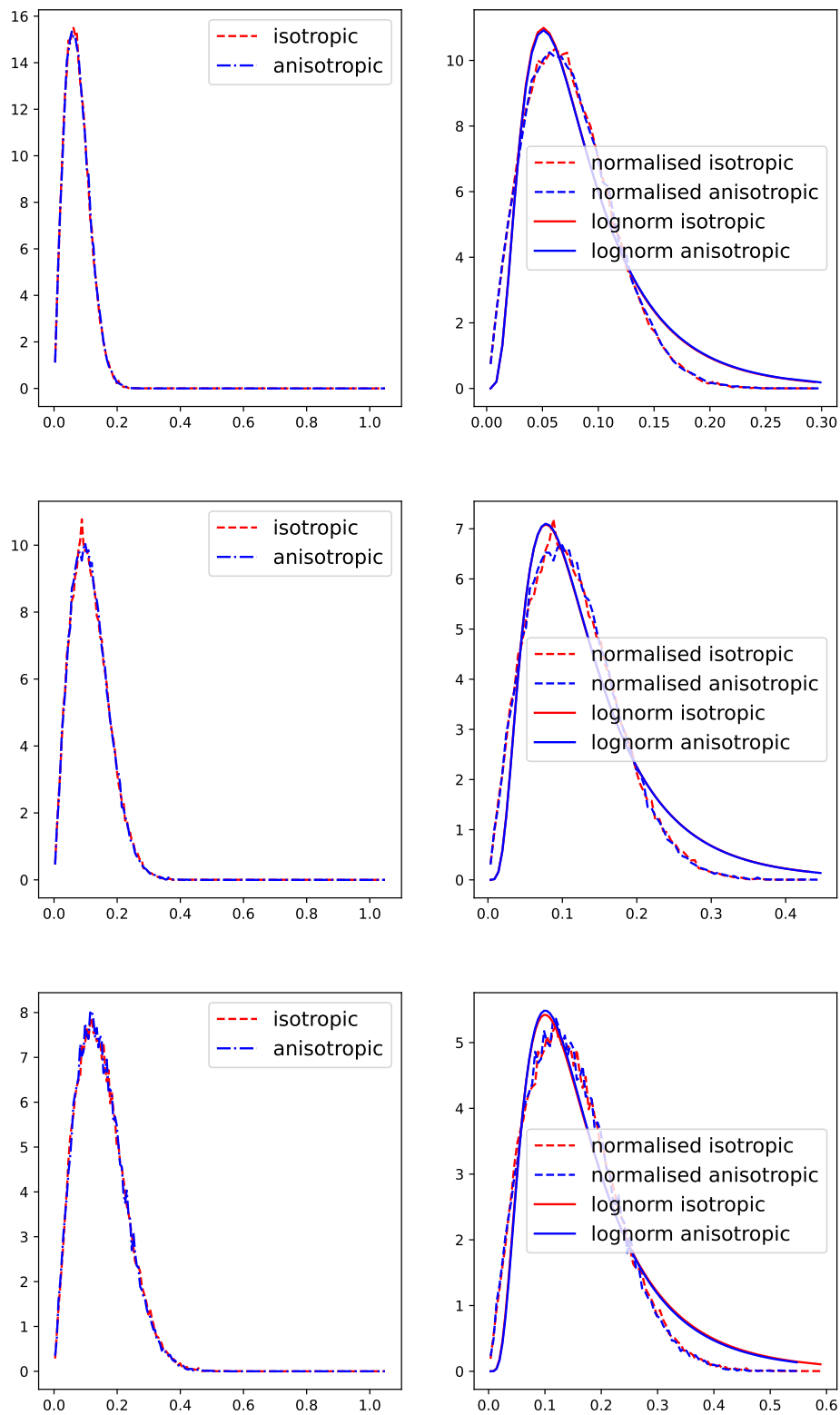


Figure A1: Histograms of isotropic and anisotropic models for different temperatures without z-direction taken into account. In descending order at 0, 1000 and 1800 K.

Only slight differences can be seen in the lineprofiles of the projected potentials at different temperatures.

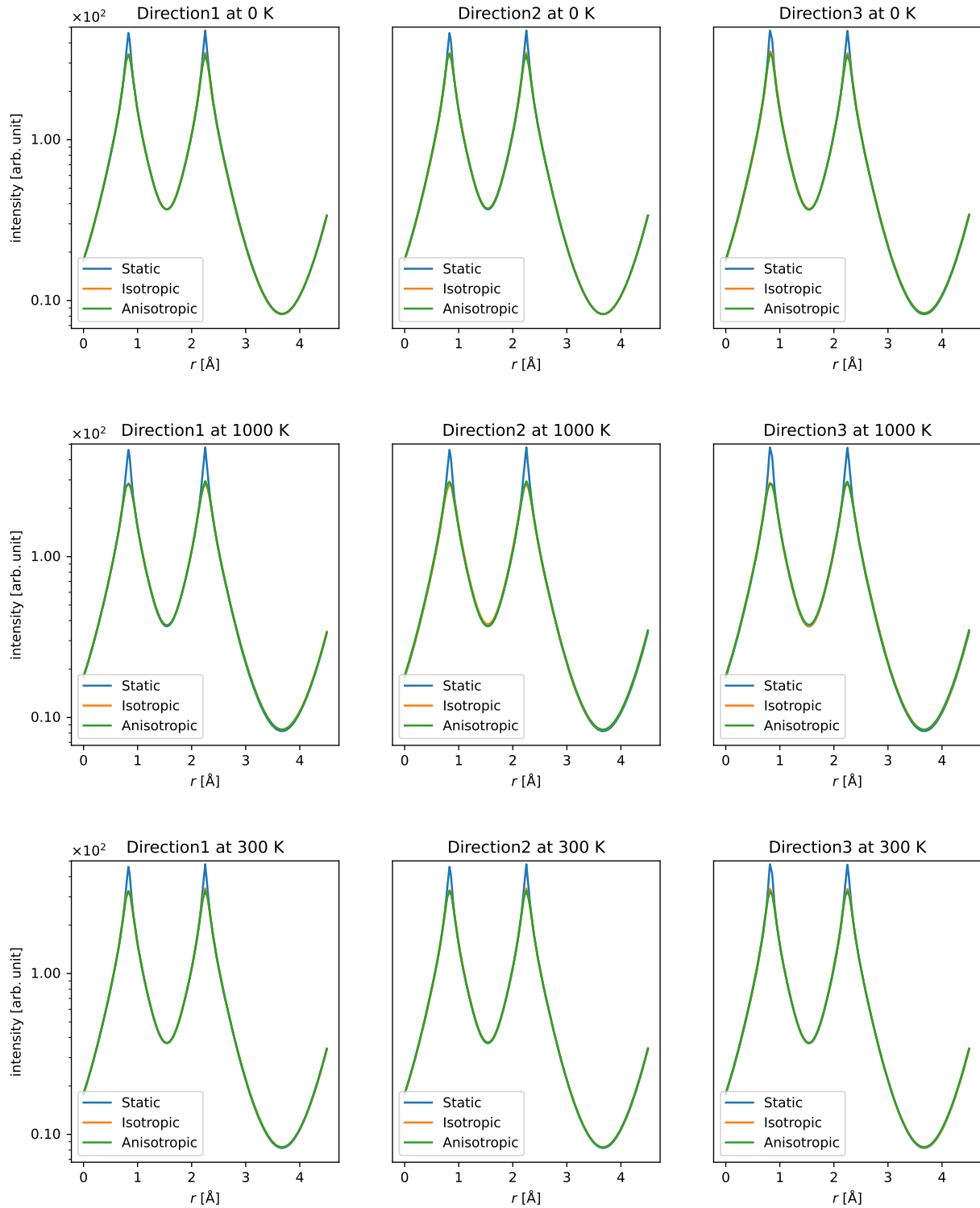


Figure A2: Lineprofiles of both models and the reference cell's projected potentials. In descending order at 0, 1000 and 1800 K.

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