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From ab-initio to machine learning potentials for hybrid
perovskite structures in molecular dynamics simulations

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Abstract

In this thesis the crystal structure of '*dynamic solids*' at finite temperature are studied. Dynamic solids are complicated to describe since they are entropically/dynamically stabilized at finite temperature. Throughout this work perovskite structures will appear as representatives for dynamically stabilized solids whereby a special emphasis is placed on the upcoming solar cell material: methylammonium perovskite (MAPbI_3). The properties of such materials have to be described by ensemble averages and can not be predicted by performing calculations on a single 0K structure. To obtain reliable results long trajectories and large simulation boxes are needed. The computation of such ensembles by means of first principles molecular dynamics is computationally very demanding. To speed up the molecular dynamics approach classical force fields are tested and compared to first principle results. The methylammonium molecules have an intrinsic dipole moment and possess a long range ordering pattern within the MAPbI_3 perovskite. These properties make a description in terms of point dipole models interesting. However, neither the in literature available classical force fields nor the point dipole model Hamiltonians are capable of describing the molecular ordering pattern observed from first principle calculations. Therefore a different approach is needed which retains the accuracy of first principles molecular dynamics, but with the computational cost of classical force fields. Here, an on-the-fly machine-learning force field was trained on ab-initio molecular dynamics simulations by the use of the SCAN exchange-correlation functional. This force field is able to describe the long range ordering pattern of the methylammonium molecules in the MAPbI_3 perovskite in agreement with the underlying first principles simulation. Moreover, the obtained force field is capable of describing the phase transition temperatures and the mechanism behind the structural transitions in agreement with experimental results. This approach was tested on other perovskite systems always giving results in good agreement with the underlying first principles calculations and experimental data.

Zusammenfassung

In dieser Arbeit wird die Kristallstruktur 'dynamischer Festkörper' bei endlicher Temperatur untersucht. Dynamische Festkörper sind kompliziert zu beschreiben, da sie bei finiter Temperatur entropisch/dynamisch stabilisiert werden. Perowskit Strukturen werden als Vertreter für dynamisch stabilisierte Festkörper verwendet, wobei ein besonderer Schwerpunkt auf das potenzielle Solarzellenmaterial, den Methyllummoniumperowskit (MAPbI_3) gelegt wird. Die Eigenschaften solcher Materialien müssen durch sogenannte Ensemble Mittelwerte beschrieben werden und können nicht durch Berechnungen vorhergesagt werden, welche auf einer einzelnen 0K-Struktur beruhen. Um zuverlässige Ergebnisse zu erhalten, müssen lange Trajektorien und große Simulationsboxen verwendet werden. Die Berechnung solcher Ensembles durch ab-initio Molekulardynamik Simulationen ist rechnerisch sehr anspruchsvoll. Zur Beschleunigung des Molekulardynamik-Ansatzes werden klassische Kraftfelder getestet und mit den ab-initio Ergebnissen verglichen. Die Methyllummoniummoleküle haben ein intrinsisches Dipolmoment und verfügen über ein weitreichendes Ordnungsmuster innerhalb des MAPbI_3 Perowskits. Diese Eigenschaften legen eine Beschreibung des MAPbI_3 mittels Punktdipol-Modellen nahe. Allerdings sind weder die in der Literatur verfügbaren klassischen Kraftfelder noch die verfügbaren Punktdipol-Modelle in der Lage, die in ab-initio Berechnungen beobachteten molekularen Ordnungsmuster zu beschreiben. Daher ist ein anderer Ansatz, der die Genauigkeit der ab-initio Molekulardynamik beibehält, aber dem rechnerischen Aufwand der klassischen Kraftfelder entspricht, erforderlich. In dieser Arbeit wird ein *on-the-fly* machine learning Kraftfeld mittels ab-initio Molekulardynamik-Simulationen unter dem Einsatz des SCAN-Austausch-Korrelation-Funktional trainiert. Dieses Kraftfeld ist in der Lage, das weitreichende Ordnungsmuster der Methyllummoniummoleküle im MAPbI_3 Perowskit in Übereinstimmung mit den zugrundeliegenden ab-initio Rechnungen zu beschreiben. Außerdem ist dieses Kraftfeld in der Lage, die Phasenübergangstemperaturen und den Mechanismus hinter den strukturellen Übergängen in Übereinstimmung mit den experimentellen Ergebnissen wiederzugeben. Dieser Ansatz wird auch an anderen Perowskiten getestet. Die erhaltenen Ergebnisse zeigen immer eine gute Übereinstimmung mit den zugrunde liegenden ab-initio Rechnungen und den experimentellen Daten.

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1 Introduction

The world surrounding us consists of atoms and molecules. The kind and the arrangement of these molecules and atoms determines the properties of the matter we can see with our bare eyes. Such properties would for example be the color, mechanical properties or electrical properties of a material. This thesis focuses on solids. From an atomistic point of view a solid consists of a repeating pattern of atoms. Figure 1.1 shows a Cesium lead bromide structure as an example for a solid.

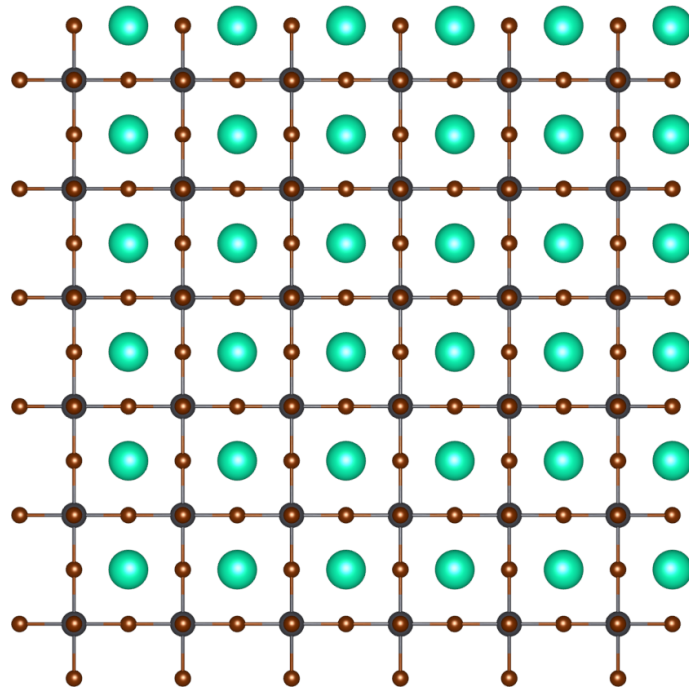


Figure 1.1: Cesium lead bromide perovskite structure as representative of a solid

The atoms of Figure 1.1 are interacting or 'feeling' each other. And at finite temperature the atoms will oscillate around their equilibrium positions. This motion is often referred to as thermal motion.

A theoretical scientists goal is to find a mathematical description to predict the everyday properties of such a solid. As a human we can not see the atoms building up the matter around us. We can only see matter as a continuum. A description in terms of a continuum can be done by phenomenological theories. A framework for such theories is given by thermodynamics. A more theoretical point of view would be to use so called first principle approaches. In these approaches the scientist takes the atoms and their interactions into account. The interactions of atoms can be described in the framework of non-relativistic quantum-mechanics, where the central equation is the Schrödinger equation. This tremendously increases the computational effort in comparison to a macroscopic description. The Schrödinger equation has to be solved for every electron building up an atom. The connection between the macroscopic theory of thermodynamics and the microscopic world of quantum mechanics is given by statistical mechanics. Statistical mechanics does not care how the atoms are interacting exactly but connects the microscopic world to the everyday macroscopic world. The scientist only supplies an equation describing the interactions between the atoms in the material of interest. These interactions can either be parametrized from experiments or can be taken from the Schrödinger equation. For a theoretical scientist it is always nice not to use experimental data in calculations but to predict them. These predictions should be as close as possible to available experimental data, telling the theoretician he/she has done good work and the underlying interaction model works. The dilemma is that interactions from first principles in terms of the Schrödinger equation are usually too expensive to compute. In this thesis this dilemma is tackled by machine-learning approaches. The machine-learning approach is trained on quantum mechanical calculations. This means, the machine-learning approach 'sees' certain arrangements of atoms and quantum mechanical calculations will tell the machine-learning algorithm what the atoms would like to do in this configuration. After the training procedure, the machine-learning algorithm knows enough atomic configurations to make predictions on what the atoms will do by itself. With this approach we are able to model the microscopic world of atoms and molecules, but are by the use of statistical mechanics able to predict macroscopic properties that we can observe in our everyday life. Properties predicted by this approach in this thesis include for example phase transition temperatures of materials.

Theoretical background

2 Basic wave mechanics

The Schrödinger equation is fundamental for a first principles description of matter. Therefore this section introduces the basic quantum mechanical concepts needed for ab-initio molecular dynamics. The Dirac notation is handy when working with quantum mechanics in theory. The Schrödinger equation is in general complicated to solve and therefore the variational principle will be presented as a tool to obtain approximate solutions. The solutions of the time independent Schrödinger equation are wavefunctions and related eigenvalues. From the wavefunction the electron density can be obtained which is the probability of finding an electron at a certain time and position. To compute forces during ab-initio molecular dynamics the Hellmann-Feynman theorem is applied and its derivation will be presented during this chapter. The forces will be computed within the Born Oppenheimer approximation: a method to decouple electronic from nuclear degrees of freedom. Classical equations of motions are the corner stone of molecular dynamics simulations. The Ehrenfest theorem defines under which circumstances the classical equations of motion are in agreement with the quantum mechanical expectation values. Real systems are composed of a large number of particles. Therefore statistical techniques are needed in order to describe matter in a classical and quantum mechanical way. The density matrix is the key to combine statistical mechanics with quantum mechanics.

2.1 Schrödinger equation

The basic ab-initio solid state theory is non-relativistic quantum mechanics for fermions and the central equation will therefore be the Schrödinger equation. The time dependent Schrödinger equation for a system composed of atomic nuclei at positions $\{\mathbf{R}_I\}$ and electrons at positions $\{\mathbf{r}_i\}$ is given by:

$$\frac{\partial \Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}, t)}{\partial t} = \hat{H} \Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}, t), \quad (\text{I.1})$$

with Ψ denoting the wavefunction and $\hat{H}$ the Hamilton operator containing all information about interactions and the kinetic energy. The wavefunction Ψ describes the state of the system and contains all information of the isolated many particle system under consideration. The wavefunction can be expressed in the real space form as shown in equation (I.1). But the wavefunction can also be expressed in momentum representation. These two representations are related by a Fourier transformation. The Hamiltonian for an N electron N_{ion} system, is given by

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \Delta_i + \sum_{i=1}^N v(\mathbf{r}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{r_{ij}} + \sum_{I=1}^{N_{ions}-1} \sum_{J=I+1}^{N_{ions}} \frac{Z_I Z_J}{R_{IJ}} - \frac{1}{2} \sum_{I=1}^{N_{ions}} \Delta_I, \quad (\text{I.2})$$

where the first term is the kinetic energy of the electrons with Δ_i denoting the Laplacian $\Delta = \nabla \cdot \nabla$ with respect to the electronic coordinates. The second term describes the interaction of the electrons with some external potential, arising due to the nuclei of the atoms. This external potential is given by

$$v(\mathbf{r}_i) = - \sum_{I=1}^{N_{ions}} \frac{Z_I}{r_{iI}}, \quad (\text{I.3})$$

where Z_I is the charge of the considered nucleus and $r_{iI} = |\mathbf{r}_i - \mathbf{R}_I|$ is the distance between electron i and nucleus I . The third term in equation (I.2) is the electrostatic Coulomb repulsion between the N electrons, with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ describing the distance between the particles. The fourth term of equation (I.2) denotes the electrostatic repulsion between the nuclei forming the molecule or the crystal. $R_{IJ} = |\mathbf{R}_I - \mathbf{R}_J|$ denotes the distance between the ions. The last term is the kinetic energy of the nuclei where the Laplacian is now with respect to nuclear coordinates. The Hamilton operator can be written in short form

$$\hat{H} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn} + \hat{T}_n, \quad (\text{I.4})$$

where the order of the terms is the same as in equation (I.2). The Schrödinger equation can also be written in a time independent form

$$\hat{H} \psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}, t_0) = E \psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}, t_0), \quad (\text{I.5})$$

where the time was fixed to a certain value t_0 . Equation (I.5) is an eigenvalue equation and the solutions are stationary states. The Schrödinger equation is a linear second order partial differential equation. The solutions of the time independent Schrödinger equation are spanning a space of eigenstates often written in Dirac's notation $|\psi\rangle$. These states can be considered as vectors forming a Hilbert space with a certain dimension. This dimension can also be infinity if the basis is continuous. The space spanned by the eigenstates is a linear and normed space. The dot product between vectors of an orthonormal basis spanning a Hilbert space is given by

$$\langle \psi_i | \psi_j \rangle = \int_{-\infty}^{\infty} \psi_i^* \psi_j d^N r = \delta_{ij}. \quad (\text{I.6})$$

Here, the notation $\langle \psi |$ was introduced, denoting a 'bra' vector. The bras are forming the dual space with respect to the 'ket' vectors. From equation (I.6) it can be seen that the bra is the complex conjugate to the ket vector. With this we can write any state $|\Phi\rangle$ in a Hilbert space by a superposition of the basis states $|\psi_i\rangle$. A big advantage of the Dirac notation is the independence of the states with respect to variables like position, momentum or energy. A ket vector can be expanded in terms of the basis vectors in the abstract space as

$$|\Phi\rangle = \sum_{i=1}^N c_i |\psi_i\rangle. \quad (\text{I.7})$$

To obtain the expansion coefficients c_i the overlap of the vector $|\Phi\rangle$ with the basis vectors $|\psi_i\rangle$ spanning the Hilbert space is computed by

$$f_i = \langle \Phi | \psi_i \rangle. \quad (\text{I.8})$$

Now consider the expansion shown in equation (I.7) but for a continuous basis (like for example the position basis). In the position basis the expansion would look like

$$|\Phi\rangle = \int_{-\infty}^{\infty} \psi(\mathbf{r}) |\mathbf{r}\rangle d^3r, \quad (\text{I.9})$$

with $|\mathbf{r}\rangle$ denoting the basis vectors of the position representation spanning the Hilbert space. To obtain the expansion coefficients $\psi(\mathbf{r})$ equation (I.8) can be used in its continuous form

$$\psi(\mathbf{r}) = \langle \Phi | \mathbf{r} \rangle \quad (\text{I.10})$$

The orthonormality relation for a continuous basis is given by

$$\langle \mathbf{r}' | \mathbf{r} \rangle = \delta(\mathbf{r}' - \mathbf{r}). \quad (\text{I.11})$$

The solutions of the time independent Schrödinger equation gives the stationary states of our quantum system. The first step for solving a differential equation is the definition of appropriate boundary conditions. In this work only solids are considered and hence the Born von Karman boundary conditions are used. If the stationary states $|\psi_i\rangle$ of the Schrödinger equation are known, then the expectation value of a quantity given by an operator $\hat{A}$ is computed with

$$\langle A_i \rangle = \frac{\langle \psi_i | \hat{A} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle}. \quad (\text{I.12})$$

The denominator is only needed if the states $|\psi_i\rangle$ are not normalized.

2.2 Variational principle

The Schrödinger equation can only be solved analytically for simple problems as the harmonic oscillator, a single particle in a central potential or a simple periodic potential. Therefore clever approaches are needed to compute approximate but as accurate as possible solutions. One of the methods is the variational method. In this method a trial wavefunction is expanded in some basis set. This basis set can be any type of functions that seem appropriate for the considered problem. For a molecule one could for example take a Gaussian basis set with varying variance and centers of the Gaussian functions. For solids, plane wave basis sets are very popular and widely used. Trial wavefunctions can be constructed as

$$|\tilde{\psi}\rangle = \sum_{i=1}^{N_{\text{Basis}}} c_i |i\rangle, \quad (\text{I.13})$$

where the $|i\rangle$ denotes a function of the basis set used to expand the wavefunction and the $c_i = \langle i | \tilde{\psi} \rangle$ denote expansion coefficients equivalent to those shown in equation (I.7). The choice of the basis set is crucial for the description of a physical problem. The basis functions are usually chosen based on symmetry arguments or the asymptotic behavior expected for the wavefunction of the system under consideration. The energy functional for a wavefunction ψ expanded in terms of a basis set is given by

$$E[\tilde{\psi}] = \frac{\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle}. \quad (\text{I.14})$$

The variational method assumes that the so computed energy will always give an upper bound to the real ground state energy E_0

$$E[\tilde{\psi}] \geq E_0. \quad (\text{I.15})$$

This will always be true since the ground state is the lowest possible energy state available for a system. By inserting the trial function expansion (I.13) into the energy functional (I.14)

$$E[\tilde{\psi}] = \frac{\sum_{i=1} c_i^2 E_i}{\sum_{i=1} c_i^2}, \quad (\text{I.16})$$

is obtained. To get this equation an orthonormal set of basis functions was assumed. By using inequality (I.15) together with (I.16) it can be shown that

$$\sum_{i=1} c_i^2 E_i \geq E_0 \sum_{i=1} c_i^2 = E_0 \quad (\text{I.17})$$

holds. The second equality follows because the sum $\sum_{i=1} c_i^2 = 1$. The first equality only holds if the true ground state is found. Only then the computed energy equals the ground state energy. Another very intuitive picture is given by Parr and Yang in their Book Density-Functional Theory of Atoms and Molecules[1]. Let's assume the basis functions used to expand the trial functions are the eigenstates of the Hamiltonian spanning the Hilbert space for the considered operator. One of those eigenstates has to be the true ground state. Hence equation (I.16) will only be the ground state if all $c_i = 0$ except the one corresponding to the ground state which has to be unity. Therefore the energy described by the energy functional will be an upper bound to the true ground state E_0 . Introducing the matrix elements of the Hamiltonian $H_{ij} = \langle i|H|j \rangle$ and the overlap integral $O_{ij} = \langle i|j \rangle$ the derivative of equation (I.16) is

$$\frac{\partial E[\tilde{\psi}]}{\partial c_i} = \frac{\sum_j c_j H_{ij}}{\sum_{i,j} c_i^* c_j O_{ij}} - E \frac{\sum_j c_j O_{ij}}{\sum_{i,j} c_i^* c_j O_{ij}} + \frac{\sum_j c_j^* H_{ji}}{\sum_{i,j} c_i^* c_j O_{ij}} - E \frac{\sum_j c_j^* O_{ji}}{\sum_{i,j} c_i^* c_j O_{ij}} = 0. \quad (\text{I.18})$$

The first two terms of this equations are conjugate transpose to the pair formed by the third and fourth term. Therefore it is sufficient to solve the following determinant for E to obtain the best approximation to the real ground state energy

$$\begin{vmatrix} H_{11} - EO_{11} & H_{12} - EO_{12} & \cdots & H_{1N} - EO_{1N} \\ H_{21} - EO_{21} & H_{22} - EO_{22} & \cdots & H_{2N} - EO_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - EO_{N1} & H_{N2} - EO_{N2} & \cdots & H_{NN} - EO_{NN} \end{vmatrix} = 0. \quad (\text{I.19})$$

2.3 Electron density

A general single particle wave function depends on the position ($\mathbf{r}$) and spin coordinates ($\mathbf{s}$). The generalized coordinate combining spin and position is denoted as $\mathbf{x}$. Real physical systems consist of many particles and therefore a many body wavefunction is needed. A good approximation for a many body N particle wavefunction $|\mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_N\rangle$ is a product state of single particle wavefunctions $|\mathbf{x}_i\rangle$

$$|\mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_N\rangle = |\mathbf{x}_1\rangle |\mathbf{x}_2\rangle \cdots |\mathbf{x}_N\rangle. \quad (\text{I.20})$$

The many-body wavefunction has to satisfy certain symmetry conditions. Fermionic wavefunctions have to be antisymmetric under the exchange of two particles. And only one particle is allowed to occupy the same state. Bosons on the other hand have to be symmetric under the exchange of particles and it does not matter how many particles occupy the same state. To generate a proper bosonic wavefunction one would have to add all permutations of the product shown in equation (I.20). For fermionic systems two particles are not allowed to occupy the same state. From this it follows that if one is dealing with non-interacting fermions there will be a Pauli repulsion between the particles such that they will always occupy different quantum states. To obtain correct antisymmetric wavefunctions for fermions one can use Slater determinants or write the expansion explicitly [2]

$$|\mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_N\rangle = \frac{1}{N!} \sum_P (-1)^P \hat{P} |\mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_N\rangle \quad (\text{I.21})$$

where $\hat{P}$ denotes the permutation operator, $(-1)^P$ denotes the parity of the actual permutation and the sum is over all possible permutations. A wavefunction built up like this will always be antisymmetric under the exchange of two particles. From the wavefunction it is possible to define an electron density

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{x}_1, \cdots, \mathbf{x}_N)|^2 ds_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N, \quad (\text{I.22})$$

where the integration is carried out over all spin states and all positions except for particle 1 were the integration is only done over the spin states. The factor N denotes the number of particles. The density defined in (I.22) gives the number of particles when integrated over the whole space

$$\int_{-\infty}^{\infty} \rho(\mathbf{r}) d^3r = N. \quad (\text{I.23})$$

The electron density has to satisfy general laws and properties. The density has to decrease monotonically by increasing the distance to the nucleus for atoms[1, 3]. And the electron density has to be finite at the

nucleus with a value of $\rho(0)$. Terms as $\frac{1}{2}\Delta - \frac{Z_\alpha}{r_\alpha}$ are dangerous to cause the density to be infinite. For this reason there exists a cusp condition [1, 4] given by

$$\left. \frac{\partial}{\partial r_\alpha} \bar{\rho}(r_\alpha) \right|_{r_\alpha=0} = -2Z_\alpha \bar{\rho}(0), \quad (\text{I.24})$$

preventing the electron density from diverging at the nucleus.

2.4 The Hellmann-Feynman theorem and forces

The Hellmann-Feynman theorem[5] shows the computational way to obtain derivatives of the energy. This is very important for ab-initio molecular dynamics since the forces are only obtained if the derivative of the total energy can be computed with respect to the ionic coordinates. The Hellmann-Feynman theorem states

$$\frac{dE}{d\lambda} = \frac{\langle \Psi_\lambda | \frac{\partial H(\lambda)}{\partial \lambda} | \Psi_\lambda \rangle}{\langle \Psi_\lambda | \Psi_\lambda \rangle}. \quad (\text{I.25})$$

The proof of the theorem for normalized wavefunctions ($\langle \Psi_\lambda | \Psi_\lambda \rangle = 1$) can be achieved by using the product rule on the total energy

$$\begin{aligned} \frac{dE_\lambda}{d\lambda} &= \left\langle \frac{\partial \Psi_\lambda}{\partial \lambda} \middle| H(\lambda) \middle| \Psi_\lambda \right\rangle + \left\langle \Psi_\lambda \middle| H(\lambda) \middle| \frac{\partial \Psi_\lambda}{\partial \lambda} \right\rangle + \left\langle \Psi_\lambda \middle| \frac{\partial H(\lambda)}{\partial \lambda} \middle| \Psi_\lambda \right\rangle = \\ &= E_\lambda \left\langle \frac{\partial \Psi_\lambda}{\partial \lambda} \middle| \Psi_\lambda \right\rangle + E_\lambda \left\langle \Psi_\lambda \middle| \frac{\partial \Psi_\lambda}{\partial \lambda} \right\rangle + \left\langle \Psi_\lambda \middle| \frac{\partial H(\lambda)}{\partial \lambda} \middle| \Psi_\lambda \right\rangle = \\ &= E_\lambda \frac{d}{d\lambda} \langle \Psi_\lambda | \Psi_\lambda \rangle + \left\langle \Psi_\lambda \middle| \frac{\partial H(\lambda)}{\partial \lambda} \middle| \Psi_\lambda \right\rangle \end{aligned} \quad (\text{I.26})$$

By integration of equation (I.26) from λ_1 to λ_2 an equation for the change in energy is obtained,

$$E(\lambda_2) - E(\lambda_1) = \int_{\lambda_1}^{\lambda_2} \frac{\langle \Psi_\lambda | \frac{\partial \hat{H}(\lambda)}{\partial \lambda} | \Psi_\lambda \rangle}{\langle \Psi_\lambda | \Psi_\lambda \rangle} d\lambda = \frac{\langle \Psi_\lambda | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi_\lambda \rangle}{\langle \Psi_\lambda | \Psi_\lambda \rangle} \quad (\text{I.27})$$

This result is analogous to the first order energy correction in perturbation theory[1, 6, 7]. The Hellmann-Feynman theorem can be considered as a first order energy perturbation by some parameter λ which could for example be the position of some ion. This can be derived by considering the eigenvalue equations of $\hat{H}(\lambda_1)$ and $\hat{H}(\lambda_2)$

$$\hat{H}(\lambda_1) |\Psi_{\lambda_1}\rangle = E_{\lambda_1} |\Psi_{\lambda_1}\rangle \quad \hat{H}(\lambda_2) |\Psi_{\lambda_2}\rangle = E_{\lambda_2} |\Psi_{\lambda_2}\rangle. \quad (\text{I.28})$$

These two equations can be subtracted and rearranged such that

$$E(\lambda_2) - E(\lambda_1) = \frac{\langle \Psi_{\lambda_2} | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi_{\lambda_1} \rangle}{\langle \Psi_{\lambda_2} | \Psi_{\lambda_1} \rangle} \quad (\text{I.29})$$

This equation is also known from first order perturbation theory with $\hat{V} = \hat{H}(\lambda_2) - \hat{H}(\lambda_1)$ and shows the equivalence of the Hellmann-Feynman theorem to first order perturbations [1, 6, 7].

The gradient with respect to the ionic coordinates of the total energy is the force acting on some ion. Therefore the Hellmann-Feynman theorem is crucial for doing ab-initio molecular dynamics. The theorem tells us that it is sufficient to look at the gradient of the Hamiltonian with respect to the ionic coordinates. By using this theorem on the Hamiltonian of (I.2)

$$\mathbf{F}_I = -\nabla E = \langle \Psi | \nabla \hat{H} | \Psi \rangle = -Z_\alpha \sum_{i=1}^N \frac{\mathbf{r}_i - \mathbf{R}_I}{r_{iI}^3} + Z_I \sum_{J \neq I}^{N_{ions}} \frac{\mathbf{R}_J - \mathbf{R}_I}{R_{IJ}^3}, \quad (\text{I.30})$$

is obtained. From this it follows the force acting on an ion I is a sum of forces arising due to all the electrons and a second term arising due to all the other nuclei. So the Hellmann-Feynman theorem supplies us with a tool to compute forces from first principles.

2.5 The Born-Oppenheimer approximation

To simplify the solutions to the Schrödinger equation for atomic systems the Born-Oppenheimer approximation [8] is used. Since the electrons are much lighter than the nuclei their motion can be decoupled. The Born-Oppenheimer approximation is a two step procedure. First one solves the electronic part of equations (I.1) and (I.2) for a fixed nuclear configuration $\{\mathbf{R}_I\}$. From this the electronic part of the wavefunction is obtained. The second step is to solve the nuclear part of the Schrödinger equation in the mean field of the electrons computed in the previous step. This can be formalized as

$$\begin{aligned} \hat{H} = \hat{H}_{el} + \hat{H}_n = & -\frac{1}{2} \sum_{i=1}^N \Delta_i + \sum_{i=1}^N v(\mathbf{r}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{r_{ij}} + \\ & + \sum_{I=1}^{N_{ions}-1} \sum_{J=I+1}^{N_{ions}} \frac{Z_I Z_J}{R_{IJ}} - \frac{1}{2} \sum_{I=1}^{N_{ions}} \Delta_I, \end{aligned} \quad (\text{I.31})$$

where the first three terms belong to the electronic Hamiltonian $\hat{H}_{el}$ and the last two terms belong to the nuclear Hamiltonian $\hat{H}_n$. The solution to the electronic part of the Schrödinger equation is

$$\hat{H}_{el} \psi_{el}(\mathbf{r}; \{\mathbf{R}_I\}) = E_{el} \psi_{el}(\mathbf{r}; \{\mathbf{R}_I\}). \quad (\text{I.32})$$

From this the wavefunction for the electrons in the nuclear configuration $\{\mathbf{R}_I\}$ is obtained. And with the knowledge of the electronic wavefunction the contribution of the electrons to the energy expectation value is obtained by $\langle \psi_{el}(\mathbf{r}; \{\mathbf{R}_I\}) | \hat{H}_{el} | \psi_{el}(\mathbf{r}; \{\mathbf{R}_I\}) \rangle$. With the knowledge of the electronic wavefunction it is possible to compute the nuclear wavefunction in an effective electronic field as an eigenvector of the Hamiltonian

$$\begin{aligned} \hat{H}_n = \langle \hat{H}_{el} \rangle + \sum_{I=1}^{N_{ions}-1} \sum_{J=I+1}^{N_{ions}} \frac{Z_I Z_J}{R_{IJ}} - \frac{1}{2} \sum_{I=1}^{N_{ions}} \Delta_I = \\ = -\frac{1}{2} \sum_{I=1}^{N_{ions}} \Delta_I + E_{pot}(\{\mathbf{R}_I\}), \end{aligned} \quad (\text{I.33})$$

where E_{pot} defines the sum of the average electronic and potential energy due to nuclei for the actual configuration. The energy E_{pot} serves as a potential energy surface in which the nuclei move during ab-initio molecular dynamics. This surface is called the Born-Oppenheimer energy surface of nuclear motion [6, 7]. The eigenvalue of equation (I.33) for the nuclear wavefunction $\Phi_n(\mathbf{R})$ is obtained from

$$\left[\hat{H}_n + \langle \hat{H}_{el} \rangle \right] \Phi_n(\mathbf{R}) = \left[-\frac{1}{2} \sum_{\alpha=1}^{N_n} \Delta_\alpha + E_{pot}(\{\mathbf{R}\}) \right] \psi = E_n \Phi_n(\mathbf{R}), \quad (\text{I.34})$$

The Born-Oppenheimer approximation shows a way in which the wavefunctions of the nuclear and electronic part can be obtained separately under the assumption that the nuclei move much slower compared to the electrons. From this it follows that the total wavefunction can be considered as a product wavefunction of the nuclear and the electronic part

$$\Psi_{tot}(\mathbf{r}, \mathbf{R}) = \psi_{el}(\mathbf{r}, \{\mathbf{R}\}) \Phi_n(\mathbf{R}). \quad (\text{I.35})$$

A every exciting way to look at the Born-Oppenheimer approximation is to think of two disjoint Hilbert spaces $\mathbb{H}_{el}$ spanned by the states of the electronic Hamiltonian $\hat{H}_{el}$ and a second Hilbert space $\mathbb{H}_n$ spanned by the nuclear states of the Hamiltonian $\hat{H}_n$. The electronic Hilbert space is depending parametrically on the nuclear coordinates and vice versa. The Hilbert space of the combined system (electrons and nuclei) is then given by the direct sum $\mathbb{H}_{tot} = \mathbb{H}_{el} \otimes \mathbb{H}_n$. Lets assume the states spanning $\mathbb{H}_{el}$ are given by $|\Phi\rangle$ and the states spanning $\mathbb{H}_n$ are given by $|\psi\rangle$. Then the total wavefunction in the combined position representation is given by

$$\begin{aligned} \Psi_{tot}(\mathbf{r}, \mathbf{R}) &= \sum_i \sum_j f_{ij} \langle \mathbf{R} | \Phi_{(n),i} \rangle \langle \mathbf{r} | \psi_{(el),j} \rangle = \\ &= \sum_i \sum_j f_{ij} \Phi_{(n),i}(\mathbf{R}) \psi_{(el),j}(\mathbf{r}) = \Phi_{(n)}(\mathbf{R}) \psi_{(el)}(\mathbf{r}), \end{aligned} \quad (\text{I.36})$$

what is the same as equation (I.35).

2.6 The Ehrenfest theorem and classical equations of motions

The next ingredient for doing ab-initio molecular dynamics are equations of motions for the nuclei that can be solved in an affordable amount of time. In quantum mechanics the particle could take any path with a weight given by $e^{iS[\mathbf{r}]}$. In classical mechanics the particle will only follow the path that minimizes the action $S[\mathbf{r}]$. This relationship is given by

$$\int_{\mathbf{r}_a}^{\mathbf{r}_b} e^{iS[\mathbf{r}]} \mathcal{D}\mathbf{r} \approx e^{iS_{cl}[\mathbf{r}]}, \quad (\text{I.37})$$

where the integral on the left hand side is over all possible paths for getting from position $\mathbf{r}_a$ to $\mathbf{r}_b$. On the right hand side the integral is approximated by the classical path. This is nothing else than a saddle point approximation for the integral. When doing ab-initio molecular dynamics it would be very cumbersome to treat the nuclear positions by wavefunctions from a computational point of view. Therefore the point particle approximation is used for the nuclei. The positions of these point particles can be viewed as the expectation values of the nuclear wavefunctions. The nuclear coordinates are propagated by Newton's equations of motion. The Ehrenfest theorem states that the momentum and position expectation values propagate according to Newton's equations of motions only when the potential is of no higher order than quadratic[9, 10]. If the wavefunction $|\Psi|^2$ describing a nuclei is very narrow along a certain path the classical path approximation of (I.37) works best. To make these statements more explicit the Ehrenfest theorem will be derived from the single particle Hamiltonian

$$H = \frac{p^2}{2m} + V(\mathbf{r}, t). \quad (\text{I.38})$$

The classical equations of motions for this Hamiltonian are given by

$$\frac{d\mathbf{r}}{dt} = \frac{1}{m}\mathbf{p} \quad \frac{d\mathbf{p}}{dt} = \mathbf{F}(\mathbf{r}, t) \quad \mathbf{F}(\mathbf{r}, t) = -\nabla V(\mathbf{r}, t) \quad (\text{I.39})$$

In quantum mechanics the propagation of the expectation values is given by the commutator relations

$$\frac{d}{dt}\langle\mathbf{r}\rangle_\Psi = \frac{1}{i}\langle[\mathbf{r}, H]\rangle_\Psi \quad \frac{d}{dt}\langle\mathbf{p}\rangle_\Psi = \frac{1}{i}\langle[\mathbf{p}, H]\rangle_\Psi, \quad (\text{I.40})$$

where the brackets $\langle.\rangle_\Psi$ are understood as the expectation values with respect to the wavefunction Ψ . The square brackets $[.,.]$ denote the commutators between the operators. The needed commutator relations are given by

$$[\mathbf{r}, H] = \frac{i}{m}\mathbf{p} \quad [\mathbf{p}, H] = -i\nabla V(\mathbf{r}, t) = i\mathbf{F}(\mathbf{r}, t). \quad (\text{I.41})$$

Combining equations (I.40) and (I.41) gives

$$\frac{d}{dt}\langle\mathbf{r}\rangle_\Psi = \frac{1}{m}\langle\mathbf{p}\rangle_\Psi \quad \frac{d}{dt}\langle\mathbf{p}\rangle_\Psi = \langle\mathbf{F}(\mathbf{r}, t)\rangle_\Psi \quad (\text{I.42})$$

During ab-initio molecular dynamics the knowledge of the wavefunction Ψ giving the needed expectation values is missing. Therefore the following approximation for the effective or average force is needed

$$\langle\mathbf{F}(\mathbf{r}, t)\rangle_\Psi = \mathbf{F}(\langle\mathbf{r}\rangle_\Psi, t). \quad (\text{I.43})$$

The $\langle\mathbf{r}\rangle_\Psi$ are the average positions of the nuclei or the classical positions that one is aware of in terms of the molecular dynamics. Hence the Ehrenfest theorem states $\langle\mathbf{r}\rangle_\Psi$ and $\langle\mathbf{p}\rangle_\Psi$ satisfy classical equations of motions only if the average forces satisfy equation (I.43)[9, 10]. To see the limits of this approximation $\nabla V(\mathbf{r}, t)$ is expanded in a Taylor series

$$\begin{aligned} \nabla_i V(\mathbf{r}, t) &= (\nabla_i V)_{cl} + (\nabla_j \nabla_i V)_{cl}(x_j - \langle x_j \rangle_\Psi) \\ &\quad + \frac{1}{2}(\nabla_k \nabla_j \nabla_i V)_{cl}(x_j - \langle x_j \rangle_\Psi)(x_k - \langle x_k \rangle_\Psi). \end{aligned} \quad (\text{I.44})$$

The subscript cl in those equations means that the terms are evaluated at the position expectation values $\langle\mathbf{r}\rangle_\Psi$. Inserting equation (I.44) with the equation for the time dependence of the momentum into equation (I.42)

$$\frac{d}{dt}\langle\mathbf{p}\rangle_\Psi = \langle\mathbf{F}(\mathbf{r}, t)\rangle_\Psi = \mathbf{F}(\langle\mathbf{r}\rangle_\Psi, t) - \frac{1}{2}(\nabla_k \nabla_j \nabla_i V)_{cl} [\langle\mathbf{r}_j \mathbf{r}_k\rangle_\Psi - \langle\mathbf{r}_j\rangle_\Psi \langle\mathbf{r}_k\rangle_\Psi], \quad (\text{I.45})$$

is obtained. Where the second term of equation (I.44) vanishes when computing the average since $\langle \mathbf{r}_j \rangle_\Psi - \langle \mathbf{r}_j \rangle_\Psi = 0$. A comparison of equations (I.43) and (I.45) shows that the expectation values of $\langle \mathbf{r} \rangle_\Psi$ and $\langle \mathbf{p} \rangle_\Psi$ propagate according to classical equations of motion only if the potential does not depend more than quadratically on the position [9, 10]. In other words, the quantum mechanical expectation values will propagate according to Newton's equations if the potential is sufficiently smooth. If the potential is not perfectly quadratically the classical equations of motions provide an approximation to the real propagation of the expectation values. And therefore ab-initio molecular dynamics can be considered as an approximative way to compute trajectories of quantum mechanical position expectation values.

2.7 The density matrix

In this section the density matrix will be introduced. The density matrix is a very useful tool when doing statistical mechanics of quantum systems. To get more familiar with the concept of a density matrix it is useful to introduce the concepts of pure and mixed states. A pure state can be considered as a state of which one has maximal knowledge in a quantum mechanical sense. An example would be a single harmonic oscillator for which one can compute all compatible expectation values. A mixed state on the other hand is a state in which one does not know exactly in which pure states the system is at the moment. One only knows the probabilities p_i satisfying $\sum_{i=1}^N p_i = 1$ that a certain pure state $|\Psi_i\rangle$ is occupied by the system. To visualize this one can think of a collection of N quantum harmonic oscillators. Any of those oscillators is in a certain state. The expectation values for mixed states are then given by statistical averages over the pure states weighted with p_i . To formalize this the density operator or density matrix is introduced

$$\rho = \sum_i |\Psi_i\rangle p_i \langle \Psi_i|. \quad (\text{I.46})$$

If the density matrix would describe a pure state one of the p_i 's would be unity and all the others would be zero. In the following some useful properties of the density matrix will be shown [9].

- The first property to be shown are the boundedness and self-adjointness of the density matrix

$$\rho^\dagger = \rho, \quad (\text{I.47})$$

where $\rho^\dagger$ is the complex transpose of ρ . To proof this property note that ρ is by definition symmetric and since a symmetric operator that is bounded is Hermitian it suffices to show the boundedness of ρ . The density matrix ρ is defined in the entire Hilbert space spanned by the states $|\varphi_i\rangle$

$$\begin{aligned} |\rho\varphi|^2 &= \sum_i \sum_j p_i p_j \langle \varphi | \Psi_i \rangle \langle \Psi_i | \Psi_j \rangle \langle \Psi_j | \varphi \rangle \leq \\ &\leq \langle \varphi | \sum_i p_i |\Psi_i\rangle \langle \Psi_i| \sum_j p_j |\Psi_j\rangle \langle \Psi_j| \varphi \rangle \leq \\ &\leq \langle \varphi | \sum_a p_a \sum_b |\Psi_b\rangle \langle \Psi_b| \sum_c p_c \sum_d |\Psi_d\rangle \langle \Psi_d| \varphi \rangle = \\ &= \langle \varphi | \sum_{i=1} p_i \sum_j p_j |\varphi\rangle = \langle \varphi | \varphi \rangle = |\varphi|^2, \end{aligned} \quad (\text{I.48})$$

where in the second line the Cauchy-Schwarz inequality was used and $|\varphi\rangle$ is some test function. From this equation it follows that $|\rho| \leq 1$ and hence the density operator is bounded. Therefore ρ is said to be self-adjoint [9].

- The second important property of the density operator

$$\rho^2 \leq \rho, \quad (\text{I.49})$$

where the equality only holds for pure states since only then a single $p_i = 1$. The proof is as follows [9] where again $|\Psi\rangle \in \mathbb{H}$ is used:

$$\begin{aligned}
\langle \Psi | \rho^2 | \Psi \rangle &= \sum_i \sum_j p_i p_j \langle \Psi | \Psi_i \rangle \langle \Psi_i | \Psi_j \rangle \langle \Psi_j | \Psi \rangle \leq \\
&\leq \sum_i \sum_j p_i p_j | \langle \Psi | \Psi_i \rangle \langle \Psi_j | \Psi \rangle | = \\
&= \left[\sum_i p_i \langle \Psi_i | \Psi \rangle \right]^2 \leq \\
&\leq \left(\sum_i p_i \right) \left(\sum_j p_j | \langle \Psi_j | \Psi \rangle |^2 \right) = \\
&= \sum_j p_j | \langle \Psi_j | \Psi \rangle |^2 = \langle \Psi | \rho | \Psi \rangle
\end{aligned} \tag{I.50}$$

This can be used as a test to check if a system is in a pure or a mixed state.

- The third property to be shown is

$$\text{Tr} [\rho] = 1, \tag{I.51}$$

Given an orthonormal basis of the Hilbert space $\{|\varphi_i\rangle\}$ it can be shown by

$$\text{Tr} [\rho] = \sum_i \langle \varphi_i | \rho | \varphi_i \rangle = \sum_i \sum_j p_i \langle \varphi_i | \Psi_i \rangle \langle \Psi_i | \varphi_i \rangle = \sum_i p_i |\Psi_i|^2 = \sum_i p_i = 1. \tag{I.52}$$

The trace condition of the density operator can be interpreted such that the system has to be at least in one of the states. Since the operator $\hat{\rho}$ is self-adjoint bounded and has unit trace it is said to be compact. Hence the eigenvectors of the density operator form an orthonormal set and the spectrum of such an operator consists of a point spectrum only [9]. For computing the expectation value of some operator $\hat{A}$ in the density matrix formulation one just uses the trace operation on the product of the density matrix and the operator

$$\begin{aligned}
\langle A \rangle &= \text{Tr} [\rho \hat{A}] = \sum_i \langle \varphi_i | \hat{A} \rho | \varphi_i \rangle = \sum_i \sum_j \langle \varphi_i | \hat{A} | \Psi_j \rangle p_j \langle \Psi_j | \varphi_i \rangle = \\
&= \sum_i \sum_j p_j \langle \Psi_j | \varphi_i \rangle \langle \varphi_i | \hat{A} | \Psi_j \rangle = \\
&= \sum_j p_j \langle \Psi_j | \hat{A} | \Psi_j \rangle = \sum_j p_j A_j.
\end{aligned} \tag{I.53}$$

By considering equation (I.53) one may recognize that the expectation value of an operator in density matrix language is just a statistical average over the quantum mechanical expectation values of the pure states. The quantities to be averaged over are the quantum mechanical expectation values of the operator $\hat{A}$ in the states $|\Psi_i\rangle$.

One may also interpret the states $|\Psi_i\rangle$ in equation (I.53) as the states describing the quantum mechanical system of interest and the states $|\varphi_i\rangle$ are describing the rest of the universe. This makes it evident that pure states are not general enough to describe a quantum mechanical system that is not containing the whole universe [11]. Another important application of this interpretation is the Born-Oppenheimer approximation. Assume the universe is now only the system of interest and this universe is split in two parts, the electronic part and the nuclear part. If one would be interested in structural properties of some material (the arrangement of the nuclei), knowledge of the nuclear states would not suffice since the probabilities p_i do not only depend on the nuclear part of the system but the whole system with the electrons included. Hence the density matrix formulation provides a generalization of quantum mechanics from pure to mixed states.

3 Basic statistical mechanics

Statistical techniques are one of the cornerstones of modern science. Whenever a scientist has to deal with a large number of degrees of freedom statistical and probabilistic approaches are indispensable. In this section fundamental concepts of statistical mechanics needed for a proper description of many particle systems will be introduced. The thermodynamic ensemble is fundamental to statistical physics and will therefore be introduced in the language of the density matrix. Ensembles can be written in closed form by maximizing entropy functions under the chosen external constraints what is known as the second law of thermodynamics. In this chapter the micro-canonical ensemble, the canonical ensemble and the grand canonical ensemble will be considered. Every ensemble is described by the corresponding partition function containing all information of a system that is accessible to a scientist. From the quantum mechanical ensembles their classical analogues will be derived as the limiting case when $\hbar \rightarrow 0$, where the canonical ensemble is used as a representative. From the classical partition functions the equipartition theorem will be derived which presents a relationship between the temperature of a statistical system and the average kinetic energy per degree of freedom. Another very important theorem of statistics is the fluctuation-dissipation theorem showing how a system that was prepared in a non-equilibrium state fluctuates to its equilibrium state.

3.1 Basics of ensemble theory

In this section the language of density matrices is used to introduce the microcanonical, the canonical and the grand canonical ensemble. The first is described by the independent variables energy E , particle number N , and the volume V . The canonical ensemble is defined by the independent variables: N , V and temperature T . For the introduction of the ensembles the concept of entropy has to be defined. The entropy is defined in one of the following ways

$$S = k_B \ln(\Omega) \quad (\text{I.54})$$

$$S = -k_B \sum_{i=1} p_i \ln(p_i) \quad (\text{I.55})$$

$$S = -k_B \text{Tr} \hat{\rho} \ln(\hat{\rho}). \quad (\text{I.56})$$

Equation (I.54) denotes the Boltzmann entropy where Ω is the multiplicity, which denotes the number of states in agreement with the external constraints imposed on the considered system. The second equation (I.55) is the Gibbs entropy defined in terms of the normalized probabilities p_i . And the third equation (I.56) relates the entropy with the density matrix [12]. This form of the entropy is the Von-Neumann entropy equation [13]. The concept of entropy is fundamental to thermodynamics and statistical physics. For systems in thermodynamic equilibrium the entropy will always be maximal. A macroscopic system that is not in thermal equilibrium would change its state until the entropy function of the system reaches a maximum. This is also known as the second law of thermodynamics[12]. Consider a microcanonical ensemble with fixed energy E and volume V , containing N particles. Imagine what happens if the system has several possibilities to arrange the particles in agreement with the energy E , volume V and particle number constraint. Since all the states have the same energy all of those states should be equally likely. Therefore the density matrix to describe a micro-canonical ensemble is given by

$$\rho(E, V, N) = \sum_{E < E' < E + \delta E} \frac{|E'\rangle \langle E'|}{\Omega(E, V, N)}, \quad (\text{I.57})$$

where $|E'\rangle$ denotes a energy eigenstate of the Hamiltonian. The sum is over all states in agreement with the total energy E of the system. The multiplicity $\Omega(E, V, N)$ denotes the total number of states available by the system under the external constraints. The probability to find the system in a certain state is the inverse of the number of possible states [14]. By considering the Boltzmann entropy equation (I.54) it can be seen that the entropy increases as the number of states accessible to the system increases. In terms of the probabilities for the Gibbs entropy p_i shown in (I.55) the entropy will be maximal if all the probabilities are the same. This is true as long as there are no external constraints altering this behavior. Therefore the Gibbs entropy can be considered as a generalization of the Boltzmann entropy to more general ensembles where the statistical weights are allowed to vary.

The next important ensemble is the canonical-ensemble (N, V, T). By using the Von-Neumann entropy one is able to find the density matrix of the canonical distribution by determining the maximum of equation (I.56) subject to constrained energy E and constrained trace of the density matrix. Therefore the Lagrange multiplier α is introduced for constraining the energy $E = \text{Tr}[\hat{\rho} \hat{H}]$. For the constraint on the trace of the density matrix (it has to be unity) the Lagrange multiplier λ is introduced. The canonical-density matrix can be obtained by solving

$$\delta \left[-k_B \text{Tr} [\hat{\rho} \ln(\hat{\rho})] + \alpha \left(\text{Tr} [\hat{\rho} \hat{H}] - E \right) + \lambda (\text{Tr} [\hat{\rho}] - 1) \right] = 0. \quad (\text{I.58})$$

The equation can either be solved by varying the probabilities and states in Hilbert space of equation (I.46) simultaneously or by varying the density matrix directly. Here the second possibility will be taken where the variation of the density matrix $\hat{\rho} = \hat{\rho}^0 + \delta \hat{\rho}$ will be used[1]. The first term in equation (I.58) can be simplified by

$$\begin{aligned} -k_B \text{Tr} [(\hat{\rho}^0 + \delta \hat{\rho}) \ln(\hat{\rho}^0 + \delta \hat{\rho})] &= -k_B \text{Tr} [\hat{\rho}^0 \ln(\hat{\rho}^0 + \delta \hat{\rho}) + \delta \hat{\rho} \ln(\hat{\rho}^0 + \delta \hat{\rho})] = \\ &= -k_B \text{Tr} \left[\hat{\rho}^0 \ln \left(1 + \frac{\delta \hat{\rho}}{\hat{\rho}^0} \right) + (\hat{\rho}^0 + \delta \hat{\rho}) \ln(\hat{\rho}^0) + \delta \hat{\rho} \ln \left(1 + \frac{\delta \hat{\rho}}{\hat{\rho}^0} \right) \right] = \\ &\approx -k_B \text{Tr} [\delta \hat{\rho} + \delta \hat{\rho} \ln \hat{\rho}^0] - k_B \text{Tr} [\hat{\rho}^0 \ln(\hat{\rho}^0)], \end{aligned} \quad (\text{I.59})$$

where from the second to the third line the approximation $\ln(1+x) \approx x$ was used and terms quadratic in $\delta\hat{\rho}$ were neglected. Also note that the second trace term in the last line is independent of the variation $\delta\hat{\rho}$. The second term of equation (I.58) becomes

$$\alpha \left(\text{Tr} \left[(\hat{\rho}^0 + \delta\hat{\rho}) \hat{H} \right] - E \right) = \alpha \text{Tr}(\hat{\rho}^0 \hat{H}) - \alpha E + \text{Tr}[(\delta\hat{\rho}) \hat{H}] = \text{Tr}[(\delta\hat{\rho}) \hat{H}], \quad (\text{I.60})$$

where $\text{Tr}(\hat{\rho}^0 \hat{H}) = E$ was used. And the third term rearranges to

$$\lambda \left(\text{Tr} [\hat{\rho}^0 + \delta\hat{\rho}] - 1 \right) = \lambda \text{Tr} [\hat{\rho}^0] - \lambda + \lambda \text{Tr}[\delta\hat{\rho}] = \lambda \text{Tr}[\delta\hat{\rho}] \quad (\text{I.61})$$

where the normalization condition $\text{Tr}[\hat{\rho}^0] = 1$ was applied. By combining equations (I.59), (I.60) and (I.61) one obtains

$$\text{Tr} \left[\delta\hat{\rho} \left(-k_B \ln(\hat{\rho}^0) - k_B + \alpha \hat{H} + \lambda \right) \right] = 0. \quad (\text{I.62})$$

The second trace term of equation (I.59) was dropped since it is independent of the considered variations and therefore only contributes as a constant to the optimization problem. The equation has to be satisfied for any variation of the density matrix and hence the term in brackets has to be zero. From this one obtains

$$\hat{\rho}^0 = e^{\frac{k_B - \lambda}{k_B}} e^{-\frac{\alpha \hat{H}}{k_B}} = C e^{-\frac{\alpha \hat{H}}{k_B}}. \quad (\text{I.63})$$

The constant C is determined from the normalization condition and the inverse temperature is introduced as $\beta = \frac{\alpha}{k_B} = \frac{1}{k_B T}$. From this the canonical density matrix subject to the constraints (T, V, N) follows

$$\hat{\rho}^0(T, V, N) = \frac{e^{-\beta \hat{H}}}{\text{Tr} [e^{-\beta \hat{H}}]} = \frac{e^{-\beta \hat{H}}}{Z(T, V, N)} \quad (\text{I.64})$$

By introducing a complete basis set $|\Psi_j\rangle$ spanning the eigenspace of the Hamilton operator $\hat{H}$ the canonical partition function Z is

$$\begin{aligned} Z(T, V, N) &= \sum_{i=1} e^{-\beta \hat{H}} |\Psi_i\rangle \langle \Psi_i| = \\ &= \sum_{i=1} \left[\sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} \hat{H}^n \right] |\Psi_i\rangle \langle \Psi_i| = \\ &= \sum_{i=1} \left[\sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} E_i^n \right] |\Psi_i\rangle \langle \Psi_i| = \\ &= \sum_{i=1} e^{-\beta E_i} |\Psi_i\rangle \langle \Psi_i|. \end{aligned} \quad (\text{I.65})$$

By inserting this result in equation (I.64) one obtains for the probability of a certain quantum state $\langle \Psi_i|$ in the canonical ensemble $\frac{e^{-\beta E_i}}{\sum_{i=1} e^{-\beta E_i}}$ [15].

The last ensemble that should be mentioned here is the grand canonical ensemble that can be obtained completely analogous to the canonical ensemble. But this time one introduces an additional Lagrange multiplier μ constraining the number of particles. With this one obtains for the grand-canonical density operator

$$\hat{\rho}^0 = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\text{Tr} [e^{-\beta(\hat{H} - \mu \hat{N})}]} = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{Q(T, V, \mu)}. \quad (\text{I.66})$$

The introduced operator $\hat{N}$ is the particle number operator and the Lagrange multiplier μ is the chemical potential [1]. For every ensemble it is possible to define a thermodynamic potential. The thermodynamic potentials U are defined as $U = -k_B T \ln(Y)$ where Y defines any of the three partition functions Ω, Z or Q , respectively. The thermodynamic potential associated with the micro-canonical ensemble is the internal energy. The potential for the canonical ensemble is known as the Helmholtz free energy and for the grand-canonical ensemble the potential is usually referred to as grand-potential or the Gibbs free energy [12].

3.2 Classical limit of basic ensemble theory ($\hbar \rightarrow 0$)

With the knowledge of the quantum mechanical partition functions this section introduces the classical partition functions as the $\hbar \rightarrow 0$ limits. The classical limit will be derived only for the canonical partition function. For the other ensembles a completely analogous procedure will work. The quantum canonical partition function in the position representation for a N-particle system is

$$\begin{aligned} Z(T, V, N) &= \sum_i e^{-\beta \mathcal{H}} |\Psi_i\rangle \langle \Psi_i| = \sum_i e^{-\beta E_i} \langle \mathbf{r} | \Psi_i \rangle \langle \Psi_i | \mathbf{r} \rangle = \\ &= \sum_i e^{-\beta E_i} \int \Psi_i(\mathbf{r}) \Psi_i^*(\mathbf{r}) d^N r, \end{aligned} \quad (\text{I.67})$$

with the quantum mechanical Hamilton operator

$$\mathcal{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \Delta + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (\text{I.68})$$

The eigenstates of this N particle Hamiltonian in position representation are given by $\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. Now the following correspondence will be shown for the classical $\hbar \rightarrow 0$ limit

$$Z(T, V, N) = \sum_i e^{-\beta E_i} \xrightarrow{\hbar \rightarrow 0} \frac{1}{N! h^{3N}} \int e^{-\beta H(\{\mathbf{r}\}, \{\mathbf{p}\})} d^{3N} r d^{3N} p, \quad (\text{I.69})$$

where $H(\{\mathbf{r}\}, \{\mathbf{p}\})$ is the classical N-particle Hamilton function belonging to the same N-particle system as the Hamilton operator $\mathcal{H}$. The integration is carried out over the whole phase space spanned by the $3N$ position and $3N$ momentum coordinates where $\mathbf{r}$ and $\mathbf{p}$ denote the 3-dimensional coordinate and momentum vector respectively[15, 16]. It was already mentioned that a many particle wavefunction has to satisfy certain symmetry conditions. To implement the anti-symmetric (fermionic) or symmetric symmetry (bosonic) into the wavefunction one can write a symmetry adapted wavefunction for state i as

$$\Psi_s(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \hat{P} \Psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (\text{I.70})$$

where the sum is over all permutations and the operator $\hat{P}$ denotes the permutation operator and the subscript s on the left hand side denotes that the resulting wavefunction satisfies the correct symmetry. Exactly this symmetry is responsible for the $\frac{1}{N!}$ factor in equation (I.69). This symmetry will be ignored for the moment since the equations get very cumbersome to write down. By introducing the momentum operator $-i\hbar \nabla_i u(\mathbf{p}_1, \dots, \mathbf{p}_N) = \mathbf{p}_i u(\mathbf{p}_1, \dots, \mathbf{p}_N)$ and its eigenfunctions

$$u(\mathbf{p}_1, \dots, \mathbf{p}_N) = e^{\frac{i}{\hbar} \sum_{k=1}^N \mathbf{p}_k \mathbf{r}_k}, \quad (\text{I.71})$$

the eigenfunctions $\Psi_i(\mathbf{r})$ of the Hamiltonian (I.68) can be rewritten as

$$\Psi_i(\mathbf{r}) = \int A_i(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} d^{3N} p. \quad (\text{I.72})$$

The coefficients $A(\mathbf{p}_1, \dots, \mathbf{p}_N)$ are defined by the Fourier transform of $\Psi_i(\mathbf{r}_1, \dots, \mathbf{r}_N)$,

$$A_i(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) = \frac{1}{h^{3N}} \int \Psi_i(\mathbf{r}_1, \dots, \mathbf{r}_N) e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} d^{3N} r. \quad (\text{I.73})$$

Insertion of the expansion in equation (I.72) into the expression for the partition function (I.67) gives

$$Z(T, V, N) = \sum_i \int \Psi_i^*(\mathbf{r}_1, \dots, \mathbf{r}_N) A_i(\mathbf{p}_1, \dots, \mathbf{p}_N) e^{-\beta \mathcal{H}} e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} d^{3N} p d^{3N} r. \quad (\text{I.74})$$

Equation (I.74) can be rewritten in terms of the Fourier transform $A_i(\mathbf{p}_1, \dots, \mathbf{p}_N)$ of the wavefunction giving

$$\begin{aligned} Z(T, V, N) &= \frac{1}{h^{3N}} \int \sum_i \left[\Psi_i^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi_i(\mathbf{r}'_1, \dots, \mathbf{r}'_N) \right] e^{-\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}'_j} \\ &\quad \times e^{-\beta \mathcal{H}} e^{\frac{i}{\hbar} \sum_{k=1}^N \mathbf{p}_k \mathbf{r}_k} d^{3N} p d^{3N} r d^{3N} r'. \end{aligned} \quad (\text{I.75})$$

The factor $\frac{1}{h^{3N}}$ follows from the normalization condition of the Fourier transform of the wavefunction. The term in brackets gives a Dirac delta function $\delta(\{\mathbf{r}_i - \mathbf{r}'_i\})$ where the brackets $\{\}$ denote the set of all N coordinate vectors. After integration over the primed position variables

$$Z(T, V, N) = \frac{1}{h^{3N}} \int e^{-\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} e^{-\beta \mathcal{H}} e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} d^{3N} p d^{3N} r, \quad (\text{I.76})$$

is obtained. Note the operator $\mathcal{H}$ contains Δ_i terms that do not commute with $\pm e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j}$. The partition function (I.76) already has the form of a phase space integral but still contains the quantum mechanical operator $\mathcal{H}$ [15, 16]. To get rid of the quantum mechanical Hamiltonian the following identity is used, relating the quantum mechanical Hamilton operator $\mathcal{H}$ with the classical Hamilton function H

$$e^{-\beta \mathcal{H}} e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} = e^{-\beta H} e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} w(\mathbf{p}_1, \dots, \mathbf{r}_N) = F(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta), \quad (\text{I.77})$$

This function is defined such that by inserting expression (I.77) in equation (I.76) one obtains the partition function $Z(T, V, N)$ as a phase space integral in terms of classical quantities only

$$Z(T, V, N) = \int e^{-\beta H} w(\mathbf{p}_1, \dots, \mathbf{r}_N) d^{3N} p d^{3N} r. \quad (\text{I.78})$$

To determine $w(\mathbf{p}_1, \dots, \mathbf{p}_N)$ it is possible to apply the quantum mechanical Hamiltonian in the exponential of (I.77) to $e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j}$ on the left hand side of equation (I.77) directly. A simpler way to determine the functions $w(\mathbf{p}_1, \dots, \mathbf{p}_N)$ is to compute the derivative of (I.77) with respect to β what is given by

$$\begin{aligned} \frac{\partial F(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta)}{\partial \beta} &= \frac{\partial}{\partial \beta} \left(1 - \beta \mathcal{H} + \frac{\beta^2 \mathcal{H}^2}{2} \right) e^{-\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} = \\ &= -\mathcal{H} e^{-\beta \mathcal{H}} e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} = -\mathcal{H} F(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta). \end{aligned} \quad (\text{I.79})$$

This gives a differential equation to determine $F(\mathbf{p}_1, \dots, \mathbf{p}_N, \beta)$ with boundary condition

$$F(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta = 0) = e^{-\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j}. \quad (\text{I.80})$$

The boundary condition is read off from equation (I.77) [16, 15]. This boundary condition implies that $w(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{r}_N, \beta = 0) = 1$ in the limit of infinite temperature. This differential equation provides a systematic tool for determining the function $F(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta)$ and hence to determine $w(\mathbf{p}_1, \dots, \mathbf{r}_N)$. Since this differential equation is in general very cumbersome to solve an expansion of $w(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta)$ in powers of $\hbar$ is used. This gives

$$w(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta) = \sum_{l=0}^{\infty} \hbar^l w_l(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta). \quad (\text{I.81})$$

This procedure will not give an analytic solution for the unknown function but will supply the first few expansion coefficients what will be sufficient to see the classical limit of the canonical partition function $Z(T, V, N)$. To compute the derivatives when inserting the expansion (I.81) into equation (I.79) the following identities

$$\begin{aligned} \nabla_i e^{-\beta H} &= e^{-\beta K} \nabla_i e^{-\beta U} = -\beta e^{-\beta H} \nabla_i U \\ \nabla_i^2 e^{-\beta H} &= e^{-\beta H} \nabla_i^2 U + \beta^2 e^{-\beta H} (\nabla_i U)^2 \\ \nabla_i e^{\frac{i}{\hbar} \sum_j \mathbf{p}_j \mathbf{r}_j} &= \frac{i}{\hbar} \mathbf{p}_i e^{\frac{i}{\hbar} \sum_j \mathbf{p}_j \mathbf{r}_j} \\ \nabla_i^2 e^{\frac{i}{\hbar} \sum_j \mathbf{p}_j \mathbf{r}_j} &= -\frac{2m}{\hbar^2} K_i e^{\frac{i}{\hbar} \sum_j \mathbf{p}_j \mathbf{r}_j}, \end{aligned} \quad (\text{I.82})$$

are used. K_i in the last line denotes the kinetic energy of particle i . Insertion of expansion (I.81) up to linear order in equation (I.77) and computing the derivative with respect to β by the product rule gives

$$\frac{\partial F}{\partial \beta} = \left\{ \left[\frac{\partial w_0}{\partial \beta} + \hbar \frac{\partial w_1}{\partial \beta} + \mathcal{O}(\hbar^2) \right] - H [w_0 + \hbar w_1 + \mathcal{O}(\hbar^2)] \right\} e^{-\beta H} e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j}. \quad (\text{I.83})$$

With this an expression of the derivative $\frac{\partial F}{\partial \beta}$ in terms of classical quantities was obtained. Next one has to compute $-\mathcal{H}F$. This is done by inserting expansion (I.81) into the right hand side of equation (I.79).

This gives

$$\begin{aligned}
-\mathcal{H}F &= \left(\frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_i - U(\mathbf{r}_1, \dots, \mathbf{r}_N) \right) e^{-\beta H} e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} w(\mathbf{p}_1, \dots, \mathbf{p}_N) \\
&= -U(\mathbf{r}_1, \dots, \mathbf{r}_N) F + e^{-\beta H} e^{\frac{i}{\hbar} \sum_{j=1}^N \mathbf{p}_j \mathbf{r}_j} \frac{\hbar^2}{2m} \times \\
&\quad \times \sum_{i=1}^N \left[-\frac{2i\beta \mathbf{p}_i (\nabla_i U)}{\hbar} (w_0 + \hbar w_1 + \mathcal{O}(\hbar^2)) - \right. \\
&\quad \left. -\frac{2m}{\hbar^2} K_i (w_0 + \hbar w_1 + \mathcal{O}(\hbar^2)) + \frac{2i}{\hbar} \mathbf{p}_i (\nabla_i w_0 + \hbar \nabla_i w_1 + \mathcal{O}(\hbar^2)) + \mathcal{O}(\hbar^2) \right],
\end{aligned} \tag{I.84}$$

where only terms up to linear order in $\hbar$ were kept. Equating (I.83) and (I.84) gives

$$\begin{aligned}
\left[\frac{\partial w_0}{\partial \beta} + \hbar \frac{\partial w_1}{\partial \beta} + \mathcal{O}(\hbar^2) \right] - H [w_0 + \hbar w_1 + \mathcal{O}(\hbar^2)] &= \\
= -(U + K) (w_0 + \hbar w_1 + \mathcal{O}(\hbar^2)) + \frac{i\hbar}{m} \sum_{i=1}^N [\mathbf{p}_i \nabla_i w_0 - \beta w_0 \mathbf{p}_i \nabla_i U],
\end{aligned} \tag{I.85}$$

with $K = \sum_i K_i$ the total kinetic energy. In the limit of $\hbar \rightarrow 0$ equation (I.85) becomes

$$\frac{\partial w_0}{\partial \beta} - H w_0 = -(U + K) w_0. \tag{I.86}$$

This shows that $\frac{\partial w_0}{\partial \beta}$ has to vanish, otherwise (I.86) is not satisfied implying w_0 is a constant. From the boundary condition (I.80) and the definition of F in (I.77) it follows $w(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta = 0) = 1$. Combining this with the expansion for w in (I.81) one obtains

$$1 = w_0(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta = 0) + \hbar w_1(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta = 0) + \hbar^2 w_2(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta = 0) + \dots \tag{I.87}$$

Because the w_i are independent of $\hbar$ but do depend on β it follows

$$\begin{aligned}
w_0(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta = 0) &= 1 \\
w_i(\mathbf{p}_1, \dots, \mathbf{r}_N, \beta = 0) &= 0 \quad i > 1.
\end{aligned} \tag{I.88}$$

From this and equation (I.78) we see that in the classical limit the quantum mechanical partition functions turn into classical phase space integrals

$$Z(T, V, N) = \int e^{-\beta H} d^{3N} p d^{3N} r, \tag{I.89}$$

what is the desired result. This shows that the quantum statistical description coincides with a classical statistical description of an N-particle system in the case of very high temperatures or in the case when $\hbar$ is zero.

3.3 Equipartition theorem

In the last section an equation for the classical partition function was derived. This section will use this result to derive the equipartition theorem. The equipartition theorem states that the energy of a system is equally distributed over all its degrees of freedom entering the Hamiltonian function quadratically. Formally this can be written as

$$\langle E_{Kin,1} \rangle = \frac{3}{2} k_B T. \tag{I.90}$$

where $E_{Kin,1}$ is the kinetic energy per particle. The kinetic energy is expressed in terms of quadratic momentum coordinates. This equation will be derived from the canonical partition function of a classical system

$$\begin{aligned}
Z(N, V, T) &= \int e^{-\beta H(\{\mathbf{r}\}, \{\mathbf{p}\})} d^{3N} p d^{3N} r = \\
&= \int e^{-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}} d^{3N} p \int e^{-\beta V(\mathbf{r}_1, \dots, \mathbf{r}_N)} d^{3N} r.
\end{aligned} \tag{I.91}$$

This equation shows that the total partition function $Z(T, V, N)$ can be written as a product partition function of kinetic $Z_{Kin}(T, V, N)$ and potential energy part $Z_{Pot}(T, V, N)$. The kinetic energy part of the partition function is a $3N$ dimensional gaussian integral

$$Z_{Kin} = Z_{Kin,1}^N = (2m\pi k_B T)^{\frac{3N}{2}}, \quad (\text{I.92})$$

Because the kinetic energy part of the partition function is the same for all N particles this decomposition into a product is possible. From this it is already possible to deduce the meaning of the equipartition theorem for the kinetic energy part of the Hamiltonian. The kinetic energy of a system distributes equally over all dynamic degrees of freedom. To obtain a relation between the dynamical degrees of freedom and the temperature, equation (I.92) is used and the average $\mathbf{p}^2$ per particle is computed by

$$\langle \mathbf{p}^2 \rangle = -k_B T \frac{\partial \ln(Z_{Kin,1})}{\partial \frac{1}{2m}} = \frac{1}{Z_{Kin,1}} \int \mathbf{p}^2 e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p = 3mk_B T. \quad (\text{I.93})$$

When removing the integral after the second equal sign this term is usually referred to as the Maxwell Boltzmann distribution. Rearranging this equation gives the equipartition theorem in a more familiar way

$$\langle E_K \rangle = \frac{3}{2} k_B T. \quad (\text{I.94})$$

Therefore we see that every degree of freedom contributes $\frac{1}{2} k_B T$ to the average kinetic energy. The factor 3 in equation (I.94) arises since a 3 dimensional space was assumed in which the particles are moving. In principle the equipartition theorem holds for any degree of freedom entering the Hamiltonian quadratically. And the partition function has to be separable in terms of the single degrees of freedom. This states that the separation treatment is only possible for non interacting degrees of freedom. Therefore it is possible to say that every positional degree of freedom subject to a potential kx^2 contributes $\frac{1}{2} k_B T$ to the total potential energy what can be derived completely analogously to the dynamical degrees of freedom.

Another result that can be directly obtained from the equipartition theorem is the magnitude of the temperature fluctuations in the canonical ensemble. The equipartition theorem in equation (I.93) shows a direct proportionality between temperature and expectation value of the squared momentum. The fluctuations in the squared momentum will be directly proportional to temperature fluctuations. Therefore we are going to compute the momentum fluctuations

$$\frac{\text{Var}(\mathbf{p}^2)}{\langle \mathbf{p}^2 \rangle^2} = \frac{\langle \mathbf{p}^4 \rangle - \langle \mathbf{p}^2 \rangle^2}{\langle \mathbf{p}^2 \rangle^2}. \quad (\text{I.95})$$

This equation is obtained as follows

$$\begin{aligned} \langle \mathbf{p}^4 \rangle - \langle \mathbf{p}^2 \rangle^2 &= (k_B T)^2 \frac{\partial^2 \ln(Z_{Kin,1})}{\partial \left(\frac{1}{2m}\right)^2} = \\ &= -k_B T \frac{\partial}{\partial \frac{1}{2m}} \frac{\int \mathbf{p}^2 e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p}{\int e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p} = \\ &= \frac{\int \mathbf{p}^4 e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p}{\int e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p} - \frac{\int \mathbf{p}^2 e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p}{\left(\int e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p\right)^2} \int \mathbf{p}^2 e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p \\ &= \frac{\int \mathbf{p}^4 e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p}{\int e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p} - \left(\frac{\int \mathbf{p}^2 e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p}{\int e^{-\beta \frac{\mathbf{p}^2}{2m}} d^3 p} \right)^2 = 3(mk_B T)^2, \end{aligned} \quad (\text{I.96})$$

and from this the relative fluctuations in momentum are determined as

$$\frac{\text{Var}(\mathbf{p}^2)}{\langle \mathbf{p}^2 \rangle^2} = \frac{1}{3}. \quad (\text{I.97})$$

Therefore, the momentum in a canonical ensemble will not be constant but fluctuates around a constant value[17]. From the direct proportionality between the kinetic energy and the average temperature it is possible to show

$$\frac{\text{Var}(T)}{\langle T \rangle_{NVT}^2} = \frac{\langle T^2 \rangle_{NVT} - \langle T \rangle_{NVT}^2}{\langle T \rangle_{NVT}^2} = \frac{1}{3N}. \quad (\text{I.98})$$

This equation shows that the temperature in a canonical ensemble is not a constant but fluctuates around an equilibrium value and the magnitude of the fluctuations decrease with increasing system size.

3.4 The fluctuation dissipation theorem

The fluctuation dissipation theorem gives a relation between a system's absorption or relaxation rates to correlations between spontaneous fluctuations at different times. For a system in thermal equilibrium it is possible to relate phenomenological parameters like rate constants or macroscopic response functions to microscopic dynamics and fluctuations. For example, when a weak electric field is applied to an ionic crystal the atoms will displace slightly from their equilibrium positions resulting in a macroscopic dipole moment. After switching the field off the atoms will move back to their equilibrium positions. The process of moving back is governed by thermal fluctuations. The thermal fluctuations could also displace the atoms in a way like the electric field. Resulting in a macroscopic dipole moment. The connection between these kind of processes is summarized by the following form of the fluctuation-dissipation theorem

$$\bar{A}(t) = \langle A \rangle - \beta [\langle \Delta \mathcal{H} A(t) \rangle - \langle A(t) \rangle \langle \Delta \mathcal{H} \rangle], \quad (\text{I.99})$$

where the $A(t)$ is a macroscopic quantity that can be measured and $\Delta \mathcal{H}$ can be any perturbation driving the system away from equilibrium. In the rest of this chapter the fluctuation-dissipation theorem will be derived and discussed in more detail. A good starting point is the introduction of correlation functions. Correlation between random variables is a very important measure in statistical mechanics to observe relations between those variables. Assume two time dependent signals $A(t)$ and $B(t)$. Then their correlation can be measured by a correlation function

$$C(t - t') = \langle A(t)B(t') \rangle - \langle A \rangle \langle B \rangle = \langle \delta A(t) \delta B(t') \rangle, \quad (\text{I.100})$$

where the brackets denote ensemble averages and the instantaneous fluctuations of the signals are given by

$$\delta A(t) = A(t) - \langle A \rangle. \quad (\text{I.101})$$

It is important to note that the correlation of two signals does not depend on the absolute times t and t' but on their differences. Such correlation functions can also be expressed in terms of the fluctuation dissipation theorem. Assume an unperturbed system with Hamiltonian $\mathcal{H}$ and some dynamical variable $A(r^{3N}, p^{3N})$ depending on time via the coordinates and momenta. The statistical average of this quantity is given by an integral of the quantity times its statistical weight over the whole phase space.

$$\langle A \rangle = \frac{\text{Tr} [e^{-\beta \mathcal{H}(r^{3N}, p^{3N})} A(r^{3N}, p^{3N})]}{\text{Tr} [e^{-\beta \mathcal{H}(r^{3N}, p^{3N})}]}, \quad (\text{I.102})$$

where the trace operation denotes a classical phase space integral like it was shown in section 3.2. Now assume the perturbation $\Delta \mathcal{H}$ is introduced and the system is prepared such that at $t = 0$ it is in an equilibrium state of the perturbed Hamiltonian $\mathcal{H} + \Delta \mathcal{H}$. At $t = 0$ the perturbation given by

$$\Delta \mathcal{H} = -f A, \quad (\text{I.103})$$

is switched off. The quantity f is some field that couples with A . From this it follows that the equilibrium value of A at time zero is given by

$$\bar{A}(0) = \frac{\text{Tr} [e^{-\beta(\mathcal{H} + \Delta \mathcal{H})} A]}{\text{Tr} [e^{-\beta(\mathcal{H} + \Delta \mathcal{H})}]}, \quad (\text{I.104})$$

and with increasing time the quantity $\bar{A}(t)$ changes according to

$$\bar{A}(t) = \frac{\text{Tr} [e^{-\beta(\mathcal{H} + \Delta \mathcal{H})} A(t)]}{\text{Tr} [e^{-\beta(\mathcal{H} + \Delta \mathcal{H})}]}, \quad (\text{I.105})$$

where $A(t)$ denotes the value of $A(r^{3N}, p^{3N})$ when the initial point in phase space was given by (r^{3N}, p^{3N}) . It is important to note that the Hamiltonian determining the dynamics of $A(t)$ at $t > 0$ is given by $\mathcal{H}$ since the perturbation was switched off [18, 12]. The perturbation $\Delta \mathcal{H}$ is assumed to be small and equation (I.105) can be expanded in a power series of the perturbation

$$\bar{A}(t) = \frac{\text{Tr} [e^{-\beta \mathcal{H}} (1 - \beta \Delta \mathcal{H}) A(t)]}{\text{Tr} [e^{-\beta \mathcal{H}} (1 - \beta \Delta \mathcal{H})]} + \mathcal{O}((\beta \Delta \mathcal{H})^2). \quad (\text{I.106})$$

Collecting terms of same power in the perturbation gives

$$\bar{A}(t) = \frac{\text{Tr} [e^{-\beta \mathcal{H}} A(t)] - \beta \text{Tr} [e^{-\beta \mathcal{H}} \Delta \mathcal{H} A(t)]}{\text{Tr} [e^{-\beta \mathcal{H}} (1 - \beta \Delta \mathcal{H})]} + \mathcal{O}((\beta \Delta \mathcal{H})^2). \quad (\text{I.107})$$

The second term is just the correlation between the variables $\Delta\mathcal{H}$ and $A(t)$ what is given by $\langle A(t)\Delta\mathcal{H} \rangle - \langle A(t) \rangle \langle \Delta\mathcal{H} \rangle$. From this it follows

$$\bar{A}(t) = \langle A \rangle - \beta [\langle \Delta\mathcal{H}A(t) \rangle - \langle A(t) \rangle \langle \Delta\mathcal{H} \rangle] + \mathcal{O}((\beta\Delta\mathcal{H})^2). \quad (\text{I.108})$$

Note that the denominator of equation (I.107) was replaced by $\text{Tr}[e^{-\beta\mathcal{H}}]$ what can be done since it has to be the normalization constant in the unperturbed ensemble. The average $\langle A(t) \rangle = \langle A \rangle$ because the value of $A(t)$ is fluctuating around the same average value for all time steps. Equation (I.108) is a form of the fluctuation-dissipation theorem and it relates the relaxation from a prepared non equilibrium state to spontaneous microscopic fluctuations of the system[18]. Now replace $B(t)$ in equation (I.100) by $A(0)$ then one obtains a self correlation function of the quantity $A(t)$ as

$$C(t) = \langle \delta A(0)\delta A(t) \rangle. \quad (\text{I.109})$$

This replacement also makes it clear that the correlation function will only depend on time differences and not on absolute times[18, 12, 12]. From equation (I.100) it can be noted that $\delta A(t) = A(t) - \langle A \rangle$. Now insert the expression for $\Delta\mathcal{H}$ into expression (I.108) and compute $\Delta\bar{A}(t) = \bar{A}(t) - \langle A \rangle$ to obtain

$$\Delta\bar{A} = \beta f \langle \delta A(0)\delta A(t) \rangle + \mathcal{O}(f^2). \quad (\text{I.110})$$

In the last equation $\Delta\bar{A}(t)$ denotes the spontaneous and $\delta A(t)$ the instantaneous fluctuations of the variable $A(t)$. This relation is known as the Onsager regression hypothesis that was known already before the fluctuation dissipation theorem[18].

In the language of the fluctuation-dissipation theorem one can introduce generalized susceptibilities. Therefore assume the spontaneous fluctuations $\Delta\bar{A}(t; f)$ of a system are related to a time dependent perturbation $f(t)$ by

$$\Delta\bar{A}(t; \lambda f) = \lambda \Delta\bar{A}(t; f), \quad (\text{I.111})$$

then the most general equation to express this relationship in linear form is given by the functional

$$\Delta\bar{A}(t) = \int_{-\infty}^{\infty} \chi(t, t') f(t') dt' + \mathcal{O}(f^2). \quad (\text{I.112})$$

Where $\chi(t, t')$ is known as the generalized response function. This response function tells how strong a system will react to a certain external perturbation $f(t)$. Therefore the relationship between the response of the system and the external perturbation is given by a functional and the generalized susceptibility can also be obtained by a functional derivative of $\Delta\bar{A}(t)$ by $f(t')$ written as $\chi(t, t') = \frac{\delta \Delta\bar{A}(t)}{\delta f(t')}$. Hence $\chi(t, t')$ can also be considered as the rate of change of the system due to a change in the external perturbation $f(t')$ [18].

4 Lattice oscillations in crystals

In a crystal atoms are oscillating around their equilibrium positions. These oscillations are in the classical mechanical picture referred to as lattice oscillations and as phonons in a quantum mechanical picture. Lattice oscillations can be described in a simplified picture where atoms couple only to their nearest neighbors by a harmonic potential. This approximation gives a lot of insight in the behavior of lattice oscillations and will be shown in this section. The lattice oscillations can be directly related to the phonon concept. In terms of phonon quasi-particles the phonon density of states and the correlation between different phonon modes will be shown. The phonon density of states can be computed from velocity autocorrelation functions in a molecular dynamics simulation. In this approach all anharmonicities of the potential will be taken into account. A statistical treatment of the dynamic structure factor and its relation to the phonon dispersion relation will be shown as a tool to include anharmonic contributions to the dispersion relation.

4.1 The harmonic approximation to the lattice oscillations

A crystal is build up of repeating unit cells that contain a certain number of different atoms. The most simple unit cell is a primitive unit cell containing only a single atom. A whole crystal can be described by a vector $\mathbf{r}_n$ describing the position of the unit cell

$$\mathbf{r}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad (\text{I.113})$$

with $\mathbf{n} = (n_1, n_2, n_3)$ being a set of integers describing the position of the unit cell within the crystal. The vectors $\{\mathbf{a}_i\}$ are the basis vectors, which span the unit cell. A unit cell can in principle contain any number of atoms. The total number of atoms per unit cell is denoted by ν and $\mathbf{u}_s(\mathbf{n})$ will be the displacement of atom s from its equilibrium position. Assuming the atoms are coupled by a harmonic potential, the interaction energy of two atoms is given by kx^2 with x being the distance between the two considered atoms. From this the Lagrangian of the crystal in terms of the displacement vectors $\mathbf{u}_s(\mathbf{n})$ follows

$$\mathcal{L} = \frac{1}{2} \sum_{\mathbf{n}, s} m_s \dot{\mathbf{u}}_s^2(\mathbf{n}) - \frac{1}{2} \sum_{\substack{\mathbf{n}, \mathbf{n}' \\ s, s'}} \Lambda_{\alpha\beta}^{ss'}(\mathbf{n} - \mathbf{n}') u_{s\alpha}(\mathbf{n}) u_{s'\beta}(\mathbf{n}'), \quad (\text{I.114})$$

where the indexes α, β denote the Cartesian components of the displacement vectors and m_s is the mass of a specific atom. The matrix $\Lambda_{\alpha\beta}^{ss'}$ contains the harmonic coupling terms between pairs of atoms. Because the interactions between the atoms have to be symmetric the coupling constant matrix [12] has to be symmetric too. Therefore the force constant matrix satisfies the following symmetry condition

$$\Lambda_{\alpha\beta}^{ss'}(\mathbf{n} - \mathbf{n}') = \Lambda_{\alpha\beta}^{s's}(\mathbf{n}' - \mathbf{n}). \quad (\text{I.115})$$

Another symmetry of the matrix $\Lambda_{\alpha\beta}^{ss'}(\mathbf{n} - \mathbf{n}')$ can be obtained by the following argument. If the whole crystal is translated by a constant displacement vector that is the same for all atoms the resulting force acting on any atom has to stay the same. This rule is known as the acoustic sum rule and can formally be written as

$$\sum_{\mathbf{n}, s} \Lambda_{\alpha\beta}^{ss'}(\mathbf{n}) = 0 \quad (\text{I.116})$$

From the Lagrangian in equation (I.114) the equations of motion are obtained as

$$m_s \ddot{u}_{s,\alpha}(\mathbf{n}) = \sum_{\mathbf{n}', s'} \Lambda_{\alpha\beta}^{ss'}(\mathbf{n} - \mathbf{n}') u_{s',\beta}(\mathbf{n}'). \quad (\text{I.117})$$

The form of the differential equation suggests to use a superpositions of monochromatic plane waves for the solutions of the equations of motions [12, 19]

$$\mathbf{u}_s(\mathbf{n}) = \mathbf{e}_s(\mathbf{k}) e^{i(\mathbf{k}\mathbf{r}_n - \omega t)}. \quad (\text{I.118})$$

In the foregoing equation the vector $\mathbf{e}_s \in \mathbb{C}^3$ is the amplitude and the orientation of the polarization of the plane wave. The vector $\mathbf{k}$ belongs to the reciprocal lattice of the crystal reflecting the crystal symmetry. These reciprocal lattice vectors define the frequency grid of the spatial Fourier transform. ω is related to the temporal frequencies of the crystal system. With this Ansatz equation (I.117) takes the form

$$\omega^2 m_s e_{s\alpha}(\mathbf{k}) e^{i(\mathbf{k}\mathbf{r}_n - \omega t)} = \sum_{\mathbf{n}', s'} \Lambda_{\alpha\beta}^{ss'}(\mathbf{n} - \mathbf{n}') e_{s'\beta}(\mathbf{k}) e^{i(\mathbf{k}\mathbf{r}_{n'} - \omega t)}. \quad (\text{I.119})$$

The factor $e^{i(\mathbf{k}\mathbf{r}_n - \omega t)}$ can be brought to the right hand side and the summation over $\mathbf{n} - \mathbf{n}'$ can be replaced by the crystal sum over $\mathbf{n}$ since this gives the same sum without a center of mass shift. Application to equation (I.119) gives

$$\begin{aligned} \omega^2 m_s e_{s\alpha}(\mathbf{k}) &= \sum_{\mathbf{n}, s'} \Lambda_{\alpha\beta}^{ss'}(\mathbf{n}) e_{s'\beta}(\mathbf{k}) e^{-i\mathbf{k}\mathbf{r}_n} = \\ &= \sum_{s'} \Lambda_{\alpha\beta}^{ss'}(\mathbf{k}) e_{s'\beta}(\mathbf{k}). \end{aligned} \quad (\text{I.120})$$

In the last line the Fourier transform of the force constant matrix was introduced by

$$\Lambda_{\alpha,\beta}^{ss'}(\mathbf{k}) = \sum_{\mathbf{n}} \Lambda_{\alpha\beta}^{ss'}(\mathbf{n}) e^{-i\mathbf{k}\mathbf{r}_n}. \quad (\text{I.121})$$

From this the algebraic system

$$\sum_{s'} \Lambda_{\alpha\beta}^{s,s'} e_{s',\beta}(\mathbf{k}) - \omega^2 m_s e_{s,\alpha} = 0 \quad (\text{I.122})$$

is obtained. This system can be solved in the form of an eigenvalue equation. The eigenvalues are obtained for every set of indexes (s', β, s, α) from the following determinant

$$\det \left| \Lambda_{\alpha\beta}^{s,s'}(\mathbf{k}) - \omega^2(\mathbf{k}) m_s \delta_{s,s'} \delta_{\alpha\beta} \right| = 0. \quad (\text{I.123})$$

The order of the determinant is 3ν since every atom contributes three Cartesian components and there are in total ν atoms per unit cell. Because of the symmetries of $\Lambda_{\alpha\beta}^{s,s'}(\mathbf{n} - \mathbf{n}')$ mentioned in the beginning the matrix $\Lambda_{\alpha\beta}^{s,s'}(\mathbf{k})$ is hermitian. This argument is made more explicit by writing

$$\Lambda_{\alpha\beta}^{s,s'}(\mathbf{k}) = \Lambda_{\beta\alpha}^{s',s}(-\mathbf{k}) = \left[\Lambda_{\beta\alpha}^{s',s}(-\mathbf{k}) \right]^*, \quad (\text{I.124})$$

and comparing with equation (I.121). Therefore the matrix $\Lambda_{\alpha\beta}^{s,s'}(\mathbf{k})$ is hermitian and hence the eigenvalues ω will be real. A set of eigenvalues for every value of $\mathbf{k}$ will be obtained and the relation $\omega_{\alpha,s} = \omega_{\alpha,s}(\mathbf{k})$ is called the dispersion relation. For every value of $\mathbf{k}$, 3ν eigenvalues are obtained known as the branches of the dispersion relation. Another property that follows from the hermiticity of $\Lambda_{\alpha\beta}^{s,s'}$ is the orthogonality of the eigenvectors $e_{s,\alpha}$ as long as they belong to different eigenvalues. Equation (I.118) shows that any displacement of the atoms in the crystal can be expressed in terms of this eigenvectors or eigenmodes. Therefore this procedure shows a decomposition of the motions of a crystal in terms of noninteracting normalmodes. The free propagation of the normal modes is a consequence of the harmonic interaction potential used between the atoms. If higher order interactions would be included the eigenmodes would interact with each other. Because a crystal is built of symmetric building blocks the time reversal invariance $\omega(\mathbf{k}) = \omega(-\mathbf{k})$ follows. This is in agreement with the time invariance symmetry in classical mechanics. Another property worth to mention, is the so called Bravais lattice invariance stating

$$\mathbf{k} \rightarrow \mathbf{k} + \mathbf{b} \quad \omega(\mathbf{k}) = \omega(\mathbf{k} + \mathbf{b}), \quad (\text{I.125})$$

where $\mathbf{b}$ is a vector of the reciprocal lattice defined by $\mathbf{a}_n \mathbf{b}_m = 2\pi \delta_{nm}$. This property follows from the fact that the wave-vector $\mathbf{k}$ enters the equations only via the complex exponential $e^{i\mathbf{k}\mathbf{r}_n}$ and because $\mathbf{b}$ belongs to the reciprocal lattice of the crystal lattice[12]. Therefore it is sufficient to analyze the dispersion relation within the first Brillouin zone.

4.2 Phonons

In the previous section the vibrations of a crystal were decomposed into normal modes by applying the harmonic picture. Those normal modes are able to describe the directions and the magnitudes of the displacements of the atoms from their equilibrium positions at any time instance. In quantum theory one introduces the concept of phonons, which are quasi-particles propagating through the crystal. The energy of a phonon is given by $\epsilon = \hbar\omega$. The quasi-momentum of the phonon is defined by

$$\mathbf{p} = \mathbf{p} + 2\pi\hbar\mathbf{b} \quad (\text{I.126})$$

The momentum of the phonon is called quasi momentum because it is not uniquely defined. The reason for the invariance with respect to the constant term $2\pi\hbar\mathbf{b}$ follows from the periodicity of the reciprocal lattice. This is the same effect like it was already discussed in equation (I.125). Everything said about lattice vibrations in the previous paragraph directly applies to the phonon picture. In the harmonic picture the phonons are propagating through the crystal without interacting with each other. Therefore the harmonic crystal can be considered as a non-interacting or ideal phonon gas. In a real crystal however the phonons will interact. This is described by scattering processes conserving the quasi momentum

$$\sum \mathbf{p} = \sum \mathbf{p}' + 2\pi\hbar\mathbf{b}. \quad (\text{I.127})$$

Since we are dealing with quasi momenta, the momentum conservation has to be satisfied only up to an additive constant related to the reciprocal lattice $\mathbf{b}$. The number of phonons in a certain state is equivalent to the intensity of the classical wave describing this state. From this it follows that phonons will obey Bose-Einstein statistics. The number of phonons in a certain phononic eigenstate is determined by the actual equilibrium state of the considered material. Therefore the number of phonons will not be conserved and has to be determined from the equilibrium condition. The free energy of the phonon

gas has to be minimal in thermal equilibrium for a given volume V and temperature T . The necessary condition for the phonon gas to be in equilibrium with respect to the phonon particle number is given by $\frac{\partial F}{\partial N_{Ph}} = 0$. From thermodynamics it is known that the derivative of the free energy with respect to the particle number is the chemical potential $\left(\frac{\partial F}{\partial N_{Ph}}\right)_{T,V} = \mu_{Ph}$. It follows, the chemical potential of a phonon has to be zero. Otherwise the free energy would describe a non-equilibrium state [12, 20]. The average occupation number n_i of a normal mode can be computed from the partition function. The energy of a harmonic oscillator is given by $\hbar\omega_\alpha$ and if n phonons are occupying this state it contributes $n_\alpha \hbar\omega_\alpha = n_\alpha \epsilon_\alpha$ to the total energy E_i of the system in state i . The partition function for independent harmonic oscillators is given by

$$\begin{aligned} Z &= \sum_i e^{-\beta E_i} = \sum_{\substack{n_1=0 \\ n_2=0 \\ \vdots}} e^{-\beta[n_1\epsilon_1+n_2\epsilon_2+\dots+n_j\epsilon_j+\dots]} = \\ &= \prod_{j=1} \left[\sum_{n_j=0}^{\infty} e^{-\beta n_j \epsilon_j} \right] = \\ &= \prod_{j=1} \left[\frac{1}{1 - e^{-\beta \epsilon_j}} \right] \end{aligned} \quad (\text{I.128})$$

where the product is over all possible states and in the last line the equation for the geometric series was used. To obtain the average occupation number $\langle n_j \rangle$ the derivative of the log of the partition function I.128 with respect to the energy of a certain state is computed.

$$\begin{aligned} \langle n_j \rangle &= -\frac{1}{\beta} \frac{\partial \ln[Z]}{\partial \epsilon_j} = \\ &= k_B T \frac{\partial}{\partial \epsilon_j} \sum_j (1 - e^{-\beta \epsilon_j}) = \\ &= \frac{e^{-\beta \epsilon_j}}{1 - e^{-\beta \epsilon_j}} = \frac{1}{e^{\beta \epsilon_j} - 1}. \end{aligned} \quad (\text{I.129})$$

This distribution was first derived by Planck for the black body radiation and is therefore commonly referred to as the Planck distribution [12, 18]. The classical limit of this distribution can be obtained by considering the case in which the term in the exponential gets small. This is either the case in the high temperature limit or in the case where the Planck constant is approaching zero. In the classical limit the exponential can be expanded as $e^{Kx} \approx 1 + Kx$ and therefore

$$\langle n_j \rangle \approx \frac{k_B T}{\epsilon_j} \quad (\text{I.130})$$

The correlation between different phonon modes is zero. This can be shown by computing the correlation function $\langle \delta n_i \delta n_j \rangle$ with $\delta n_i = n_i - \langle n_i \rangle$. $\delta n_i \delta n_j$ is nothing else than a covariance matrix

$$\begin{aligned} \langle \delta n_i \delta n_j \rangle &= \langle (n_i - \langle n_i \rangle) (n_j - \langle n_j \rangle) \rangle = \\ &= \langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle \end{aligned} \quad (\text{I.131})$$

It was already shown in equation (I.96) that the variance or the covariance in the canonical ensemble can be obtained by the second derivative of the partition function

$$\Sigma = \frac{1}{\beta^2} \frac{\partial^2 Q}{\partial \epsilon_i \partial \epsilon_j} = \begin{cases} 0 & \text{if } i \neq j \\ \frac{e^{\beta \epsilon_i}}{(e^{\beta \epsilon_i} - 1)^2} & \text{if } i = j, \end{cases} \quad (\text{I.132})$$

giving a diagonal covariance matrix Σ . This result can be used to build a self-correlation function for the phonon state population $n_i(t)$ in terms of some external distortion $\Delta H = -f n_i$ by the use of equations (I.109) and (I.111).

$$C(t) = \beta f \langle n_i(0) n_i(t) \rangle \quad (\text{I.133})$$

This equation shows that the phonon modes will relax independently to the equilibrium states after being distorted by some external perturbation f . From the self-correlation function the frequencies of the relaxation process can be obtained.

4.3 Phonon density of states from ensemble averages

The phonon density of states is defined by the equation

$$\langle g(\omega) \rangle = \sum_{\mathbf{k}, \alpha} \delta(\omega - \omega_\alpha(\mathbf{k})), \quad (\text{I.134})$$

where α denotes the branch index. In this section the equivalence of equation (I.134) and the Fourier transform of the velocity autocorrelation function will be shown. The phononic density of states in terms of the velocities is given by

$$\langle g(\omega) \rangle = \int \frac{\langle \dot{\mathbf{u}}(t) \dot{\mathbf{u}}(0) \rangle}{\langle \dot{\mathbf{u}}(0) \dot{\mathbf{u}}(0) \rangle} e^{i\omega t} dt, \quad (\text{I.135})$$

where $\langle . \rangle$ denotes a thermal average and $\dot{\mathbf{u}}$ are the atomic velocities. The quantity in the denominator is the average squared velocity in the system at time step 0. The numerator is the average correlation of the velocities at time step t and the initial velocities. The velocity autocorrelation of a single particle $G_s(\mathbf{n}, t)$ in unit cell $\mathbf{n}$ and of type s is

$$G_s(\mathbf{n}, t) = \dot{\mathbf{u}}_s(\mathbf{n}, t) \dot{\mathbf{u}}_s(\mathbf{n}, 0). \quad (\text{I.136})$$

To obtain a thermal average of this quantity it is possible to sum over all unit cells $N_{\text{unit cells}}$ forming the considered supercell

$$\langle G_s(t) \rangle = \langle \dot{\mathbf{u}}_s(t) \dot{\mathbf{u}}_s(0) \rangle = \frac{1}{N_{\text{unit cells}}} \sum_{\mathbf{n}} \dot{\mathbf{u}}_s(\mathbf{n}, t) \dot{\mathbf{u}}_s(\mathbf{n}, 0). \quad (\text{I.137})$$

The velocities can be rewritten in terms of the normal modes of the phonons shown in equation (I.118). A general atomic displacement is given by

$$\mathbf{u}_s(\mathbf{n}, t) = \sum_{\mathbf{k}, \alpha} \mathbf{e}_{\alpha, s}(\mathbf{k}) e^{i(\mathbf{k}\mathbf{n} - \omega_\alpha(\mathbf{k})t)}, \quad (\text{I.138})$$

where α is the branch index of the dispersion relation. The velocity follows from the time derivative of equation (I.138)

$$\frac{d\mathbf{u}_s(\mathbf{n}, t)}{dt} = \sum_{\mathbf{k}, \alpha} -i\omega_\alpha(\mathbf{k}) \mathbf{e}_{\alpha, s}(\mathbf{k}) e^{i(\mathbf{k}\mathbf{n} - \omega_\alpha(\mathbf{k})t)}. \quad (\text{I.139})$$

With this equation (I.136) takes the form

$$G_s(\mathbf{n}, t) = \sum_{\mathbf{k}, \alpha} \omega_\alpha^2(\mathbf{k}) \mathbf{e}_{\alpha, s}^2(\mathbf{k}) e^{-i\omega_\alpha(\mathbf{k})t}. \quad (\text{I.140})$$

The thermal average of (I.137) is obtained with (I.140) as

$$\langle G_s(t) \rangle = \frac{1}{N_{\text{unit cells}}} \sum_{\mathbf{n}} \sum_{\mathbf{k}, \alpha} \omega_\alpha^2(\mathbf{k}) \mathbf{e}_{\alpha, s}^2(\mathbf{k}) e^{-i\omega_\alpha(\mathbf{k})t}. \quad (\text{I.141})$$

And the Fourier transform of equation (I.141) is

$$\begin{aligned} \langle G_s(\omega) \rangle &= \frac{1}{N_{\text{unit cells}}} \sum_{\mathbf{n}} \sum_{\mathbf{k}, \alpha} \omega_\alpha^2(\mathbf{k}) \mathbf{e}_{\alpha, s}^2(\mathbf{k}) \int_{-\infty}^{\infty} e^{-i\omega_\alpha(\mathbf{k})t} e^{i\omega t} dt = \\ &= \frac{1}{N_{\text{unit cells}}} \sum_{\mathbf{n}} \sum_{\mathbf{k}, \alpha} \omega_\alpha^2(\mathbf{k}) \mathbf{e}_{\alpha, s}^2(\mathbf{k}) \delta(\omega - \omega_\alpha(\mathbf{k})). \end{aligned} \quad (\text{I.142})$$

Every normal mode of a certain atom type contributes $\omega_\alpha^2(\mathbf{k}) \mathbf{e}_{\alpha, s}^2(\mathbf{k})$ to the phonon density of states. If a system is composed of several atom types s an averaging of the Fourier transformed velocity autocorrelation in equation (I.142) over the different atom types has to be carried out

$$\langle G(\omega) \rangle = \frac{1}{N_{\text{types}}} \sum_{s=1}^{N_{\text{types}}} \langle g_s(\omega) \rangle =$$

$$\begin{aligned}
 &= \frac{1}{N_{\text{types}} N_{\text{unit cells}}} \sum_{s=1}^{N_{\text{types}}} \sum_{\mathbf{n}} \sum_{\mathbf{k}, \alpha} \omega_{\alpha}^2(\mathbf{k}) \mathbf{e}_{\alpha, s}^2(\mathbf{k}) \delta(\omega - \omega_{\alpha}(\mathbf{k})) = \\
 &= \sum_{\mathbf{k}, \alpha} \omega_{\alpha}^2(\mathbf{k}) \langle \mathbf{e}_{\alpha}^2(\mathbf{k}) \rangle \delta(\omega - \omega_{\alpha}(\mathbf{k})).
 \end{aligned} \tag{I.143}$$

This equation shows how the different branches contribute to $\langle G(\omega) \rangle$. The contributions of the different branches to the density of states can be simplified by the equipartition theorem. Every velocity degree of freedom will contribute on average $\langle \mathbf{u}_s^2 \rangle = \frac{3k_B T}{m_s}$ to the total energy. From this it follows that it is possible to rewrite equation (I.143)

$$\langle G(\omega) \rangle = \frac{1}{N_{\text{types}}} \sum_s \frac{3k_B T}{m_s} \sum_{\mathbf{k}, \alpha} \delta(\omega - \omega_{\alpha}(\mathbf{k})) \tag{I.144}$$

Now, to obtain from the function $\langle G(\omega) \rangle$ the phonon density of states one has to divide by $\langle \dot{\mathbf{u}}_s^2(0) \rangle = \frac{3k_B T}{m_s}$

$$\begin{aligned}
 \langle g(\omega) \rangle &= \frac{1}{N_{\text{types}}} \sum_s \frac{G_s(\omega)}{\langle \dot{\mathbf{u}}_s^2(0) \rangle} = \\
 &= \frac{1}{N_{\text{types}}} \sum_s \frac{\frac{3k_B T}{m_s} \sum_{\mathbf{k}, \alpha} \delta(\omega - \omega_{\alpha}(\mathbf{k}))}{\frac{3k_B T}{m_s}} =
 \end{aligned} \tag{I.145}$$

$$= \sum_{\mathbf{k}, \alpha} \delta(\omega - \omega_{\alpha}(\mathbf{k})). \tag{I.146}$$

The last line of equation (I.146) is equivalent to the definition of the phonon density of states in equation (I.134). Therefore it is possible to obtain the phonon density of states directly from ensemble averages of the velocity autocorrelation functions. The computation of the phonon density of states by the Fourier transform of the velocity autocorrelation function is not restricted to the harmonic picture. The harmonic approximation was only used in this section to show the equivalence of equations (I.134) and (I.135) in a simple way.

4.4 Dynamic structure factor

In the section about the harmonic approximation the dispersion relation was introduced. During a molecular dynamics simulation the potential will not be harmonic in general. To measure the phonon dispersion relation from molecular dynamics simulations the dynamic structure factor can be used. The dynamic structure factor is the spatial and temporal Fourier transform of the density-density correlation function containing the dynamical and spatial correlations of the considered material. In the following the density-density correlation will be introduced and the relationship to the phonon dispersion relation will be shown. The density-density correlation function is given by

$$A(\mathbf{r}, \mathbf{r}', t) = \langle \rho(\mathbf{r}' + \mathbf{r}, 0) \rho(\mathbf{r}', t) \rangle. \tag{I.147}$$

For point particles the normalized density function is given by

$$\rho(\mathbf{r}, t) = \frac{1}{N} \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i(t)), \tag{I.148}$$

and the density-density correlation function for point particles becomes [21, 22]

$$A(\mathbf{r}, \mathbf{r}', t) = \frac{1}{N^2} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta(\mathbf{r}' + \mathbf{r} - \mathbf{r}_i(t)) \delta(\mathbf{r} - \mathbf{r}_j(0)) \right\rangle. \tag{I.149}$$

The van-Hove equation is obtained by integrating equation (I.149) over all space,

$$A(\mathbf{r}, t) = \int_{\mathbb{R}^3} A(\mathbf{r}, \mathbf{r}', t) d^3 r' = \frac{1}{N} \left\langle \sum_i^N \sum_j^N \delta(\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_j(0)) \right\rangle \tag{I.150}$$

Decomposing the van-Hove equation into a self part ($i = j$) and a part for different particles equation (I.150) becomes

$$\begin{aligned} A(\mathbf{r}, t) &= \frac{1}{N} \left\langle \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_i(0)) \right\rangle \\ &+ \frac{1}{N} \left\langle \sum_i^N \sum_{j \neq i}^N \delta(\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_j(0)) \right\rangle = \\ &= A_{\text{self}}(\mathbf{r}, t) + A_{\text{different}}(\mathbf{r}, t) \end{aligned} \quad (\text{I.151})$$

At $t = 0$ the self correlation part becomes a Dirac delta distribution and the part of different particles is the pair-correlation function $g(\mathbf{r})$

$$A(\mathbf{r}, 0) = \delta(\mathbf{r}) + g(\mathbf{r}). \quad (\text{I.152})$$

The physical interpretation at $t \neq 0$ for the self part is the probability to find particle i at $\mathbf{r}_i(t)$ at time t knowing the particle was initially at position $\mathbf{r}_i(0)$. Or the probability that the particle i was traveling along the vector $\mathbf{r}(t) - \mathbf{r}_i$ within a time interval t [22]. The part for distinct particles at $t \neq 0$ can be interpreted as the probability to find a different particle $j \neq i$ at $\mathbf{r}_j(t)$ when a particle i was at position $\mathbf{r}_i(0)$ at time $t = 0$ [22]. With this interpretation it is clear that the dynamic behavior of the considered system is coded in the Van Hove equation. To relate this equation to the phonon frequencies at different vectors $\mathbf{k}$ the spatial and temporal Fourier transform has to be computed. The spatial Fourier transform gives

$$\begin{aligned} S(\mathbf{k}, t) &= \int A(\mathbf{r}, t) e^{i\mathbf{k}\mathbf{r}} d^3r = \\ &= \int \frac{1}{N} \left\langle \sum_i^N \sum_j^N \delta(\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_j(0)) \right\rangle e^{i\mathbf{k}\mathbf{r}} d^3r = \\ &= \left\langle \sum_i^N \sum_j^N e^{i\mathbf{k}(\mathbf{r}_i(t) - \mathbf{r}_j(0))} \right\rangle. \end{aligned} \quad (\text{I.153})$$

From this equation the dynamic structure factor is defined via a temporal Fourier transform

$$\begin{aligned} S(\mathbf{k}, \omega) &= \int \left\langle \sum_i^N \sum_j^N e^{i\mathbf{k}(\mathbf{r}_i(t) - \mathbf{r}_j(0))} \right\rangle e^{-i\omega t} dt = \\ &= \sum_i^N \sum_j^N e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} \int \left\langle e^{i\mathbf{k}(\mathbf{u}_i(t) - \mathbf{u}_j(0))} \right\rangle e^{-i\omega t} dt, \end{aligned} \quad (\text{I.154})$$

where $\mathbf{R}_i$ and $\mathbf{R}_j$ denote the equilibrium positions of atoms i and j and $\mathbf{u}_i(t)$ and $\mathbf{u}_j(t)$ are the displacements from the equilibrium positions. A comparison of the dynamic structure factor with the expansion in equation (I.138) shows that the frequencies sampled during the molecular dynamics simulation will be those of the phonons in the case of a crystal. Therefore the dynamic structure factor includes all the dynamic behavior of a crystal without making any assumptions about the underlying physics. It represents a statistical way in terms of correlation functions to describe the dynamical properties of a system.

5 Density functional theory

The Born-Oppenheimer approximation allows to split the electronic and the nuclear parts of the Hamiltonian for a fixed nuclear configuration. This section will introduce the density functional theory (DFT) to solve the electronic part of the Hamiltonian (I.2). The electronic Hamiltonian is

$$\hat{H}_{el} = -\frac{1}{2} \sum_{i=1}^N \Delta_i - \sum_{i=1}^N \sum_{\alpha=1}^{N_{ions}} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{r_{ij}}. \quad (\text{I.155})$$

The Hohenberg-Kohn theorems are fundamental for the density functional theory. The first Hohenberg-Kohn theorem relates the external potential to the electronic density in a unique way. And the second theorem states that the true ground state electron density minimizes the energy for some given external potential. The v and N representability will be introduced as conditions that there exist electron density for a given external potential. The Levy-constrained search can be used to compute the true ground state if the system of interest possesses a degenerate ground state. The Kohn-Sham formulation of DFT will be introduced because in this way the DFT is applied in modern ab-initio codes. The problem of the correct exchange-correlation functional will be laid out by the adiabatic connection theorem.

5.1 The Hohenberg-Kohn theorems

To start the chapter about density functional theory (DFT) the Hohenberg-Kohn theorems are mentioned since they are fundamental for determining the electronic ground state.

The first Hohenberg Kohn theorem states: *'The external potential $v(\mathbf{r})$ is determined up to an arbitrary additive constant, by the electron density'* [23, 1]. This implies that ρ uniquely determines the external potential $v(\mathbf{r})$ and the number of electrons (shown in equation (I.23)). To proof this theorem assume there exist two external potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$ belonging to the same non-degenerate electron ground state density $\rho(\mathbf{r})$. Then there exist two Hamiltonians $\hat{H}'$ and $\hat{H}$ with eigenfunctions Ψ' and Ψ . Using the minimum energy principle of the ground state and using Ψ' as a trial function for $\hat{H}$

$$E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle - \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle = E'_0 + \int_{-\infty}^{\infty} \rho(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r} \quad (\text{I.156})$$

Now doing the same thing again but with Ψ as the trial function and $\hat{H}'$ as the Hamiltonian

$$E'_0 < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle - \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle = E_0 - \int_{-\infty}^{\infty} \rho(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r}, \quad (\text{I.157})$$

is obtained. Adding equations (I.156) and (I.157)

$$E_0 + E'_0 < E'_0 + E_0, \quad (\text{I.158})$$

what is clearly wrong. Therefore by reductio ad absurdum it was proved that the electronic density uniquely determines $v(\mathbf{r})$ and therefore the properties of the particle system [23, 1]. It follows, that it is possible to rewrite the Schrödinger equation in terms of the density $\rho(\mathbf{r})$. The electronic energy functional in terms of the electron density is given by

$$E_v[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r}) d^N r + F_{HK}[\rho]. \quad (\text{I.159})$$

with

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho] \quad (\text{I.160})$$

where

$$V_{ee} = \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^N r d^N r' + \text{non classical terms} \quad (\text{I.161})$$

The electronic energy functional can be split into a part depending on the considered system $v(\mathbf{r})$ and a second term $F_{HK}[\rho]$ that is independent of the considered system and can therefore be considered as a unique functional. The functional $F_{HK}[\rho]$ only depends on the electronic degrees of freedom and is a sum of kinetic energy and potential energy. The potential energy equation (I.161) is a sum of the classical Coulomb term and non classical terms, the exchange-correlation energy [23, 1]. The exchange correlation energy will be discussed in more detail in a later section.

In the following a variational principle for the electronic density will be established. The second Hohenberg-Kohn theorem states: *'For a trial density $\tilde{\rho}(\mathbf{r})$, such that $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int \tilde{\rho}(\mathbf{r}) d^N r = N$*

$$E_0 \leq E_v[\tilde{\rho}] \quad (\text{I.162})$$

where $E_v[\tilde{\rho}]$ is the energy functional of equation (I.159). To proof this theorem is straightforward, if the first Hohenberg-Kohn theorem was already proven.

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) d^N r + F_{HK}[\tilde{\rho}] = E_v[\tilde{\rho}] \geq E_v[\rho]. \quad (\text{I.163})$$

This is analogous to the already shown variational principle but for electron densities [23, 1]. The ground state density can also be determined by Lagrangian multipliers. The constraint follows from the conservation of the number of electrons N in the system.

$$\delta \left[E_v[\rho] - \mu \left(\int \rho(\mathbf{r}) d^N r - N \right) \right] = 0 \quad (\text{I.164})$$

This can be simplified by variational calculus. If one evaluates the variation of equation (I.164) one obtains the Euler-Lagrange equation for this problem

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta F_{HK}[\rho]}{\delta \rho(\mathbf{r})} \quad (\text{I.165})$$

where μ is the chemical potential. To close this section it should be stressed that the functional $F_{HK}[\rho]$ is unique and independent of the considered system. Therefore, if this functional would be known exactly a theory based on the Hohenberg Kohn theorems would be exact in a mathematical sense [23, 1]. But the major problem with $F_{HK}[\rho]$ are the non classical terms, the exchange-correlation functional.

5.2 The v representability and N representability

The previous section showed that the electronic ground state density $\rho(\mathbf{r})$ uniquely determines the potential $v(\mathbf{r})$. Now the question arises if there exist for every potential $v(\mathbf{r})$ a ground state density. A density $\rho(\mathbf{r})$ is said to be v representable if it is the density of the antisymmetric ground state wavefunction belonging to some Hamiltonian H that contains $v(\mathbf{r})$ [1]. From the first Hohenberg-Kohn theorem it follows that there exists a surjection between the ground state wavefunction (there could be several ground state wavefunctions leading to the same ground state density), belonging to some Hamiltonian and the v -representable ground state density. If a trial ρ is used for the variational principle it is important that this trial wavefunction is v -representable because otherwise the variational principle fails. This is caused by the fact that the functionals included in the energy equation (I.159) are only defined for v -representable wavefunctions. The exact condition if a wavefunction is v -representable is still unknown [1]. On the other hand there exists a sufficient but weaker condition, the N -representability. A density is said to be N -representable if

$$\rho(\mathbf{r}) \geq 0, \quad \int \rho(\mathbf{r}) d^N r = N \quad \text{and} \quad \int |\nabla \rho^{\frac{1}{2}}|^2 d^N r < \infty. \quad (\text{I.166})$$

This property is weaker but sufficient since any ground state electron density can be formed from a set of M smooth orthonormal orbitals $\{\varphi_k(\mathbf{r})\}$ with $M \geq N$. The ground state density can be expanded in terms of these orbitals as

$$\rho(\mathbf{r}) = \sum_{k=1}^M \lambda_k |\varphi_k(\mathbf{r})|^2 \quad (\text{I.167})$$

where the expansion coefficients have to satisfy $\sum_k \lambda_k = N$. An electron density constructed in this way is automatically N -representable.

5.3 Degenerate ground states and the Levy-constrained search

In the last section it was described that the ground state density can be obtained from the ground state wavefunction by quadrature in a unique way. But when determining the ground state wavefunction Ψ_0 from the density ρ_0 there exist infinitely many solutions to the problem. The question is how to find the true ground state wavefunction associated with the real ground state density. Assume a ground state wavefunction Ψ_{ρ_0} integrating to ρ_0 is given. Then the minimum energy principle says

$$\langle \Psi_{\rho_0} | \hat{H} | \Psi_{\rho_0} \rangle \geq E_0 \quad (\text{I.168})$$

By inserting for the functionals of E_0 and the Hamiltonian $\hat{H}$ one obtains

$$\langle \Psi_{\rho_0} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho_0} \rangle + \int \rho_0(\mathbf{r}) v(\mathbf{r}) d^N r \geq \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle + \int \rho_0(\mathbf{r}) v(\mathbf{r}) d^N r. \quad (\text{I.169})$$

From this equation it follows

$$\langle \Psi_{\rho_0} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho_0} \rangle \geq \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle. \quad (\text{I.170})$$

It follows that the true ground state wavefunction minimizes the unique functional $F_{HK}[\rho]$. By taking this fact it is possible to define a constrained search algorithm

$$F_{HK}[\rho_0] = \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle = \text{Min}_{\Psi \rightarrow \rho_0} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \quad (\text{I.171})$$

The minimization is done within the space of all antisymmetric wavefunctions giving the correct ground state density ρ_0 and minimizing the Hohenberg-Kohn functional $F_{HK}[\rho]$ [1]. If the search would not be constrained one would have to test all antisymmetric wavefunctions in the N -particle Hilbert space. With the Levy-constrained search one only looks for solutions in the Hilbert space that give the correct ground state densities. Another advantage of this search algorithm is that the wavefunctions don't have to be v -representable since this term does not occur in equation (I.171). Therefore it is possible to extend the

search algorithm to all N-representable wavefunctions. To find the ground state energy and density one does the energy minimization in two steps

$$\begin{aligned} E_0 &= \text{Min}_{\Psi} = \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i) | \Psi \rangle = \\ &= \text{Min}_{\rho} \left[\text{Min}_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i) | \Psi \rangle \right] = \end{aligned} \quad (\text{I.172})$$

$$= \text{Min}_{\rho} \left[\text{Min}_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int \rho(\mathbf{r}) v(\mathbf{r}) d^N r \right] \quad (\text{I.173})$$

The first step is the minimization to find the electron density for the ground state and in a second step the search for the minimum energy wavefunction belonging to this ground state density is carried out. An input density ρ is supplied to the inner minimization that searches all wavefunctions giving the input density. The outer minimization checks for all densities such that the the ground state density will be found. Finally, the Levy- constrained search algorithm gets rid of the v -representability of the densities and searches for all N-representable antisymmetric wavefunctions in the Hilbert space to give the correct ground state electron density[1].

5.4 Kohn–Sham density functional theory

Because the functionals $T[\rho]$ and $V_{ee}[\rho]$ are not known exactly, Kohn and Sham introduced a non-interacting reference system for which the two functionals can be written down exactly. Formally this can be done by introducing independent orbitals ϕ in the Hohenberg-Kohn energy functionals[24, 1]

$$\begin{aligned} E[\rho] &= T_S[\rho] + J[\rho] + E_{XC}[\rho] = \\ &= \sum_{i=1}^N \sum_s \int \phi_i(\mathbf{r}) \left(-\frac{1}{2} \Delta \right) \phi_i(\mathbf{r}) d^N r + J[\rho] + E_{XC}[\rho] + \int v(\mathbf{r}) \rho(\mathbf{r}) d^N r, \end{aligned} \quad (\text{I.174})$$

$$(\text{I.175})$$

where $J[\rho]$ denotes an approximate for the electrostatic energy and $E_{XC}[\rho]$ is the exchange-correlation functional given by

$$E_{XC} = T[\rho] - T_S[\rho] + V_{ee}[\rho] - J[\rho]. \quad (\text{I.176})$$

The electron density is expressed in terms of the non interacting reference system wavefunctions

$$\rho(\mathbf{r}) = \sum_{i=1}^N \sum_s |\phi_i(\mathbf{r}, s)|^2. \quad (\text{I.177})$$

So the energy functional was rewritten in terms of N-independent orbitals. The set of orbitals $\{\phi_i\}$ have to satisfy certain criteria to be useful. The orbitals have to posses finite kinetic energy and must be square integrable. Therefore the second derivatives have to exist and the functions and their second derivatives have to be square integrable. The density computed from the orbitals has to be N-representable and the used orbitals have to be orthonormal

$$\int \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) d^N r = \delta_{i,j}. \quad (\text{I.178})$$

If this condition would not be met, the formula for the kinetic energy would break down because it would not be possible to sum the individual orbital energies. The orthonormality condition automatically imposes the normalization of the electron density. Now the variational principle is reformulated in terms of the new constraints and the orbitals. Therefore the functional

$$\Omega[\{\phi_i\}] = E[\rho] - \sum_i \sum_j \epsilon_{ij} \int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d^N r, \quad (\text{I.179})$$

is defined. With the minimum energy condition

$$\delta\Omega[\{\phi_i\}] = 0. \quad (\text{I.180})$$

This equation is rewritten in terms of local operators and single particle energies

$$\hat{h}_{eff}\phi_i = [-\frac{1}{2}\Delta + v_{eff}(\mathbf{r})]\phi_i = \sum_j \epsilon_{ij}\phi_j. \quad (\text{I.181})$$

It should be noted that the single particle operator $\hat{h}_{eff}$ is hermitian and therefore ϵ_{ij} is a hermitian matrix that can be diagonalized by unitary transformations. By transformations to equation (I.181) it becomes

$$[-\frac{1}{2}\Delta + v_{eff}(\mathbf{r})]\phi_i = \epsilon_i\phi_i. \quad (\text{I.182})$$

The effective potential is given by

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3N_{r'} + v_{XC}(\mathbf{r}) \quad (\text{I.183})$$

Equations (I.182),(I.183) together with the equation for the electron density (I.177) are known as the Kohn-Sham equations in their canonical form. They form a set of non-linear equations that can be solved iteratively. The total energy of the electronic system can be obtained by computing the density and inserting in equation (I.175). Therefore the Kohn-Sham approach projects the many-body problem on a set of N independent nonlinear equations. These equations treat the kinetic energy of the single particle systems exact. The theory includes the quantum mechanical exchange-correlation part exactly even if the form of this term is not known. The theory can be improved by finding better approximations for the exchange-correlation part. This will be discussed in more detail in section 5.5. Last it should be noted that every orbital in ϕ_i can in general accommodate two electrons while the effective potential $v_{eff}(\mathbf{r})$ does not contain any spin degrees of freedom. Hence one can choose spin orbitals $\varphi(\mathbf{r})\alpha(s)$ containing only a single electron. The total density decomposes in spin densities. The spin density for an even number of electrons is given by

$$\rho(\mathbf{r}) = 2\rho^\uparrow(\mathbf{r}) = 2\rho^\downarrow(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\varphi_i(\mathbf{r})|^2 \quad (\text{I.184})$$

and for an odd number of electrons

$$\rho(\mathbf{r}) = \rho^\uparrow(\mathbf{r}) + \rho^\downarrow(\mathbf{r}). \quad (\text{I.185})$$

5.5 The exchange-correlation functional

The last ingredient to compute the electronic ground-state structure within the Born-Oppenheimer approximation under the use of DFT is the exchange correlation functional. This section will introduce the adiabatic connection theorem. This theorem states that the interacting many-body problem can be projected accurately onto a Hamiltonian of a non-interacting system[25]. To show what is meant by this, a Hamiltonian depending on a real parameter λ is introduced as

$$\hat{H}_\lambda = \hat{T} + \lambda\hat{V}_{ee} + \hat{V}_{ext}^\lambda. \quad (\text{I.186})$$

The $\lambda = 0$ case denotes the non-interacting Hamiltonian and $\lambda = 1$ would describe the fully interacting system. The external potential $\hat{V}_{ext}^\lambda$ also depends on the introduced parameter. In the non-interacting case the external potential $\hat{V}_{ext}^0$ is a single particle potential. The non-interacting Schrödinger equation is given by

$$\hat{H}_0 |\Psi_0\rangle = (\hat{T} + \hat{V}_{ext}^0) |\Psi_0\rangle, \quad (\text{I.187})$$

with the ground state electron density $\rho_0(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle$. The ground state wavefunction $|\Psi_0\rangle$ is expressed by a single Slater determinant. Now the interaction is switched on adiabatically. This can be visualized by changing λ to $\lambda + d\lambda$ and maintaining the external potential. Therefore the wavefunction changes from $|\Psi_0\rangle$ to $|\Psi'_0\rangle$ and the Hamiltonian for this system is $\hat{H}'_0 = \hat{T} + d\lambda\hat{V}_{ee} + \hat{V}_{ext}^0 = \hat{H}_0 + d\lambda\hat{V}_{ee}$ with corresponding electron density $\rho'(\mathbf{r})$. It is assumed that it is possible to alter the external potential in such a way that the ground state electron density is restored[25]. By doing so the new Hamiltonian will look like

$$\hat{H}_\lambda = \hat{H}_0 + d\lambda(\hat{V}_{ee} + \hat{V}_{ext}^{0'}). \quad (\text{I.188})$$

This new Hamiltonian will have eigenstates $|\Psi_{d\lambda}\rangle$ having the same density ρ_0 as the non-interacting Hamiltonian $\hat{H}_0$. Now it is possible to repeat this step over and over until one reaches the fully interacting system. This is only possible under the assumption that the potentials connecting the non-interacting with the interacting system exist. Note that the potential $\hat{V}_{ext}^1$ will depend on the choice of the non-interacting reference system, $\hat{V}_{ext}^0$. The ordering of the eigenstates will not necessarily be conserved. The state $|\Psi_1\rangle$ is not restricted to the ground state of $\hat{H}^1$ even if one started with a wavefunction $|\Psi_0\rangle$ being the ground state of the non-interacting Hamiltonian[25]. With the help of the Hellmann-Feynman theorem it is possible to obtain a variational principle when computing the derivative with respect to λ and integrating from the non-interacting system to the interacting system. From this the energy functional for the interacting system is computed

$$\begin{aligned}\langle\Psi_1|\hat{H}_1|\Psi_1\rangle &= \langle\Psi_0|\hat{H}_0|\Psi_0\rangle + \int_0^1 \langle\Psi_\lambda|\hat{V}_{ee} + \frac{\partial\hat{V}_{ext}^\lambda}{\partial\lambda}|\Psi_\lambda\rangle d\lambda = \\ &= \langle\Psi_0|\hat{H}_0|\Psi_0\rangle + \int_0^1 \langle\Psi_\lambda|\hat{V}_{ee}|\Psi_\lambda\rangle d\lambda + \int V_{ext}^1(\mathbf{r})\rho_0(\mathbf{r})d^3r.\end{aligned}\quad (\text{I.189})$$

If a physical system with external potential V_p is considered, then the potential is not arbitrary but well defined. For example, by the ions building up a crystal in which the electrons are moving. Since the last term of equation (I.189) is independent of λ it holds for an arbitrary adiabatic-connection. But only under the assumption that there exists such a connection between the interacting and non-interacting system. With this it is possible to write a variational energy functional for the physical system

$$E_i[V_{ext}^0] = \langle\Psi_0|\hat{H}_0|\Psi_0\rangle + \int_0^1 \langle\Psi_\lambda|\hat{V}_{ee}|\Psi_\lambda\rangle d\lambda + \int V_p^1(\mathbf{r})\rho_0(\mathbf{r})d^3r \geq E_0. \quad (\text{I.190})$$

The label i in equation (I.190) denotes the number of the state, since it was mentioned before that the ordering of the states is not necessarily conserved. And the exact form of the energy functional will depend on the choice of V_{ext}^0 what is contained in $\hat{H}_0$. This energy functional can be rewritten by introducing the exchange-correlation hole density

$$\rho_{XC}^i(\mathbf{r}, \mathbf{r}') = \rho_0^i(\mathbf{r}) - \frac{\int_0^1 \sum_{\sigma, \sigma'} \langle\Psi_\sigma^*(\mathbf{r})\Psi_{\sigma'}^*(\mathbf{r}')\Psi_\sigma(\mathbf{r})\Psi_{\sigma'}(\mathbf{r}')\rangle_\lambda^i d\lambda}{\rho_0}, \quad (\text{I.191})$$

and the exchange-correlation energy depending on the exchange-correlation hole

$$E_{XC}^i = -\frac{1}{2} \int \int \rho_0^i(\mathbf{r}) \frac{\rho_{XC}^i(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' d^3r. \quad (\text{I.192})$$

Using the last two equations (I.191) and (I.192) together with the energy functional (I.190)

$$E_i[V_{ext}^0] = T_i[V_{ext}^0] + E_{es}[\rho_0^i(\mathbf{r})] + E_{XC}^i[V_{ext}^0] + \int V_{ext}^1(\mathbf{r})\rho_0(\mathbf{r})d^3r, \quad (\text{I.193})$$

is obtained. With this the the ground state energy E_i can be computed by varying the external potential $\hat{V}_{ext}^i$ in the non-interacting limit. For every step the lowest energy that can be obtained from the variational principle for the considered potential is used. This procedure is very time consuming because the energy optimizations has to be done for every potential connecting the interacting with the non-interacting system. Moreover, this procedure only works if there exists an adiabatic connection between the true ground state and some non-interacting system[25]. Therefore, in practice approximations to the exchange-correlation-energy (I.192) are used. The approximations rely on an expansion of the correct exchange correlation potential in terms of the density

$$E_{XC}[n] = \int \rho(\mathbf{r}) \epsilon_{XC}^{approx}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \tau(\mathbf{r}), \dots) d^3r, \quad (\text{I.194})$$

where τ is a kinetic-energy density. The order of the approximations are usually referred to as the Jacobs Ladder of density functional theory. The first step of the ladder is build by the local density approximation (LDA) which expresses the exchange-correlation energy in terms of the local density only. The next step of the ladder is build by the generalized gradient functionals relying on the electron density and it's gradient. Meta-GGAs are the third step of this ladder and also take into account the kinetic-energy density. An overview of the performance of such functionals will be shown later in this thesis, where they are tested on the methylammonium-lead-iodide perovskite.

6 Molecular dynamics simulation

So far it was shown, for studying a material in a statistical way, a Hamiltonian (I.2) has to be defined and the solutions to the resulting Schrödinger equation have to be computed. The Born-Oppenheimer approximation was used to partially decouple the electronic degrees of freedom from the ionic/nuclear degrees of freedom. The electronic part of the Schrödinger equation is solved independently by DFT. It is very cumbersome to study a material's structure in terms of nuclear/ionic wavefunctions and therefore the Ehrenfest theorem shows that the nuclear coordinates (the expectation values of the nuclear wavefunction) propagate according to Newton's equations of motion if the forces (given by the Hellmann-Feynmann theorem) are sufficiently smooth. Moreover, these approximations reduce the quantum mechanical density-matrix representation for the ensembles to classical phase space integrals. This section will show algorithms to propagate the ions according to Newton's equations of motion. Furthermore, algorithms to control the temperature or pressure during the simulation will be introduced. The shake algorithm will be shown as a representative for imposing geometrical constraints during a simulation.

6.1 Verlet-algorithm and the Liouville formulation

A 'good' algorithm for solving Newton's equations of motions should preserve the properties of those equations. The first of these properties is the time reversibility. Classical dynamics posses time inversion symmetry. A good propagation algorithm must not violate this property. The second important property satisfied by classical statistical mechanics is the conservation of the phase space distribution function formulated by the Liouville theorem[12]. Imagine a very big system divided in a huge number of noninteracting subsystems. Every subsystems is in a certain thermodynamic state defined by its momentum and position coordinates. The probability distribution of the coordinates is described by the phase space distribution function $\rho(\{\mathbf{r}\}, \{\mathbf{p}\})$. If the system is in thermal equilibrium the entropy associated with the phase space distribution has to be maximal. This principle was introduced in section 3.1. From this maximum entropy principle it follows, when propagating an equilibrium system the phase space distribution has to be conserved. Therefore, the flow in and out of every phase space point has to be zero. This can be formulated with a continuity equation, called the Liouville equation

$$\frac{d\rho(\{\mathbf{r}\}, \{\mathbf{p}\})}{dt} = \sum_{i=1}^N \left[\dot{\mathbf{r}}_i \frac{\partial \rho(\{\mathbf{r}\}, \{\mathbf{p}\})}{\partial \mathbf{r}_i} + \dot{\mathbf{p}}_i \frac{\partial \rho(\{\mathbf{r}\}, \{\mathbf{p}\})}{\partial \mathbf{p}_i} \right] = i\hat{L}\rho(\{\mathbf{r}\}, \{\mathbf{p}\}), \quad (\text{II.1})$$

where the sum is over all particles in the system. On the most right hand side the Liouville operator $\hat{L}$ was introduced. The criterion for time reversal and invariant phase space volume are closely related[17] and, when violated, usually cause long term energy drifts during the simulation.

In the following it will be shown how the Liouville equation can be used to obtain proper algorithms for molecular dynamics simulations. The time derivative of $\rho(\{\mathbf{r}\}, \{\mathbf{p}\})$ is given by the Liouville operator and the following differential equation

$$\frac{\partial \rho}{\partial t} = i\hat{L}\rho, \quad (\text{II.2})$$

can be used to obtain the propagation of the phase space distribution function with time. A solution to this relation is given by

$$\rho(\{\mathbf{r}(t)\}, \{\mathbf{p}(t)\}) = e^{i\hat{L}t}\rho(\{\mathbf{r}(0)\}, \{\mathbf{p}(0)\}). \quad (\text{II.3})$$

The Liouville operator can be decomposed into a position and momentum part. The position part $i\hat{L}_r = \dot{\mathbf{r}}(t) \frac{\partial}{\partial \mathbf{r}}$ shifts the position coordinates by the used time increment Δt . This can be seen by using a Taylor expansion in equation (II.3) resulting in

$$\begin{aligned} \rho(\{\mathbf{r}(t + \Delta t)\}, \{\mathbf{p}(t)\}) &= e^{i\hat{L}_r \Delta t} \rho(\{\mathbf{r}(t)\}, \{\mathbf{p}(t)\}) = \\ &= \sum_{n=0}^{\infty} \frac{(\{\dot{\mathbf{r}}\} \Delta t)^n}{n!} \frac{\partial^n}{\partial \{\mathbf{r}\}^n} \rho(\{\mathbf{r}(t)\}, \{\mathbf{p}(t)\}). \end{aligned} \quad (\text{II.4})$$

The symbol $\{\dot{\mathbf{r}}\}$ denotes the velocity vector of all N particles with length $3N$, and $\frac{\partial^n}{\partial \{\mathbf{r}\}^n}$ is the n th derivative with respect to the atomic coordinates. The momentum part $i\hat{L}_p$ of the Liouville operator can be treated analogously. It will shift the momentum coordinates by a time step Δt . In general decomposing the Liouville operator in momentum and position part will only work if the two operators contained in the exponential commute, which is not the case for position and momentum. The Trotter identity can be used to decompose a non-commuting exponential e^{A+B}

$$e^{\hat{A}+\hat{B}} = \lim_{P \rightarrow \infty} \left[e^{\frac{\hat{A}}{2P}} e^{\frac{\hat{B}}{P}} e^{\frac{\hat{A}}{2P}} \right], \quad (\text{II.5})$$

which is only true in the limit when P is infinity. For finite P it can be shown that the error introduced is of the order $e^{\mathcal{O}(1/P^2)}$ [17]. The Liouville formulation in combination with the Trotter identity can be used to obtain the Velocity-Verlet algorithm by setting $P = 2$ and identifying $\hat{A} = i\hat{L}_p \Delta t$ and $\hat{B} = i\hat{L}_r \Delta t$. With this an approximate to the propagator for a single time step is

$$e^{i\hat{L}\Delta t} \approx e^{\frac{i\hat{L}_p \Delta t}{2}} e^{i\hat{L}_r \Delta t} e^{\frac{i\hat{L}_p \Delta t}{2}}. \quad (\text{II.6})$$

From this it follows, the propagation for a single time step can be decomposed by applying the exponentials on the right hand side of equation (II.6) consecutively[17]. This results in the following propagation scheme

$$e^{\frac{i\hat{L}_p \Delta t}{2}} \rho[\mathbf{p}(t), \mathbf{r}(t)] = \rho \left[\mathbf{p}(t + \frac{\Delta t}{2}), \mathbf{r}(t) \right] \quad (\text{II.7})$$

$$e^{i\hat{L}_r\Delta t}\rho\left[\mathbf{p}\left(t+\frac{\Delta t}{2}\right),\mathbf{r}(t)\right]=\rho\left[\mathbf{p}\left(t+\frac{\Delta t}{2}\right),\mathbf{r}(t+\Delta t)\right] \quad (\text{II.8})$$

$$e^{\frac{i\hat{L}_p\Delta t}{2}}\rho\left[\mathbf{p}\left(t+\frac{\Delta t}{2}\right),\mathbf{r}(t+\Delta t)\right]=\rho[\mathbf{p}(t+\Delta t),\mathbf{r}(t+\Delta t)] \quad (\text{II.9})$$

which is the Velocity-Verlet algorithm in the kick-drift form also known as the Leapfrog algorithm. This can be rewritten in the following form that will be more useful in practice

$$\mathbf{p}_i\left(t+\frac{\Delta t}{2}\right)=\mathbf{p}_i(t)+\frac{\Delta t\mathbf{F}_i(t)}{2} \quad (\text{II.10})$$

$$\mathbf{r}_i(t+\Delta t)=\mathbf{r}_i(t)+\mathbf{v}_i\left(t+\frac{\Delta t}{2}\right)\Delta t \quad (\text{II.11})$$

$$\text{Compute force for configuration }\{\mathbf{r}_i(t+\Delta t)\} \quad (\text{II.12})$$

$$\mathbf{p}_i(t+\Delta t)=\mathbf{p}_i\left(t+\frac{\Delta t}{2}\right)+\frac{\Delta t\mathbf{F}_i(t+\Delta t)}{2} \quad (\text{II.13})$$

6.2 Constant temperature computer simulations

In section 3.3 it was shown that the temperature in a real canonical ensemble has to fluctuate around an equilibrium value T . Therefore, when constant temperature molecular dynamics are done the temperature has to fluctuate too. Velocity rescaling would result in a wrong simulation, since it neglects temperature fluctuations. In general there are two approaches for thermostating in molecular dynamics simulations, stochastic approaches and deterministic approaches. An example for a stochastic thermostat would be the Langevin thermostat and the Nosé–Hover thermostat would be an example for a deterministic thermostat. The Langevin thermostat relies on the generalized Langevin equation

$$\dot{\mathbf{p}}=\mathbf{F}-\gamma_i\mathbf{p}_i+f_i, \quad (\text{II.14})$$

what is a modification of Newton's equations. The Newtonian equations of motion are extended by a friction term $\gamma_i\mathbf{p}_i$ and a random force f_i term. The random force term f_i can be considered as collisions of the particles with some fictitious heat bath. The original force term $\mathbf{F}_i$ is obtained from the used force field or from the Hellmann-Feynman theorem when doing ab-initio molecular dynamics. The random force has to be an uncorrelated Gaussian random number with variance

$$\sigma_i^2=\frac{2m_i\gamma_ik_BT}{\Delta t}. \quad (\text{II.15})$$

By solving this equation of motion for every particle with some propagation algorithm, canonical particle trajectories are obtained. This thermostat style is called stochastic since a random force is added to the equation of motion. The friction parameter is a free parameter that can be chosen before starting the molecular dynamics simulation. The larger the friction parameter the larger the influence of the thermostat on the momenta will be. One usually tries to choose this parameter such that it is possibly small but still the temperature should fluctuate around the desired value.

The Nosé–Hover thermostat relies on an extended Lagrangian scheme introducing fictitious degrees of freedom to maintain the temperature during a molecular dynamics simulation. The Nosé–Hover Lagrangian is

$$\mathcal{L}_{NH}=\sum_{i=1}^N\frac{m_i}{2}\dot{\mathbf{r}}_i^2-U(\mathbf{r}_1,\dots,\mathbf{r}_N)+\frac{Q}{2}\dot{s}^2-gk_BT\ln(s), \quad (\text{II.16})$$

where Q represents a fictitious mass associated with the virtual degree of freedom s representing the heat bath[17]. g is some parameter that will be determined in the following where it will be shown that this Lagrangian gives a canonical ensemble if $g=3N+1$. The Hamiltonian belonging to this Lagrangian is given by

$$\mathcal{H}_{NH}=\sum_{i=1}^N\frac{\mathbf{p}_i^2}{2m_i}+U(\mathbf{r}_1,\dots,\mathbf{r}_N)+\frac{p_s^2}{2Q}+gk_BT\ln(s), \quad (\text{II.17})$$

To see that this Lagrangian is able to generate the desired canonical ensemble the micro-canonical partition function Ω_{NH} for a system with $3N+1$ degrees of freedom and energy E is written as

$$\Omega_{NH}=\frac{1}{N!}\int\delta[\mathcal{H}_{NH}-E]dp_sdsd^{3N}pd^{3N}r. \quad (\text{II.18})$$

To simplify the notation the rescaled momenta $\mathbf{p}' = \mathbf{p}/s$ and the Hamiltonian equation

$$\mathcal{H}(\mathbf{p}', \mathbf{r}) = \sum_{i=1}^N \frac{\mathbf{p}'^2}{2m_i} + U(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (\text{II.19})$$

are introduced. The following property of the Dirac delta function is essential to rewrite the delta function of equation (II.18)

$$\delta[h(s)] = \frac{\delta(s - s_0)}{|h'(s_0)|}, \quad (\text{II.20})$$

where $h(s) = \frac{g}{\beta} \ln(s)$. This makes it possible to rewrite the micro-canonical partition function (II.18) into a canonical partition function Z_{NH} as

$$\begin{aligned} Z_{NH} &= \frac{\beta}{gN!} \int s^{3N+1} \delta \left[s - e^{-\beta \frac{\mathcal{H}(\mathbf{p}', \mathbf{r}) + p_s^2/(2Q) - E}{g}} \right] dp_s d^3N p' d^{3N} r ds = \\ &= \frac{\beta}{gN!} e^{\frac{\beta E(3N+1)}{g}} \int e^{-\frac{\beta(3N+1)}{g} \frac{p_s^2}{2Q}} dp_s \int e^{-\beta \frac{3N+1}{g} \mathcal{H}(\mathbf{p}', \mathbf{r})} d^{3N} p d^{3N} r = \\ &= \frac{C}{N!} \int e^{-\beta \frac{3N+1}{g} \mathcal{H}(\mathbf{p}', \mathbf{r})} d^{3N} p d^{3N} r = \frac{C}{N!} \int e^{-\beta \mathcal{H}(\mathbf{p}', \mathbf{r})} d^{3N} p d^{3N} r \end{aligned} \quad (\text{II.21})$$

From this equation it follows that the parameter g has to be set to $(3N + 1)$, the degrees of freedom of the extended system to obtain a canonical ensemble. By inserting for g into the Hamiltonian (II.17) one can readily obtain the equations of motions for the extended system. The mass Q of the fictitious degree of freedom is a parameter that can be chosen freely. The smaller the mass of the heat bath is chosen the stronger the temperature will fluctuate in the Nosé-Hoover scheme[17].

A complete analogous picture applies when thinking of barostats. Again it can be shown from the canonical partition function that the pressure will not be constant during a molecular dynamics simulation but will fluctuate around an equilibrium value. The Langevin scheme can be applied directly if a stochastic barostat is desired. Introducing another degree of freedom in the extended Lagrangian of the Nosé-Hoover scheme makes it possible to couple the system to a deterministic barostat.

6.3 Constrained Molecular Dynamics

The time step in a molecular dynamics simulation is always limited by the fastest modes of motion. Considering for example a simulation box filled with ethane molecules. Every molecule will have very high frequency C–H bonds limiting the time step of the simulation. If the dynamic behavior of the hydrogens is of no interest, it is possible to use renormalization group theory to get rid of this high frequency motions. To make this practically usable an algorithm is needed, imposing constraints on the high frequency motions of the system during the molecular dynamics simulation. Assume the bond lengths (or angles) in the molecules have to be constrained to increase the usable time step during the simulation. These constraints can be defined as

$$\sigma_\alpha(\mathbf{r}_i, \mathbf{r}_j) = r_{ij}^2 - d_{ij}^2, \quad (\text{II.22})$$

where d_{ij}^2 is the desired bond length between atoms i and j [17, 26]. The quantity $\sigma_\alpha(\mathbf{r}_i, \mathbf{r}_j)$ will be zero if the bond length has the desired length. These holonomic constraints can be imposed by an extended Lagrangian

$$\mathcal{L}' = \mathcal{L} - \sum_{\alpha} \lambda_{\alpha} \sigma_{\alpha}(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (\text{II.23})$$

where the λ_{α} 's are Lagrange multipliers. From this extended Lagrangian it is possible to derive equations of motion

$$m_i \ddot{\mathbf{r}}_i = -\frac{\partial U}{\partial \mathbf{r}_i} - \sum_{\alpha} \lambda_{\alpha} \frac{\partial \sigma_{\alpha}}{\partial \mathbf{r}_i} = \mathbf{F}_i + \sum_{\alpha} \mathbf{G}_{\alpha}(\mathbf{r}_i), \quad (\text{II.24})$$

where the second term on the right can be considered as a constraining force[17, 26]. If the restrictions on the bond lengths are satisfied the constraining force of (II.24) will vanish. To obtain a solution for the Lagrange multipliers λ_{α} the second derivative of (II.22) with respect to time is computed

$$\frac{\partial^2 \sigma_{\alpha}}{\partial t^2} = \frac{\partial}{\partial t} \{\dot{\mathbf{r}}\} \nabla \sigma_{\alpha} = \{\ddot{\mathbf{r}}\} \nabla \sigma_{\alpha} + (\{\dot{\mathbf{r}}\} \{\dot{\mathbf{r}}\}) : (\nabla \nabla \sigma_{\alpha}). \quad (\text{II.25})$$

In this equation $\{\dot{\mathbf{r}}\}$ denotes a collection of all 3 dimensional velocity vectors of the N particles and is therefore a $3N$ dimensional velocity vector and $\{\ddot{\mathbf{r}}\}$ is the corresponding acceleration vector. The nabla

operator is understood as a $3N$ dimensional derivative vector, taking the derivatives with respect to the x,y,z components of the N particles. The term $(\{\dot{\mathbf{r}}\}\{\dot{\mathbf{r}}\})$ is a $3N \times 3N$ matrix containing the product terms $\dot{r}_i \dot{r}_j$ and $(\nabla \nabla \sigma_\alpha)$ is the matrix containing the second derivatives of the constraint with respect to the atomic positions. The dyadic product $:$ is defined as $\sum_{i,j} A_{ij} B_{ji}$. By inserting equation (II.24) for the second time derivative of the position in (II.25) the following equation for the constraints

$$\begin{aligned} \frac{\partial^2 \sigma_\alpha}{\partial t^2} &= \sum_i \frac{1}{m_i} \left[F_i + \sum_\beta G_\beta(r_i) \right] \nabla_i \sigma_\alpha + \sum_i \sum_j \dot{r}_i \dot{r}_j (\nabla_i \nabla_j \sigma_\alpha) = \\ &= \sum_i \frac{1}{m_i} F_i \nabla_i \sigma_\alpha - \sum_i \frac{1}{m_i} \sum_\beta \lambda_\beta \nabla_i \sigma_\beta \nabla_i \sigma_\alpha + \sum_i \sum_j \dot{r}_i \dot{r}_j (\nabla_i \nabla_j \sigma_\alpha) = \\ &= \mathcal{F}_\alpha - \mathbf{\Lambda} \mathcal{M}_\alpha + \mathcal{T}_\alpha = 0, \end{aligned} \quad (\text{II.26})$$

is obtained. The sums i and j run over all $3N$ atomic coordinates and the sum β is over all included constraints. In the last line of (II.26) the equation was rephrased in matrix notation[17] and an exact solution can be found for $\{\lambda_\alpha\}$. In practice, an approximative method is used to compute the positions of the next time step (Verlet-algorithm). So there is no need to compute the λ 's exactly since the exact constraining force will be of no use when approximative positions are used. Moreover, one would have to do a matrix inversion of the form

$$\mathbf{\Lambda} = \mathcal{M}^{-1} (\mathcal{F} + \mathcal{T}) \quad (\text{II.27})$$

for every time step what can be very time consuming if the number of constraints is large. To make a more applicable scheme, the positions at time step $t + \Delta t$ are given as

$$\mathbf{r}_i^{\text{constrained}}(t + \Delta t) = \mathbf{r}_i^{\text{unconstrained}}(t + \Delta t) - \frac{\Delta t^2}{m_i} \sum_\alpha \lambda_\alpha \nabla_i \sigma_\alpha(t), \quad (\text{II.28})$$

what follows from (II.24). A Taylor expansion can be used to approximate the constraint up to linear order

$$\begin{aligned} \sigma_\alpha^{\text{constr}}(t + \Delta t) &= \sigma_\alpha^{\text{unconstr}}(t + \Delta t) + \\ &+ \sum_{i=1} \left(\frac{\partial \sigma_\alpha(t + \Delta t)}{\partial \mathbf{r}_i} \right) [\mathbf{r}_i^{\text{constr}}(t + \Delta t) - \mathbf{r}_i^{\text{unconstr}}(t + \Delta t)]. \end{aligned} \quad (\text{II.29})$$

By inserting (II.28) for $\mathbf{r}_i^{\text{constr}}(t + \Delta t) - \mathbf{r}_i^{\text{unconstr}}(t + \Delta t)$ in equation (II.29) and assuming the constraint is satisfied $\sigma_\alpha^{\text{constr}}(t + \Delta t) = 0$

$$\sigma_\alpha^{\text{unconstr}}(t + \Delta t) = \sum_i \frac{\Delta t^2}{m_i} \nabla_i \sigma_\beta(t + \Delta t) \sum_\alpha \lambda_\alpha \nabla_i \sigma_\alpha(t), \quad (\text{II.30})$$

is obtained. Equation (II.30) can be rephrased in a matrix equation

$$\sigma^{\text{unconstr}}(t + \Delta t) = \Delta t^2 \mathcal{M} \mathbf{\Lambda} \quad (\text{II.31})$$

and the Lagrange multipliers $\mathbf{\Lambda}$ are obtained by inverting $\mathcal{M}$. But since a truncated Taylor expansion was used in (II.29) an iterative scheme has to be used. First the positions of the Verlet-integration are taken and the vector $\mathbf{\Lambda}$ is computed. Then the positions are updated according to equation (II.28) and the iteration is repeated until the constraints are satisfied. This would cause a high computational effort since for every iteration a matrix inversion has to be done. This is only affordable for a low number of constraints. Therefore in practice the SHAKE scheme[17, 27] is used. In the SHAKE algorithm equation (II.28) is approximated by

$$\mathbf{r}_i^{\text{constr}}(t + \Delta t) - \mathbf{r}_i^{\text{unconstr}}(t + \Delta t) \approx - \frac{\Delta t^2 \lambda_\alpha}{m_i} \nabla_i \sigma_\alpha(t). \quad (\text{II.32})$$

By inserting this in the Taylor expansion for the constraint in (II.29) and solving for λ_α

$$\lambda_\alpha \Delta t^2 = \frac{\sigma_\alpha^{\text{unconstr}}(t + \Delta t)}{\sum_{i=1} \frac{1}{m_i} \nabla_i \sigma_\alpha(t + \Delta t) \nabla_i \sigma_\alpha(t)}, \quad (\text{II.33})$$

is obtained. This procedure is applied to all constraints σ_α one after another. Assume $\mathbf{r}_i^{\text{unconstr}}(t + \Delta t)$ is known from free propagation with the Verlet algorithm. And all the gradients with respect to the atomic positions $\nabla_i \sigma_\alpha(t)$ are known from the preceding molecular dynamics step. Then the iterative scheme for the SHAKE algorithm looks as follows

- compute $\sigma_\alpha^{unconstr}(t + \Delta t)$ by equation (II.22)
- compute $\sum_{i=1} \frac{1}{m_i} \nabla_i \sigma_\alpha(t + \Delta t) \nabla_i \sigma_\alpha(t)$
- solve for λ_α in equation (II.33)
- update atomic positions $\mathbf{r}_i^{constr}(t + \Delta t)$ by equation (II.32)
- check how close the actual values are to the desired constraining value criterion
- $\mathbf{r}_i^{unconstr}(t + \Delta t) = \mathbf{r}_i^{constr}(t + \Delta t)$

This scheme is then repeated until all the constraints are satisfied within some tolerance criterion. This procedure will increase the usable time step during the molecular dynamics simulation tremendously by the cost of solving equation (II.33) iteratively for every time step.

7 Long range interactions

Electrostatic lattice models form a major part of this thesis. In those models the fast computation of long-range electrostatic interaction energies is central. Long range interactions under periodic boundary conditions are complicated to compute because of the partial convergence of the sums in the Coulomb interaction. This section introduces the Ewald summation which is a method to convert conditionally convergent electrostatic sums to strictly converging sums.

7.1 Long-range interaction and Ewald summation

When dealing with interacting point charges or point dipoles in molecular dynamics or Monte-Carlo simulations a crucial step is to evaluate the electrostatic potential related to the charges

$$\begin{aligned}\phi(\mathbf{r}) &= \frac{1}{4\pi\epsilon_0} \sum_{\mathbf{l}} \sum_{j=1}^{N_{cell}} \frac{q_j}{|\mathbf{r} - (\mathbf{r}_j + \mathbf{l})|} \\ &= \frac{1}{4\pi\epsilon_0} \sum_{i=1} \frac{q_i}{|\mathbf{r} - \mathbf{r}_i|},\end{aligned}\tag{II.34}$$

where the sum $\mathbf{l}$ runs over all periodic replicas of the cell. The sum j is over all atoms contained in the repeated unit-cell and q_j is the point charge of the considered atom. The sum over i denotes a combined index over all images and atoms in each replicated unit-cell. This is done to simplify the notation. To obtain meaningful results the sum has to converge to a certain value and this is exactly the problem. The sums for electrostatic potentials be it monopoles or dipoles are only conditionally converging [28, 29, 30, 31]. A very rigorous treatment of developing the equations for the Ewald formulation of the electrostatic potential was done by Leeuw *et.al.* [29, 30, 31]. Here, a much simpler and more intuitive way to develop the Ewald summation will be shown. Since there is a very nice physical picture that can be exploited to make the lattice sums for the electrostatic potential strictly converging. The following mathematical identity will be central when developing the Ewald summation

$$\frac{1}{r} = \frac{f(r)}{r} + \frac{1 - f(r)}{r}.\tag{II.35}$$

This identity is equivalent with the physical picture shown in figure II.1. Oppositely charged Gaussian charge distributions are added to the point charge grid shown in the top right of figure II.1. This shields the original point charges and forces the sum shown in (II.34) to converge strictly. To compute the electrostatic energy with the scheme shown in figure II.1 or (II.35) three contributions have to be computed. A short range part taking into account the interactions between the point screened by Gaussian charges. A spurious self-interaction term arising due to point charges and Gaussian charges at the same positions. And last the long-range part taking into account the interactions of the Gaussian charge distributions with the point charges. Therefore the total Coulomb energy is given by a sum of 3 terms

$$U_{Coulomb} = U_{long} + U_{short} + U_{self}.\tag{II.36}$$

The fictitious Gaussian charge distributions are given by

$$\rho_G(r) = q_i \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha r^2},\tag{II.37}$$

where r denotes the distance to the center of the point charge and α determines the width of the Gaussian. The electrostatic potential arising due to the Gaussian charge distributions in the Ewald sum is referred to as the Fourier part and will be discussed in the next section[17].

7.1.1 Ewald summation

The first thing that we compute is the so called Fourier part, which is the interaction between the Gaussian charges shown in the lower right of figure II.1. The charge distribution of a Gaussian charge grid is given by

$$\rho_1(\mathbf{r}) = \sum_i q_i \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha(\mathbf{r}-\mathbf{r}_i)^2},\tag{II.38}$$

where the sum i has to be understood in the same way as in (II.34). The electrostatic potential of a charge distribution is given by the Poisson equation [32, 17, 19]

$$-\Delta\phi_1(r) = 4\pi\rho_1(r),\tag{II.39}$$

where Δ is the Laplace operator ∇^2 . This equation can be rewritten in Fourier space where a derivative with respect to the coordinates becomes a multiplication with the conjugated variable k

$$k^2\phi(k) = 4\pi\rho_1(k).\tag{II.40}$$

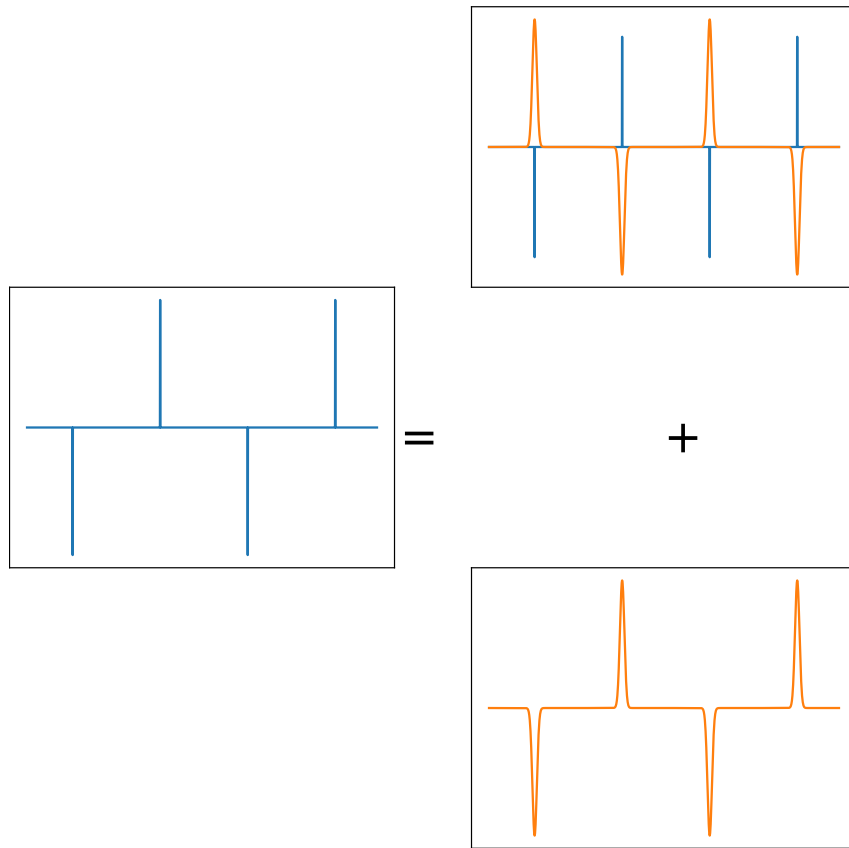


Figure II.1: Scheme depicting the mathematical identity of equation (II.35) behind the Ewald summation. **Left:** In — the original point charge distribution. **Right top:** The original point charge distribution — screened by oppositely charged Gaussian distributions — (short-range and self interaction part) **Right bottom:** Gaussian distributions — to restore original point charge distribution (long-range part)

Therefore the Fourier transform of the charge density $\rho_1(k)$ is needed. The computation of the Fourier transform for a single Gaussian will be derived in the following. The Fourier transform of a Gaussian charge is defined as

$$f(k) = \int_{\mathbb{R}} e^{-\alpha r^2} e^{ikr} dr. \quad (\text{II.41})$$

This integral is solved via a differential equation by taking the derivative with respect to k [19]

$$\frac{\partial \rho(k)}{\partial k} = - \int_{\mathbb{R}} (ir) e^{-\alpha r^2} e^{ikr} dr = \frac{i}{2\alpha} \int_{\mathbb{R}} \left(\frac{\partial}{\partial r} e^{-\alpha r^2} \right) e^{ikr} dr. \quad (\text{II.42})$$

Using integration by parts to the most right hand side gives the following equation

$$\frac{\partial \rho(k)}{\partial k} = -\frac{k}{2\alpha} \rho(k). \quad (\text{II.43})$$

This is a separable differential equation and is solved to give

$$\rho(k) = C e^{-\frac{k^2}{4\alpha}}. \quad (\text{II.44})$$

The integration constant is given from the case $k = 0$ where the integral in equation (II.41) is just the norm of the Gaussian. In the case of a Gaussian shown in equation (II.37) this constant is $C = q_i$. To compute the Fourier transform of the charge density $\rho_1(r)$ the shifting property of the Fourier transform is needed. The shifting property is given by

$$\begin{aligned} \int_{\mathbb{R}} e^{-\alpha(r-r_j)^2} e^{-ikr} dr &= \int_{\mathbb{R}} e^{-\alpha l^2} e^{-ik(r_j+l)} dl = \\ &= \rho(k) e^{-ikr_j}. \end{aligned} \quad (\text{II.45})$$

With this knowledge the Fourier transform of the charge density (II.38) can be written down directly

$$\rho_1(\mathbf{k}) = \frac{1}{V} \sum_i q_i e^{-\mathbf{k} \cdot \mathbf{r}_i} e^{-\frac{k^2}{4\alpha}}, \quad (\text{II.46})$$

where the factor $\frac{1}{V}$ is a normalization by the cell volume. By using equation (II.39) together with equation (II.46) the electrostatic potential

$$\phi(k) = \frac{4\pi}{Vk^2} \sum_i q_i e^{-\mathbf{k} \cdot \mathbf{r}_i} e^{-\frac{k^2}{4\alpha}}, \quad (\text{II.47})$$

in Fourier space is obtained. This potential is strictly converging except for $\mathbf{k} = \mathbf{0}$ where it diverges. This term can be ignored, which assumes the box is embedded in a medium with infinite dielectric constant [17]. To obtain the desired equation for the interactions between the Gaussian charges the Fourier transform of equation (II.47) multiplied by the point charges has to be computed. This long-range contribution to the Ewald sum is given by

$$\begin{aligned} U_{\text{Long}} &= \frac{1}{2} \sum_i q_i \phi(r_i) = \frac{1}{2} \sum_i q_i \sum_{\mathbf{k} \neq \mathbf{0}} \phi(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}_i} \\ &= \frac{1}{2} \sum_i \sum_j \sum_{\mathbf{k} \neq \mathbf{0}} \frac{4\pi q_i q_j}{Vk^2} e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)} e^{-\frac{k^2}{4\alpha}} \\ &= \frac{V}{2} \sum_{\mathbf{k} \neq \mathbf{0}} \frac{4\pi}{k^2} |\rho(\mathbf{k})|^2 e^{-\frac{k^2}{4\alpha}}, \end{aligned} \quad (\text{II.48})$$

with

$$\rho(\mathbf{k}) = \frac{1}{V} \sum_i q_i e^{-i\mathbf{k} \cdot \mathbf{r}_i}, \quad (\text{II.49})$$

being just the Fourier transform of the point charges. The sums in equation (II.48) for the potential energy contain spurious self interaction terms for the cases where $i = j$ [17]. The correction of this self-interaction terms will be treated in the next section.

7.1.2 Self-interactions

The spurious self-interaction is arising due to a point charge at position $\mathbf{r}_i$ and a Gaussian charge distribution at the same position. To compute the electric field of the Gaussian at its center the Poisson equation is used. This problem is spherically symmetric and therefore the Poisson equation in spherical coordinates is used

$$-\frac{\partial^2 (r\phi(r))}{\partial r^2} = 4\pi r\phi(r). \quad (\text{II.50})$$

This equation can be solved by integrating both sides of (II.50) with respect to r

$$\begin{aligned} -\frac{\partial (r\phi(r))}{\partial r} &= 4\pi \int_{\infty}^r r\rho_G(r)dr = \\ &= -4\pi q_i \left(\frac{\alpha}{\pi}\right)^{3/2} \int_r^{\infty} r e^{-\alpha r^2} dr = \\ &= -2\pi q_i \left(\frac{\alpha}{\pi}\right)^{3/2} \int_{r'(r)}^{\infty} e^{-\alpha r'^2} dr' = \\ &= -2q_i \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha r^2}. \end{aligned} \quad (\text{II.51})$$

where the substitution $r' = r^2$ was used from the second to the third line. By repeating this step equations

$$r\phi(r) = 2q_i \left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^r e^{-\alpha r^2} dr = q_i \text{erf}(\sqrt{\alpha}r) \quad (\text{II.52})$$

and

$$\phi(r) = \frac{q_i}{r} \text{erf}(\sqrt{\alpha}r) \quad (\text{II.53})$$

are obtained. To derive these equations the definition of the error function $\int_0^r e^{-\alpha r^2} dr = \frac{\sqrt{\pi}}{2\sqrt{\alpha}} \text{erf}(\sqrt{\alpha}r)$ was used. The focus lies in the value of the potential at the origin $r = 0$. The error function is evaluated at this point and gives $2q_i\sqrt{\frac{\alpha}{\pi}}$. Therefore the self interaction term is evaluated and gives

$$U_{\text{self}} = \frac{1}{2} \sum_i q_i \phi(r_i) = \sqrt{\frac{\alpha}{\pi}} \sum_i q_i^2 \quad (\text{II.54})$$

This term does not depend on the positions of the particles but only on the number of particles[17].

7.1.3 Short-range part of the Ewald summation

What remains is to compute the short range part of the Ewald summation. This is the interaction of the point charges with the oppositely charged Gaussian distributions. This interaction is shown in Figure II.1 on the top right. Here it should be mentioned that if the Fourier part corrected by the spurious self interaction is added to the short range part (computed in this section) the interaction due to the point charges on the left hand side of Figure II.1 is obtained. The electrostatic potential arising due to the Gaussian charges was already computed and is shown in (II.53). So the electrostatic potential due to the point charges and oppositely charged Gaussians is given by

$$\phi_2(r) = \frac{q_i}{r} - \frac{q_i}{r} \text{erf}(\sqrt{\alpha}r). \quad (\text{II.55})$$

By comparing this equation with the identity shown in equation (II.35) we identify the second term with the function just written down. The electrostatic interaction follows from equation (II.55) as

$$U_{\text{short}} = \frac{1}{2} \sum_i \sum_{j \neq i} \frac{q_i q_j}{r_{ij}} \text{erfc}(\sqrt{\alpha}r_{ij}). \quad (\text{II.56})$$

By summing the three derived contributions the electrostatic energy in terms of strictly converging sums can be written as

$$U_{\text{Coulomb}} = \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{4\pi}{k^2} |\rho(\mathbf{k})|^2 e^{-\frac{k^2}{4\alpha}}$$

$$\begin{aligned}
 & -\sqrt{\frac{\alpha}{\pi}} \sum_i q_i^2 \\
 & + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{q_i q_j}{r_{ij}} \operatorname{erfc}(\sqrt{\alpha} r_{ij}).
 \end{aligned} \tag{II.57}$$

A completely analogous picture applies for point dipoles. It only has to be noted that a dipole is interacting with the electric field and not with the electrostatic potential. The electric field is related to the potential by $\mathbf{E} = -\nabla\phi(\mathbf{r})$. With this the Ewald sum can be obtained from equation II.57 by replacing the point charges q_i by $-\mathbf{p}_i \nabla_i$ where $\mathbf{p}$ denotes the dipole vector. With this the electrostatic dipole-dipole interaction can be computed as

$$\begin{aligned}
 U_{\text{dipole-dipole}} &= \frac{1}{2} \sum_{\mathbf{k} \neq \mathbf{0}} \frac{4\pi V}{k^2} |M(\mathbf{k})|^2 e^{-\frac{k^2}{4\alpha}} \\
 & - \frac{2\pi}{3} \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_i \mathbf{p}_i^2 \\
 & + \frac{1}{2} \sum_i \sum_{j \neq i} \mathbf{p}_i \mathbf{p}_j B(r_{ij}) - (\mathbf{p}_i \mathbf{r}_{ij}) (\mathbf{p}_j \mathbf{r}_{ij}) C(r_{ij}),
 \end{aligned} \tag{II.58}$$

with

$$B(r) = \mathbf{r} = \frac{\operatorname{erfc}(\sqrt{\alpha} r)}{r^3} + 2\sqrt{\frac{\alpha}{\pi}} \frac{e^{-\alpha r^2}}{r^2}, \tag{II.59}$$

$$C(r) = 3 \frac{\operatorname{erfc}(\sqrt{\alpha} r)}{r^5} + 2\sqrt{\frac{\alpha}{\pi}} \left(2\alpha + \frac{3}{r^2}\right) \frac{e^{-\alpha r^2}}{r^2} \tag{II.60}$$

and last

$$M(\mathbf{k}) = \frac{1}{V} \sum_j i \mathbf{p}_j \mathbf{k} e^{i \mathbf{k} \mathbf{r}_j}. \tag{II.61}$$

7.2 Ewald sum implementation

In this thesis systems containing dipolar molecules are studied by means of Monte-Carlo models for which the Ewald sum had to be implemented. For the Monte-Carlo simulation the Metropolis Rosenbluth algorithm [33] was used. In the present work every dipolar molecule is treated as a point dipole on a fixed grid. This will be discussed in more detail in section VI. For now it is only important that the considered system is treated as point dipoles and the structure update is done by flipping one dipole at a time. One could directly exploit equation (II.58) to compute the energy after every update and check if the step is accepted or rejected. This would result in the computation of all the pair interactions after every flip of a dipole. To reduce the computational cost matrices were introduced containing the coupling between pairs of dipoles. The short range part of the Ewald sum in terms of pair interaction matrices is given by

$$U_{\text{short}} = \frac{1}{2} = \sum_i \sum_{j'} U_{i,j}^{\text{short}}, \tag{II.62}$$

where the matrix element U_{ij}^{short} is

$$U_{ij}^{\text{short}} = (\mathbf{p}_i \mathbf{p}_j) B(r_{ij}) - (\mathbf{p}_i \mathbf{r}_{ij}) (\mathbf{p}_j \mathbf{r}_{ij}) C(r_{ij}). \tag{II.63}$$

U_{ij}^{short} is a matrix containing the pairwise interaction terms of the short range part and therefore after flipping a dipole one only has to update the fields containing the flipped dipole. The size of the matrix is $N \times N_{\text{cut}}$ where N_{cut} is the number of dipoles within the cutoff for every dipole. Moreover since $U_{ij}^{\text{short}} = U_{ji}^{\text{short}}$ it is sufficient to store only half of those interactions. The same technique is applied to the long-range interaction part. The matrix element $|M(\mathbf{k})|_{ij}^2$ which is given by

$$|M(\mathbf{k})|_{ij}^2 = \frac{1}{V^2} (\mathbf{p}_i \mathbf{k}) (\mathbf{p}_j \mathbf{k}) e^{i \mathbf{k} (\mathbf{r}_i - \mathbf{r}_j)}. \tag{II.64}$$

is used. And after carrying out the sum over $\mathbf{k}$ one obtains the pairwise equation for the long-range part of the potential

$$U_{\text{long}} = \frac{1}{2} \sum_{i,j} \sum_{\mathbf{k} \neq \mathbf{0}} |M(\mathbf{k})|_{ij}^2 e^{-\frac{k^2}{4\alpha}} = \frac{1}{2} \sum_{i,j} U_{i,j}^{\text{long}} \tag{II.65}$$

So U_{ij}^{long} is a $N \times N$ matrix containing the pairwise long-range interactions. After flipping a dipole one only updates the fields containing the flipped dipole. After each dipole flip only one column of the matrix has to be computed. Because of the symmetry of the interaction matrix $U_{i,j}^{\text{long}} = U_{j,i}^{\text{long}}$, the updated column of the matrix is the same as the row that has to be updated. This structure of the matrix also gives the possibility for a vectorized implementation of $U_{i,j}^{\text{long}}$ in a Fortran90 code.

8 Speeding up electronic structure computations

The projector augmented-wave method (PAW)[34] is a tool to speed up electronic structure computations. The valence electron wavefunctions show strong oscillations in the nuclear regions what makes them expensive to describe with a plane wave basis set. The difficulty arises because a very large number of plane waves is needed to describe high oscillatory states [35, 34]. It is known that core states only show small contributions to the chemistry of atoms. The properties of atoms to form bonds and the type of bonds is determined by the electrons in the atomic valence states. Therefore the core electrons and their wavefunctions will only show minor variations with respect to the chemical environment surrounding the atom. The focus to describe solids or molecules is therefore on the valence electrons.

8.1 The projector augmented wave method

The basic idea of the PAW [34] method is to define a cutoff sphere around every atom. Within this cutoff sphere the wavefunctions of the valence electrons $|\Psi\rangle$ are described in terms of a partial wave $|\phi_i\rangle$ expansion

$$|\Psi\rangle = \sum_i c_i |\phi_i\rangle. \quad (\text{II.66})$$

The valence all electron (AE) wavefunction for a single electronic state $|\Psi\rangle$ is a solution of the all electron Kohn-Sham equations. Outside the core region the valence wavefunction will be expanded in terms of plane waves $|\phi\rangle$ because in this interstitial region the electronic wavefunctions are smooth. The cutoff distance will be chosen for every atom type J individually and denoted by r_c^J [35]. At this cutoff radius the partial wave expansion and the plane wave expansion are adjusted to match in terms of their function values and their derivatives [34]. The PAW method takes the all electron wavefunction and projects it onto a smooth pseudo wavefunction. This can be considered as a linear mapping between the real Hilbert space formed by the physical valence wavefunctions $|\Psi\rangle$ onto a pseudo Hilbert space (PS) formed by smoothed pseudo wavefunctions $|\tilde{\Psi}\rangle$ [34]. This transformation will look like

$$|\Psi\rangle = \mathcal{T} |\tilde{\Psi}\rangle \quad (\text{II.67})$$

and expectation values in PS will be computed by $\langle A \rangle = \langle \tilde{\Psi} | \hat{A} | \tilde{\Psi} \rangle$ where the operator transforms as $\hat{A} = \mathcal{T}^\dagger A \mathcal{T}$. The physical all electron wavefunction and the pseudo wavefunction have to match outside the augmentation sphere r_c^J and therefore the transformation operator can be written as a sum of local contributions $\hat{\mathcal{T}}^J$ over the augmentation spheres

$$\mathcal{T} = 1 + \sum_J \hat{\mathcal{T}}^J, \quad (\text{II.68})$$

with $\hat{\mathcal{T}}^J$ being the transformation operator within augmentation sphere r_c^J . This implies, the transformation from the pseudo basis $|\tilde{\phi}_i\rangle$ to the real basis function $|\phi_i\rangle$ inside the augmentation sphere r_c^J is given by $|\phi_i\rangle = (1 + \hat{\mathcal{T}}^J) |\tilde{\phi}_i\rangle$. A natural choice for the all electron partial waves $|\phi_i\rangle_i$ are radial solutions of the Schrödinger equation for the isolated atom. The index i denotes a combination index J, l, m denoting atom number and angular momentum quantum numbers l, m . The partial waves $|\phi_i\rangle$ and $|\tilde{\phi}_i\rangle$ have to be the same outside the cutoff radius [34]. The pseudo wavefunction $\tilde{\Psi}$ can be expanded by pseudo partial waves within r_c^J

$$|\tilde{\Psi}\rangle = \sum_i c_i |\tilde{\phi}_i\rangle. \quad (\text{II.69})$$

The coefficients $\{c_i\}$ are the same for the pseudo wavefunction and the all electron wavefunction within r_c^J

$$|\Psi\rangle = \mathcal{T} |\tilde{\Psi}\rangle = \sum_i c_i |\phi_i\rangle. \quad (\text{II.70})$$

From this it follows that the all electron wavefunction $|\Psi\rangle$ and the pseudo wavefunction are related by

$$|\Psi\rangle = |\tilde{\Psi}\rangle - \sum_i c_i |\tilde{\phi}_i\rangle + \sum_i c_i |\phi_i\rangle. \quad (\text{II.71})$$

The coefficients c_i can be obtained by introducing projector functions $|\tilde{p}_i\rangle$

$$c_i = \langle \tilde{p}_i | \tilde{\Psi} \rangle, \quad (\text{II.72})$$

where the projector functions have to satisfy

$$\sum_i |\tilde{p}_i\rangle \langle \tilde{\phi}_i| = 1. \quad (\text{II.73})$$

There has to be a projector function $|\tilde{p}_i\rangle$ for every $|\tilde{\phi}_i\rangle$ within the augmentation spheres r_c^J . This results in a linear transformation from the pseudo wavefunction to the all electron wavefunction [34]

$$\mathcal{T} = 1 + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{p}_i|. \quad (\text{II.74})$$

The all electron partial waves $|\phi_i\rangle$ are obtained by integrating the radial Schrödinger equation for the isolated atom outward

$$\left(-\frac{1}{2} \Delta + v_{eff} - \epsilon_i^1 \right) |\phi_i\rangle = 0 \quad (\text{II.75})$$

where v_{eff} is the effective all electron potential and ϵ_i^1 is the set of energies. The lowest lying energy per angular momentum state ϵ_i^1 is usually chosen to be the lowest bound valence state of the considered site[34].

Room-temperature dynamic correlation between methylammonium molecules in lead-iodine based perovskites: An ab initio molecular dynamics perspective [†]

The high efficiency of lead organo-metal-halide perovskite solar cells has raised many questions about the role of the methylammonium (MA) molecules in the Pb-I framework. Experiments indicate that the MA molecules are able to 'freely' spin around at room temperature even though they carry an intrinsic dipole moment. We have performed large supercell (2592 atoms) finite temperature ab-initio molecular dynamics calculations to study the correlation between the molecules in the framework. An underlying long range anti-ferroelectric ordering of the molecular dipoles is observed. The dynamical correlation between neighboring molecules shows a maximum around room temperature in the mid-temperature phase. In this phase, the rotations are slow enough to (partially) couple to neighbors via the Pb-I cage. This results in a collective motion of neighboring molecules in which the cage acts as the mediator. At lower and higher temperatures the motions are less correlated.

[†]Lahnsteiner J., Kresse G., Kumar A., Sarma D., Franchini C., Bokdam M., Phys. Rev. B 94, 214114 Published 28 December 2016

9 Introduction

The spectacular rise of perovskite photovoltaics[36] has sparked much research effort into the physical mechanisms behind these materials' good photovoltaic performance. From a solid state physics perspective, the answer seems simple: the well suited electronic structure of methylammonium lead-iodide (MAPbI₃). With a band gap of ~ 1.6 eV[37, 38, 39, 40, 41] and a high absorption coefficient[37, 40, 41], it is expected to be a high efficiency solar cell material for the solar radiation spectrum observed on earth.[42] Density Functional Theory (DFT) calculations have shown that an *s-p* mixture in the valence band maximum (VBM) and *p*-states in the conduction band minimum (CBM), combined with a direct band gap lead to an absorption coefficient up to an order of magnitude higher than GaAs.[43] However, the crystal structure of MAPbI₃ is completely different from GaAs. It even possesses temperature depended dynamical contributions arising from the organic constituent. The perovskite structure of MAPbI₃ is composed of three iodine atoms (monovalent anions) combined with a lead atom (divalent cation) and a CH₃NH₃ (MA) molecule (monovalent cation). The Pb-I framework forms the perovskite structure out of PbI₆ octahedra and the molecules are trapped in the cavities. Whether the cubic perovskite structure is stable or becomes orthorhombic or tetragonal is determined by the temperature[41] combined with a balance between the size of the molecule and the Pb-I bond length.[44] NMR experiments have indicated that at high temperatures (>300 K) the MA molecule exhibits complete orientational disorder.[45, 46] This means that the MA molecules have enough kinetic energy to overcome the rotational barriers and can rotate in their 'cage'. Around room temperature this process has a typical relaxation time of ~ 5 ps.[47] These rotations apparently do not effect the charge carriers in the system, since very long electron-hole diffusion lengths have been reported.[48, 49] From an electronic point of view this is not surprising, because the Pb-I framework is electronically decoupled from the molecule.[50] The VBM/CBM are well separated from the HOMO/LUMO of the molecule, respectively. Therefore all conducting states for holes and electrons are dominated by the framework. At the same time the dispersion at the VBM and CBM is large, resulting in low effective masses.[51] However, this picture applies to 0 K and does not take into account the dynamics of the MA molecules, their order or lack thereof at room temperature (RT). A partial alignment of these polar molecules could result in polar domains. Piezoresponse force microscopy measurements seem to indicate that polar domains form and that spontaneous polarization occurs at RT.[52, 53] A DFT based analysis indicates that at high temperature ferroelectricity is suppressed by the large configurational entropy and only below 50 K ferroelectric (FE) ordering would be present.[54] A strong argument against a polar structure is the absence of second harmonic generation in time-resolved pump-probe measurements.[55] The presence of polarized domains at RT is however still debated.

In a recent work we showed that polar phonons in MAPbI₃ increase the static dielectric constant to ~ 30 , but that they are too slow to effectively screen the excitonic state in the system.[56] The rotational dynamics of the polar MA molecules and the corresponding screening occurs at even lower frequencies.[57, 58, 59] Therefore even when the temperature is raised to RT, *i.e.* when the molecules rotate, the excitons are not screened by polar phonons nor by rotating polar molecules.[56] However, understanding of the dynamics of the molecules at finite temperatures is necessary to describe thermal transport[60, 61] as well as the screening of free charge carriers.[62] The dynamics and (dis)order of the MA molecules in MAPbI₃ has been extensively investigated, both experimentally and theoretically. Experiments showed the ability of molecules to reorient at RT with relaxation times in the range (1-10 ps).[45, 63, 64, 65, 47, 66] The dynamics of the MA molecules in the PbI framework were also studied by *ab-initio* molecular dynamics reporting relaxation times in roughly the same picosecond time scale.[67, 68, 69, 70, 71, 72] Most *ab-initio* studies were performed with small systems. A recent study of the relaxation time as a function of temperature using a reasonably large super cell indicates an absence of spatial correlation at RT.[71] However, a precise assessment of finite size effects in *ab-initio* calculations is still missing. MA dynamics in large supercells have been studied by classical molecular dynamics.[73] In agreement with experiment[47] a transition from the anti-ferroelectric ordering in the orthorhombic phase to thermally activated directional disorder in the tetragonal and cubic phases was reported.[73] However, the accuracy of model potentials are questionable and there is the need of an *ab-initio* validation. In particular, no systematic analysis of the spatial and dynamical correlation has been reported.

In this work we study the long range order of the MA molecules in MAPbI₃ by means of large scale *ab-initio* molecular dynamics (MD) calculations at finite temperatures. We show that the dynamics of the molecules is not a completely random thermal motion. Besides the possible dipole-dipole interaction between the intrinsic dipole moments of the molecules[74], the order of the molecules is also mediated by long range cage stress and strain effects as well as deformations or rotations of the PbI₆ octahedra and their long range order. In the low temperature (<150 K) phase this leads to an anti-ferroelectric arrangement of the molecules.[75, 76, 77] At higher temperatures the ordering pattern changes.

The paper is organized as follows. In the next section, the details of the computational method are

presented. Hereafter, we present the different super cell structures and their implications. We discuss in section 12 the dynamics of the molecules individually and in section 13 the correlation with their neighbors. We discuss the results in 14, and in the last section we summarize our findings in conclusions.

10 Computational method

For the first-principles molecular dynamics calculations we use a plane-wave basis and the projector augmented wave (PAW) method[34] as implemented in the VASP code[78, 79, 80]. The PBEsol (Perdew, Burke, Ernzerhof modified for solids)[81] functional is used. Relatively shallow pseudo-potentials are used, for Pb the $(6s^26p^2)$, for I the $(5s^25p^5)$, for C the $(2s^22p^2)$ and for N the $(2s^22p^3)$ orbitals are included in the valence. This makes it possible to set a relatively low energy cut-off of 250 eV for the plane-wave basis.

Super cells of dimension $n \times n \times n$, $n = 2, 4, 6$ were constructed out of pseudo-cubic unit cells (12 atoms) with experimental lattice constants ($a, b = 6.3115 \text{ \AA}$, $c = 6.3161 \text{ \AA}$)[41] as described in Ref. [56]. In order to construct an unbiased starting structure, all molecules in the supercell are randomly (R) rotated over three axis before starting the MD run. In the supercell all atoms were allowed to move while keeping the lattice vectors fixed.

Gaussian smearing with $\sigma = 0.05 \text{ eV}$ is used to broaden the one-electron levels. The Brillouin zone is sampled by the Γ point only for the large $4 \times 4 \times 4$ (4-cell) and $6 \times 6 \times 6$ (6-cell) supercells and by a $(2 \times 2 \times 2)$ Γ -centered Monkhorst-Pack grid for the $2 \times 2 \times 2$ supercell (2-cell). Using only a single k-point for the 2-cell results in significant errors in the calculated forces. The Kohn-Sham orbitals are updated in the self-consistency cycle until an energy convergence of 10^{-4} eV is obtained. A Langevin thermostat[82] is applied to simulate a canonical ensemble (at constant temperature). The trajectory is formed by propagating the structure with the calculated Hellmann-Feynman forces with time steps of 2.0/3.0 fs and increased hydrogen masses of 4/8 a.u. for the 2/4/6-cell, respectively. The hydrogen masses are increased to allow for a larger time step for the large cell-sizes. Additionally in the 6-cell the Pb and I masses have been decreased to 20 a.u. These changes in the masses are possible since the DFT functional does not depend on the mass and since the partition function factorizes into a momentum and position dependent part ($\rho(X, P) = e^{-U(X)\beta} e^{-P^2/(2M)\beta}$) so that results for the configurational part X are independent of the chosen masses (M). The down side is that the dynamical properties (velocities, average reorientation times, etc.) are no longer exact. However, differences in the dynamical properties between calculations where the same masses are used remain meaningful.

Unit cells for the different crystal phases have been constructed based on experimental crystal structures determined by X-ray diffraction. For the orthorhombic structure the Pb-I positions of Baïke *et al.*[77] were used ($a = 8.8362 \text{ \AA}$, $b = 8.5551 \text{ \AA}$, $c = 12.5804 \text{ \AA}$) and for the tetragonal structure the Pb-I positions of Stoumpos *et al.*[41] were used ($a = 8.8490 \text{ \AA}$, $b = 8.8490 \text{ \AA}$, $c = 12.6420 \text{ \AA}$). The molecules were placed in an arbitrary but unpolarized pattern and a high temperature MD (500 K, Pb-I framework kept fixed) was performed, allowing the molecules to reorient them-selves. Several low energy structures were picked from the MD trajectory and for those all atoms were thoroughly relaxed (forces $< 10^{-5} \text{ eV/\AA}$) into their instantaneous ground state while keeping the lattice vectors fixed. The resulting lowest energy configurations are shown in Figure III.1.

11 Molecular Dynamics: unit and supercells

In the MAPbI_3 structure the different MA molecules can interact with each other, either directly via the electrostatic forces (they are cations and have an intrinsic dipole moment) or indirectly by their collective pushing and pulling on the Pb-I framework. The potential energy related to dipole-dipole interactions between the different molecules falls off like r^{-3} , and we expect that this interaction only influences the nearest neighbors. However, it is clear that a single unit cell, be it orthorhombic (4 formula units), tetragonal (4 formula units) or cubic (1 formula unit) is prone to finite size effects/self-interaction errors and might therefore be artificially stabilized in a particular ordering pattern. If these effects are ignored and one starts with the structures obtained by X-ray diffraction[77, 41] for the three different phases, well ordered patterns are obtained as shown in Figure III.1. These structures agree (at various levels of accuracy) with the orthorhombic[83, 84, 85] and tetragonal[86, 87] molecular ordering patterns found in other first principles studies. The three crystal phases have distinct molecular ordering patterns:

The *orthorhombic phase* has an AFE ordering pattern of the MA molecules, with two molecules lying flat in the ab -plane with a $\sim 60^\circ$ angle between them. The layer on top has the same relative orientation in the plane, but the molecules are 180° degree rotated resulting in a zero net dipole moment. The PbI_6 octahedra are rotated by $\sim 15^\circ$ degree in the plane, one clockwise, the other counterclockwise. The

octahedra in the layer below have the same rotations in the ab -plane. An alternating $\pm 11^\circ$ tilt from the c -axis of neighboring octahedra results in a zigzag pattern in the c -direction.

In the *tetragonal phase* the octahedra are aligned to the c -axis, but in the ab -plane the octahedra in the two layers do not have the same rotations. They are rotated by $\sim 12^\circ$ degree, again one clockwise, the other counterclockwise. But in the second layer the order is reversed, counterclockwise, clockwise. In this Pb-I framework the MA molecules have an orthogonal orientation (when projected) in the ab -plane to all their nearest neighbors and have a $\sim 30^\circ$ out of the ab -plane tilt. The resulting angle between all nearest neighboring molecules thereby becomes $\sim 75^\circ$. The total MA pattern is here slightly FE.

In the *cubic phase* the octahedra are almost not rotated and all molecules are aligned in a FE ordering pattern. At the according temperature this state is dynamically unstable and the molecules are rotating.[45, 46]

Overall, we see that the nitrogen (most electronegative) side of the molecules are close to the iodines. The average distance of the N atom to nearest neighbor (n.n.) I atoms is $3.58 \pm 0.04 \text{ \AA} / 3.64 \pm 0.02 \text{ \AA}$ and of the C atom to n.n. I atoms $3.94 \pm 0.02 \text{ \AA} / 4.02 \pm 0.09 \text{ \AA}$, for the orthorhombic/tetragonal structure, respectively. The N-H bonds align to the N-I directions, thereby forming hydrogen bonds.[88, 89] All H-I bonds with a length $\leq 3 \text{ \AA}$ have been indicated in Fig. III.1 by the dashed (orange) lines. This orientation reduces the electrostatic energy between the negatively charged iodines and positively charged molecule. It dominates over the intermolecular dipole-dipole interaction as can be seen in the tetragonal structure (with its rotated octahedra), where it stabilizes the FE pattern.

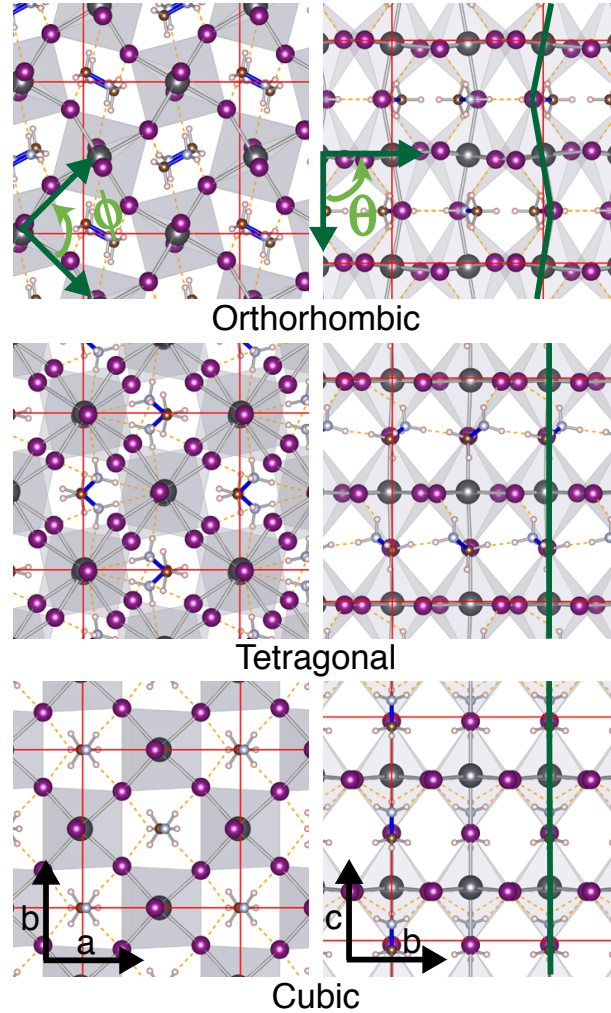


Figure III.1: (color online) The three different MAPbI₃ crystal phases. The unit cells (48 atoms, 4 molecules, solid red lines) are indicated, except for the cubic phase where a $\sqrt{2} \times \sqrt{2} \times 2$ supercell of the pseudo-cubic unit cell is shown. The dashed orange lines show the hydrogen bonds between the NH₃ groups and the iodines. The left/right column shows a top/side view, respectively. The polar coordinates reference frame $\{\phi, \theta\}$ to describe the orientation of the C-N bond of the MA molecule is drawn on the top.

Table 1: Overview of structures evaluated by molecular dynamics. Super cells of $n \times n \times n$ cubic unit cells, starting with an unpolarized-random (R) or polarized-aligned (A) MA ordering pattern, have been propagated for T picoseconds in steps of dt femtoseconds, with hydrogen mass M_H and at different temperatures.

Size	T (ps)	dt (fs)	M_H (a.u.)	Temp (K)
$2 \times 2 \times 2$ (R1)	86	2.0	4	300
$2 \times 2 \times 2$ (R2)	63	2.0	4	300
$2 \times 2 \times 2$ (R3)	64	2.0	4	300
$2 \times 2 \times 2$ (A)	84	2.0	4	300
$4 \times 4 \times 4$ (R)	21	2.0	4	100
$4 \times 4 \times 4$ (R)	27	2.0	4	150
$4 \times 4 \times 4$ (R)	42	2.0	4	200
$4 \times 4 \times 4$ (R)	24	2.0	4	250
$4 \times 4 \times 4$ (R)	23	2.0	4	300
$4 \times 4 \times 4$ (A)	31	2.0	4	300
$4 \times 4 \times 4$ (R)	31	2.0	4	400
$6 \times 6 \times 6$ (R)	8	3.0	8	150
$6 \times 6 \times 6$ (R)	13	3.0	8	300

Now we move on to supercells and see if and how these ordering patterns prevail at finite temperature. Previous ab-initio MD calculations have used relatively small supercell structures of 8 formula units (cubic)[68, 90] or 32 formula units (tetragonal)[90, 91, 69]. Only Carignano *et al.*[69] have systematically studied the effect of the supercell size and performed a calculation on a 108 formula unit (tetragonal) super cell. Using classical molecular dynamics Mattoni *et al.* have studied a 256 formula unit (orthorhombic) supercell.[73] An overview of the supercells that we have evaluated at room temperature and below is presented in Table 8. We have constructed $n \times n \times n$ supercells of the pseudo-cubic structure (1 formula unit), thereby containing $N = n^3$ molecules. This is hereafter referred to as n -cell. The lattice parameters of the pseudo-cubic structure are fixed at the experimental values, while all internal coordinates have been fully relaxed at the DFT level. During the MD all atoms are allowed to move, but the cell volume and shape are kept fixed. Since we are evaluating large cells this approximation seems acceptable and the error diminishes going from $n = 2$ to $n = 6$. From the trajectory of all atoms we extract the orientation of all MA molecules (C-N bond vector) in polar coordinates projected on the unit sphere $(\phi_i(t), \theta_i(t))$. The coordinate frame is aligned to the Pb-I framework as shown in Fig. III.1. Initially, all molecules in the super cells have been randomly rotated over three axis to generate an unbiased starting structure. We have tested this in comparison to a starting structure with aligned molecules and found that this approach results in shorter equilibration times. For example, the first 20 ps of an MD trajectory at 300 K for an initially aligned 4-cell involve a reorientation of the molecules so that the initial long range order is practically destroyed. Starting from a random state avoids these long equilibration times. This can be seen in Figure III.1, where the average polarization based on the molecular contribution only,

$$P_{\text{mol}}(t) = \left| \frac{1}{N} \sum_{i=1}^N \hat{\mathbf{p}}_i(t) \right|, \quad (\text{III.1})$$

has been plotted for a polarized-aligned (A) and a unpolarized-random (R) starting structure. This is not the full polarization of the structure, which would include contributions from the cage, but merely the contribution of the intrinsic dipole moment vector $(\hat{\mathbf{p}}_i)$ of each molecule. Here we assume that the dipole of each molecule is equally strong and that it does not change in time. After initial equilibration time, both calculations show a fluctuating behavior around a mean value. The mean value depends on the starting configuration and does not converge to a common value within the available compute time. The higher degree of fluctuation might indicate that the (A) system is not yet as well equilibrated as the (R) system.

12 Dynamics of Individual Molecules

We now want to determine how rotationally mobile the individual molecules are. In Figure III.1 the coordinates $(\phi_i(t), \theta_i(t))$ of 10 randomly chosen molecules in the 6-cell have been plotted over a time frame of 8 ps. The area covered by the paths increases with temperature. At 150 K the average orientation of most of the dipoles is maintained. At 300 K the covered area of the path ways are so

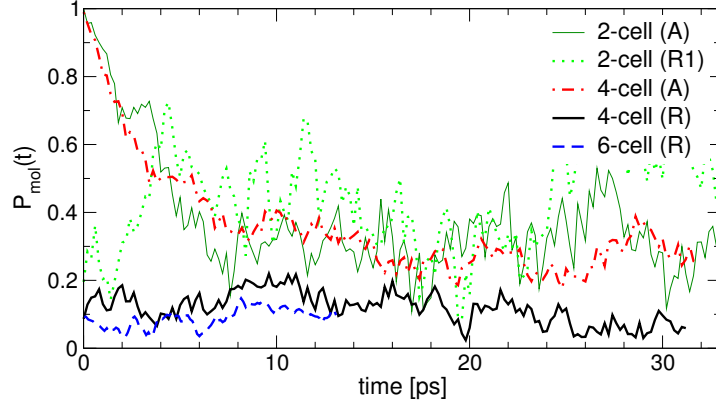


Figure III.1: (color online) Molecular polarization $P_{\text{mol}}(t)$ in the 2-cell, 4-cell and 6-cell at 300K starting from an unpolarized-random (R) structure. The polarization resulting from a polarized-aligned (A) starting structure in the 4-cell is given for comparison.

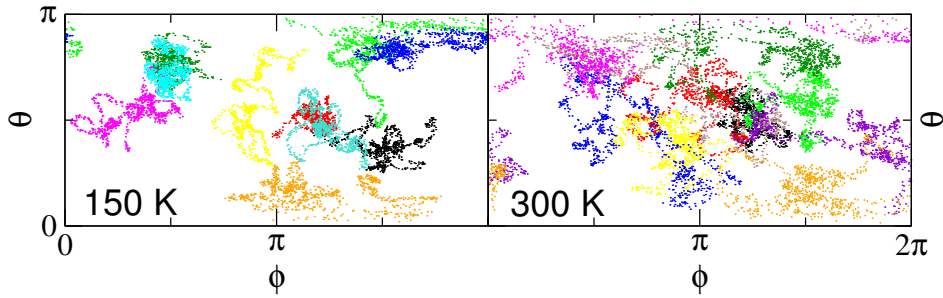


Figure III.1: (color online) The polar plot of 10 randomly chosen dipoles in the 6-cell shows the rotational mobility $(\phi_i(t), \theta_i(t))$ in a time frame of 8 ps at 150 K and 300 K.

large that reorientation of the molecules by 180° is possible. How exactly the molecules move at 300 K is not yet clear, whether they perform free rotations or whether they jump from one preferential orientation to the next, as was recently suggested.[66]

The average reorientation time (τ_{mol}) of the N molecules can be extracted from the autocorrelation function

$$r_{\text{mol}}(t - t_0) = \frac{1}{N} \sum_{i=1}^N \hat{\mathbf{p}}_i(t_0) \cdot \hat{\mathbf{p}}_i(t), \quad (\text{III.2})$$

where the dot product traces the change of the molecule's orientation in time with respect to its orientation at $t = t_0$. The autocorrelation function is smoothed by applying a time averaging over N_T different starting times t_0 ,

$$\langle r_{\text{mol}}(t) \rangle = \frac{1}{N_T N} \sum_{j=0}^{N_T-1} \sum_{i=1}^N \hat{\mathbf{p}}_i(\Delta t j) \cdot \hat{\mathbf{p}}_i(t + \Delta t j), \quad (\text{III.3})$$

where $\Delta t = \frac{T}{2(N_T-1)}$ for $N_T > 1$. Within this definition $\langle r_{\text{mol}}(t) \rangle$ is computable only for half of the total MD trajectory time T . In Figure III.2 a), the autocorrelation functions of MA molecules in the 2,4, and 6-cell structure at 300 K are shown. τ_{mol} is the time at which the autocorrelation function reaches the value $\frac{1}{e}$. Even though the autocorrelation functions are averaged with Eq. III.3 and long MD trajectory were used, the relaxation times are different and depend on the starting configuration. In the 2-cell, using the aligned (A) molecules as a starting structure results in faster dynamics than randomly (R) oriented molecules. However, even between different random structures, R1, R2 and R3 the τ_{mol} values

Table 2: The relaxation time (τ_{mol}) in picoseconds for a n -cell at 300 K starting from a polarized-aligned (A) and unpolarized-random (R) structures.

n	2 (A)	2 (R1)	2 (R2)	2 (R3)	4 (A)	4 (R)	6 (R)
τ_{mol}	4.8	7.6	7.6	11.3	8.5	6.8	5.4

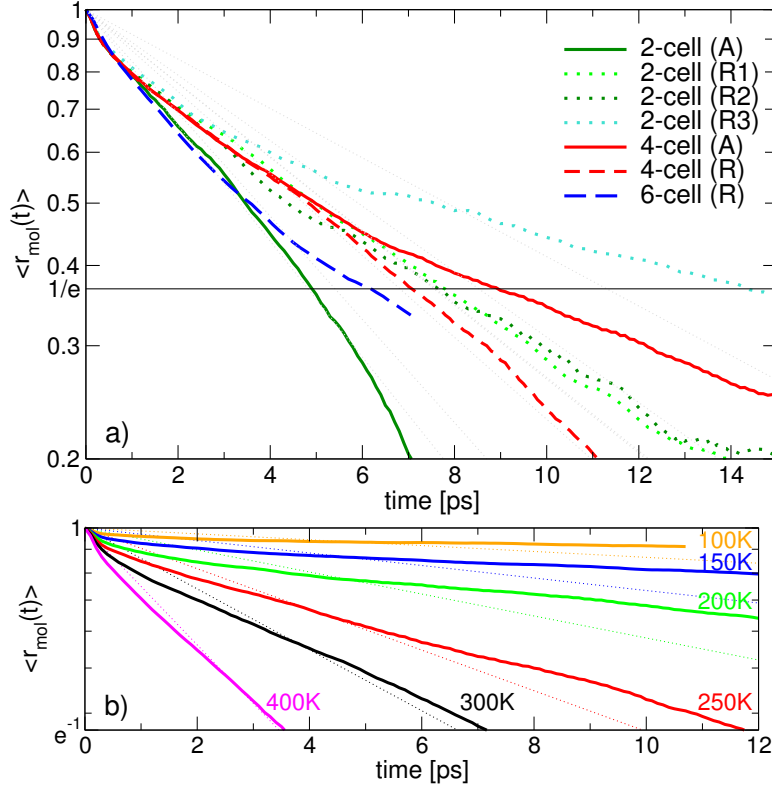


Figure III.2: (color online) Autocorrelation function $\langle r_{\text{mol}}(t) \rangle$ of MA molecules in semi-log plot. a) At 300 K in the 2,4, and 6-cell structures magenta starting from random (R) and aligned (A) configuration of the molecules. b) At various temperatures in between 100-400 K in the 4-cell. The dashed lines indicate exponential fits.

differ. Some starting configurations are energetically more disfavored and might therefore be easier to break down. This means that with the present results for the 2-cell we have an uncertainty in the τ_{mol} value of about ± 3 ps. To reduce the uncertainty, one has to improve the statistics. This can be done by averaging over many more MD trajectories using different random starting configurations.

The values τ_{mol} for the different systems have been tabulated in Table 2. They have been obtained by fitting an exponentially decaying function to the curves. These calculations show that τ_{mol} in the 4-cell is at least of the same order as in the 2-cell, however with the present data we cannot conclude with certainty that the reorientation time is not affected by finite size effects. Note that the τ_{mol} values are overestimated because the hydrogen masses have been raised. This raises the molecule's moment of inertia, while the DFT forces remain unchanged. The 6-cell shows a slightly lower reorientation time, this is possibly an artifact from the lower Pb and I masses (see Computational Details Section).

Figure III.2 b) shows the autocorrelation function in the 4-cell for various temperatures. The corresponding τ_{mol} values are 3.5, 6.9, 9.9, 18, 32 and 69 ps for 400, 300, 250, 200, 150 and 100 K, respectively. For temperatures below 200 K these numbers do not have a significant meaning. At these temperatures the autocorrelation function is not well described by a simple exponential.[73] Analysis with jump models on temperature dependent neutron scattering data shows relaxation time values of the same order.[47] Compared to this experiment the here presented results in the mid-temperature phase (150-300 K) are slightly lower.

In order to understand the molecular order at 300 K, the polar distribution of the orientation $(\phi_i(t), \theta_i(t))$ of all molecules in the cell over the entire simulation time (T) is plotted in Figure III.3. The distribution is plotted for the 2, 4 and 6-cell. Provided that a sufficiently long simulation time is taken at 300 K, the polar distributions are independent of the precise starting configuration. Here, MD trajectories from different starting molecular orderings (A/R) were combined in a single polar plot. The polar distributions of trajectories starting from the aligned and the three random structures for the 2-cell have been combined (A+3R). For the 4-cell, the full trajectory starting from the random configuration and the second half of the trajectory of the aligned starting configuration have been combined (A+R). This removes the strong artificial bias of aligned ordering. The differences in the distribution between the 2-cell and the larger 4,6-cells are small. The remaining differences are predominantly related to

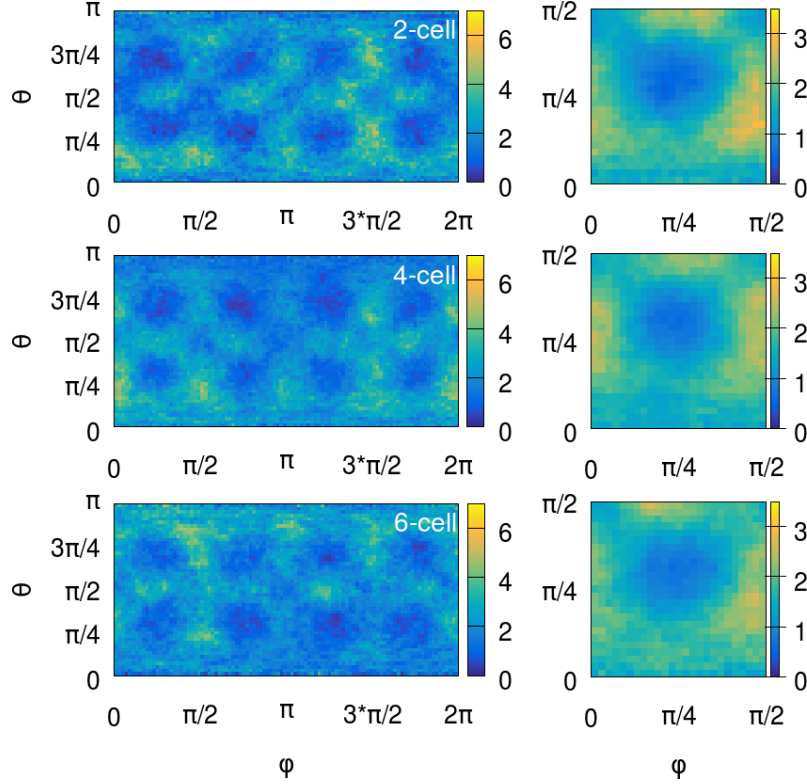


Figure III.3: (color online) Polar angle distribution of the MA molecules at 300 K in the 2-cell (top), 4-cell (middle) and 6-cell (bottom). The plots show the full rotational space (left) and the down-folded plot (right) into $\frac{1}{8}$ of the full space.

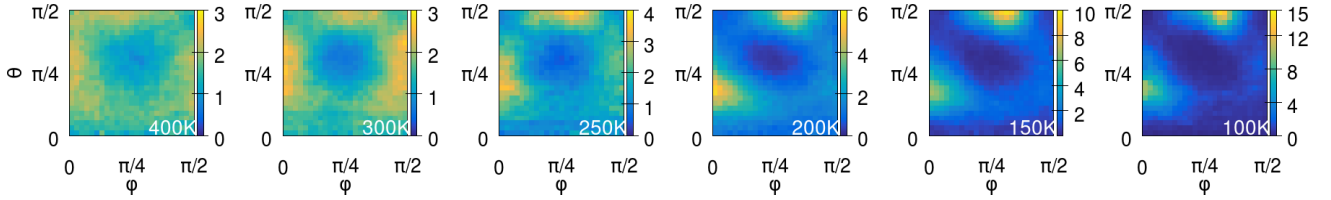


Figure III.4: (color online) From left to right, down-folded polar angle distribution of the MA molecules at 400, 300, 250, 200, 150, 100 K in the 4-cell.

the insufficient statistics. This means that the effective potential in which the molecules move does not depend strongly on cell size. (The effective potential can be obtained by a Boltzmann inversion of the polar distribution.) Combined with the foregoing observation of similar τ_{mol} times this indicates that the dynamics of the individual molecules are roughly the same in the 2-, 4- and 6-cell. The polar plots presented in Fig. III.3 are in agreement with the 300 K ab-initio/classical MD calculations in Refs. [69, 73], respectively. The regular pattern in the polar plots shows the presence of cubic symmetry. Therefore we have down-folded the polar plots into a single octant, shown on the right. The hole in the middle of the down-folded plot corresponds to the room-diagonal of the Pb-I cube. This orientation is systematically avoided by the MA molecules. Instead, the preferred direction is close to the face diagonal. The plot also shows that almost all orientations except the room-diagonal have a fairly high probability. These results agree with the picture arising from NMR measurements. At room temperature the molecules are rotating freely in a potential with several preferred high symmetry directions.[46]

When the temperature of the system is lowered, a more anisotropic polar angle distribution appears. In Figure III.4 the down-folded polar plots of a 4-cell at temperatures between 400 and 100 K are shown. When cooling down, the pattern changes from a ring with three spots, to just two spots below 200 K. We are not able to pin-down the phase transition temperature to the orthorhombic/low-temperature phase (exp. ~ 150 K[41]) exactly. Figure III.4 indicates that the low-temperature phase in our supercell approach is related to the freezing in of the molecules into two preferred orientations in the down-folded polar plot. The high temperature patterns show a similar polar distribution as the ones calculated by the

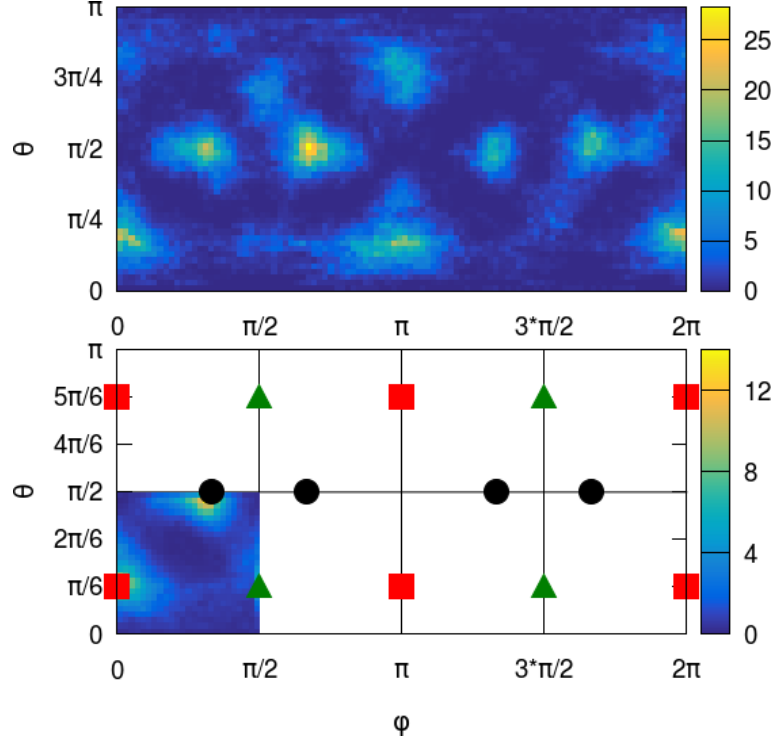


Figure III.5: (color online) *Top*: Polar angle distribution of the MA molecules at 100 K in the 4-cell. *Bottom*: Ideal molecular ordering of the orthorhombic structure with the molecules in the xy -plane (black circles), the xz -plane (red squares) and in the yz -plane (green triangles) with a $\frac{\pi}{3}$ relative orientation. The down-folded polar angle distribution is included for comparison.

classical MD calculations of Mattoni *et al.* in Ref. [73]. However, for temperatures below 250 K there are some differences. The most prominent difference appears at 100 K, where we find two distinct spots in the down-folded polar plot instead of one. The first and most dominant spot is close to $(\phi = \frac{\pi}{3}, \theta = \frac{\pi}{2})$, a direction where the molecules are in the xy -plane and are slightly tilted off the face diagonals of the Pb-I framework. The second spot close to $(\phi = 0, \theta = \frac{\pi}{6})$ is absent in Ref. [73]. What has happened is more easy to identify in the full polar plot, as shown in Figure III.5 (top). As mentioned before in the orthorhombic structure (Fig. III.1) all molecules lie flat in the xy -plane with a $\sim 60^\circ$ angle to their neighbors and an AFE stacking in the z -direction. These four distinct orientations are presented by the black circles in the symmetrical polar plot of Fig. III.5 (bottom). The second spot describes also such a pattern, but with the molecules in the xz -plane (presented by the red squares). This shows that, while cooling down the system, we acquired two competing orthorhombic phases (xy and xz , circles and squares in Fig. III.5) in the supercell. This low-temperature phase does not represent the ground state minimum, but as the result of the rapid cooling rate the system has been trapped in a local minimum. To avoid confusion we refer to this mixed phase in the supercell as low-temperature phase. We furthermore note that the condensation into ordered phases with molecules lying in the xy or xz plane occurred even though we used the pseudo-cubic initial structure.

The general picture that appears in Fig. III.4 about the transition of the molecular order in the supercell from the low-temperature (100 K) to the high-temperature (300 K) phase is one of three competing orthorhombic phases, with molecules in the xy , xz and yz planes. When the temperature increases, more than one phase can be present and the ideal spots start to blur out. This process goes on until a closed ring is formed for temperatures > 300 K. Within the available simulation time, we have not observed a 'pure' tetragonal phase in the mid-temperature regime. According to the unit cell of Fig. III.1 the tetragonal phase should result in four spots at $\{\phi = n \cdot \frac{\pi}{2}, \theta = \frac{\pi}{3}\}$ with $n = 0, 1, 2, 3$. Therefore our mid-temperature phase is most likely a mixture between the orthorhombic phases rather than a representative of the tetragonal structure. We return to this point in Fig. III.2.

At this point we have presented the orientation of the set of all molecules and their average reorientation times, but we do not know about the order between neighboring molecules. To this end, one needs to study the correlation between molecules.

13 Correlation between molecules

In the previous two sections we have described the behavior by averaging over all molecules (Sec. 11) and the behavior of each molecule individually (Sec. 12). In this section the correlation between the orientation of a molecule and its nearest neighbors (n.n.) is studied both in time (*dynamical correlation*) and on time average (*static correlation*).

13.1 Static correlation

The dot product between the unitary dipole vectors of molecules i and j

$$d_{i,j}(t) = \hat{\mathbf{p}}_i(t) \cdot \hat{\mathbf{p}}_j(t), \quad (\text{III.4})$$

indicates whether the molecules are parallel (1), orthogonal (0) or anti-parallel (-1) arranged. All other relative orientations are within the range $([-1, 1])$. We focus on the orientation of one molecule with respect to molecules at different distances/directions: $|\mathbf{q}| = |(k, l, m)|$. Here k, l, m are integers ($1, \dots, n$ for an n -cell) describing the connecting vector between molecules i and j on a cubic grid. Figure III.1 shows the time averaged distribution of $d_{i,j}$ over the whole trajectory of the MD simulation for the 2,4,6-cell at 300 K. The first observation is that all relative orientations occur in all simulated n -cells. Secondly, the shape of the distribution, characterized by the positions of the maxima and minima, does not depend very significantly on the cell size. Uncorrelated dipoles would result in a flat distribution, therefore some correlation prevails at 300 K. The differences between the 2-, 4- and 6-cell are related to the limited simulation time for the large supercells. Initially the molecules have a random orientation, therefore it takes simulation time to bring the flat distribution to the converged attenuated distribution. For the computationally less expensive 2-cell calculations these results are very close to the fully converged distribution for $|\mathbf{q}| = 1$ and $\sqrt{2}$. Note that a combined trajectory of ~ 300 ps corresponding to four MD runs starting from different molecular ordering (A+3R) were necessary.

In the 1st n.n. shell ($|\mathbf{q}| = \sqrt{1}$) of Fig. III.1, one 'sharp' peak at $d_{i,j} = -1$ is observed, here the molecules are AFE aligned. A second broad peak is found at $d_{i,j} = 0.4$, indicating a $\sim 66^\circ$ angle between the neighboring dipoles. Going to the 2nd n.n. shell ($|\mathbf{q}| = \sqrt{2}$), a similar pattern is observed, but mirrored. The sharp peak at $d_{i,j} = 1$ indicates a FE alignment between a molecule and its 2nd n.n. The broad peak is also observed, but is now at $d_{i,j} = -0.4$ indicating a $\sim 114^\circ$ angle. For the 4- and 6-cells, the third distribution ($|\mathbf{q}| = \sqrt{3}$) is almost exactly the same as the first. When going even further to the 4th ($|\mathbf{q}| = \sqrt{4}$) and 7th ($|\mathbf{q}| = \sqrt{8}$) shells the same pattern prevails. This alternating or 'mirror' pattern is not an effect of the supercell size, since it is does not diminish going from the 4- to the 6-cell.

The distributions in Figs. III.1 a-c) show an average over the different directions, all neighbors at the same distance have been added. This is possible because there is almost no cubic symmetry breaking, as can be seen in Figs. III.1 d-e). The static correlation along the cubic axis ($\mathbf{q}_x, \mathbf{q}_y$ and $\mathbf{q}_z$) are shown in Fig. III.1 d) and for all face-diagonal neighbors ($\mathbf{q}_{xy}, \mathbf{q}_{yz}$ and $\mathbf{q}_{xz}$ separately) in Fig. III.1 e). The curves have the same shapes and maxima, but the relative intensity per peak varies slightly.

Analysis of Fig. III.1 confirms the picture deduced from the polar angle plots, that the molecular ordering pattern at 300 K is a mixture of orthorhombic phases smeared out by the high temperature. Plots of the distribution in the 4-cell at different temperatures further justify this view. The distributions for the 1st and 2nd n.n. shell are shown in Figure III.2. For comparison the distribution in the perfect orthorhombic and tetragonal cells of Fig. III.1 have been plotted by the solid (black) and dashed (red) histograms, respectively. When the system is cooled down the sharp AFE and broad $\sim 60^\circ$ orientation peaks grow in relative intensity. These two peaks correspond to the molecular ordering pattern in the orthorhombic phase and are the same for the xy , yz and xz -orientations. However, stress between the different phases in the supercell and the finite temperature can explain the shift and broadening of the peaks. The ratio between the most and least likely orientation is simultaneously increased from a factor 2 at 300 K to a factor of 25 at 100 K, indicating the freezing in of a fixed ordered pattern going hand in hand with an increase of static correlation. Again, no clear signature of the tetragonal phase is found in the 4-cell.

13.2 Dynamical correlation

As a measure of dynamical correlation between the MA molecules, we have calculated the Pearson correlation coefficient of the $\theta_i(t)$ trajectories of neighboring molecules. Here we use the square Pearson correlation coefficient

$$r_{i,j}^2 = \left(\frac{\sum_{t=t_0}^T (\theta_i(t) - \bar{\theta}_i)(\theta_j(t) - \bar{\theta}_j)}{\sigma_i^2 \sigma_j^2} \right)^2, \quad (\text{III.5})$$

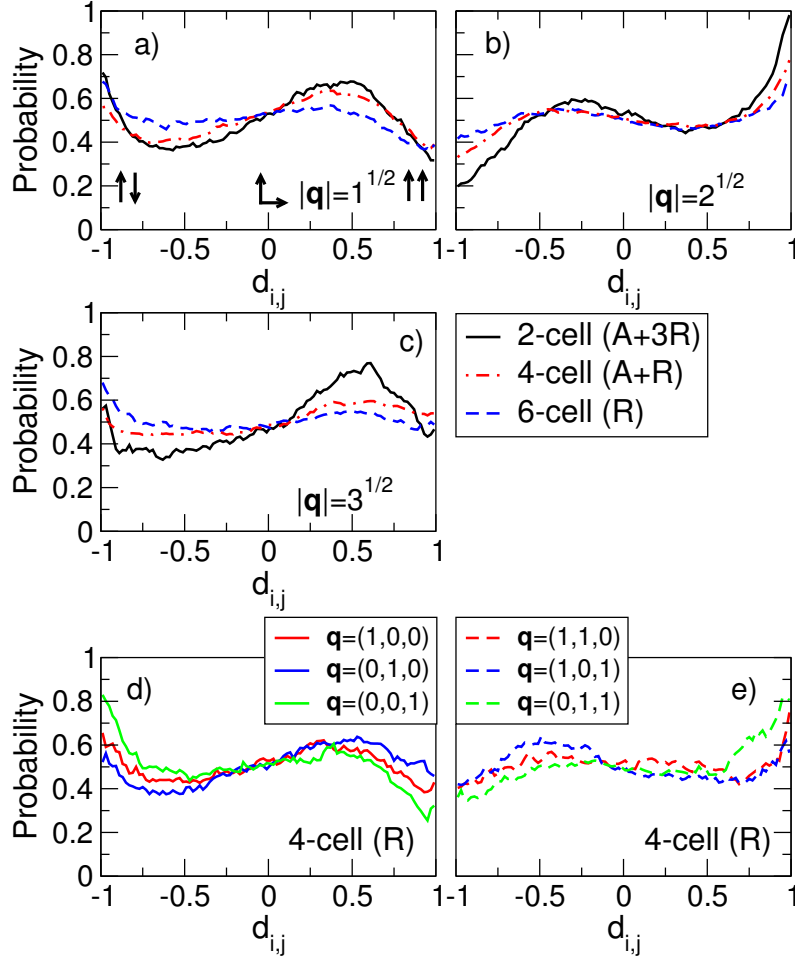


Figure III.1: (color online) Static correlation between molecules at 300 K in the a) 1st, b) 2nd and c) 3rd n.n. shells expressed by the distribution of $d_{i,j}$, going from AFE ($\uparrow\downarrow$) to FE ($\uparrow\uparrow$) alignment. The red/blue/green lines correspond to the 2-cell/4-cell/6-cell, respectively. The three different directions for the d) 1st (cubic axis) and the e) 2nd (face-diagonal) n.n. in the 4-cell at 300 K. (Integral of the $d_{i,j}$ distributions are normalised to one.)

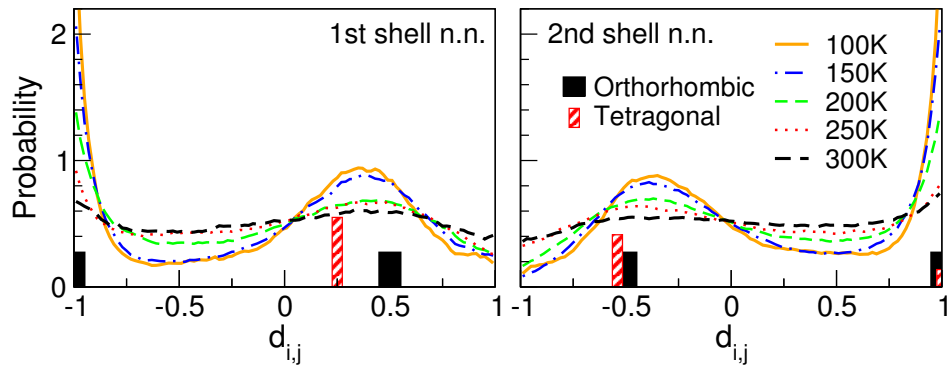


Figure III.2: (color online) Static correlation between molecules in the 1st (left) and 2nd (right) n.n. shell of the 4-cell at temperatures between 100 and 300 K expressed by the distribution of $d_{i,j}$. The dot product values corresponding to the ideal molecular ordering pattern in the orthorhombic/tetragonal phase are shown (in arb. units) by the filled/striped histograms, respectively.

with σ^2 the variance and $\bar{\theta}$ the mean of $\theta(t)$. It is an estimate of the fraction of the two signals showing linear correlation. In Figure III.3 the average values r_c^2 are plotted. This is the average $r_{i,j}^2$ over all pairs i, j with distance $d = |\mathbf{r}_i - \mathbf{r}_j|$ and ranges between 0-100%. 12 ps long trajectories of the 4-cell MD calculations at different temperatures have been used. Qualitatively the same picture appears when the

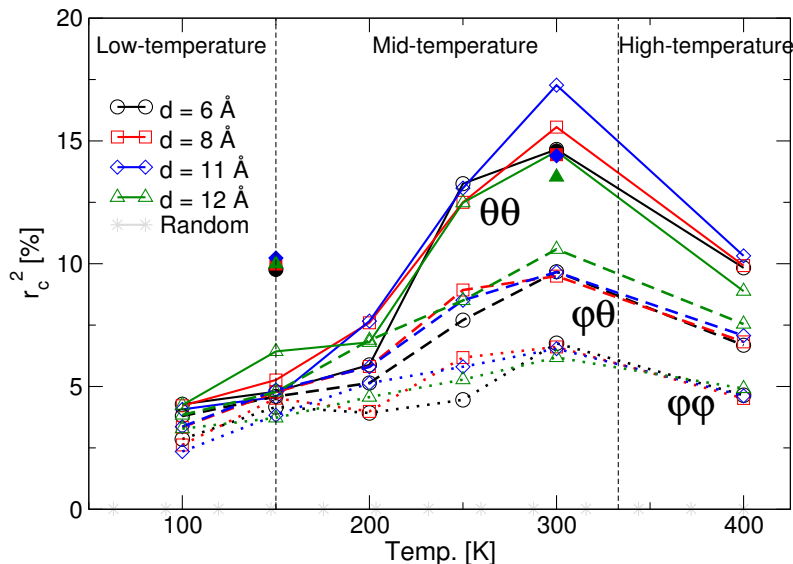


Figure III.3: (color online) Dynamical correlation between molecules in the first four n.n. shells of the 4-cell at temperatures between 100 and 300K expressed by square Pearson correlation coefficient (r_c^2) for $\theta_i\theta_j$, $\phi_i\theta_j$ and $\phi_i\phi_j$. The filled symbols correspond to the $\theta_i\theta_j$ correlation in the 6-cell. Experimental phase transition temperatures have been indicated by the dashed lines.

dynamical correlation of $\phi_i(t)$ with $\phi_j(t)$ (dashed lines) or $\phi_i(t)$ with $\theta_j(t)$ (dotted lines) are calculated. Random dipoles placed on the 4-cell grid result in a mere $\sim 0.02\%$ correlation. Remarkably, the dynamical correlation is temperature dependent and, even more remarkably, is independent of the distance, at least in the 4-cell considered here. This means that the movement of the molecules in the mid-temperature range is partly a collective motion. A recent Monte Carlo simulation based on a simplified model Hamiltonian of interacting MA molecules in MAPbBr_3 suggested correlation in clusters of 3 neighboring molecules.[92] We cannot predict an effective rotation cluster size (because of the limited supercell size), but in the 4-cell it seems to be greater than 3. The filled symbols in Fig. III.3 correspond to the $\theta_i\theta_j$ correlation in the 6-cell. At 300 K the same level of dynamic correlation as in the 4-cell is found, but at 150 K the value is larger. Presumably this is caused by the very limited simulation time and therefore too short equilibration time.

14 Discussion

In this next to last section, we would like to hypothesize about the origins of the dynamics of the MA molecules. J. Li *et.al.* already referred to it in Ref. [93] as the 'chicken and egg paradox' present in this system. Do the molecules determine the rotations of the PbI_6 octahedra or do the molecules follow the octahedra? Their conclusion was that the two mechanisms work synergetically. The here presented results shed new light on this issue from a time and temperature dependent viewpoint. We focus now on the, at first sight, peculiar temperature dependence of the dynamical correlation in Fig. III.3. A peak in the dynamical correlation at finite temperature is unusual. In most cases dynamical correlation decreases when temperature goes up. For example, the correlation between two next nearest neighboring atoms in a cubic crystal performing the (very correlated) motion associated to a phonon mode. If the temperature increases, modes tend to broaden and higher lying modes become occupied. This will lower the dynamical correlation between the atoms. However in Fig. III.3, in the low-temperature phase, the molecules do not possess enough kinetic energy to overcome the potential barrier imposed by the Pb-I framework. Therefore at low temperatures, where the molecules only oscillate (random thermal motion) around their equilibrium positions and rotate along the C-N axis, the motion between neighboring molecules is less correlated. In the intermediate temperature phase the reorientation times (τ_{mol}) become finite. The molecules then have enough kinetic energy to overcome the potential barrier. However, because neighboring octahedra are rotated with respect to each other in the low and mid-temperature range, the potential landscape in these phases are expected to be less isotropic compared to the high-temperature (pseudo-cubic) phase. It is therefore likely that a molecule in the mid-temperature regime can only rotate if (some of) its surrounding molecules rotate as well. The collective reorientation prevents large stress and strain interactions with the Pb-I framework. When the temperature is raised (but remaining in the mid-

temperature regime) more (concerted) reorientation pathways become available and the average level of dynamical correlation increases. When the temperature is raised even further into the high-temperature phase the kinetic energy lies above the barriers imposed by the now more isotropic potential landscape of the cage and the molecules rotate independently. Overall, we suggest that the Pb-I framework is the mediator here, coupling molecule i with j and not the electrostatic dipole-dipole interaction, which would be distance dependent.

15 Conclusion

Large supercell ab-initio molecular dynamics calculations of the perovskite solar cell material MAPbI₃ have been performed. The dynamics of the initially randomly oriented MA molecules has been studied and carefully analyzed with respect to the supercell size. We find that at 300 K the $2 \times 2 \times 2$ (2-cell, 96 atoms), $4 \times 4 \times 4$ supercell (4-cell, 768 atoms) as well as the $6 \times 6 \times 6$ (6-cell, 2592 atoms) supercells result very similar polar angle distributions of the molecules if the molecular dynamics trajectories are long enough. However, a small supercell (2-cell) can artificially constrain the dynamics of the molecules, it is more sensitive to the initial random orientations of the molecules. Therefore either long (> 100 ps) trajectories have to be calculated or a combination of multiple shorter runs starting from different independent random starting configurations has to be made. The average reorientation times (τ_{mol}) in the three supercells are of the same order. The molecules can rotate with a τ_{mol} time of ~ 7 ps. This is an upper bound because increased hydrogen masses have been used. The molecules systematically avoid the room-diagonal orientation and prefer the (slightly tilted off) face-diagonal orientations of the 'cubical' Pb-I cage.

At room temperature all relative orientations between neighboring molecules can occur. However, signs of an ordering pattern related to the orthorhombic structure smeared out by the high temperature are visible. When the temperature is lowered to 100 K the molecular ordering pattern condenses into a mixture of orthorhombic phases within the supercell. The dynamical correlation, expressed by the Pearson correlation coefficient between the $\theta(t)$ trajectories of neighboring molecules in the 4-cell, shows, in the considered temperature range of 100-400 K, a value between 5-15%. A purely random system of the same size would result in a mere 0.02% correlation. At room temperature a maximum in the dynamical correlation is observed. In this mid-temperature phase the molecules possess enough thermal energy to rotate and this process is slow enough to couple to neighbors via the Pb-I cage. The range of the coupling extends throughout the entire considered supercell. This results in (partially) collective motion of neighboring molecules driven by stress and strain interactions which are mediated by the Pb-I framework. The role of intermolecular dipole-dipole interactions is most likely negligible in this process. At lower temperatures the motions are less correlated, because the molecules randomly oscillate around their fixed orientations. Also at higher temperatures there is less correlation, because the molecules spin around freely.

Finite-temperature structure of the MAPbI₃ perovskite: Comparing density functional approximations and force fields to experiment [†]

Determining the finite temperature structure of the hybrid perovskite MAPbI₃ is a challenge for both experimental and theoretical methods. A very powerful computational method that can resolve the atomic structure is molecular dynamics (MD). The resulting structure depends on the density functional approximation (DFA) in the case of *ab initio* MD and the force field in classical MD. We compare the structure between 250 K and 400 K obtained with different DFAs and force fields in one consistent manner. The symmetry of the PbI₃ framework is analyzed as well as the relative ordering of the neighboring organic molecules inside the framework. The distribution function of the molecules is used to map out an effective energy surface for the rotation of a single molecule. This surface is accurately modeled by a pair of cubic harmonics. Available experimental data in literature are discussed and compared to the structure obtained with the different methods. The spread in these data is still too large to uniquely determine the method that 'best' describes the perovskite, however promising candidates and outliers have been identified.

[†]Lahnsteiner J., Kresse G., Heinen J., Bokdam M. Phys. Rev. Materials 2, 073604 Published 16 July 2018

Table 3: Experimental measurements of the molecular reorientation time (τ) and rotational barrier as obtained by various experimental techniques.

T [K]	Phase	time [ps]	barrier [meV]	method
300K	tetragonal	13.8	13.5	QENS [66]
-	tetragonal	-	101	Permittivity [97]
330K	tetragonal	0.463	52	NMR [45]
300K	tetragonal	3	-	IR [65]
350K	cubic	2.72	94	QENS [47]
300K	tetragonal	5.37	78	Permittivity [63]
300K	tetragonal	1.0	27	IR [64]
289K	cubic	-	108	NMR [108]

16 Introduction

The stark rise in photovoltaic efficiency of hybrid perovskites and its potential use in very thin, flexible and cheap solar cells has spiked interest in the condensed matter community. The most successful perovskite until now is the Methylammonium Lead-Iodide (MAPbI₃). The interesting dynamics of the molecules in this ionic crystal at finite temperatures and their hypothesized influence on the electronic properties[74, 62] warrant thorough investigation of its atomic structure. This perovskite system has already been studied with experimental techniques such as X-ray diffraction (XRD)[41, 77, 94, 95, 96], dielectric spectroscopy[97, 98], infra-red (IR) spectroscopy[65], nuclear magnetic resonance (NMR) spectroscopy[45, 99] or quasi-elastic-neutron scattering (QENS)[64, 47]. From the theoretical side, extensive density functional theory (DFT) studies have been performed. With *ab initio* molecular dynamics (MD) simulations, insight into the finite temperature structure has been obtained[69, 100, 101, 102, 103, 70]. Because of the necessary dimensions of the supercell to avoid spurious interactions and the limitations in computational resources, classical force fields[73, 104, 105] have been designed and parametrized relying on DFT calculations. Furthermore, the complexity of the material has inspired the construction of model Hamiltonians[68, 66, 106, 107], describing the interactions of Methylammonium (MA) dipoles on a grid, in order to determine the essential underlying physics.

Out of all these studies, a general picture arises. The MAPbI₃ perovskite adopts a stable tetragonal unit cell at room temperature (RT), while allowing for considerable movement of the Pb-I framework as well as the MA molecules. The accuracy of the different experimental methods are, however, limited, allowing for different interpretations at the level of the PbI octahedra and the MA molecules orientations. Firstly, many experiments propose rotations of MA molecules at finite temperature [97, 65, 66, 95, 98], but the measured speed of this process differs as well as the related energy barriers. At 300 K, the QENS measured rotational energy barrier for the molecular carbon nitrogen axes (CN-axes) is 13.5 meV and has a reorientation time of 13.8 ps in the tetragonal MAPbI₃ structure[66]. From dielectric permittivity measurements Onoda-Yamamuro *et.al.* [97] obtained 101 meV for the rotational barrier of the CN-axes. In a second work by Onoda-Yamamuro *et.al.* using QENS, a rotational barrier of 27 meV and a reorientation time of 1.0 ps was found [64]. Wasylishen *et.al.* used ²H and ¹⁴N NMR spectroscopy to determine the values of the rotational barrier of the CN-axes as 52 meV[45]. The experiment was carried out at 330 K for the tetragonal MAPbI₃ phase and 0.463 ps was obtained as the reorientation time. IR spectroscopy measurements were done by Bakulin *et.al.* at 300 K and they obtained a reorientation time of 3 ps[65]. Chen *et.al.* used QENS analysis on cubic MAPbI₃ at 350 K and obtained 70 meV for the rotational barrier and 2.7 ps for the reorientation time[47]. These experimental data are summarized in Table 3. Secondly, there are several experimental studies that obtain the molecular orientations. Measurements of the second harmonic generation signal at different delay time by Govinda *et.al.*, rule out the possibility of a transient ferroelectric state of the molecules under photoexcitation[98]. Whitfield *et.al.* proposes, based on synchrotron X-ray powder diffraction and time of flight neutron diffraction analysis, that the MA molecules in the cubic phase are dynamically disordered but prefer to be aligned along the principal cubic axes [95]. In the work by Weller *et.al.* powder neutron diffraction analysis is used to determine that the MA molecules in the cubic MAPbI₃ phase also align the MA molecules along the cubic axes $\langle 100 \rangle$ [94]. On the other hand, the work of Franz *et.al.*, where X-ray powder diffraction, neutron powder diffraction and synchrotron X-ray diffraction was used, reports that the molecules are oriented along the $\langle 221 \rangle$ directions of the cubic lattice[96].

In the present work the atomic structure of the MAPbI₃ perovskite is studied in a wide temperature range around the tetragonal-cubic phase transition by two computational methods: *ab initio* molecular dynamics and classical molecular dynamics. Multiple different density functional approximations (DFAs)

and force fields are analyzed in one consistent manner. Note that the choice of the DFA is a very critical one. In Ref. [109] we have reported on this issue by assessing the accuracy of different density functionals compared to accurate many body perturbation theory calculations. In short, the SCAN density functional was shown to outperform most standard and van der Waals corrected density functionals. Here, we report on our attempts to find the 'best' method by comparing calculated physical parameters to the experimentally obtained equivalents. Out of the molecular dynamics data, we determine the structure of the PbI framework by mapping the orientation of the PbI_6 octahedra onto distribution functions. Hereafter, a similar procedure is applied to the MA molecules. By a Boltzmann inversion of the MA distribution function, we calculate an effective energy surface for molecular rotation within the Pb-I perovskite cage. The corrugation energy for the molecules is then defined as the difference between the highest and lowest energy on this surface. Note that the experimental rotational barrier will be lower than this corrugation energy, because multiple reorientation pathways with a lower barrier exist on the surface. We show that this surface can be accurately described by a pair of cubical harmonics. By averaging over the autocorrelation functions of each individual molecule we obtain the reorientation times of the MA molecules. Besides the local orientation of the molecules, also the relative orientation with respect to the nearest neighbors is analyzed. We will show that the current level of accuracy and consistency in and between experiments is insufficient to assign a single 'best' density functional or force field for finite temperature structure calculations of the hybrid perovskites.

The paper is organized as follows: in Section 17 the applied computational methodology is explained. The structural analysis methods are presented in Section 18. The results of the calculations are presented in Section 19. These results are discussed and compared to experiment in Section 31. In the last Section 21, we summarize the outcomes in conclusions.

17 Computational methods

17.1 DFT

All the DFT calculations in this paper were carried out using VASP[78, 110, 79] (Vienna ab initio simulation package). The electronic minimization was computed within the projector augmented wave (PAW)[80] formalism. The Brillouin zone was sampled using 4 k-points which are set according to the cubic symmetry of the $2 \times 2 \times 2$ supercell and include the Γ , R, M and Z points. For the broadening of the one electron levels we use Gaussian smearing with $\sigma = 0.05$ eV. To treat the electron-electron exchange-correlation energy we use several different density functional approximations. The following DFAs were selected to represent a wide range of commonly used functionals: the local density approximation (LDA)[24], Perdew-Burke-Ernzerhof (PBE)[111], optPBE (vdW DFT functional based on PBE)[112], PBE with Grimme D3 vdW correction (PBE-D3)[113], PBE revised for solids (PBEsol)[81], Tkatchenko-Scheffler with vdW correction (TS)[114] and, a new meta-GGA, strongly constrained appropriately normed (SCAN)[115]. The energy cutoff for the size of the plane wave basis set was set to 250 eV for all functionals except of SCAN, for which 300 eV was used. SCAN uses the kinetic energy gradient of the wave function and therefore more accurate orbitals are required. These relatively small plane-wave basis sets are possible, because only the outer shell electrons are treated explicitly for every atom. For Pb the $(6s^26p^2)$, for I $(5s^25p^5)$, C $(2s^22p^2)$, N $(2s^22p^3)$ and H $(1s^2)$ orbitals are included in the valence shell of the pseudo-potential. The one electron orbitals are determined and converged until the stopping criterion (10^{-4} eV) for the self consistent electronic cycle is reached. The effect of spin-orbit coupling on the structure is negligible[116] and therefore was not included.

17.2 *ab initio* Molecular Dynamics

After the electronic ground state of a system has been obtained, an *ab initio* MD trajectory can be calculated by computing the forces acting on the ions using the Hellmann-Feynman theorem. The Born-Oppenheimer surface is explored by propagating the ions forward in time with a small time step. The temperature was maintained during the MD simulations by a Langevin thermostat [82, 117]. The time step was set to 10 fs for all MD calculations except when the SCAN functional was used; here a time step of 8 fs seconds was used. The smaller time step for the SCAN functional was used to get higher precision orbitals within an acceptable number of electronic minimization steps. These relatively large time steps are possible because the internal degrees of freedom of the MA molecules were constrained. The rotation of the NH_3 relative to the CH_3 group over the C–N bond was not constrained, thereby allowing the C_3 rotation of the molecule. To constrain the remaining internal degrees of freedoms, bond lengths and certain bond angles, the Shake algorithm [118, 119] was applied. This algorithm creates virtual forces for the desired degrees of freedom to maintain their values during the simulations. Additionally,

Table 4: Length (in ps) of the continues *ab initio* MD trajectories and between brackets the parallel tempering times, for pseudo-cubic $2 \times 2 \times 2$ MAPbI₃ supercells. The additional parallel tempering calculations are used for the calculation of the distribution functions.

DFA:	250 K	300 K	350 K	400 K
LDA	600	401	400	400
PBE	200	200	200	200
PBEsol	200	200	200	200
optPBE	375 (450)	200 (450)	200 (450)	200 (450)
PBE-D3	200 (200)	296 (200)	600 (200)	617 (200)
TS	500 (750)	200 (750)	200 (750)	200 (750)
SCAN	230 (264)	220 (264)	204 (264)	207 (264)

increased hydrogen masses of 4 a.u where used. The hereby reduced motion in the system makes the Shake algorithm converge faster. The increased hydrogen mass lowers the reorientation time by 10%. This was checked by comparison of two MD simulations with the same starting structure. Keep in mind that the choice of the starting structure potentially has a more sizable influence on the reorientation times than the heavier hydrogen masses[101]. As a further validity check, we compared a constrained MD simulation (Shake algorithm applied) with an unconstrained MD, the hydrogen masses were fixed to the same value but the time step was decreased to 2 fs. This test made clear that the internal molecular degrees of freedom do not influence the here presented results at all. The total simulation times are tabulated for each functional and temperature in Table 4. To improve the sampling efficiency, a parallel tempering scheme[96] was used additionally for optPBE, PBE-D3, TS and SCAN. For each DFA, four MD trajectories run in parallel with their thermostats set to 250, 300, 350 and 400 K. During the run, the temperatures can switch between the trajectories depending on the energy differences, see Ref. [109] for more details. Parallel tempering was used for the van der Waals corrected functionals, because the van der Waals forces hinder or slow down the dynamics. The dynamics using the other DFAs is so fast that it is not necessary to use the parallel tempering approach. The obtained probability distributions are the same for fixed temperature MDs (provided sufficiently long trajectories are used) as when the parallel tempering scheme is used. This was checked explicitly for the PBEsol and PBE functionals. The disadvantage of parallel tempering is that the self correlation times (τ) for the MA molecules cannot be extracted from the autocorrelation function. Therefore >200 ps long NVT trajectories were calculated additionally.

17.3 Structural Models Considered

The central objects of study in this work are $2 \times 2 \times 2$ supercells of MAPbI₃ with pseudo-cubic symmetry. The imposed lattice constants are adapted from single crystal XRD analysis[41]. The lattice constants are set to $a = b = 6.312 \text{ \AA}$ and $c = 6.316 \text{ \AA}$, therefore our supercells have a small tetragonal distortion of 0.06%. The volume of a unit cell is $V = 251 \text{ \AA}^3$. According to Wahl et al., the properties of perovskite systems are very sensitive to the unit cell volume[120]. Our initial calculations showed a sensitive dependence of the molecular orientation on the unit cell volume. Therefore, additional MD simulations of cubic unit cells with a smaller volume of $V = 245 \text{ \AA}^3$ and a lattice constant of $a = 6.257 \text{ \AA}$ were calculated for comparison. This is the equilibrium volume for tetragonal MAPbI₃ using the SCAN functional at room temperature[109].

The considered MAPbI₃ unit cell has $3 \cdot 12 = 36$ atomic degrees of freedom. After applying the constraints to the MA molecules, only 19 degrees of freedom remain. One standardized frozen MA geometry is used for all MD calculations even though different DFAs are used. This approximation was checked by calculating the optimal bond lengths and dipole moments of the MA molecule in vacuum for different functionals. As can be seen in Table 5, the differences in bond lengths between the various functionals are minor. The intrinsic dipole moment is between 2.1 and 2.2 D for all functionals, except for the LDA which contracts the C-N bond length too much and thereby reduces the dipole to 2.0 D. The PBEsol optimized molecular geometry is used for all simulations in this work. To obtain a starting configuration the molecules are placed in the PbI₃ framework with random starting orientations. Hereafter the MD trajectory is calculated and at every time step the geometry is analyzed.

17.4 Classical Molecular Dynamics

Classical molecular dynamics calculations were performed with RASPA 2.0 Molecular Software Package for Adsorption and Diffusion in (Flexible) Nanoporous Materials[121]. The forces were calculated ac-

Table 5: Molecular bond lengths (in Å) and dipole moments μ (in Debye) for the relaxed ground state structure of the Methylammonium molecule in vacuum as obtained for different DFAs.

DFA:	CN	CH	NH	μ
LDA	1.487	1.070	1.063	2.00
optPBE	1.510	1.096	1.062	2.12
PBE	1.511	1.097	1.058	2.17
PBE-D3	1.523	1.098	1.059	2.13
PBEsol	1.500	1.100	1.061	2.17
SCAN	1.508	1.093	1.058	2.17
TS	1.511	1.097	1.058	2.17

cording to two different force fields parametrized based on DFT data by Mattoni *et.al.* [73] and another one by Handley *et.al.* [105]. The force fields were implemented in the RASPA code. The simulations were done in the NVT ensemble. To maintain the temperature a Nose-Hoover thermostat was used. The time step during the MD was set to 0.5 fs and every 5th step a sample was taken which is equivalent to taking a sample every 2.5 fs. Before starting sampling, an equilibration period of 5 ps was calculated. In total 2,000,000 steps were computed without counting the equilibration steps. This corresponds to a total sample number of 40,000 steps and a total simulation time (without equilibration time) of 1,000 ps. For the van der Waals and the Coulomb interactions the cutoff radii were set to 12 Å which is slightly smaller than half of the box size. The electrostatic interactions are calculated with the Ewald summation method and the precision is set to 10^{-9} . The lattice vectors are the same as for the *ab initio* molecular dynamics, but larger $4 \times 4 \times 4$ super-cells were used and the constraints on the molecules were omitted.

18 Structure Analysis method

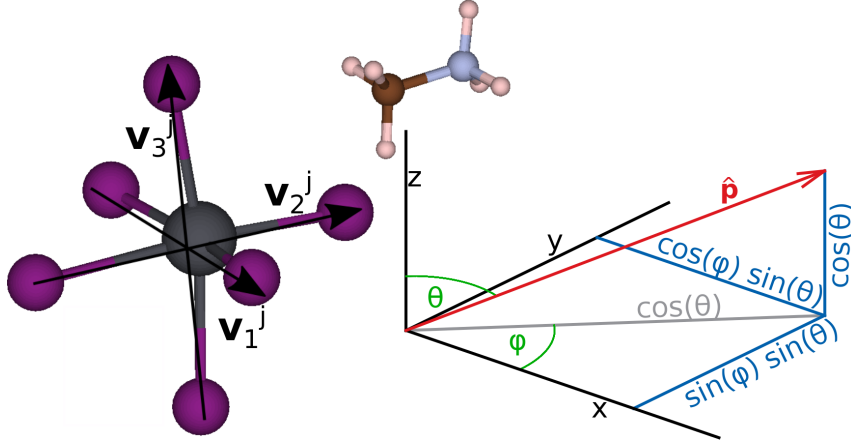


Figure IV.1: The j^{th} lead atom with surrounding iodine atoms. $\hat{\mathbf{v}}_\nu^j$ denotes the iodine-iodine vectors defined in positive Cartesian direction ν . The PbI framework creates a cubical cavity in which the MA molecule reorients. This movement is described by the unit vector $\hat{\mathbf{p}}$ parallel to the C-N axis and is expressed in spherical coordinates (θ, ϕ) .

18.1 Effective potential energy surface by Boltzmann inversion

The spherical angular distribution function $\rho(\theta_i, \varphi_i)$ of the vector $\hat{\mathbf{p}}$ describing the C–N axes of the MA molecule is extracted from the finite temperature MD trajectories. As illustrated in Figure IV.1, θ denotes the angle of $\hat{\mathbf{p}}$ with the $\hat{\mathbf{z}}$ direction of the coordinate frame, and φ is the angle in the $\hat{\mathbf{x}}\hat{\mathbf{y}}$ -plane, chosen to be zero when aligned with the $\hat{\mathbf{x}}$ -axes. After assigning the molecules for all time frames to the directions (θ_i, φ_i) , the cubic symmetry of the lattice is invoked to down-fold these spherical distributions onto a single octant. The same procedure was used in Ref. [101], where it was shown that the dynamical correlation between the neighboring molecules is low. Here, we approximate the spherical angular distribution function $\rho(\theta_i, \varphi_i)$ to be independent of the other molecules as well as of the cage. Therefore we can average over all molecules, $\rho(\theta, \varphi) = \frac{1}{N} \sum_i \rho(\theta_i, \varphi_i)$. The probability distribution $\rho(\theta, \varphi)$ for a particular

molecular orientation can be written as,

$$\rho(\theta, \varphi) = \frac{e^{-\beta E(\theta, \varphi)}}{\int_0^\pi \int_0^{2\pi} e^{-\beta E(\theta, \varphi)} d\varphi d\theta} = \frac{e^{-\beta E(\theta, \varphi)}}{\mathcal{Z}}, \quad (\text{IV.1})$$

with $\beta = \frac{1}{k_B T}$, k_B the Boltzmann constant, T the temperature and $\mathcal{Z}$ the partition function in the independent molecule picture. The potential energy surface of the molecules is calculated from the down folded polar distributions by a Boltzmann inversion. The effective energy surface $E(\theta, \varphi)$ denotes the energy of a molecule being oriented along a certain direction. Taking the natural logarithm of Eq. (IV.1) and solving for $E(\theta, \varphi)$ we obtain

$$E(\theta, \varphi) = -k_B T (\ln(\rho(\theta, \varphi)) - \ln(\mathcal{Z})). \quad (\text{IV.2})$$

This inversion technique determines the energy surface up to an unknown additive constant. This suffices, since we are only interested in energy differences. In this work, the energy surfaces are defined such that the minimum value of the energy surface is set to zero.

18.2 Modelling the potential energy surface

To compare the energy surfaces obtained with the different methods, a small set of cubic harmonics is fitted to the energy surfaces. Since pseudo-cubic cells are used, cubic harmonics possess the correct symmetry as long as there is no sizable symmetry breaking. The applied cubic harmonic functions can be written as

$$f_1(\alpha_x, \alpha_y, \alpha_z) = \alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_x^2 \alpha_z^2, \quad (\text{IV.3})$$

and

$$f_2(\alpha_x, \alpha_y, \alpha_z) = \alpha_x^2 \alpha_y^2 \alpha_z^2. \quad (\text{IV.4})$$

Here the α_i are the directional cosines of the C–N bond vectors ($\hat{\mathbf{p}}$). The directional cosines α_i are calculated by

$$\alpha_x = \hat{\mathbf{x}} \cdot \hat{\mathbf{p}}, \quad \alpha_y = \hat{\mathbf{y}} \cdot \hat{\mathbf{p}}, \quad \alpha_z = \hat{\mathbf{z}} \cdot \hat{\mathbf{p}}.$$

The cubic lattice and the PbI_3 cage impose symmetry on the polar distributions and energy surfaces of the molecules. The essential symmetry can be captured by a superposition of these cubic harmonics

$$E_{fit}(\hat{\mathbf{p}}) = C_1 [\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_x^2 \alpha_z^2] + C_2 \alpha_x^2 \alpha_y^2 \alpha_z^2 + C_3. \quad (\text{IV.5})$$

The potential energy surface imposed by different methods can hereby be reduced to three parameters C_1, C_2 and C_3 . The optimal parameters are calculated by least-square fittings of Eq. (IV.5) to the energy surfaces obtained from MD simulations. This step was done with the DGLS routine, part of the Lapack library[122]. In this way the noise, which remains even after the long MD trajectories, is averaged out.

The symmetry of the cubic harmonics terms of Eq. (IV.5) and the high symmetry orientations of the molecule are graphically represented on the top of Figure IV.3. Depending on the ratio between C_1 and C_2 , the maximal corrugation energy (ΔE) and the minimal corrugation energy ($\Delta E_{\min}$) can be calculated. In this model, the height of the potential barrier along the path from the $\hat{\mathbf{x}}$ orientation over the face-diagonal $\frac{1}{\sqrt{2}}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$ to the $\hat{\mathbf{z}}$ orientation is

$$\Delta E_{x \rightarrow xz} = \frac{C_1}{4}. \quad (\text{IV.6})$$

The barrier from the $\hat{\mathbf{x}}$ orientation over the room-diagonal $\frac{1}{\sqrt{3}}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$ to the $\hat{\mathbf{z}}$ orientation is

$$\Delta E_{x \rightarrow xyz} = \frac{C_1}{3} + \frac{C_2}{27}. \quad (\text{IV.7})$$

The barrier from the face-diagonal orientation over the room-diagonal to another face-diagonal is

$$\Delta E_{xz \rightarrow xyz} = \frac{C_1}{12} + \frac{C_2}{27}. \quad (\text{IV.8})$$

Lastly, when C_1 and C_2 have opposite sign (and C_2 is sufficiently large) a saddle point $\hat{\mathbf{s}}(C_1, C_2)$ appears on the surface. The barrier from the face-diagonal orientation over $\hat{\mathbf{s}}$ to another face-diagonal ($\Delta E_{xz \rightarrow s}$) was determined numerically.

18.3 Reorientation times of the molecules

For the calculation of the reorientation times (τ) of the MA molecules, the autocorrelation function averaged over all molecules is computed,

$$r(t - t_0) = \frac{1}{N} \sum_{i=1}^N \hat{\mathbf{p}}_i(t_0) \cdot \hat{\mathbf{p}}_i(t). \quad (\text{IV.9})$$

Here N denotes the number of molecules in the cell and $\hat{\mathbf{p}}_i(t_0)$, $\hat{\mathbf{p}}_i(t)$ are the C–N unit vectors at time t_0 and $t \geq t_0$, respectively. The autocorrelation function is obtained by computing a time average of Eq. (IV.9) over N_T different starting times,

$$\langle r(t) \rangle = \frac{1}{N_T} \sum_{j=0}^{N_T-1} r(t - \Delta t \cdot j), \quad (\text{IV.10})$$

with $\Delta t = \frac{T}{2(N_T-1)}$ for $N_T > 1$. In this work Δt was set to $100\times$ the MD time step, resulting in one pico-second. Hereafter, the reorientation times of the molecules are extracted by fitting $f(t) = e^{-\tau t}$ to the autocorrelation function. Since the obtained functions $\langle r(t) \rangle$ are not simple exponentials, the fit was made in two steps. First, a fit was made including the entire data range, from this we determined the half-life period τ followed by a second fit in the range $[0, \tau]$. This procedure was iterated until convergence was reached (usually after two iterations).

18.4 Molecular ordering pattern

A statistical measure for the relative orientation of the molecules is obtained by calculating the dot product between its neighboring molecules,

$$d(t) = \frac{1}{N} \sum_{i=1}^N \sum_{j \in n.n.} \hat{\mathbf{p}}_i(t) \cdot \hat{\mathbf{p}}_j(t). \quad (\text{IV.11})$$

This quantity is calculated for every time step (t) of the MD trajectory and binned into a histogram, thereby forming the probability distribution for the relative molecular orientations. This distribution is computed separately for the first, second and third nearest neighbor molecules j .

19 Results

19.1 Structure of the PbI_3 framework

In the MAPbI_3 perovskite every lead atom is bonded to six nearest neighbor iodine atoms forming an octahedron with lead in the center. As illustrated in Figure IV.1, four iodines lie in the xy plane and two along the z axes. The Pb–I bond is a mixture of a covalent and an ionic bond. Considering the MA^+ molecule as one undividable element in the ABX_3 perovskite structure, the Pb–I bond constitutes the largest contribution to the cohesive energy of the crystal. The MA^+ molecules are only weakly bonded to the framework and are electronically decoupled from it. A crucial step for the theoretical description of a material is the choice of an applicable approximation, in this case a density functional or a classical force field. To asses the different methods we have extracted the I–I bond vectors ($\mathbf{v}_\nu^j$) from the MD trajectories. The I–I bonds are chosen such that in the center of the bonds a lead atom is located, see Fig. IV.1. The vectors $\mathbf{v}_\nu^j$ are rescaled to unity as denoted by $\hat{\mathbf{v}}_\nu^j$. Next they are transformed to spherical coordinates $(\theta_\nu^j, \phi_\nu^j)$ and assigned to a two-dimensional probability distribution. This representation describes the rotation of an octahedron as a whole. Another possibility is to define lead-iodine bond vectors and transform them to spherical coordinates. This representation would also be capable to capture the internal deformations of an octahedron, but has not been pursued in the present work.

As an example of the probability distribution of the I–I vectors, the distribution obtained from a classical MD trajectory calculated with the Mattoni force field[73] is shown in Figure IV.1(a). It shows that the I–I vectors point along the Cartesian x, y, z -directions forming a cubic framework. The projection of spherical coordinates to a rectangular plot smears out the intensity of the 'north and south poles' ($\theta \pm \pi$) over a large area. Computing the integral around the x, y and z directions shows that all are equally likely. Because almost perfectly cubic supercells ("pseudo-cubic" from here on) are used, the probability distribution does not differ between the three different orthogonal I–I vectors associated with an octahedron. We will therefore zoom-in (throughout this work) on a single square around the

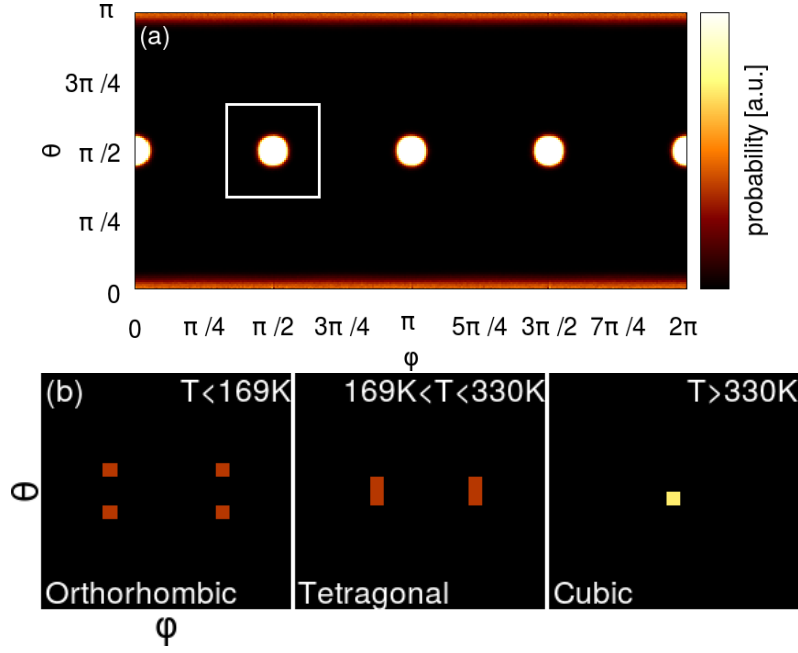


Figure IV.1: Probability distribution for angles (θ, ϕ) corresponding to the I–I bond vectors extracted from (a) an MD trajectory calculated with the Mattoni force field at 350 K and (b) typically optimized orthorhombic, tetragonal and cubic structures from Ref. [101]. (In (b) only the square area around the $\hat{y}$ direction is shown.)

y -direction (see Fig. IV.1(a)) and show the $\{\frac{\pi}{3} \leq \phi \leq \frac{2\pi}{3}, \frac{\pi}{3} \leq \theta \leq \frac{2\pi}{3}\}$ window of the plot. This zoom-in functions as a descriptor for the PbI framework are illustrated in Fig. IV.1(b). Here we have analyzed typical structures obtained by DFT PBEsol optimization of experimental orthorhombic, tetragonal and cubic unit cells[101]. The XRD experiments indicate that the iodine-iodine vectors form a characteristic tilting pattern in the xy -plane depending on the temperature[95, 94]. Qualitatively, this tilting pattern is the same along the x and y directions. When the temperature is increased, a transition from four spots in the orthorhombic phase, to two in the tetragonal phase and finally to one spot in the cubic phase is observed. In the orthorhombic structure neighboring octahedra are clockwise/counter-clockwise rotated in the xy -plane and tilted to the left/right in the z -direction. This results in four spots. The tilting in the z -direction is removed (or reduced) in the tetragonal phase and two spots remain. In the cubic structure the rotations are also removed and an, on average, simple cubic framework remains as indicated by just one spot. We will use these three characteristic distributions as a guideline to determine which structure is dominating in the MD simulations. But we need to be aware that such an assignment remains very cursory for the following reasons: (i) all simulations were performed for cubic or close to cubic cells and the tetragonal distortion was absent. (ii) This implies that tetragonally ordered structures can temporarily develop with the x , y or z axis standing out. Such patterns might prevail over a substantial simulation time, but can dynamically change in the course of the simulations from say x to y order. (iii) The exact nature of the tetragonal phase is still unknown. For instance, it could be either related to a static tetragonal order, or what we believe is more likely, it could be a highly dynamical phase that fluctuates between orthorhombic local minima.[109] (iv) Related to these issues, our simulations do not allow us to define a proper order parameter for the tetragonal phase, for instance, because the c/a ratio was kept fixed.

19.2 Temperature dependence of the PbI₃ framework

Figure IV.2 shows the probability distributions of the I-I vectors for the different computational methods at temperatures between 250 K and 400 K. We first focus on the results obtained at 350 K as shown in the third row. The different methods display distinct patterns. Since the tetragonal to cubic transition temperature is ~ 330 K, the simulations should show signs of the cubic phase and the distribution function must be symmetric around the cubic axes. The XC-functionals PBEsol, LDA, PBE, SCAN, TS and the Mattoni force field show a clear maximum along the cubic axes. The radius of the circles differ, indicating differences in the stiffness of the PbI framework. The smaller the radius, the stiffer the framework. On average, the I–I bonds appear to be perfectly aligned with the Cartesian axes. PBE-D3 and to some

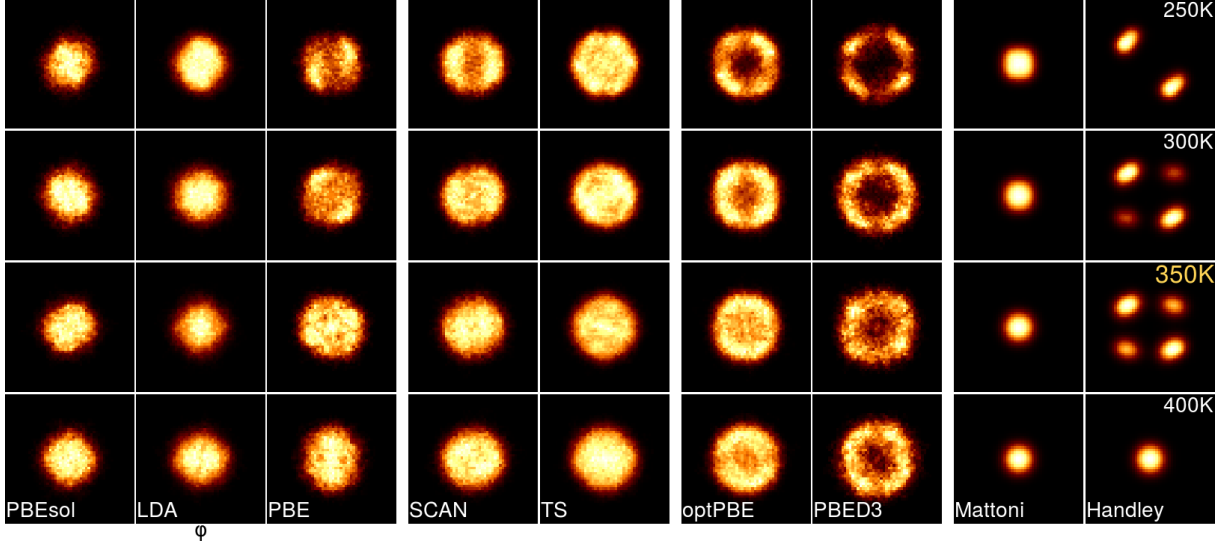


Figure IV.2: Probability distribution of angles (θ, ϕ) of the I–I bond vectors for the different methods in the temperature range from 250 K to 400 K. The center of each plot denotes the $\hat{y}$ direction $(\pi/2, \pi/2)$. The lower left and the upper right corner of each square are the $(\pi/3, \pi/3)$ and $(3\pi/2, 3\pi/2)$ directions, respectively. The brighter the color the more frequent the orientation occurs.

extent optPBE show a slightly different pattern, indicating a framework consisting of alternating rotated and tilted PbI octahedra. The distribution of the Handley force field shows four distinct sharp spots. This indicates a very rigid PbI framework with tilted clockwise/counter clockwise orientations of the octahedra in the xy -plane.

To study to what extent these methods can describe the cubic to tetragonal phase transition, the distributions at 250, 300 and 400 K have also been calculated. The columns in Fig. IV.2 show the temperature dependence of the orientational probability distributions of the I-I bonds for every method. As explained before, we expect some change but due to the deficiencies enumerated above the assignment needs to be rather cursory. The methods are arranged in four groups according to the stiffness of the framework and the shape of the distributions. If the method is able to describe the cubic to tetragonal transition, we expect to see a reduction of symmetry of the distribution ($1 \rightarrow 2$ spots) at some temperature between 400 to 250 K. The first group consists of PBEsol, LDA and PBE. This group shows deformed circularly shaped distributions around the principal axes and a stiffer framework compared to the remaining XC-functionals. The second group containing SCAN and TS shows softer framework bonds and circular distributions for temperatures above 250 K. The third group consists of optPBE and PBE-D3, they tend to avoid the directions along the principal axes. This behavior is more pronounced with decreasing temperature, especially for PBE-D3. The force fields make up the fourth group and show the stiffest description of the framework. Mattoni shows circular spots for all temperatures, whereas the Handley force field shows a “transition” not observed with any of the DFAs. Comparing Fig. IV.2 with Fig. IV.1(b) one can interpret the SCAN and PBE distributions at 250 K and the optPBE at 300 K as tetragonal like patterns. An orthorhombic like pattern can be seen in the four spots of the PBE-D3 and optPBE distributions at 250 K.

19.3 Potential energy surface of the molecules

After having characterized the structural degrees of freedom of the PbI framework, we turn our attention to the MA^+ molecules. The orientation of all molecules are extracted from the MD trajectories, and the potential energy surface as a function of the molecular orientation is calculated by a Boltzmann inversion of the distribution function. The raw potential energy surfaces are shown in Figure IV.3 (2nd row). Cubic harmonic functions (Eq. IV.5) are fitted to them and the resulting model potential energy surfaces are shown in the 3rd row. The model consists of two cubic harmonic terms (C_1 and C_2), with characteristic symmetries as illustrated in the legend of Fig. IV.3 (top) and an offset (C_3). Depending on the sign, the C_1 term suppresses or enhances the face diagonal (xz, xy, yz) and room diagonal (xyz) orientations of the molecule in the cubic PbI cage. The C_2 term only affects the room diagonal (xyz) orientations. A linear combination of the two accurately describes the original MD surfaces as is verified by calculating the Pearson-correlation coefficient between the two, see Tables 13 & 14 of the Appendix. As rule of

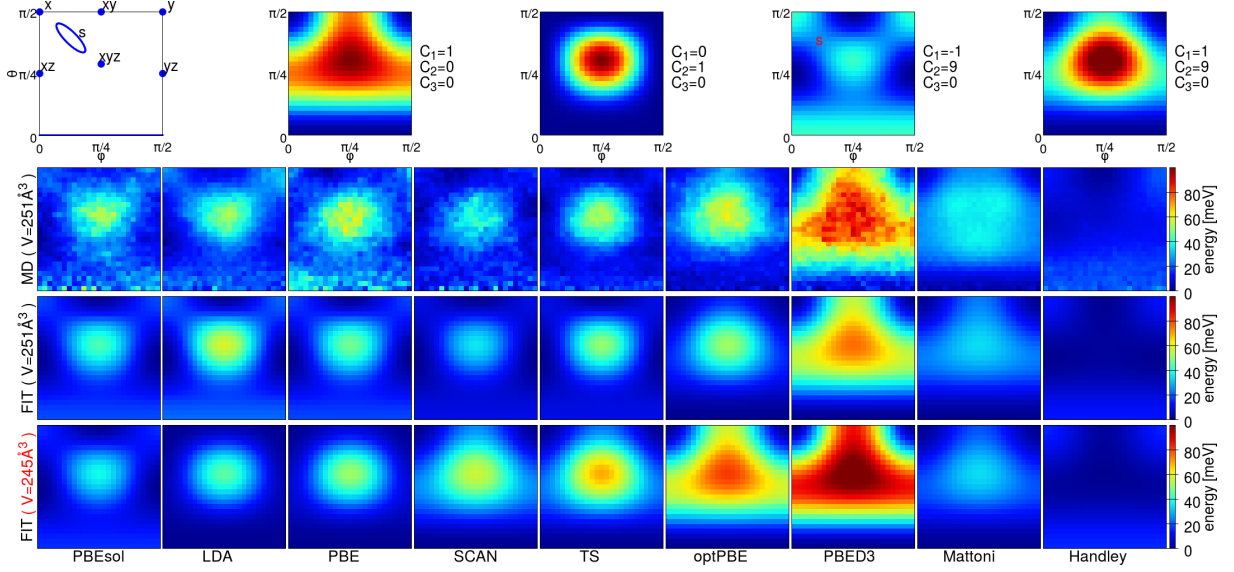


Figure IV.3: Effective potential energy surfaces of the MA^+ molecules for different DFAs and force fields at 350 K. **1st row:** (From left to right) The high symmetry orientations, cubic harmonic functions f_1 , f_2 and two linear combinations of them. **2nd row:** Energy surfaces at $V = 251 \text{ \AA}^3$ obtained by Boltzmann inversion of distribution function $\rho(\theta, \varphi)$. **3rd row:** Fitted energy surfaces at $V = 251 \text{ \AA}^3$. **4th row:** Fitted energy surfaces at $V = 245 \text{ \AA}^3$.

thumb, correlation values above 0.9 indicate that the simulated data is well described. All obtained fitting parameters for the different methods and temperatures are documented in Tables 15 and 16 of the Appendix.

We focus now on the model results obtained at 350 K as shown in Figure IV.3. At this temperature the system is cubic and the molecules can preform complete reorientations since the minimal corrugation energy ($\Delta E_{\min}$) on the potential energy surface is of the order of $\sim \frac{1}{2}k_bT$. Depending on the symmetry of the surface, $\Delta E_{\min}$ can be any of the four barriers expressed by Eqs. (IV.6-IV.8) and $\Delta E_{xz \rightarrow s}$. The darker blue areas in the energy surface plots indicate the more likely molecular orientations. At this temperature all orientations occur during the MD, but some occur more often than others. The PBEsol functional tends to orient the molecules along the face diagonals xy , xz and yz as does the LDA, PBE, SCAN and the TS functional. This symmetry of the potential energy surface is captured by the sign of C_1 . Since $C_1 < 0$, the barrier between an axes orientation and the face diagonal ($\Delta E_{x \rightarrow xz}$) is negative, as can be seen in Eq. (IV.6). In the second category with $C_1 > 0$, to which PBE-D3, optPBE as well as the Mattoni force field belong, the MA molecules are primarily directed along the principal axes x, y and z . The Handley force field is an outlier, its shows a almost flat energy surface, which favors the room diagonals xyz and slightly disfavors the principal axes orientations. Table 6 shows the maximal (ΔE) and minimal ($\Delta E_{\min}$) corrugation energies for the different XC-potentials and temperatures. ΔE is defined as the difference between the extrema of the fitted energy surfaces. ΔE is slightly decreasing with temperature, making it easier for the molecules to undergo reorientations. At the same time, the framework becomes more flexible at higher temperatures. At 350 K and 400 K the corrugation energies for the different DFAs differ only slightly. At 350 K all, with the exception of two, methods show $\Delta E_{\min} \sim 13 \text{ meV}$ and $\Delta E \sim 43 \text{ meV}$. The PBE-D3 functional constrains the molecules more and the Handley force field shows a significantly flatter surface. The temperature has no effect on the dominant symmetry of the energy surface, the preferred orientations remain the same.

The volume of the supercell has a large effect on the potential energy surface. Supercells with only a 2.4% smaller volume ($245 \text{ \AA}^3$) can already have different preferred orientations for the molecules, as shown in the last row of Fig. IV.3. By contracting the cell, LDA and PBE show a slight preference for the molecules to be oriented along the principal axes. The SCAN and the TS functional are now aligning the molecules along the principal axes. The other methods do not switch the preferred orientations for the molecules. The potential energy surface for the SCAN ($V = 245 \text{ \AA}^3$, $\frac{c}{a} = 1$) calculation, is very similar to the tetragonal ($V = 245 \text{ \AA}^3$, $\frac{c}{a} = 1.01$) calculation presented in Ref. [109]. The effect of the tetragonal distortion is that a higher fraction of the molecules align along the x, y axes compared to the z axes[109].

Table 6: Reorientation times τ (in ps) and the minimal ($\Delta E_{\min}$) and maximal (ΔE) corrugation energies (in meV) of the effective potential energy surfaces of the MA molecules in MAPbI₃.

T	250 K			300 K			350 K			400 K		
	τ	$\Delta E_{\min}$	ΔE	τ	$\Delta E_{\min}$	ΔE	τ	$\Delta E_{\min}$	ΔE	τ	$\Delta E_{\min}$	ΔE
PBEsol	18	14	50	8.1	15	50	7.2	14	43	3.8	14	42
LDA	12	17	48	5.5	17	48	4.1	13	43	2.4	14	43
PBE	19	12	55	7.3	15	54	7.2	14	47	4.2	12	45
SCAN	9	10	48	5.2	10	41	3.5	8	35	2.2	9	34
TS	99	11	61	14	10	59	14	9	50	5.1	10	47
optPBE	52	20	67	31	20	62	10	14	51	6.0	13	44
PBE-D3	**	56	78	47	48	74	19	55	76	9.6	49	75
Mattoni	1.9	17	38	1.3	19	33	1.0	23	34	0.7	25	34
Handley	1.6	19	19	1.4	16	16	0.9	12	12	0.5	14	14

19.4 Reorientation times of the MA molecules

In Figure IV.4, the autocorrelation functions $\langle r(t) \rangle$ calculated from continues MD trajectories are shown. The reorientation times were determined by fitting $e^{-\frac{t}{\tau}}$ to the autocorrelation functions as described in Section 18. Table 6 shows the reorientation times for the different functionals and temperatures. The stars denote that the MD simulation became trapped in a local minimum and therefore the reorientation time can not be determined. For a free rotator with a fixed center of mass, the reorientation time τ scales with the temperature as $\frac{1}{\sqrt{T}}$. As expected, the reorientation times decrease with increasing temperature, but do not scale as for the free rotator. Only for the Handley force field, this model results in a fit with a low rms error, consistent with the previously observed flat potential energy surface. Some irregularities are observed in the PBE and TS reorientation times. One possibility is that the randomized starting configurations influenced the reorientation time. This can occur even for reasonably long MD trajectories of a $2 \times 2 \times 2$ supercell, see for more details Ref. [101]. The system can become (temporarily) trapped in a phase where the 4-fold rotation about an axis perpendicular to the C-N bond is suppressed.

19.5 Relative orientation of neighboring molecules

In the cubic MAPbI₃ crystal, every MA molecule is surrounded by 6 nearest neighbors (n.n.) molecules, 12 second n.n. and 8 third n.n. Figure IV.5 shows the relative ordering of the molecules with respect to the neighboring molecules ($d_{i,j}$) in the different shells for the two different volumes. The distributions are calculated using Eq. (IV.11) at 350 K. A parallel/anti-parallel orientation of two molecules yields $d = 1/-1$, respectively, and an orthogonal configuration yields $d = 0$. In all graphs, the red line shows the ordering with respect to the first n.n., the green line to the second n.n. and the blue line to the third

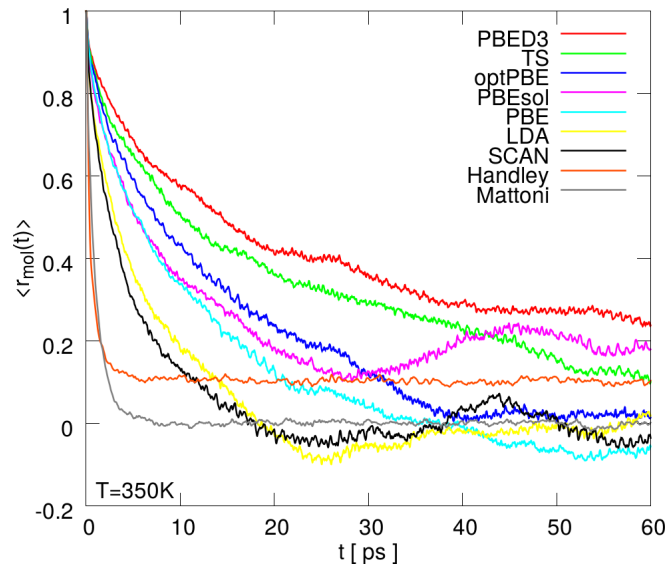


Figure IV.4: Autocorrelation functions $\langle r(t) \rangle$ of the MA molecules at 350 K for different DFAs and force fields.

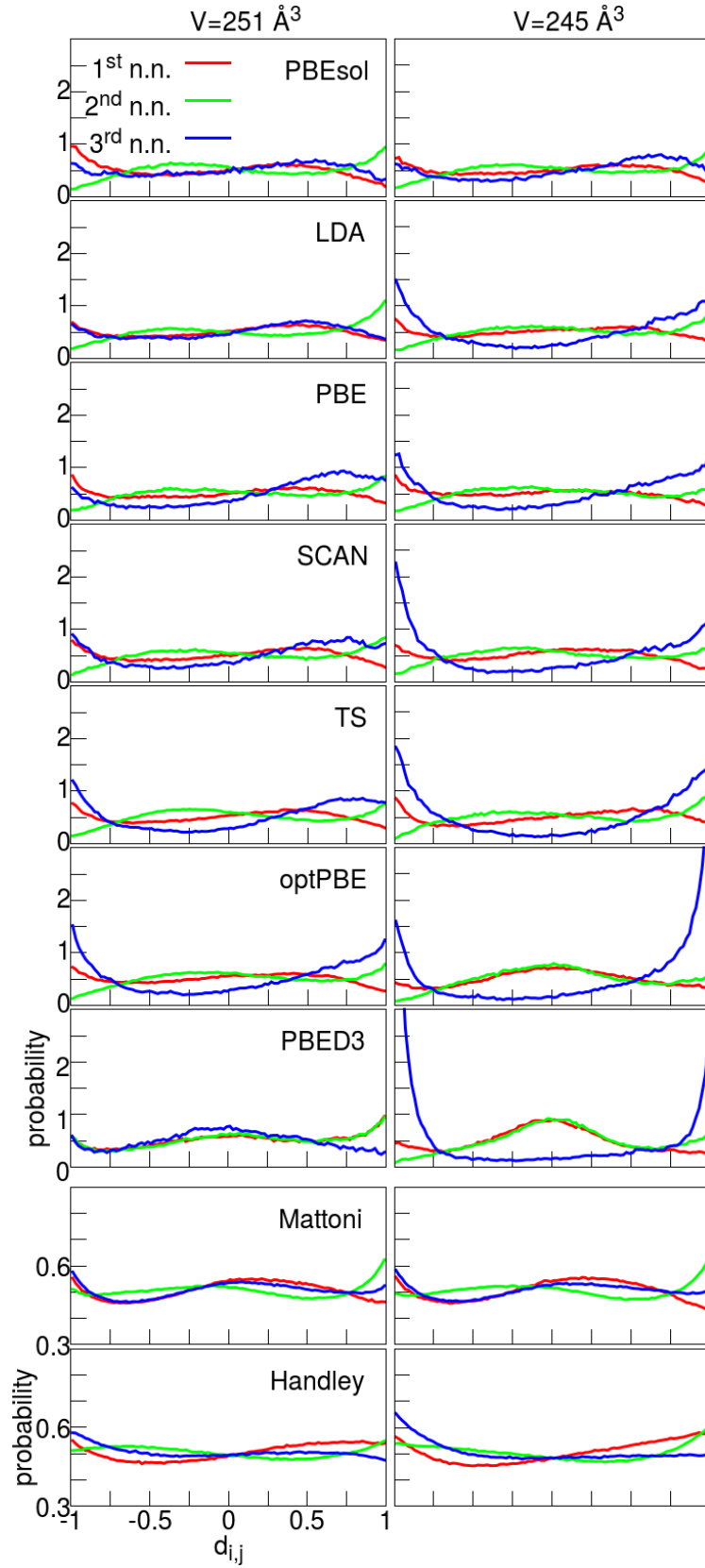


Figure IV.5: Probability distributions of relative molecular orientations ($d_{i,j}$) at 350 K. The left column corresponds to a unit cell volume of 251 Å^3 and the right column to 245 Å^3 . Three different nearest neighbor shells are shown: 1st (red), 2nd (green) and 3rd (blue). Note the different scales for the probability axes for the force fields compared to the DFAs.

Table 7: ${}_{\text{N}}\text{H-I}$ and ${}_{\text{C}}\text{H-I}$ hydrogen bond lengths and their variances for various functionals and temperatures. Units for bond lengths is $\text{\AA}$ and the variance (σ^2) in units of $\text{\AA}^2$.

	T	PBEsol		LDA		PBE		SCAN		TS		optPBE		PBE-D3		Mattoni		Handley		exp.[96]	exp.[94]
		mean	σ^2	mean	σ^2	mean	σ^2	mean	σ^2	mean	σ^2	mean	σ^2	mean	σ^2	mean	σ^2	mean	σ^2	mean	mean
${}_{\text{N}}\text{H-I}$	250 K	2.75	0.05	2.72	0.05	2.75	0.05	2.79	0.05	2.79	0.05	2.78	0.05	2.81	0.04	2.83	0.07	2.63	0.09	2.84	3.12
	300 K	2.76	0.05	2.73	0.05	2.77	0.06	2.81	0.06	2.81	0.06	2.81	0.05	2.81	0.05	2.85	0.07	2.65	0.09		
	350 K	2.77	0.06	2.74	0.06	2.79	0.06	2.82	0.06	2.82	0.05	2.81	0.06	2.82	0.05	2.87	0.07	2.68	0.10		
	400 K	2.79	0.07	2.75	0.06	2.80	0.06	2.83	0.06	2.82	0.06	2.83	0.06	2.82	0.06	2.89	0.08	2.69	0.10		
${}_{\text{C}}\text{H-I}$	250 K	3.24	0.05	3.24	0.06	3.21	0.05	3.20	0.05	3.23	0.04	3.19	0.04	3.15	0.04	3.23	0.04	2.87	0.07	3.09	-
	300 K	3.22	0.06	3.22	0.06	3.19	0.05	3.20	0.05	3.22	0.05	3.18	0.05	3.14	0.04	3.22	0.05	2.87	0.08		
	350 K	3.21	0.06	3.21	0.07	3.18	0.05	3.19	0.05	3.20	0.05	3.17	0.05	3.13	0.05	3.21	0.05	2.86	0.08		
	400 K	3.19	0.07	3.19	0.07	3.18	0.06	3.19	0.06	3.19	0.06	3.16	0.05	3.13	0.05	3.20	0.05	2.85	0.09		

n.n. shell. Extending the simulation time indicates that the results are well converged. Note that there is only one third n.n. for every MA molecule in the $2 \times 2 \times 2$ super cell, therefore the distribution shows more noise.

In the calculations with the pseudo-cubic volume of $251 \text{ \AA}^3$, a trend in the relative ordering patterns is observed. This trend has the same order of the functionals as in the effective potential energy surfaces. Both PBEsol and LDA show an alternating pattern for the different n.n. shells. The first and third n.n. distributions are, within the statistical uncertainty, the same and the second is a mirror image of the first. The peaks in the distribution for the first and third n.n. correspond to an anti-aligned or an 60° configuration. The peaks for the second n.n. are at a 140° or an aligned configuration. The distributions for PBE, SCAN and TS look similar, but the third nearest neighbor shows a small deviation from the more perfect alternating n.n. probability distribution. PBE-D3 and optPBE show a different relative ordering and do not show an alternating behavior at all. This is consistent with the potential energy surface which shows a different symmetry. The distributions of the different shells are almost the same and show, compared to the other functionals, a strong preference for orthogonal relative orientations.

When the volume of the cell is reduced to $245 \text{ \AA}^3$ only small changes are observed in the distributions for the first and second n.n. shell. However, the ordering in third n.n. shell is strongly affected. In the most volume sensitive case, PBE-D3, the third n.n. order almost exclusively parallel and anti-parallel, while the first and second n.n. order orthogonal to the central MA molecule. Its potential energy surface shows that the eight molecules in the supercell prefer to occupy the six $\pm x$, $\pm y$, $\pm z$ axes orientations with equal probability. Since the barriers between these states are high at this volume the system is frustrated. The small volume reduction has almost no effect on the force fields. The distributions are more uniform compared to the DFAs, in agreement with the calculated "flat" potential energy surfaces.

19.6 Iodine-hydrogen bond analysis

The lack of chemical bonding of the MA^+ molecule to the PbI framework makes that iodine-hydrogen bonds have an important influence on the molecular order[123, 89, 93]. The hydrogen atoms of the $\text{CH}_3\text{-NH}_3^+$ molecules can bond weakly to iodine atoms. To analyze these bonds at finite temperature, the hydrogens are assigned to two groups throughout the MD trajectory. The first group contains the carbon-hydrogens (${}_{\text{C}}\text{H}$) and the second nitrogen-hydrogens (${}_{\text{N}}\text{H}$). Next the distance of each hydrogen is computed to the closest iodine atom. The three shortest ${}_{\text{N}}\text{H-I}$ and ${}_{\text{C}}\text{H-I}$ distances are then assigned to histograms shown in Fig. IV.6. An approximately Gaussian probability distribution for the iodine-hydrogen bonding lengths is found. The average value and the variance of those distributions are shown in Table 7. The difference of the average values between the different functionals is very small and there is no clear trend visible with respect to the functionals. This also holds for the variance. For all functionals the ${}_{\text{N}}\text{H-I}$ bonding length is increasing with temperature whereas the ${}_{\text{C}}\text{H-I}$ is decreasing with temperature. This indicates that the molecules connect with the nitrogen side to the iodine atoms via hydrogen bonding. At higher temperatures the hydrogen bonding weakens and the molecules will move more to the center of the PbI cages. The ${}_{\text{N}}\text{H}$ atoms remain closer to the iodines in agreement with the higher electronegativity of the nitrogen atom. The force fields are able to reproduce the temperature trend suggested by the ab initio simulations. However, the average values of the Handley force fields are significantly shorter and the Mattoni force field shows too long ${}_{\text{N}}\text{H-I}$ bonds.

20 Discussion

In this section the structural parameters calculated with the different computational methods are compared to available experimental data. We study which calculated structural properties can act as effective selection criteria to determine the most accurate computational method(s) for MAPbI_3 .

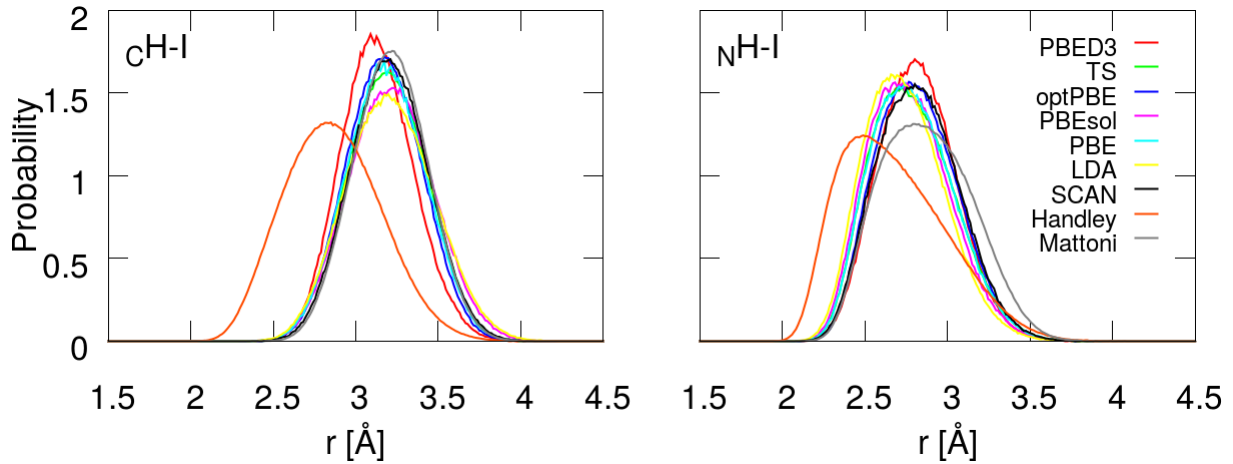


Figure IV.6: Probability distributions for the shortest C-H-I (left) and N-H-I (right) bonds at 350 K for various XC-functionals and force fields.

20.1 Structure: PbI_3 framework and MA orientations

From many experiments, it is known that the perovskite has cubic symmetry above ~ 330 K and that the framework (at least on time-average) should be aligned with the principal axes[41, 77, 94, 95, 96]. This means the orientational distributions of the I–I vectors in the framework should resemble symmetrically smeared spots, where the radius of smearing indicates the stiffness of the framework. The tetragonal phase is stable from ~ 160 K to ~ 330 K and the PbI octahedra show clockwise-counterclockwise rotations resembling a PbI zigzag pattern in the xy -plane[95, 94, 96]. In the probability distributions for the framework shown in this work, this agrees with spots left and right of the y -direction. Below ~ 160 K the perovskite possesses the orthorhombic structure which shows a 3-dimensional zigzag pattern in and out of the xy -plane [95, 94]. In the framework probability distributions this would result in 4 spots distributed around y direction. These three typical structural characteristics are shown in Fig. IV.1(b).

In all calculations the volume of the supercell has been fixed at the experimental volume at 400 K. When comparing this description to the obtained I–I distribution functions of Fig. IV.2, it is clear that at 350 K LDA, PBE, PBEsol, SCAN, TS, optPBE and the Mattoni force field describe the perovskite framework in agreement with experiment. However, LDA, PBEsol, TS and the Mattoni force field do not show a sign for a transition to a different phase when the temperature is decreased. The optPBE functional does show a sign, however a pattern resembling the orthorhombic phase starts building already at 250 K. The remaining functionals, SCAN and PBE, are able to describe the cubic phase but also show the zigzag pattern of the PbI octahedra in the tetragonal phase when the temperature is lowered. According to experiment the tetragonal phase should already be observed in the simulations at 300 K. However, since the lattice constants are kept fixed during all our simulations, the onset of the cubic to tetragonal phase transition is likely to be shifted in temperature.

The experimentally observed MA^+ orientations in the high temperature (~ 350 K) pseudo-cubic phase from three different sources are illustrated in the polar plot of Figure IV.1. In the work of Franz *et*

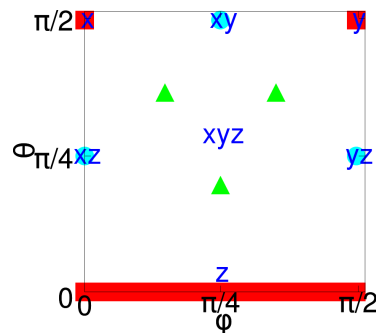


Figure IV.1: Experimental orientations found by Whitfield *et al.* [95] and Weller *et al.* [94] (red squares), Franz *et al.* [96] (green triangles) and Kawamura *et al.* [124] (turquoise circles). The labels indicate the high symmetry directions in the reduced polar distribution.

al. the molecules are shown to have a preference for a tilted of room diagonal orientation. None of the here shown methods show a preference for this orientation. At the same temperature, Whitfield *et al.* [95] and Weller *et al.* [94] observed that the molecules preferentially align along the Cartesian axes. For the simulations done at 251 Å³ only PBE-D3, optPBE and the Mattoni force field are in agreement with this experimental observation. By decreasing the unit cell volume to 245 Å³ also SCAN and TS are preferentially aligning the molecules along the principal axes. And Kawamura *et al.* [124] observed molecules orienting along the face diagonals for the cubic phase. This is in agreement with the results obtained by the non van der Waals DFAs for the simulations in the cubic volume. The large spread in the experimental data suggest that a common experimental consensus is still missing.

20.2 Energy and time related to MA reorientation

According to the here used definition of the maximal corrugation energy (ΔE) it is an upper bound to the rotational barrier for the molecules. The barrier is a statistically averaged rotation of the molecule over all pathways on the energy surface, connecting the initial with the final state, that are accessible at the considered temperature. However, this is not the only complicating factor, when comparing rotational barriers measured in experiment (see Table 3) with the barrier heights calculated in this work (see Table 6). The spread in the values among the different experiments is much larger than the spread for the different DFAs. This is not only due to the different experimental and sample conditions, but also due to the different underlying models used to extract a barrier from the experimentally recorded signals. All of the computational methods show corrugation energies (see Table 3) of roughly the same magnitude. Only PBE-D3 functional and the Handley force field can be considered to be outliers, because the corrugation energies are too large or too low, respectively. A very similar and closely related problem appears when comparing the reorientation times (τ) of the molecules. In the experimental data for the tetragonal structure at 300 K, a spread in the data from 0.5 ps to 14 ps is reported. The spread in the reorientation times obtained from the MD calculations at 350 K is of the same order. By comparing the MD data with the experimental data at 350 K, we see that the PBE-D3 functional (19 ps) differs the most from the experimental value of 2.7 ps. By comparison, SCAN fits best to the experimental reorientation time.

The experimentally measured hydrogen-iodine bond lengths ($_{\text{N}}\text{H-I}$, $_{\text{C}}\text{H-I}$) are included in Table 7. Comparing with the experimental work of Franz *et al.* [96] at 350 K, all density functionals and the Mattoni force field yield shorter $_{\text{N}}\text{H-I}$ and larger $_{\text{C}}\text{H-I}$ bond lengths. Weller *et al.* [94] reports a change in the $_{\text{N}}\text{H-I}$ bond lengths depending on the temperature: 2.61-2.81 (100 K), 3.15-3.18 (180 K) and 3.12-3.52 (352 K). The spread between the experimental data at 350 K is too large to make a best choice between the methods. The Handley force field does not give a correct description of the hydrogen bonding in the perovskite. According to the 0 K DFT structure optimization work of Li *et al.* hydrogen bonding is well described by PBE in hybrid perovskites [93]. All methods show approximately the same increase in $_{\text{N}}\text{H-I}$ as function of temperature as PBE, except for PBE-D3. We speculate that the thermal motion of the PbI framework and the MA molecule softens the hydrogen bonding and this contributes to an effective potential surface which allows reorientation of the MA molecules even at room temperature.

21 Summary and Conclusions

A comparison of *ab initio* and classical molecular dynamics methods applied to the hybrid perovskite MAPbI₃ was presented. Based on one consistent structural analysis, various density functional approximations (DFAs) and force fields were compared to experimental data. Currently, the spread in the experimental data is too large to uniquely determine the most accurate computational approach for this highly dynamic ionic crystal. However, promising candidates and outliers have been identified.

The PbI octahedra create a cavity for the molecules to move in. By calculating the distribution function of the PbI octahedra orientations at temperatures between 250 K and 400 K, we have shown that the PBE and SCAN functionals show changes in the structure that can well be related to the experimentally observed phase transition from the cubic to the tetragonal structure. For other DFAs, the evidence is less conclusive. PBEsol and LDA show no clear cut structural change upon cooling, whereas for the optPBE and PBE-D3 (and to some extent TS) the order increases, but the observed ordering rather points to an orthorhombic-like instead of tetragonal order. As eluded to in the main text, there are caveats to this statement. Since tetragonally distorted unit cells have not been considered, and since the simulation times are still short—albeit quite long by usual first principles standards—we are left with somewhat unambiguous results. In future, one would certainly like to reinspect the present results with larger unit cells, even longer simulation times, and variable cell shape simulations. Whether this will be feasible with first principle techniques in the near future remains, however, somewhat questionable.

Concerning the orientation of the MA molecules we have made the following observations. The effective potential for the molecular orientation (obtained by Boltzman inversion) can be accurately modeled by a linear combination of only two cubical harmonics. In the cubic phase at 350 K, all here considered DFAs and force fields show an effective potential energy surface and reorientation time for the MA molecules consistent with rotational freedom. The maximal corrugation energy lies between 30-50 meV, and the reorientation time lies between 4-14 ps. The van der Waals corrected PBE-D3 functional is the only exception yielding 76 meV and 19 ps. This seems fairly large and not quite consistent with most experimental findings. All DFAs agree that the molecules avoid a C-N orientation along the room diagonal. Whether the face diagonal or the principle axes are preferred, however, depends on the functional. In the high temperature cubic phase, the simple local and semi-local functionals prefer orientations along the face diagonals, whereas optPBE and PBE-D3 orient the molecules preferably along the principal axes.

A greatly troublesome outcome of our work is that the volume of the simulation cell can quite drastically change the results. In the present work, we have used two volumes for our simulations, the experimental volume of the high temperature cubic phase and the optimal volume of the tetragonal phase as predicted by the SCAN functional[109]; this corresponds to a 2 % volume change. For the SCAN and optPBE functional, this 2 % volume change changes the preferred C-N orientation of the molecules from along the principle axes to along the face diagonal. These observed changes upon a small volume decrease clearly imply that significant attention needs to be paid to the considered volumes. It also means that even in the experiment the molecules might change their preferred orientation between the lower volume tetragonal phase and the larger volume cubic phase. That such a small change of the volume can have such a drastic effect on the order of the molecules is unheard of, and requires a careful re-evaluation of simulations performed in the past.

Returning to the molecular order, we have also investigated the relative order of neighboring molecules. In particular at higher temperature (350 K), the molecular orientations are fairly random with a modest long range order. At the lower volume, the PBE-D3 and optPBE functionals lead to a more pronounced long range order than functionals without vdW corrections. This is in line with what one would expect and correlates with the slower reorientation time of the molecules for vdW functionals.

Finally, let us briefly comment on the available classical force fields. Neither the Mattoni *et al.* nor the Handley *et al.* force fields yield results that are close to any of the considered DFA functionals. Both yield a very rigid PbI framework. Additionally, the Mattoni force field shows (in the here chosen setup of fixed lattice vectors) no sign of a phase transition; the PbI bonds are always aligned to the principle axis. The Handley force field does yield a transition, most likely to the orthorhombic phase around 350 K. For the orientation of the MA molecule, the Han91dley force field shows no preferred order and resultantly a free rotator behavior with far too short reorientation times. The Mattoni force field performs better, but the reorientation speed is still too fast compared to the DFAs. Clearly the present force fields for MAPbI₃ are not satisfactory, and improvements are called for.

Taking all things together, our conclusion is that the PBE and SCAN functionals are showing a very reasonable performance in line with the experimental data. However, we have given PBE a somewhat unfair “bonus” here: the simulations were done at the experimental volume, although PBE predicts far too large volumes. Given the large volume sensitivity discussed above, we can not predict how PBE would perform had we adopted the theoretically optimized volume. This leaves SCAN as the best choice for MD simulations, and we recall that the SCAN functional predicts a tetragonal instability at temperatures close to the experimentally observed cubic to tetragonal transition temperature[109]. A final word of caution needs to be made concerning the PBE-D3 functional. As clearly shown in Fig. IV.3, the molecules are very immobile even at 350 K in the cubic structure. Also there is hardly any structural change for the PbI framework between 400 K and 250 K. We feel that this is not in agreement with the experimental data, but due to the large spread in the outcomes of the different experimental works, it is difficult to make a final judgment.

Phase Transitions of Hybrid Perovskites Simulated by Machine-Learning Force Fields Trained on the Fly with Bayesian Inference[†]

Realistic finite temperature simulations of matter are a formidable challenge for first principles methods. Long simulation times and large length scales are required, demanding years of computing time. Here we present an on-the-fly machine learning scheme that generates force fields automatically during molecular dynamics simulations. This opens up the required time and length scales, while retaining the distinctive chemical precision of first principles methods and minimizing the need for human intervention. The method is widely applicable to multielement complex systems. We demonstrate its predictive power on the entropy driven phase transitions of hybrid perovskites, which have never been accurately described in simulations. Using machine learned potentials, isothermal-isobaric simulations give direct insight into the underlying microscopic mechanisms. Finally, we relate the phase transition temperatures of different perovskites to the radii of the involved species, and we determine the order of the transitions in Landau theory.

[†]Jinnouchi R., **Lahnsteiner J.**, Karsai, F., Kresse, G., Bokdam M., Phys. Rev. Letters 122, 225701 Published 7 June 2019,
(Application of the *on-the-fly* machine-learning force field to the MAPbI₃ perovskite and determining the mechanism of the phase transitions)

22 Introduction

Predicting the finite temperature properties of materials from first principles (FP) has always been a dream of materials scientists but it has hardly been achieved except for the simplest of solids. The main obstacle is that the required system sizes and simulation times are simply not attainable using standard FP techniques. Training force fields using machine learning (ML) techniques is an obvious solution to the problem. However, what has prevented ML from being widely applied is the construction of suitable reference structures. In conventional approaches[125, 126], training structures are selected using chemical intuition, FP calculations are performed for them, and machine-learned force fields (MLFF) are fitted. Later, when the user realizes that structures outside the present training set need to be included, additional structures are added, and the force field is retrained. This is a time-consuming trial and error process often taking months for a single material, and it is practically untraceable for multielemental complex materials. On-the-fly machine learning has been suggested as an alternative possibly reducing human intervention[127, 128]. The prime progress in the present work is that the predicted (Bayesian) error is used to decide whether FP calculations are required or can be bypassed. We put our generally applicable algorithm to the test by applying it to a puzzling material exhibiting very fast hydrogen dynamics, as well as very slow rotational dynamics. The on-the-fly ML allows us to predict phase diagrams with FP quality, with so far unprecedented efficiency.

We have chosen hybrid perovskites as a first application of our scheme, because the slow rotational dynamics of the molecules makes straightforward FP molecular dynamics exceedingly time consuming. Furthermore, hybrid perovskites possess a huge scientific and technological potential. Methylammonium (MA)PbI₃ is a promising solar cell material[37, 129, 130] with a high charge-carrier mobility[49]. Many experimental and theoretical studies have been performed on its atomic structure and dynamical properties[131, 64, 77, 124, 41, 95, 63, 45, 47, 50, 73, 101, 109, 132] and they have revealed that experimentally this material exhibits two entropy-driven phase transitions from an orthorhombic to a tetragonal phase at 160 K, and from a tetragonal to a cubic phase at 330 K. Estimates of the transition temperatures from FP have not been reported to date and are elusive to be obtained using standard FP techniques alone, owing to the fact that the transitions are entropy driven. Although in the orthorhombic phase the molecules and the cage are essentially frozen, in the cubic phase the MA molecules and the cage reorient rapidly exploring a large phase space. Moreover, recent theoretical studies[132] indicate that the available semiempirical force fields are not accurate and that only few fairly expensive density functionals describe the instabilities of the cage and the interaction between the molecules and the cage with sufficient accuracy[109].

23 On-the-fly machine-learning force field

For the description of the machine learned potential energy surface, we use a variant of the Gaussian approximation potential (GAP) pioneered by Bartók and coworkers[126]. In GAP, the potential energy U of a system with N_a atoms is described as a summation of *local* atomic potential energies U_i ,

$$U = \sum_{i=1}^{N_a} U_i = \sum_{i=1}^{N_a} \sum_{i_B=1}^{N_B} w_{i_B} K(\mathbf{X}_i, \mathbf{X}_{i_B}). \quad (\text{V.1})$$

Each U_i is expressed as a linear combination of the kernel function $K(\mathbf{X}_i, \mathbf{X}_{i_B})$ and weight factors w_{i_B} . The kernel measures the similarity between the local configuration around atom i and the reference local configuration i_B . For the descriptor $\mathbf{X}_i$ and the kernel K , we adopted a variant of the Smooth Overlap Atomic Positions (SOAP)[133] (see Supplemental Materials (SM)[134]). Equation (V.1) allows to describe the energy, forces and stress tensor (EFS) for a given structure as $\phi \mathbf{w}$. Here, $\mathbf{w} = \{w_{i_B}\}$ and ϕ is a matrix containing $K(\mathbf{X}_i, \mathbf{X}_{i_B})$ and its derivatives with respect to the coordinates and lattice vectors. Similarly, the EFSs on all training structures can be summarized as $\Phi \mathbf{w}$, where Φ collects ϕ for all training structures. The parameters $\mathbf{w}$ and the uncertainty σ in the predicted EFS are simultaneously determined to reproduce the FP EFSs using the Bayesian theorem [135] as and weight factors w_{i_B} . The kernel measures the similarity between the local configuration around atom i and the reference local configuration i_B . For the descriptor $\mathbf{X}_i$ and the kernel K , we adopted a variant of the Smooth Overlap Atomic Positions (SOAP)[133] (see Supplemental Materials (SM)[134]). Equation (V.1) allows to describe the energy, forces and stress tensor (EFS) for a given structure as $\phi \mathbf{w}$. Here, $\mathbf{w} = \{w_{i_B}\}$ and ϕ is a matrix containing $K(\mathbf{X}_i, \mathbf{X}_{i_B})$ and its derivatives with respect to the coordinates and lattice vectors. Similarly, the EFSs on all training structures can be summarized as $\Phi \mathbf{w}$, where Φ collects ϕ for all training structures. The parameters $\mathbf{w}$ and the uncertainty σ in the predicted EFS are simultaneously

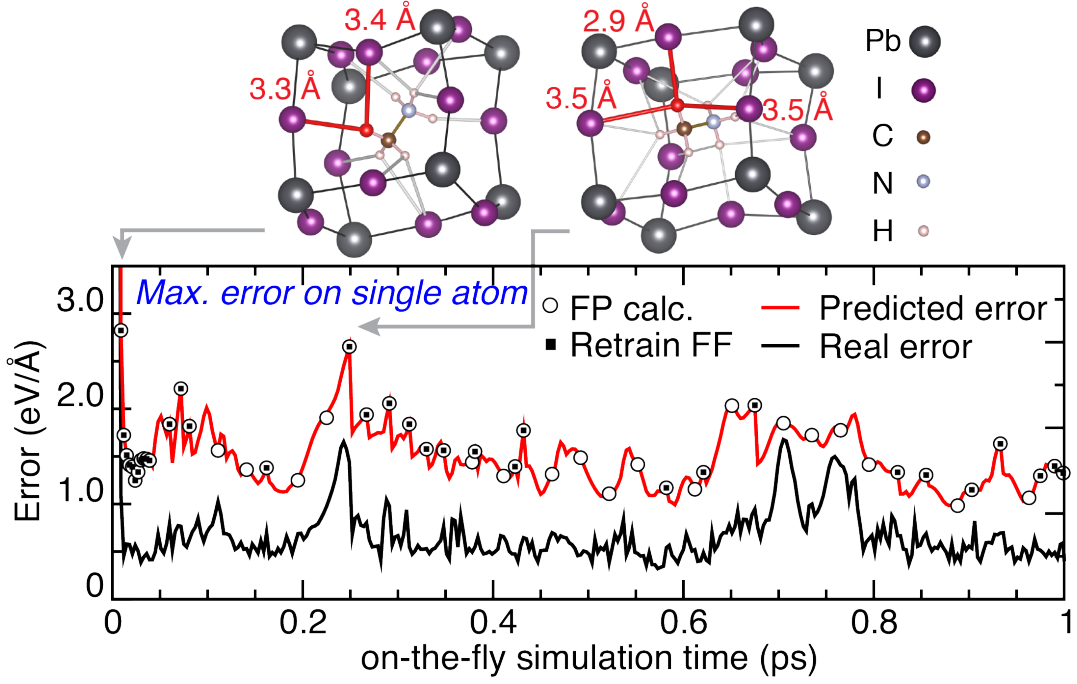


Figure V.1: The error in the force field during the first pico-second of the on-the-fly simulation. The predicted (Bayesian) error for the unitless force (provided by Eq. (V.3)) closely resembles the real error. A part of the structure at 0 and 0.24 ps is shown on top. The hydrogen atom that exhibits the largest real and predicted errors at 0.24 ps is drawn as a red sphere, and the H-I bonds shorter than 3.6 Å as red/gray lines. The simulation is executed on MAPbI₃ at 450 K.

determined to reproduce the FP EFSs using the Bayesian theorem [135] as

$$\mathbf{w} = [\mathbf{I}/\sigma_w^2 + \Phi^T \Phi / \sigma_v^2]^{-1} \Phi^T \mathbf{Y} / \sigma_v^2, \quad (\text{V.2})$$

$$\sigma = \sigma_v^2 \mathbf{I} + \phi^T [\mathbf{I}/\sigma_w^2 + \Phi^T \Phi / \sigma_v^2]^{-1} \phi. \quad (\text{V.3})$$

The FP data of the training structures enter in the vector $\mathbf{Y}$. $\mathbf{I}$ is the identity matrix. The parameters σ_v^2 and σ_w^2 are determined to balance the accuracy and robustness of the MLFF using the evidence approximation [135]. The on-the-fly scheme has been integrated within the VASP code [79, 110] (section A in SM[134]).

24 Computational methods

The actual training was performed using a state-of-the-art metagradient corrected functional [115] and running extensive FP simulations in all three experimentally known phases using $2 \times 2 \times 2$ unit cells[134]. To determine whether FP calculations are required, the Bayesian error Eq. (V.3) is used (see Fig. V.1). If the error is above a certain threshold, adjusted also on the fly, FP calculations are performed as indicated by the white circles. The FP data are used to refine the force field at the MD steps shown as black dots. In this manner, if the system stays in a local minimum, most FP calculations are bypassed, but after reordering of the PbI cage or the MA molecules FP calculations are performed as illustrated in Fig. V.1. The efficiency of the on-the-fly learning is demonstrated by the fact that during the training 99 % of the FP calculations are skipped reducing the computational time by almost a factor of 100 even during learning. This enables us to extensively explore the phase space involving slow molecular reorientations in the PbI₃ framework occurring on a ps timescale. The generated regression model predicts energies, forces and stress tensors with near-FP quality of 2.6 meV/atom, 0.07 eV/Å and 0.82 kbar, respectively (Section C in SM[134]).

25 Results

In Figure V.1(a), we show the simulated lattice constants of MAPbI₃ as a function of the temperature and compare them with experiment[95]. For this simulation $4 \times 4 \times 4$ unit cells were used (for determination of

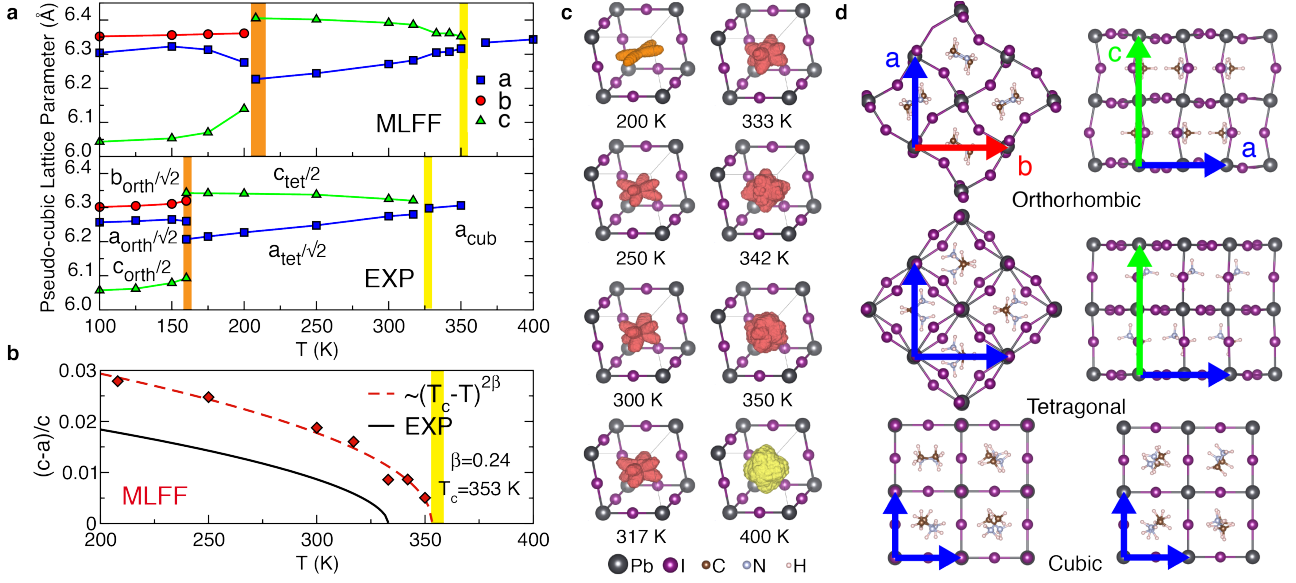


Figure V.1: Phase transitions of MAPbI_3 . (a) Simulated lattice constants compared to experiment. (b) A power law, $(T_c - T)^{2\beta}$, fitted to the simulated and experimental tetragonal distortion, $(c - a)/c$, where T_c and β are the transition temperature and the critical exponent, respectively. (c) Three-dimensional polar plots of the probability distributions of the MA molecules (C-N bond orientation) at various temperatures, ranging from 200 K to 400 K. (d) Schematic representation of the three MAPbI_3 phases as obtained by the MLFF. Experimental data shown in (a) and (b) are taken from Ref. [95], and vertical orange and yellow bars indicate the orthorhombic to tetragonal and the tetragonal to cubic phase transition temperatures, respectively.

lattice constants see section D in SM[134]). The constructed force field accurately reproduces the structure of all three phases. An analysis on the tetragonal distortion, $(c - a)/c$, shown in Fig. V.1(b) allows us to pinpoint the tetragonal to cubic phase transition temperature at 353 K. The critical exponent of 0.24 agrees well with the reported experimental results of 0.22-0.285[95] and a theoretically expected value of $1/4$ for a tricritical point on the basis of Landau theory. A careful free energy umbrella sampling[136] analysis (details in the SM[134]) was used to determine the transition temperature of 215 ± 10 K between the orthorhombic and tetragonal phase. Furthermore, for the orthorhombic to tetragonal transition, the change of the entropy at this phase transition is $1.3 \pm 0.6 k_B$ per MA molecule agreeing reasonably with the experimental value of $2.3 k_B$ [64]. The theoretical results compare well with the available experimental data and are in essence only limited by the accuracy of the density functional.

Contrary to experiment, our simulations readily provide atomic-scale insight into the entropy-driven phase transitions. As a first step, we have analyzed the orientation of the molecular C-N axis. Figure V.1(c) shows three-dimensional polar plots of the probability distribution of the molecular orientation in the PbI_3 framework at 200-400 K. In the orthorhombic phase at 200 K, the polar distribution exhibits two specific orientations predominantly along the x - or y -axis. In this phase the molecules are frozen, and their orientation alternates only spatially. In the tetragonal phase at 250 K, the molecules are also canting in $+z$ and $-z$ direction out of the xy -plane, so that eight lobes are visible. It should be noted that our previous FP MD simulations did not describe the molecular order in the tetragonal phase accurately at lower temperatures either because of the short simulation time or the fixed volume[109]. In the present simulations, at 250 K the short range molecular order is consistent with the order shown in the snapshot of Fig. V.1(d) for the tetragonal phase. Between 300 and 350 K a spherical probability distribution gradually develops, indicating that the molecules continuously obtain additional rotational freedom close to the tetragonal to cubic phase transition. In the cubic phase at 400 K, the molecules realize a nearly free rotation, whereas in the tetragonal phase, the molecules exhibit hindered reorientations. Specifically, at 350 K we predict a reorientation rate of 6.4 ps (Section F in the SM [134]) agreeing well with the experimental results of 1.0-5.4 ps at 300-350 K[64, 63, 47].

To obtain more insight on the atomic scale mechanism of the phase transitions, we performed simulations on $4 \times 4 \times 4$ unit cells using a slow heating rate of 0.5 K/ps. Even with state-of-the-art massively-parallel computers such a simulation would take several years using FP techniques alone. To unravel the microscopic mechanism of the phase transition, we introduce order parameters denoted as **O** (octahedron) and **M** (molecular) as sketched in Fig. V.1(b). The vector **O** measures the angular correlation

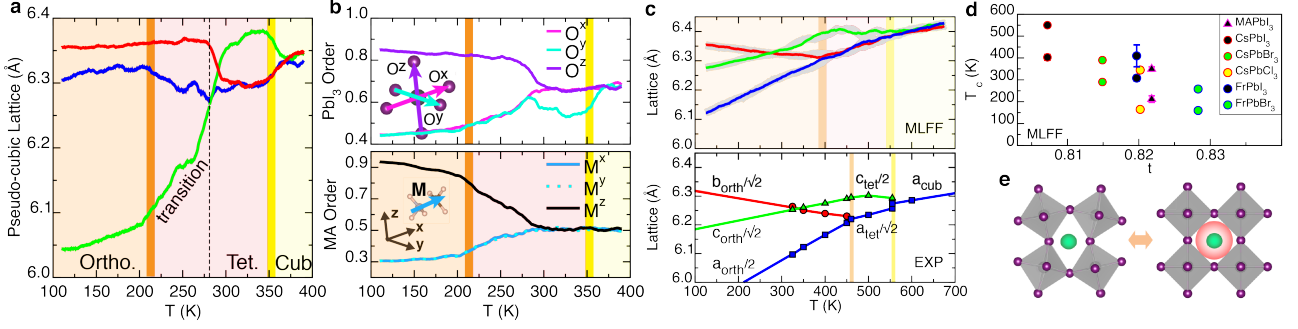


Figure V.1: Dynamics of MAPbI₃ and CsPbI₃ lattice upon heating/cooling MDs at a rate of 0.5 K/ps. Lattice constants (a) and order parameters (b) provided by the heating simulation for a $4 \times 4 \times 4$ unit cell of MAPbI₃. The black dashed line in a indicates a switch from the orthorhombic to tetragonal representation. The bond vectors used in the order parameters are sketched in the inset. (c) Simulated lattice constants for a $6 \times 6 \times 6$ unit cell of CsPbI₃ compared with experiments of CsPbI₃. Results for heating are shown using colored lines, whereas results for cooling are shown using gray lines. Experimental data shown in (c) are taken from Ref. [137]. (d) Phase transition temperatures of perovskites in dependence on the Goldschmidt tolerance factor. The circles and triangles represent the data for various ABX_3 perovskites. Lattice and order parameters for these perovskites are presented in the SM[134]. (e) Sketch of the thermal radius (r_A) of the cation.

between adjacent PbI₆ octahedra along the x -, y - and z -axis and resolves the ordering of the frame. O^x , for example, approaches unity when adjacent octahedra along the x -axis are tilted in the same direction, while it approaches zero when adjacent octahedra are tilted oppositely. Similarly, the vector $\mathbf{M}$ measures the angular correlation between adjacent MA molecules and resolves the molecular order[134]. Figure V.1 (b) shows that below 220 K adjacent octahedra are tilted in the same direction along the z -axis, while they are oppositely rotated in the xy -plane. A corresponding trend appears in the molecular order parameter. This is the typical pattern of the orthorhombic phase as illustrated in Fig. V.1(d). Between 220 K and 270 K, thermal fluctuations allow the molecules to reorient, and the three elements of the molecular order parameter gradually merge to 0.5, which corresponds to the 90-degree angle between neighboring molecules in the tetragonal phase. The octahedral order parameter changes rather abruptly to the tetragonal pattern after the transition in the molecular order parameter has finished (drop of O^y in Fig. V.1(b) at 270 K). These results clearly indicate that the transition of the PbI₆ octahedra occurs after the reorganization of the molecules has completed, in other words, the molecules seem to inhibit the transition. The exact same trend is observed in a constant temperature MD at 220 K shown in Section D in the SM[134].

All in all, our simulations suggest that the orthorhombic to tetragonal transition is first order. The transition region in Figs. V.1(a) and (b) is a result of the still fairly fast heating compared to experiment and slow dynamics of the MA molecules. The second transition from the tetragonal to the cubic phase, however, is continuous, since the lattice parameters and order parameters evolve smoothly. This also agrees with the reversibility, i.e. upon cooling the cubic to tetragonal transition is readily observed (see Fig. D1 in the SM[134]) and the hysteresis between heating and cooling is small.

The phase diagram of MAPbI₃ is well known experimentally. In order to test the methodology for a less well-studied material, we move to CsPbI₃, where the experimentally observed phases strongly depend on the process of heating and annealing as well as sample preparation, and thus, their interpretations are still controversial[137, 138]. Figure V.1(c) shows the simulated lattice constants as a function of the temperature. The force-field generation and MD simulations are described in the SM[134]. Our MD simulations show two now clearly continuous phase transitions between orthorhombic and tetragonal at 403 ± 13 K, and between tetragonal and cubic at 550 ± 5 K. These transitions are also fully reversible and are observed both under heating (shown as colored lines) and cooling (shown as gray lines). The simulated lattice constants agree well with the experimental results reported by Marronier *et al.*[137]. The difference between MAPbI₃ and CsPbI₃ is related to the slow, extra rotational degrees of freedom of the MA molecule, which become accessible only in the tetragonal and cubic phases, whereas for Cs only lateral rattling movements become progressively more pronounced upon heating.

Although both perovskites exhibit similar crystallographic structures, the transition temperatures of MAPbI₃ are significantly lower than those of CsPbI₃. In order to better understand the origin of this difference, we further extend our on-the-fly scheme to other inorganic perovskites ABX_3 (A =Cs or Fr, B =Pb, and X =I, Br or Cl). Comparison of the transition temperatures with the Goldschmidt

tolerance factor[?], $t = (r_A + r_X)/(\sqrt{2}(r_{\text{Pb}} + r_X))$, indicates that the different transition temperatures relate reasonably well with the size of the ions. Here, r_A , r_{Pb} and r_X denote the ionic radii of cation A , Pb and halogen X , respectively. The determination of these radii is described in Section G in the SM[134]. Figure V.1(d) illustrates that the transition temperatures of the hybrid perovskites decrease with increasing tolerance factor. This trend can be explained by the mechanism described below. The calculated tolerance factors of the inorganic perovskites indicate that the PbX_6 octahedra need to tilt in order to allow the formation of multiple bonds between the cation A and the halogen X . Without tilting, the Pb-halogen distance ($r_{\text{Pb}} + r_X$) is too large compared to the optimal cation-halide distance ($r_A + r_X$). The prediction is consistent with the fact that all six perovskites exhibit the orthorhombic phase at low temperature. The situation, however, changes with rising temperature. The effective radius of the cation A increases by thermal fluctuations (as schematically shown in Fig. V.1(e)) and the tilting of the octahedra becomes unnecessary. Thus, the phase transition occurs. The necessary amount of the thermal fluctuation depends on the radii. The larger the cation A or the smaller the halide X radius, the smaller is the necessary fluctuation. Therefore, the transition temperatures decrease with increasing tolerance factor.

26 Summary and conclusion

In summary, we have shown here that the combination of FP calculations with on-the-fly ML has the potential to lead to a paradigm shift in the modeling of complex materials at finite temperature. On-the-fly ML enables an exceedingly efficient sampling of structures over a large phase space with very little human intervention. Our scheme is straightforwardly applicable to complex multielemental materials and can be easily applied to other materials science problems such as ionic diffusion or catalytic reactions. For hybrid perovskites, we obtain excellent qualitative agreement with experiment as well as useful new insights. We observe the temperature driven transition from the orthorhombic, over the tetragonal to the cubic phase to be omnipresent in Pb-perovskites. However, MAPbI_3 is in fact unique with a first-order orthorhombic to tetragonal phase transition, related to the unfreezing of the molecular rotational degrees of freedom.

Long-range order imposed by short-range interactions in methylammonium lead iodide: Comparing point-dipole models to machine-learning force fields [†]

The crystal structure of the MAPbI₃ hybrid perovskite forms an intricate electrostatic puzzle with different ordering patterns of the MA molecules at elevated temperatures. For this perovskite three published model Hamiltonians based on the point-dipole (pd) approximation combined with short-range effective interactions are compared to a recently developed machine-learning force field. A molecular order parameter is used to consistently compare the transformation of the anti-ferroelectric ordering in the orthorhombic phase upon raising the temperature. We show that the ground states and the order-disorder transition of the three models are completely different. Our analysis indicates that the long-range order in the low-temperature orthorhombic phase can be captured by pd-based models with a short cutoff radius, including the nearest and next-nearest neighbor molecules. By constructing effective atomic interactions the ordering can already be described within a 6 Å radius. By extracting the coupling energetics of the molecules from density functional theory calculations on MA_xCs_{1-x}PbI₃ test systems, we show that the pd-approximation holds at least for static structures. To improve the accuracy of the pd-interaction an Ewald summation is applied combined with a distance dependent electronic screening function.

[†]Lahnsteiner J., Jinnouchi R., Bokdam M., Phys. Rev. B 100, 094106 Published 12 September 2019

27 Introduction

The finite temperature structure of the promising Methylammonium-Lead Iodide (MAPbI_3) hybrid perovskite solar cell material is characterized by a vast number of accessible macro-states related to the orientational degree of freedom of the Methylammonium (MA) molecule. Above ~ 333 K, a cubic crystal structure is formed by PbI_6 octahedra enclosing MA molecules. Below ~ 150 K, an orthorhombic lattice is formed, with molecules in a long-range ordered pattern. The $\text{MA}^+\text{Pb}^{2+}\text{I}_3^-$ system is held together by a mixture of covalent and ionic bonds, whereby the MA molecule is chemically decoupled from the PbI framework. Weak (hydrogen, van der Waals) bonds link the MA molecule to the framework[123, 88, 89, 93], and the intrinsic dipole moment ($|\mathbf{p}|$) of the molecules couples them, even more weakly, to each other[74]. There is a large spread in the reported MA preferred orientations as well as in their rotation barriers (10-100 meV), see Ref. [132] and references therein. On one thing all seem to agree, at room temperature and above the molecules show entropic disorder[63] in their orientations. It is important to understand the ordering pattern (or lack thereof) of the MA molecules, since the orientation of the molecules are connected to various physical effects (screening, charge localization, polarons, Rashba) which affect electronic device properties[74, 139, 140, 141, 142, 62, 143, 144, 145, 98]. Previous first-principles based molecular dynamics (FPMD) calculations have indicated that a soft long-range ordering pattern between neighboring MA molecules remains at room temperature [101, 132]. This order is a remnant of the highly ordered molecular pattern in the low-temperature orthorhombic phase. This order has been well resolved in experiment and is sketched in Figure VI.1. This pattern also shows the lowest energy in DFT calculations[83, 84, 85, 86, 88, 101]. However, the length and time scales required to model the finite temperature structure occurring in real devices exclude a straightforward application of FPMD methods. Therefore effective model Hamiltonians that describe the potential energy surface of MA molecules on a lattice could be of great help in understanding the local structure at defects[146] and domain boundaries[147]. The presence of the reorienting molecules makes it difficult to apply models used for other perovskites, like BaTiO_3 [148]. Therefore point-dipole (pd) based model Hamiltonians[68, 66, 149, 92, 106, 107, 150, 151, 147], a rigid rotor cluster expansion[152] and classical force fields[73, 105] have been designed. Often pd-models have been constructed in such a way that the heat capacity as function of temperature and/or phase transitions resemble experimental data. In some cases the coupling energies of certain inter-molecular ordering patterns have been fitted to DFT energies calculated for (relaxed) surrogates of the structure at different temperatures obtained from the experiment[131, 64, 77, 41, 124, 95]. The local microscopic structure is in most experiments only observed on a time and space average. These surrogates show dynamic instabilities that manifest themselves as imaginary phonon frequencies in FP calculations[58, 153]. This indicates that the higher temperature crystal phases are possibly entropically stabilized. When many different micro-states of the molecular orientation are accessible, the related gain in entropy can shift the Gibbs free energy of the system such that the tetragonal and cubic phases are stabilized under certain temperature and pressure conditions.

In this work, we compare the inter-molecular structure at elevated temperature described by three recently published pd-based models[68, 66, 107, 106] to a highly accurate machine learned force field (MLFF)[154]. The MLFF has the advantage that it learns *on-the-fly* during FPMD and generates ensembles that are practically indistinguishable from FPMD at much lower computational cost. By Monte Carlo calculations we study the change of this ordering pattern for the different models when the temperature is slowly raised. We show that the models have completely different ground states as well as excited states. Only one of the three considered models (Model III [106]) shows similar phase

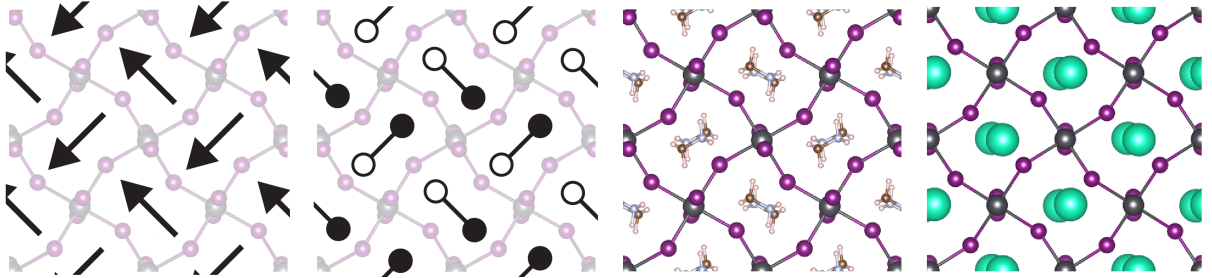


Figure VI.1: The low temperature orthorhombic structure of MAPbI_3 in the i) point-dipole model, ii) monopole model and iii) the machine-learning force field. Arrows indicate the point-dipoles $\hat{\mathbf{p}}$, and their monopole based equivalents are shown by the black & white circles. The low temperature orthorhombic structure of CsPbI_3 [138] is shown in the last figure.

transitions as the MLFF. With DFT calculations on cubic $\text{MA}_x\text{Cs}_{1-x}\text{PbI}_3$ supercells we demonstrate that the pd-approximation of the MA molecule has a limited accuracy. By summing the dipole-dipole (d-d) electrostatic energy by means of an Ewald sum and by introducing a distance dependent model screening function we improve the accuracy. We show that the d-d coupling effectively splits the degeneracy of the states imposed by the short-range part of the Hamiltonian. These short-range interactions are the dominant energetic terms as can already be inferred from the experimentally observed long-range order in the low-temperature structure (Fig. VI.1). The molecules do not display a "striped" configuration (anti-ferroelectric aligned columns of head-to-tail dipoles) as would be expected for pure d-d interactions, but rather close to orthogonal orientations. Our analysis indicates that essence of this long-range order can be reduced to effective interactions within a 6 Å radius.

This paper is organized as follows. In Section 28 we introduce the different model Hamiltonians, followed by a description of the applied Monte Carlo strategy and computational details in Section 29. The results are presented in Section 30 and, for readability, split into several subsections. The paper is closed with a discussion in Section 31 and its conclusions are summarized in Section 32.

28 Model Hamiltonians

Several model Hamiltonians describing the interactions of MA dipoles on a grid have been proposed in the last five years[68, 66, 149, 92, 106, 107, 150, 151, 147]. In these models an effective Hamiltonian splits the total interaction energy of all N molecules in the cell in a short-range framework-dipole interaction and a long-range dipole-dipole interaction: $H = H_{\text{sr}} + H_{\text{lr}}$. The interaction terms are often very similar in these models, therefore we will limit the analysis to three representatives. For the models here considered (hereafter referred to as, I[68, 66], II[107], III[106]), the long-range part (H_{lr}) is based on the electrostatic interaction energy of two point-dipoles

$$U(\mathbf{p}_i, \mathbf{p}_j, \mathbf{n}_{ij}) = \frac{|\mathbf{p}|^2}{4\pi\epsilon_0\epsilon_r} \frac{1}{r_{ij}^3} (\hat{\mathbf{p}}_i \hat{\mathbf{p}}_j - 3(\hat{\mathbf{p}}_i \cdot \hat{\mathbf{n}}_{ij})(\hat{\mathbf{p}}_j \cdot \hat{\mathbf{n}}_{ij})), \quad (\text{VI.1})$$

where $\hat{\mathbf{p}}_i$ and $\hat{\mathbf{p}}_j$ denote unit dipole vectors at different lattice sites. The distance between the dipoles is given by $r_{ij} = |\mathbf{n}_{ij}|$, and $\hat{\mathbf{n}}_{ij} = \mathbf{n}_{ij}/|\mathbf{n}_{ij}|$ is the unit displacement vector. The total long-range energy is then calculated by a sum over all neighbors within the interaction radius (r_c) and then summed over all lattice sites,

$$H_{\text{lr}} = \frac{1}{2} \sum_{i=1}^N \sum_{j \in r_c} U(\mathbf{p}_i, \mathbf{p}_j, \mathbf{n}_{ij}). \quad (\text{VI.2})$$

All dipoles have the same dipole moment $|\mathbf{p}|$, but the relative permittivity ϵ_r and the long-range cutoff (r_c) depend on the model. In model II the Ewald summation technique is used to compute H_{lr} . In the three models, the prefactor in Eq. (VI.1) is treated as an effective coupling constant for which an optimally tuned value is used. These values can be compared by ϵ_r when we define the dipole moment of the MA molecule to 2.29 D[68]. This results in $\epsilon_r^{\text{I}} = 1$, $\epsilon_r^{\text{II}} = 0.73$, $\epsilon_r^{\text{III}} = 1.5$.

The short-range interaction (H_{sr}) is differently modeled in models I, II and III. In model I, it is described by a linear pair potential,

$$H_{\text{sr}}^{\text{I}} = -K \frac{1}{2} \sum_{i=1}^N \sum_{j \in \text{NN}} \hat{\mathbf{p}}_i \cdot \hat{\mathbf{p}}_j, \quad (\text{VI.3})$$

where the first sum runs over all lattice sites and the second sum over the nearest neighbors (NN). The parameter $K = 25$ meV approximates the strain on the framework and favors the parallel arrangement of dipoles. Both models II and III use a penalty potential of the form,

$$H_{\text{sr}}^{\text{II/III}} = \frac{1}{2} \sum_{i=1}^N \sum_{j \in \text{NN}} g(\hat{\mathbf{p}}_i, \hat{\mathbf{p}}_j). \quad (\text{VI.4})$$

The strength of the penalty depends on the relative orientations of NN molecules as sketched in Figure VI.1. In model II, two interaction modes are described: the pair of molecules lies "flat" in a common plane $[(\hat{\mathbf{p}}_i \times \hat{\mathbf{p}}_j) \cdot \hat{\mathbf{n}}_{ij} = 0]$ and (i) they are orthogonal and one of them points to the neighbor in the pair, then $g(\uparrow, \leftarrow) = -60$ meV, or (ii) they are pointing in the same direction, then $g(\uparrow, \uparrow) = -35$ meV. For all other NN configurations that can occur, $g = 0$ meV. Model III, also describes only two pair modes, but these modes are more restricted: the pair of molecules lies orthogonal to each other in the xy -plane

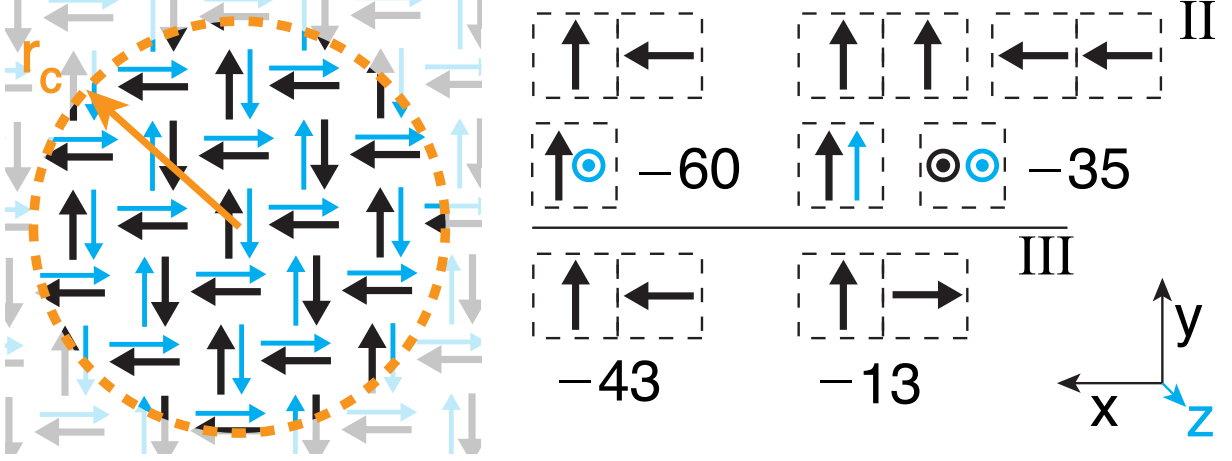


Figure VI.1: Point-dipole model on a cubic lattice with interaction radius (r_c). The pair-modes assigned in models II and III together with the corresponding penalty potentials $g(\hat{\mathbf{p}}_i, \hat{\mathbf{p}}_j)$ (in meV) are sketched on the right. The lower lying layer, into the paper z -direction, is colored in blue.

and one of them points (i) to the neighbor in the pair, then $g(\uparrow, \leftarrow) = -43$ meV, or (ii) away from the neighbor in the pair, then $g(\uparrow, \rightarrow) = -13$ meV. As before, for all other nearest neighbor configurations that can occur, $g = 0$ meV. We note that the explicit preference for the xy -plane breaks the cubic symmetry of the Hamiltonian. In reality upon cooling from cubic to the orthorhombic phase, the molecules can condense in any of the cubic planes.

In regard to the short-range interaction of Eq. (VI.4) we would like to mention the thorough work of Li *et.al.*, who have systematically analyzed the "pair-mode" concept based on $4 \times 4 \times 4$ supercell DFT calculations[150]. The pair-modes used in models II and III also appear in their study as low energy configurations.

29 Computational details

Monte-Carlo method. All the model Hamiltonians are evaluated by Monte-Carlo methods based on the Metropolis-Rosenbluth algorithm [33]. $16 \times 16 \times 16$ dipole grids based on a cubic lattice ($a = 6.3$ Å) using periodic boundary conditions were simulated. The starting configuration is a minimal representation of the molecular order in the experimental low-temperature (orthorhombic) structure. It solely consists out of x and y axes orientated molecules as sketched in Fig. VI.1, and the next plane in z direction has the same orientations anti-ferroelectrically aligned. Starting from the same configuration we calculate 20 Markov chains in parallel. The random number generator is initialized differently for every core to obtain different trajectories. Every chain equilibrates the system at the desired temperature by calculating 4×10^6 MC steps and then produces 25 equidistant samples spaced by $10 \cdot 16^3$ MC steps. Hereafter the temperature is increased by 10 K and the system is equilibrated again. This procedure is 60 times repeated, thereby raising the temperature from 0 to 600 K. Statistical averages are calculated over the chains. This setup has been carefully tested and shows converged order parameters.

Model I maps the orientational freedom of the dipoles on 26 discrete cubic orientations: $6 \times [1, 0, 0]$ (axes), $12 \times [1, 1, 0]$ (face diagonal) and $8 \times [1, 1, 1]$ (room diagonal). To avoid a bias for an orientation, we have weighted the chances in the Monte Carlo steps accordingly. Models II and III are more restrictive and allow only for the six cubic axes directions. The cutoff-radii for the long-range interaction were set as in the respective publications, ie. $r_c^I = 3a$, $r_c^{III} = 2a$. For model II the Ewald technique as presented in section 7 is used instead of the real space summation.

Density Functional Theory. For the first-principles calculations we use a plane-wave basis and the projector augmented wave (PAW) method[34] as implemented in the VASP code[78, 79, 80]. For the DFT calculations on the $\text{MA}_x\text{Cs}_{1-x}\text{PbI}_3$ test systems, the PBE (Perdew-Burke-Ernzerhof)[111] functional and standard VASP pseudo-potentials are used with a 400 eV energy cut-off for the plane-wave basis. Gaussian smearing with $\sigma = 0.05$ eV is used to broaden the one-electron levels. The Brillouin zone is sampled by a $2 \times 2 \times 2$ Γ -centered Monkhorst-Pack grid. The Kohn-Sham orbitals are updated in the self-consistency cycle until an energy convergence of 10^{-6} eV is obtained. $2 \times 2 \times 2$ CsPbI_3 super cells were constructed out of cubic unit cells with lattice constant $a = 6.3$ Å. On two sites, Cs atoms are replaced by Methylammonium (CH_3NH_3) molecules. All positions are kept fixed at their high symmetry cubic sites. The

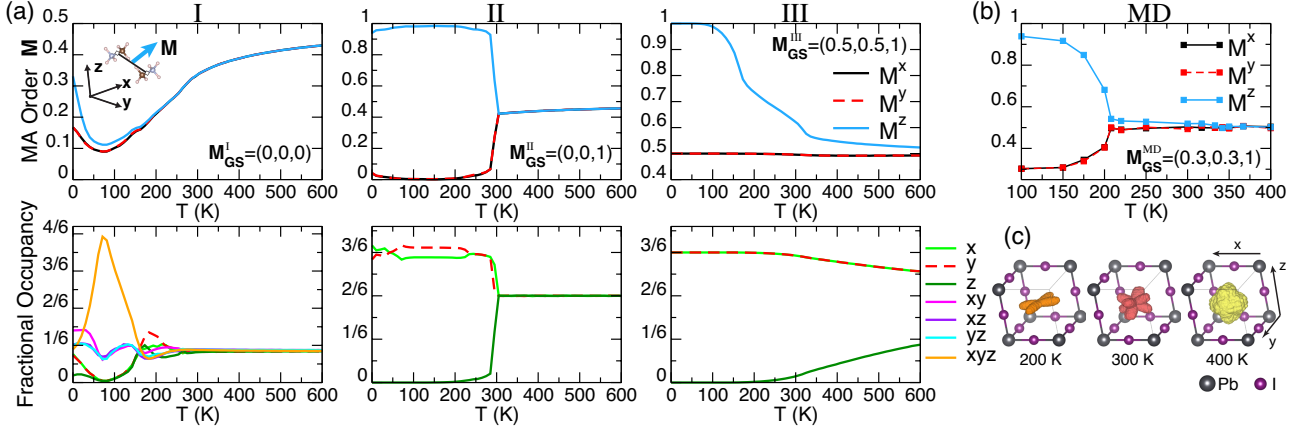


Figure VI.1: (a) Molecular order parameter ($\mathbf{M}$) and fractional occupancy of orientational states as function of temperature for models I-III. Systems (I-III) are initialized at 0 K in state $\mathbf{M}_{\text{init}} = (0.5, 0.5, 1)$ and the true ground state ordering is indicated by $\mathbf{M}_{\text{GS}}$. (b) The squares show the average order $\mathbf{M}$ obtained in constant temperature molecular dynamics (MD). (c) Three-dimensional polar distribution of the molecular C-N axes at three different temperature regimes in the MD.

central molecule is rigidly rotated in spherical coordinates around the center of the C-N bond. No ionic relaxation was performed in these test systems.

Molecular Dynamics. The machine-learned force field (MLFF) of MAPbI_3 as presented in Ref. [154] is used to generate MD trajectories. The MLFF was trained *on-the-fly* during FPMD calculations with the SCAN (Strongly Constrained Appropriately Normed) [115] exchange-correlation functional, as its relative total energies agree well with many-body perturbation theory calculations in random phase approximation [109]. The MLFF approach has the advantage that it speeds up the MD by three orders of magnitude, while retaining near FP accuracy. Note that the finite temperature structure of MAPbI_3 obtained with the MLFF is in excellent agreement with traditional FPMD [101, 132]. Further computational details are presented in Ref. [154]. Here we have calculated a 600 ps long trajectory for a $4 \times 4 \times 4$ supercell (768 atoms) in the NPT ensemble. The temperature was linearly increased from 100 to 400 K using a Langevin thermostat [82]. Since the heating trajectory shows signs of hysteresis, we have calculated the averaged molecular order parameter on constant temperature MDs. In these calculations snapshots of the heating run were equilibrated for 0.2-1.2 ns, depending on the crystal phase and temperature.

30 Results

The results of this study are presented in four subsections. We start by introducing an order parameter for the molecules that is used to compare models I-III with MD. Hereafter we study the working of the short-range and long-range interactions separately.

30.1 Molecular Order Parameter

In order to straightforwardly compare the ordering patterns of the MA molecules we calculate the molecular order parameter as briefly presented Ref. [154]. We assume an integer cubic grid $\mathbf{q} = (i, j, k)$ of dimensions $N = N_x \times N_y \times N_z$ that has on each site a unit vector $\hat{\mathbf{p}}_{\mathbf{q}}$ describing the orientation of the MA molecule. The order parameter, $\mathbf{M} = (M^x, M^y, M^z)$, is then defined as

$$M^\alpha = \frac{1}{N\pi} \sum_{\mathbf{q}} \arccos(\hat{\mathbf{p}}_{\mathbf{q}} \cdot \hat{\mathbf{p}}_{\mathbf{q}+\mathbf{n}^\alpha}), \quad (\text{VI.5})$$

where $\mathbf{n}^\alpha$ is the displacement vector to the neighboring site in the Cartesian direction α . Typical order parameters in the three different crystal phases are:

$$\begin{aligned} \mathbf{M}_{\text{ortho}} &= (0.3, 0.3, 1) \\ \mathbf{M}_{\text{tetra}} &= (0.5, 0.5, 0.53) \\ \mathbf{M}_{\text{cub}} &= (0.5, 0.5, 0.5). \end{aligned} \quad (\text{VI.6})$$

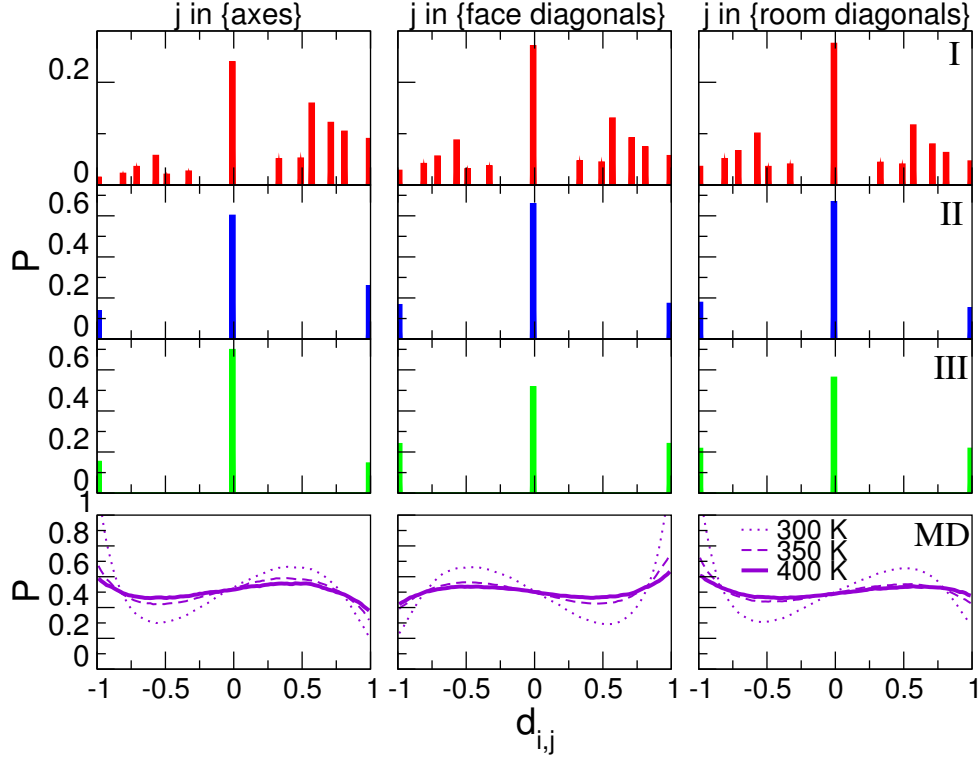


Figure VI.1: Probability distributions of the relative molecular orientations ($d_{i,j} = \hat{\mathbf{p}}_i \cdot \hat{\mathbf{p}}_j$) in the first (axes), second (face diagonal) and third (room diagonal) nearest neighbor shells at 400 K. The MD distributions at 300 and 350 K are shown additionally.

These values agree well with the experimental structures as long as the temperature is not too close to the phase transition temperature[154].

30.2 Molecular ordering at finite temperature

To compare the ordering patterns of the dipoles imposed by the model Hamiltonians, we have calculated large finite temperature ensembles by slowly heating up the experimental low temperature molecular configuration by Monte Carlo simulations. In the first row of Figure VI.1(a) the change of the order parameter ($\mathbf{M}$) during heating is shown. The initial structure for the models is described by $\mathbf{M}_{\text{init}} = (0.5, 0.5, 1)$. $\mathbf{M}_{\text{init}}$ is the closest equivalent of $\mathbf{M}_{\text{ortho}}$ described with only axes orientations of the molecules. Models I and II already break down this structure at 0 K by exothermic steps, indicating it is not the true ground state (GS). Model II switches directly to its GS, which is an anti-ferroelectric (AFE) striped pattern, $\mathbf{M}_{\text{GS}}^{\text{II}} = (0, 0, 1)$. Model I exhibits a kinetic barrier from $\mathbf{M}_{\text{init}} \rightarrow \mathbf{M}_{\text{GS}}^{\text{I}} = (0, 0, 0)$ and reaches it only partially at 75 K. The cubic symmetry breaking (indicated by different components of $\mathbf{M}$) observed at low temperature is an artefact. Its GS is the fully polarized state with molecules ordered along one of the *room diagonal* (xyz) orientations. Model III retains the initial ordering at low temperature and shows a gradual transition involving two steps to a cubic-like phase. The different behavior of model I compared to II and III does not come as a surprise, its Hamiltonian has cubic symmetry and has no short-range interaction that can stabilize "flat" molecular orientations in the xy , xz or yz planes. Models II and III do have such interactions, imposed by favoring certain pair configurations. In model II, these pairs are counted for independently in which plane they lie, therefore the observed symmetry breaking is imposed by the initial structure only.

The second row of Fig. VI.1(a) shows the fractional occupancy of each quantized molecular orientation. Model I distinguishes 26 orientations, model II and III only 6 orientations. These different degrees of freedom cannot be compared directly, but do give an intuitive picture of the structure as function of temperature. At high temperature all orientations become equally occupied. Note here that there are eight *room diagonal* orientations (xyz), compared to four *face diagonals* (xy) and two *axes* (x) orientations, therefore these directions are weighted accordingly. To build a model that describes all three crystal phases by their typical molecular orientations, one minimally needs the axes basisset. The expected occupancy of the orientations would then be for orthorhombic: $(\frac{1}{2}, \frac{1}{2}, 0)$, tetragonal $(\frac{1-\delta}{2}, \frac{1-\delta}{2}, \delta)$ and cubic: $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$.

Using the order parameter as a common reference framework, we compare the models (Fig. VI.1 a) to the MD results (Fig. VI.1 b) in order to find the best working model. Both models I and II show different ordering compared to the MD already at 0 K. Their GS ordering patterns ($\mathbf{M}_{GS}^I, \mathbf{M}_{GS}^{II}$) are totally different compared to $\mathbf{M}_{ortho}$. Model I does not mimic an orthorhombic/tetragonal to cubic phase transition, but shows a gradual changing ordering pattern with cubic symmetry. In model II, the barrier to leave the GS is roughly 300 K. The resulting transformation is manifested as a first-order phase transition (evidenced by a discontinuity in the first derivative of the order parameter) to the cubic phase. Model III shows qualitatively the best comparison with the MD. While heating up, the system undergoes two transitions at approximately 150 and 300 K. This is in agreement with the phase transitions obtained from peaks in the calculated heat capacity[106]. Similarly, the MD shows two transitions at 200 and 350 K. Each transition decreases the molecular order and brings it closer to $\mathbf{M}_{cub}$. Furthermore, it has the correct GS ($\mathbf{M}_{init}$). Still important differences between model III and the MD remain. Within the applied temperature window $\mathbf{M}_{cub}$ is not reached, and both transitions are of second order. This is at odds with experimental data indicating a first order phase transition followed by a close to tri-critical transition[95]. Interestingly, when turning off the long-range d-d interactions, model III breaks $\mathbf{M}_{init}$ down to $\mathbf{M}_{cub}$ at low temperature, even though the pair configurations only favor the xy -plane and can perfectly form the initial molecular order. We come back to this stabilizing effect in Section 30.3.

Model III can capture the essence of the long-range order in the low temperature orthorhombic phase, although it fails to reproduce the more detailed molecular orientation. These orientations are illustrated in Figure VI.1(c) by the three-dimensional distributions of the molecular C-N axis calculated from MD. An iso-surface shows the outer shell of this distribution. The three different temperatures show the typical orientations of the molecules in the three phases. These missing orientations are also important to describe the probability distributions of the relative molecular orientation ($d_{i,j} = \hat{\mathbf{p}}_i \cdot \hat{\mathbf{p}}_j$). In Figure VI.1 we see that all models show more structure at 400 K compared to the almost flat MD distributions. Furthermore, the MLFF captures the soft ordering that remains at room temperature and above, consistent with previous FPMD calculations[101]. In the first NN shell there is a broad peak at $d_{i,j} \sim 0.5$ and in the second at $d_{i,j} \sim -0.5$ and so on. When using the axes basisset, both relative orientations are mapped to $d_{i,j} = 0$. Expanding the basis with the face- and room-diagonal orientations would allow us to reach a qualitative description for these relative orientations. To get realistic microscopic structures one would have to include the dominant orientations as they occur in the MD.

30.3 Splitting of degenerate ground states by dipole-dipole interaction

In order to clarify the origin of the long-range order, we analyze the short- and long-range interactions on the molecular orientations. As shown in Section 28, the short-range interaction is the energetically dominant term in all model Hamiltonians I, II and III. It is build up of NN pair interactions, and its ground state (GS) can be studied on a $2 \times 2 \times 2$ cubic grid with periodic boundaries. Using only the 6 *axes* orientations we have calculated the total energies of all 6^8 possible ordering patterns. To illustrate the spread of these levels we have plotted the density of states (DOS) in Figure VI.2. We can roughly assess the influence of including the dipole-dipole coupling by calculating the NN interactions. In models II and III this increases the energy difference between the ground- and highest energy state (ΔE), whereas it is unaffected in model I. More importantly, many of the degenerate states are split, thereby raising the total number of different energy states (N_s). This also holds for the states occupied at room temperature (roughly those between 0-25 meV). In this small system with only NN interactions we can determine the GS exactly; model I shows a fully polarized state with multiplicity (Ω) of 6, and model II shows an AFE striped pattern also with $\Omega = 6$. Both GSs are different compared to the low temperature experimental ordering pattern of Fig. VI.1. We have summarized the characteristics of the models in Table 8, and we will now discuss model III.

In Figure VI.3, eight out of a total of $\Omega = 1024$ possible ground states of *only* the short-range interaction (Eq. (VI.4)) as parameterized in model III are sketched. The most in-plane polar states (highlighted in purple) that alternate between (1,1) and $(-1,-1)$ polarized layers is the expected ordering. The inclusion of NN dipole-dipole coupling splits the degeneracy of the GS and brings its multiplicity down from $1024 \rightarrow 32$. It couples the layers in the z -direction to each other and enforces their AFE ordering. Still all states of Fig. VI.3 and further symmetry equivalents are possible ground states. If the cutoff radius of the d-d interaction is extended to include the next NN ($r_c = \sqrt{2}a$), the GS of Fig. VI.3 splits into three energy levels. Whereby the (1,1) state is the new GS with $\Omega = 8$, followed in energy by the (1,0) and (0,0) state. This means that d-d interaction in model III stabilizes the long-range ordering pattern to $\mathbf{M} = (0.5, 0.5, 1)$ and makes it the GS. Note that including only NN coupling would enable a checkerboard pattern of the different orderings (shown in Fig. VI.3) at low temperature.

We now turn the problem around and use the unscreened long-range energy ($H_{lr}, \varepsilon_r = 1$), to analyze

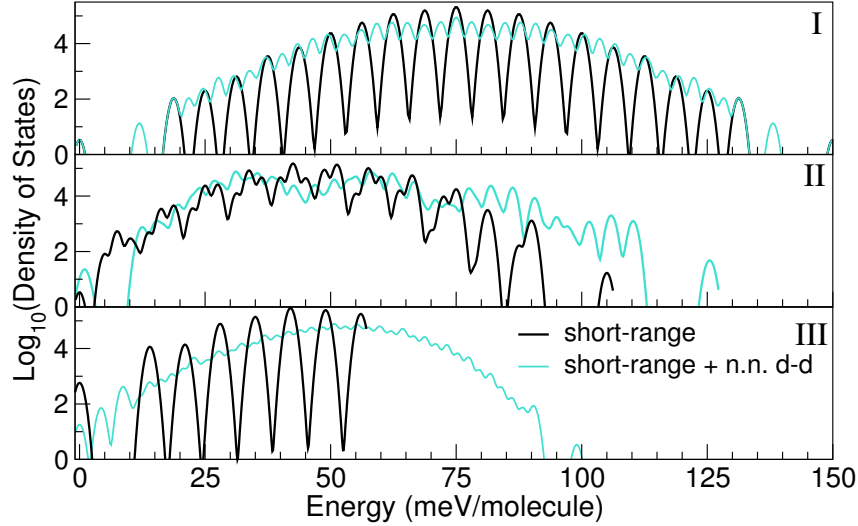


Figure VI.2: Density of states (DOS) of models I-III on a $2 \times 2 \times 2$ cubic grid with only *axes* orientations including periodic boundaries with (turquoise) and without (black) NN dipole-dipole coupling. The ground state energy is set to zero. Gaussian smearing ($\sigma = 0.5$ meV) has been applied to broaden the δ -functions at each energy level. Note that the DOS is normalized ($\int DOS(E)dE = 6^8$), and its logarithm has been plotted.

the ordering patterns obtained with the MLFF. To calculate Eq. (VI.1), the center and direction of the C-N axes are used in combination with the constant value for $|\mathbf{p}|$. In Figure VI.4 the energy and molecular order parameter are shown for a system in which the temperature was continuously raised from 100 K to 400 K. The still fairly fast heating rate results in hysteresis spreading the orthorhombic to tetragonal transition over a 50 K temperature range. The orthorhombic order $\mathbf{M}_{\text{ortho}}$ is stabilized by d-d interactions by ~ 30 meV/molecule, whereas this contribution drastically reduces in the tetragonal phase and vanishes in the cubic phase. This trend is the same in constant temperature MDs, where we obtain on time-average -29, -3.7, -2.6 and -1.7 meV/molecule at 150, 250, 300 and 400 K, respectively. These unscreened energies from an upper-bound to the real d-d interaction energy. This indicates that long-range d-d interactions stabilize the orthorhombic phase, but essentially play no role in the more disordered tetragonal and cubic phases.

30.4 Accuracy of the long-range interaction

30.4.1 The $\text{MA}_x\text{Cs}_{1-x}\text{PbI}_3$ test system

The pd-interaction plays an essential role in the stabilization of the long-range molecular order. However, the origin and validity of the selected parameters in the models is unclear. To test their accuracy, we have constructed $\text{MA}_x\text{Cs}_{1-x}\text{PbI}_3$ test systems and examined the dipole-dipole interactions by DFT calculations. The systems are based on $2 \times 2 \times 2$ CsPbI_3 cubic supercells as shown in Figure VI.5. The central Cs atom is replaced by a MA molecule which is rotated manually. The DFT total energy (E) of the rotated configurations $\{0 \leq \phi < \frac{\pi}{2}, 0 \leq \theta < \pi\}$ is used to map out the short-range interaction

Table 8: Bandwidth of the models (meV/molecule) as expressed by the standard deviation (σ) of the DOS and the energy difference between the ground- and highest state (ΔE). The multiplicity of the ground state (Ω) and the total number of different energy states (N_s) are shown in the last columns.

Model	σ	ΔE	Ω	N_s
Short-range I	12	150	6	21
Short-range I + NN dipole-dipole	15	150	6	95
Short-range II	12	105	6	41
Short-range II + NN dipole-dipole	17	126	6	257
Short-range III	9.3	56	1024	8
Short-range III + NN dipole-dipole	11	99	32	138
Short-range III + full dipole-dipole	-	-	8	-

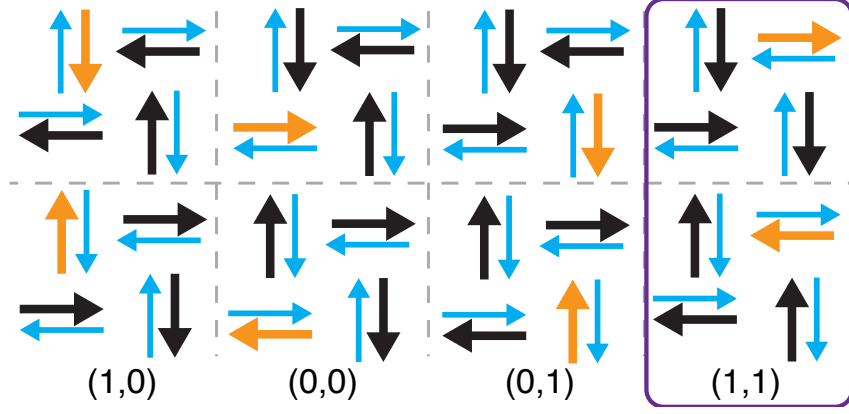


Figure VI.3: Selection of 8 possible ordering patterns in the ground state of the short-range interaction (Eq. (VI.4)) as parameterized in model III. The top xy plane is shown by the larger arrows, and the underlying (anti-ferroelectric) layer is shown in blue. To highlight the relative changes one molecule is colored orange. The in-plane polarization vectors are indicated at the bottom. Inclusion of long-range d-d coupling makes the states marked with purple the ground state.

energy $E_a(\phi, \theta)$. The obtained energy surface has a corrugation energy of ~ 80 meV with a room-diagonal orientation in the cubic PbI framework that is unfavored. Hereafter, a second Cs is replaced by a fixed MA molecule to probe the d-d coupling. As before, the central molecule is rotated, and the DFT total energies are calculated. Depending on the position of the fixed molecule, see Figs. VI.5 (b) axes $\mathbf{n} = (\pm 1, 0, 0)$ and (c) room diagonal $\mathbf{n} = (\pm 1, \pm 1, \pm 1)$ neighbors, energy surfaces $E_b(\phi, \theta)$ and $E_c(\phi, \theta)$ are obtained, respectively. Assuming the short-range interaction is unaffected by the replacement of a neighboring Cs by MA, we can extract the long-range interaction energy by calculating

$$\Delta E_x = E_x - E_a - \langle E_x - E_a \rangle, \quad (\text{VI.7})$$

where $x = \{b, c\}$ and $\langle \cdot \rangle$ the average over $\{\theta, \phi\}$. The DFT long-range interaction energy obtained in test systems (b) and (c) (shown on the bottom of Fig. VI.5) are accurately fitted by: $\Delta E_x = \alpha_x \cos \theta$, where $\alpha_b = -35$ meV and $\alpha_c = -10$ meV. In the pd-approximation these systems are described by $\Delta E_x^{\text{pd}} = H_{\text{lr}}$ using periodic-boundaries. Summing the interaction in real space and cutting off the interactions beyond

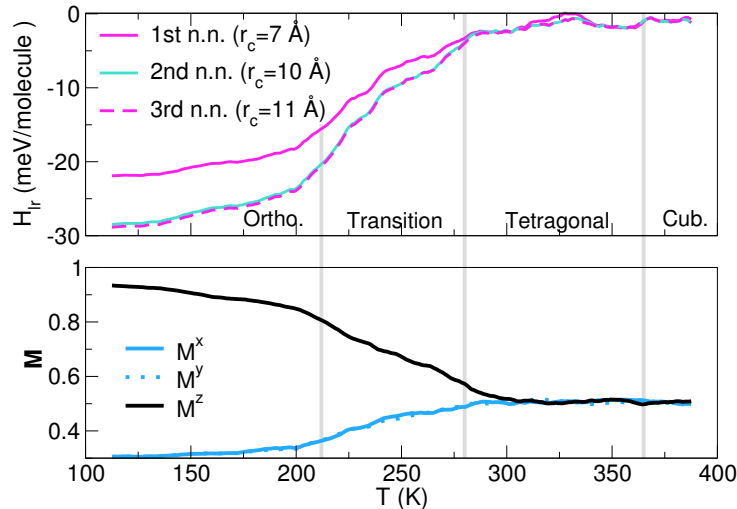


Figure VI.4: The long-range energy (H_{lr} , $\varepsilon_r = 1$) and order parameter ($\mathbf{M}$) calculated based on the molecular C-N axes extracted from a 0.5 K/ps heating run with the MLFF. The trajectory is started from a $4 \times 4 \times 4$ supercell in the orthorhombic phase and run in the NPT ensemble. Running averages with a width of 25 K are applied to smoothen the curves. The vertical gray lines sketch boundaries between the different crystal phases.

Table 9: Parameters of the model dielectric function. Fitted screening length parameter (λ) in $\text{\AA}^{-1}$ and the "ion clamped" static dielectric constant (ϵ_∞) both adapted from Ref. [56].

	λ	ϵ_∞		λ	ϵ_∞
MASnI ₃	1.05	9.18	MAPbBr ₃	1.13	5.15
FASnI ₃	1.05	8.06	FASnBr ₃	1.13	5.32
FAPbI ₃	1.05	7.10	FAPbCl ₃	1.17	4.27
MAPbI ₃	1.05	6.83	MAPbCl ₃	1.17	4.22
MASnBr ₃	1.13	5.89	FASnCl ₃	1.17	4.07
FAPbBr ₃	1.13	5.25	MASnCl ₃	1.17	4.05

$r_c = \sqrt{3}a$, the following two energies are obtained

$$\Delta E_b^{\text{pd}} = -4 \frac{C}{a^3 \epsilon_r} \cos \theta, \quad \Delta E_c^{\text{pd}} = 0, \quad (\text{VI.8})$$

where $C = \frac{|\mathbf{p}|^2}{4\pi\epsilon_0}$ is the Coulomb constant. Setting $|\mathbf{p}|$ to 2.29 D fixes the energy scale to $C/a^3 \approx 13$ meV. This means that the pd model with the real space sum and $\epsilon_r = \frac{4 \times 13}{\alpha_b} \approx 1.5$ describes the DFT result for system (b). However, it is unable to capture the cosine with amplitude α_c observed in system (c), even when the interaction radius is increased.

30.4.2 Changes to the long-range interaction

In order to understand the missing coupling in system (c), we further analyze the d-d interaction using three different electrostatic models.

First, considering the long-range nature of Eq. (VI.1), the conditional convergence of Eq. (VI.2) under the periodic boundaries that are imposed[28], H_{lr} should be calculated by an Ewald summation. Here we apply the formulation of the Ewald sum as presented in section 7. Note that the ($\mathbf{k} = 0$) term in the Ewald sum is omitted, implying that "conducting boundaries" are assumed[155].

Second, the microscopic electronic screening in this semiconductor can be more accurately described. Here, we apply the following distance dependent dielectric function

$$\epsilon_m^{-1}(r) = 1 - (1 - \epsilon_\infty^{-1}) \text{erf} \left(\frac{\lambda}{2\pi} r \right), \quad (\text{VI.9})$$

where r is the distance, and $\frac{\lambda}{2\pi}$ is the real space screening length. Equation (VI.9) is the real space version of the local model dielectric function fitted to the Many-Body Perturbation Theory calculations in the GW_0 approximation as described in the supplementary materials of Ref. [56] It was used there to screen electron-hole interactions in MAPbI₃. The Fourier transform of $\epsilon^{-1}(|\mathbf{k} + \mathbf{G}|) \rightarrow \epsilon^{-1}(r)$ is described in Appendix B. Compared to one fixed effective dielectric constant (ϵ_r) this is a more realistic screening description with proper limits, $\epsilon(0) = 1$ and $\epsilon(\infty) = \epsilon_\infty$. This screening function is closely related to the hybrid screened exchange functional, where λ is the range-separation parameter[156]. Note it only includes contributions from electronic screening, the ionic contributions are not included. We tabulate the parameters for a set of commonly studied hybrid perovskites in Table 9 and plot the inverse of $\epsilon_m^{-1}(r)$ in Figure VI.6. We recall the ϵ_r values for the three models $\epsilon_r^{\text{I}} = 1$, $\epsilon_r^{\text{II}} = 0.73$, $\epsilon_r^{\text{III}} = 1.5$. Since the dominant contribution to the total dipole-dipole interaction energy comes from NN coupling, which occurs at distances of one lattice spacing (~ 6.3 Å), setting $\epsilon_r < \epsilon_\infty$ as an effective screening parameter seems reasonable. In comparison to models I-III, the distance dependent dielectric function screens more, with a NN screening of $\epsilon_m(a) = 3.8$.

Third, the use of the pd-approximation can be circumvented by replacing the atoms with point charges, thereby creating interacting monopoles (mm). The system is sketched in Fig. VI.1 and is in total charge neutral. The same dipole moment as before is used to fix the charges: $q_C = 2.29 \times 0.20819434 \text{ e\AA} / 1.51 \text{ \AA} = 0.316e$, $q_N = -q_C$, $q_{\text{Pb}} = -2q_I$, $q_H = 0$ and $q_{\text{MA}} = q_{\text{Cs}} = -q_I$. A compensation charge q_{MA} is placed on the middle of the C-N bond. The Ewald sum is used to calculate the electrostatic energy of the monopole arrangements. Since the PbI framework and the center of mass of the molecule are fixed in this analysis, the charges q_{Pb} , q_I and q_{MA} only create a potential offset.

In Figure VI.7, we have applied the three changes to the test systems (a)-(c). The most clear improvement is that by applying the Ewald sum the cosine term is recovered for system (c). This term appears from the reciprocal space sum in the Ewald method. Note that the coupling to the second NN

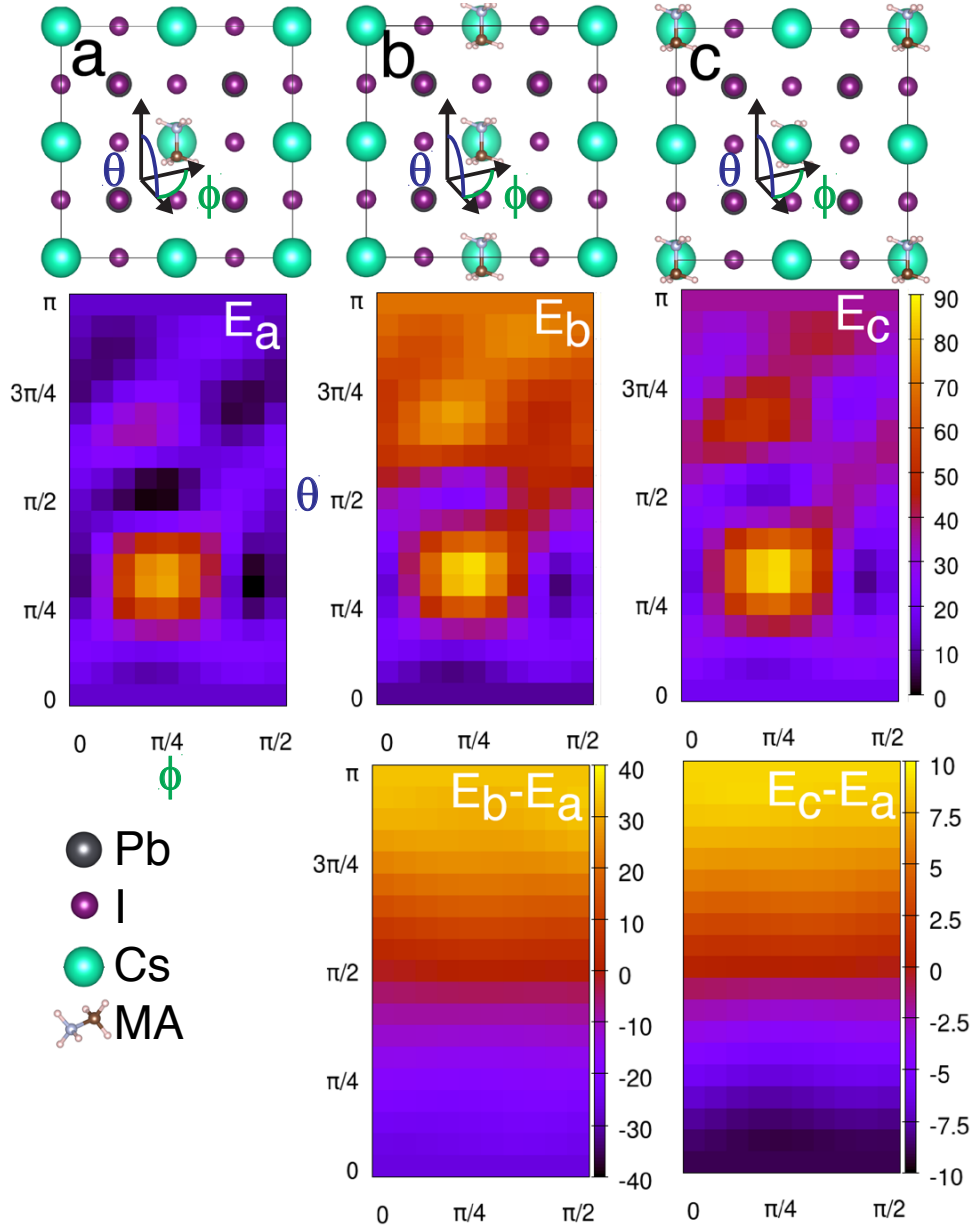


Figure VI.5: *top*: The $\text{MA}_x\text{Cs}_{1-x}\text{PbI}_3$ test system in a $2 \times 2 \times 2$ cubic supercell. a) One MA molecule rotated by $\{\phi, \theta\}$. b) A fixed MA molecule at distance $r = a$ and direction $\hat{n} = (0, 0, 1)$ replaces the Cs. c) Same as in b), but with $r = \sqrt{3}a$ and $\hat{n} = \frac{1}{\sqrt{3}}(1, 1, 1)$. *middle*: DFT total energy surfaces of systems a, b and c. *bottom*: DFT energy differences (ΔE_b , ΔE_c). The energy scale on all colorbars is in meV.

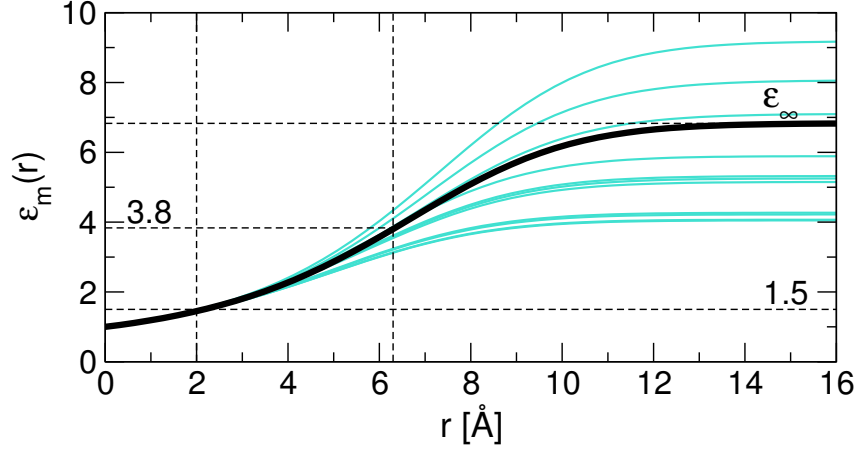


Figure VI.6: Distance dependent dielectric function $\varepsilon_m(r)$ for MAPbI₃ in the cubic phase based on the parameters of Table 9. The range of screening strengths in the wider class of hybrid perovskites is plotted by the turquoise lines.

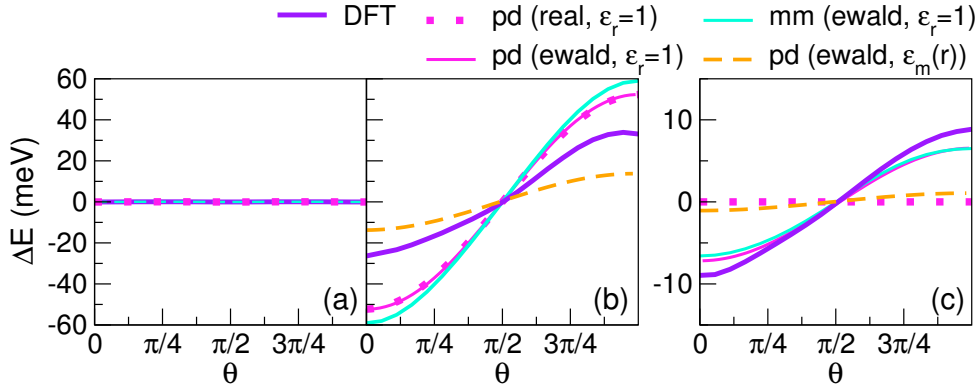


Figure VI.7: Long-range interaction energy calculated in the point-dipole (pd) and monopole-monopole (mm) approximation using the Ewald method or the real space sum. Both constant screening (ε_r) and the distance dependent screening function ($\varepsilon_m(r)$) are applied. Results are compared to the DFT data (ΔE_x) for the test systems (a), (b) and (c) in the respective figures.

$\mathbf{n} = (\pm 1, \pm 1, 0)$ are correctly accounted for in the real-space sum. The mm-model (solid cyan line) shows almost the same result as the pd-model with the Ewald sum. This means that the distance between C and N is sufficiently small compared to the NN distance a . The cosine behavior of both systems (b) and (c) are captured by the pd-model with Ewald sum and $\varepsilon_r = 1$, but their amplitudes are not. In system (b) the coupling is overestimated, while it underestimates the coupling in system (c). This is not mitigated by the distance dependent dielectric function $\varepsilon_m(r)$, which "over-screens" the coupling in both systems. The amplitude of the DFT energy is approximately $2\times$ and $8\times$ larger than the $\varepsilon_m(r)$ screened d-d interaction energy of systems (b) and (c), respectively. Overall, none of the applied electrostatic schemes can capture the strength of the interactions calculated by DFT in both systems simultaneously.

31 Discussion

With the Cs/MA-testsystem we removed what in most model studies of MAPbI₃ would be considered as the physical/chemical reasons for the short-range interactions. *Stress and strain* on the framework are removed because the framework is kept rigid under the MA rotation and the reference energy of system (a) is subtracted. We assume that the *hydrogen bonds* of the molecules with the framework are only marginally affected by the rotation of a neighboring molecule and should therefore be taken away in this scheme. The pd-approximation using the Ewald method qualitatively captures the interaction between the molecules. The inability to capture the correct amplitude of the interaction in both systems (b) and (c) simultaneously can be explained by microscopic polarization effects. H_{lr} assumes a constant dipole moment ($|\mathbf{p}|$), however in reality it is not constant but the result of an effective (depolarisation) field imposed by the surrounding ions and dipoles. These effects could possibly be captured by an anisotropic

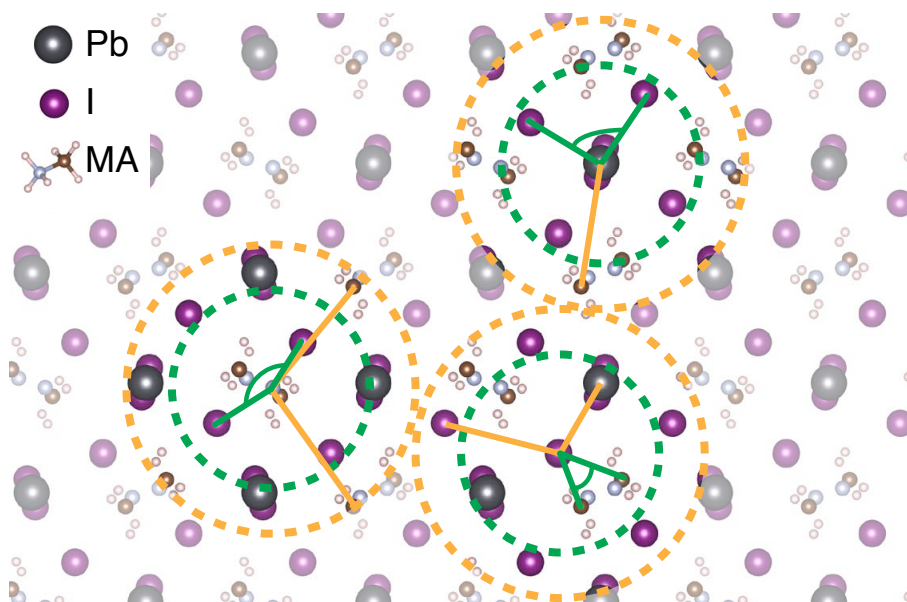


Figure VI.1: Local chemical environment around a lead, nitrogen and iodine atom as recognized in the machine learning force field. Two-body radial and three-body angular descriptors with a cut-off of 6 Å and 4 Å are sketched in orange and green, respectively.

dielectric function.

By including a distance dependent electronic screening function with a relatively large value for $\epsilon_\infty = 6.31$ we have increased the total screening of the d-d coupling compared to the previous models, especially for the second NN and beyond. The ionic screening from the PbI lattice has been omitted. In a previous study we have shown that the dielectric functions at 0 K calculated with density functional perturbation theory and at 300 K calculated with FPMD are very similar[56]. The dominant (dipole-active) oscillators related to Pb-I bonds lie between 2-10 meV (2-0.4 ps), ie. slightly faster than the MA reorientation times (several ps). This results in a sizable increase of the static dielectric constant ($\epsilon_0 = 30$) compared to the ion-clamped high frequency dielectric constant (ϵ_∞). It can therefore not be excluded that the d-d interactions are (partially) screened by the PbI lattice. This implies that the here computed d-d interaction energy is an upper bound.

The d-d coupling between the molecules is only an effective description of the electrostatics related to the ionic nature of the perovskite lattice. Without the MA cation, cubic PbI_3 is metallic in a DFT calculation. Introducing a MA or Cs turns it into a semiconductor. Each molecule donates one electron to the framework, which exactly fills up the (Pb and I states dominated) valence band. To lower the electrostatic energy, each MA^+ moves (with its nitrogen side) to a different PbI_3^- . The same mechanism also occurs in CsPbI_3 , even though the Cs cation does not have an intrinsic dipole moment. As shown in the low temperature orthorhombic phases of Figure VI.1, similar off-center displacements for the Cs cations as for the center of masses of the MA molecules occur. And, in both perovskites the PbI octahedra show a clock-wise, anti-clockwise ordering. This results in stretched and squeezed cavities in which the molecules align, because of space filling, along the extended axes. The framework imposes the long-range order of the molecules, whereas the displaced centers of masses of the cations are the result of the ionic lattice.

To capture such interactions, we have applied a machine-learning force field approach which learns a force field *on-the-fly* during FPMD[154]. The constraining effect of the PbI framework is automatically included, one of the difficult terms to model accurately. This force field is based on a purely short-range description as shown in Figure VI.1. Two-body radial and three-body angular descriptors with a cut-off of 6 Å and 4 Å, respectively, are used to represent the local chemical environment around each atom. The total energy is then defined as the sum of atomic energies assigned to each atom[126] by means of a similarity kernel. This method shows ordering patterns, lattice constants and phase transition temperatures in very good agreement with experiments. The chemical environment around a Pb atom (shown in Fig. VI.1 top right) connects both NN as well as next NN molecules. Thereby it is able to impose the AFE ordering pattern of the molecules in the orthorhombic phase. It effectively has the same reach as the minimal cutoff radius ($r_c = \sqrt{2}a$) required to split the degenerate GS of the short-range part of the model Hamiltonians. This implies that long-range d-d coupling is not necessary to capture the

molecular ordering.

32 Conclusions and Outlook

The ordering pattern of molecules in the hybrid perovskite MAPbI₃ at finite temperatures as described by three different model Hamiltonians (I-III) and an accurate MD simulation have been studied. A comparison based on the molecular order parameter ($\mathbf{M}$) has shown that model III best captures the features observed in MD. Using a discrete set of molecular orientations, model III qualitatively captures the ordered (orthorhombic) to disordered (cubic) transition upon heating, involving two second order transitions. The order-disorder transition in model I is a continuous process, while in model II the system undergoes one abrupt first-order transition. The ground state ordering pattern of model III closely resembles that of the experimental orthorhombic structure, whereas both models I and II show completely different ground state order.

In attempt to improve upon the models, we examined the accuracy of the dipole-dipole interactions using a more advanced electrostatic description with a distance dependent dielectric function and the Ewald summation technique. Although these methods enable a better quantitative description of the electrostatic interaction, the improvement was found to be not substantial. Static MA_xCs_{1-x}PbI₃ test systems were constructed to probe the d-d interaction energies in self-consistent DFT calculations. The point-dipole model is able to qualitatively describe the DFT interaction energies. However, its strength can not be consistently captured with one set of screening parameters.

We have shown that the pd-approximation (H_{lr}) effectively splits the degenerate ground state imposed by the short-range part (H_{sr}) of the Hamiltonian ($H = H_{lr} + H_{sr}$) of model III. A short cutoff radius ($r_c = \sqrt{2}a$) for the calculation of H_{lr} including the first and second NN dipole already suffices to capture the long-range AFE order of the molecules observed in the low-temperature orthorhombic phase. The d-d interaction energy calculated for ordering patterns from the MLFF shows a stabilizing effect in the orthorhombic phase, however it is practically absent in the tetragonal and cubic phases. The essence of the long-range order in the low-temperature orthorhombic phase lies in the propagation of this order by short-range interactions. The MLFF effectively captures these interactions between atoms that are no more than 6 Å apart. This analysis explains the large similarity of the MAPbI₃ and CsPbI₃ crystal lattices at low temperature, even though Cs does not have a permanent dipole-moment.

In future work, it is possible to improve the model Hamiltonians further by adopting more elaborate descriptions of H_{sr} as well as inclusion of more refined molecular degrees of freedom. However, its development and optimization *by-hand* are not tractable. In contrast, the MLFF method systematically constructs an accurate interaction model *on-the-fly* during FPMD. It enables the automatic inclusion of the constraining effect of the PbI framework as well as the effective short-range electrostatics with high accuracy, thereby realizing realistic ordering patterns of the molecules. The method can be extended to more complex systems with defects, surfaces and mixed halides or molecules.

Anharmonic phonon dispersion relation for finite temperature materials by machine-learning force-fields [†]

Phonon properties for complex solids at finite temperature are challenging to obtain. The harmonic approximation is a very strong tool at low temperatures for obtaining phonon dispersion relations. However, when the potential shows anharmonicities the approximation fails to describe the dispersion relation properly. Here we study, for the first time, the phonon dispersion by computing the dynamic structure factor by molecular dynamics with machine-learning force fields. In the first part a classical Morse potential is considered to assess the strengths and weaknesses of the two methods. In the second part both the harmonic approximation and the dynamic structure factor are applied to the Cesium lead iodide crystal. In the low temperature regime the harmonic approximation is applicable to the perovskite structure. For high temperatures the band widths of the phonon dispersion relation broaden so that a band structure picture is not applicable. The imaginary modes in the harmonic picture of the cubic Cesium Lead Bromide structure are absent in the Dynamic structure factor, indicating a dynamic stabilization of the crystal

[†]To be submitted

33 Introduction

The phonon dispersion relation is an important quantity related to many properties of a material. Especially the thermal conductivity and the elastic properties are strongly dependent on the phonon dispersion relation. The freezing and unfreezing of phonon modes with varying temperature can be responsible for a material's phase transitions. The most widely used approach to determine the phonon dispersion relation is the harmonic approximation. In the harmonic approximation the coupling between two atoms is described in terms of a polynomial of second order. This approximation is likely satisfied at low temperatures, but is likely to fail at room temperature and above. Especially dynamic solids like organic or inorganic perovskites will not be properly described by the harmonic approximation at finite temperature. There are also much simpler test systems for which the harmonic approximation will fail. Atoms coupled by a Morse potential will be very well described by the harmonic approximation at low temperature. Moreover, at higher temperatures, when the anharmonic part of the Morse potential becomes important, the harmonic approximation will not suffice. In the picture of phonon quasi-particles this states that scattering events become important between the phonons. In this work the determination of the phonon dispersion relation from measurements of the dynamic structure factor will be shown. This takes into account all possible anharmonicities or phonon scattering events up to infinite order. This approach was already employed to classical potentials like the Lennard Jones or the Morse potential[157] but never was used with machine-learning potentials giving nearly first principles accuracy. A simple Morse potential test system will be studied where the harmonic approximation will be compared to the dynamic structure factor for several temperatures. The dynamic structure factor will be applied to cesium-lead-bromide perovskite ($CsPbBr_3$). This system will be simulated by an *on-the-fly* generated machine-learning potential[154]. For this system the obtained results will be compared to the harmonic approximation. The sampling of the dynamic structure factor by means of an molecular dynamics simulation requires large supercells to obtain a dense enough q-point grid.

For low frequency modes another difficulty for the molecular dynamics simulation is the finite simulation time which has to be at least $1/\omega$ (the frequency of the lowest energy mode) to sample all frequencies needed for the analysis.

34 Computational Methods

34.1 Morse-potential molecular Dynamics

The classical molecular dynamics are performed with a molecular dynamics code implemented in the C++ programming language. The Verlet algorithm[17] in kick drift form is applied to propagate the atoms. A cubic primitive simulation box of size $16 \times 16 \times 16$ is used. The spacing between the atoms is set to $r_e = 3.733\text{\AA}$. The masses of the atoms were adjusted to 207.2 atomic mass units which is equivalent to the mass of a lead atom. The atoms are coupled by a Morse potential

$$V(r) = D_e \left(1 - e^{-\alpha(r-r_{eq})} \right)^2, \quad (\text{VII.1})$$

where D_e defines the depth of the potential and is set to 1.0meV. The parameter α defines the steepness of the potential and is set to $1.836\text{\AA}^{-1}$. r denotes the distance between the atoms. In the beginning of the simulation a nearest neighbor list is set up. This list will not be updated during the simulation. This is done to keep the simulation as simple as possible and to make a comparison between the harmonic approximation and the dynamic structure factor simpler because the system is unable to melt. The molecular dynamics simulations are equilibrated by propagating the atoms in a canonical NVT ensemble for 100 ps. A comparison between the Andersen and Langevin thermostat was done, (not shown here). Both thermostats seem to work for this simple system. In our experience a stochastic thermostat is better to use for equilibration because the different phonon modes will be occupied more homogeneously compared to deterministic thermostats. For the data shown here the Langevin equilibration was used. After the equilibration the thermostat was switched off and the molecular dynamics run was continued in the microcanonical ensemble for 400 ps. In this sense 20 trajectories were done for every temperature. The time step during the classical molecular dynamics simulations was set to 2 fs.

The written code also contains a simple routine computing the phonon dispersion relation by finite displacements in the harmonic picture. In this routine the atoms are displaced along the x, y, z directions and from this the force constant matrix is computed. This finite difference routine is used to do a comparison between the dynamic structure factor and the harmonic picture for the Morse potential.

Table 10: Unit cell lattice parameters used for $CsPbBr_3$ simulations taken from [154]

temperature [K]	$ a $	$ b $	$ c $
150K	8.37	8.16	11.79
400K	5.93	5.93	5.93

34.2 Machine Learning Molecular Dynamics simulation

To perform molecular dynamics simulations for the $CsPbBr_3$, a *on-the-fly* machine-learning force field was used. The force field and its training parameters are described in more detail in reference [154]. For the $CsPbBr_3$ two temperatures of 150 K and 400 K were simulated. The lattice constants for this simulations were taken from [154] and are reported in table 10. For the orthorhombic simulation at 150 K an orthorhombic $\sqrt{2} \times \sqrt{2} \times 2$ unit cell containing 4 lead, 4 Cs and 12 Br atoms was used. Out of this unit cell a $8 \times 8 \times 8$ supercell containing in total 10240 atoms was constructed. The supercell was propagated with a time step of 10 fs. To generate starting structures a constant temperature run with the Langevin thermostat was done. In total 2100 ps were simulated in the NVT ensemble and every 100 ps a starting structure was taken resulting in 20 starting structures. Every starting structure was then propagated in a microcanonical ensemble for 100 ps. For every microcanonical molecular dynamics simulation the dynamic structure factor is computed. For the high temperature cubic simulations at 400 K the lattice parameters were taken too from the work of Jinnouchi et.al [154]. A cubic unit cell containing 1 lead, 1 Cs and 3 bromide atoms was used. This unit cell was replicated to give a $10 \times 10 \times 10$ supercell containing 5000 atoms.

For the 400 K simulations a time step of 5 fs was used to avoid unwanted bond dissociations. In total 20 microcanonical molecular dynamics streams with 100 ps each were analyzed. The starting configurations were computed from a canonical molecular dynamics run with 100 ps between the starting configurations.

34.3 Dynamic Structure factor computation

For the computation of the dynamic structure factor the van Hove function $A(\mathbf{r}, t)$ for point particles is used [21]

$$A(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_i^N \sum_j^N \delta(\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_j(0)) \right\rangle. \quad (\text{VII.2})$$

From the Van-Hove function the dynamic structure factor is obtained via temporal and spatial Fourier transforms

$$\begin{aligned} S(\mathbf{k}, \omega) &= \int_{\mathbb{R}} \int_{\mathbb{R}^3} A(\mathbf{r}, t) e^{i\mathbf{k}\mathbf{r}} e^{-i\omega t} d^3r dt = \\ &= \int_{\mathbb{R}} \int_{\mathbb{R}^3} \frac{1}{N} \left\langle \sum_i^N \sum_j^N \delta(\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_j(0)) \right\rangle e^{i\mathbf{k}e^{-i\omega t}\mathbf{r}} d^3r dt = \\ &= \int_{\mathbb{R}} \left\langle \sum_i^N \sum_j^N e^{i\mathbf{k}(\mathbf{r}_i(t) - \mathbf{r}_j(0))} \right\rangle e^{-i\omega t} dt. \end{aligned} \quad (\text{VII.3})$$

In this equation $\mathbf{k}$ is a reciprocal lattice vector defined via the dot product with the lattice vectors $\mathbf{a}_i$ as $\mathbf{k}_j \mathbf{a}_i = 2\pi \delta_{ij}$. The dynamic structure factor contains all the dynamic information governing the motion of the system. The frequencies ω sample the phonon branches for different values of $\mathbf{k}$ known as the phonon dispersion. The average $\langle . \rangle$ is understood as a thermal average. The thermal average was computed over the 20 starting structures generated for every molecular dynamics simulation described in the foregoing sections and by using several starting configurations within the corresponding MD runs. The phonon state with energy ϵ_j is populated according to the Planck-distribution

$$\langle n_j \rangle = \frac{1}{e^{\beta \epsilon_j} - 1} \approx \frac{k_b T}{\epsilon_j}, \quad (\text{VII.4})$$

which gives the term on the far right in the classical limit. The intensities of the dynamic structure factor are weighted by the inverse Planck-distribution in the classical limit.

34.4 Phonon density of states computation

The phonon density of states can be computed from molecular dynamics simulations. The phonon density of states for a certain atom type s can be computed from velocity autocorrelation functions (VACF) $f_s(t)$ given by

$$f_s(t) = \frac{\langle \mathbf{v}_s(t) \mathbf{v}_s(0) \rangle}{\langle \mathbf{v}_s(0) \mathbf{v}_s(0) \rangle} \quad (\text{VII.5})$$

where $\mathbf{v}_s(t)$ is the velocity of a certain atom at time t . Again the brackets $\langle \cdot \rangle$ denote thermal averages. The thermal average is also computed over the 20 starting configurations and over different starting times of a single MD run. The phonon density of states per atom s can be obtained from Fourier transforming equation (VII.5)

$$g_s(\omega) = \int_{\mathbb{R}} f_s(t) e^{-i\omega t} dt. \quad (\text{VII.6})$$

The total density of states is given as a sum of the individual atomic contributions.

34.5 Harmonic approximation CsPbBr₃

To obtain the harmonic phonon band structure the phonopy[158] code is used. The phonopy code uses a minimum energy structure file. This structure file was replicated to get $8 \times 8 \times 8$ supercells for the orthorhombic and $10 \times 10 \times 10$ supercells for the cubic phase. Then atoms are displaced giving 120 different structures. For every configuration defined by its displacements the forces on the atoms are computed. The forces were computed with the potential of the machine learning forcefield introduced previously. From the set of forces and displacements the force constant matrix is obtained. For the phonopy calculations the electronic total energy was converged to 10^{-4} eV. From this force constant matrix the eigenvalues and the eigenvectors were computed giving the phonon dispersion relation and the phonon density of states. The shown phonon densities of states computed in the harmonic picture were checked for convergence with respect to the number of underlying mesh points.

35 Results

35.1 Comparison with the harmonic approximation

This section shows a comparison of the results obtained from molecular dynamics simulations with results obtained from the harmonic finite difference approach. Figure VII.1 shows the dynamic structure factor's intensities as a color map for the Morse potential at 10 K. On top the red line shows the harmonic results.

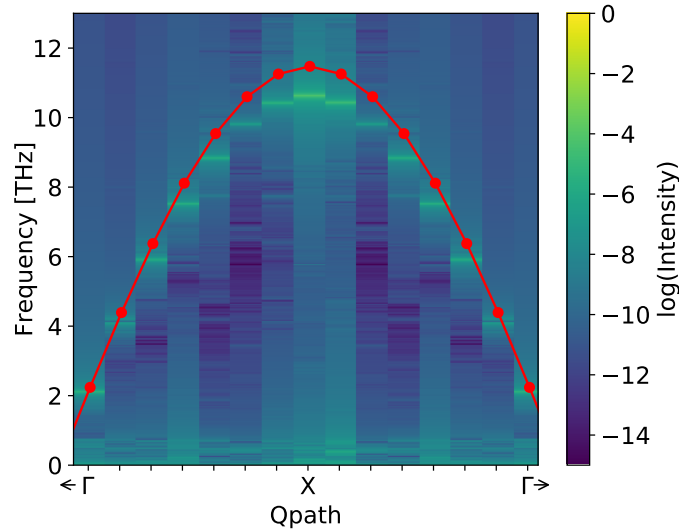


Figure VII.1: — Harmonic phonon dispersion for the Morse potential. Heat Map shows the logarithmic intensities of the dynamic structure factor sampled from a molecular dynamics simulation at $T=10$ K

By taking the intensity maxima of the dynamic structure factor of Figure VII.1 for every $\mathbf{k}$ -point, the phonon dispersion relation for this simple test system is obtained. The results obtained by the finite difference approach give an upper bound to the results from the molecular dynamics simulation. In finite temperature simulations atoms will always move along the gradient of the potential energy and therefore

they will choose the way of lowest resistance. In the used harmonic finite differences approach the atoms are only displaced along the Cartesian directions. Therefore the results of the harmonic approximation are expected to give higher frequencies than the molecular dynamics results. The deviation of the results are getting larger with increasing frequency. But still the two approaches agree at 10 K

35.2 Temperature dependence of the phonon dispersion relation for the Morse crystal

We now present an analysis of the temperature dependence of the phonon dispersion relation for the Morse potential. Figure VII.2 (A) shows the dynamic structure factor on the left and the phonon density of states on the right. The blue line in the plot for the dynamic structure factor is obtained from fitting Lorentz distributions to the molecular dynamics data. Since the variance for the Lorentz distribution (a special case of the Cauchy distribution) is not defined, the distance between the half heights of the peak was used as a measure for the variance. This figure shows good agreement between the data obtained from the dynamic structure factor and the velocity autocorrelation functions. The peak positions in the frequency domain agree perfectly. The velocity autocorrelation functions converge faster than the dynamic structure factor. Therefore if there is no interest in the $\mathbf{k}$ -point resolution of the phonon properties it is more advisable to study phonon density of states.

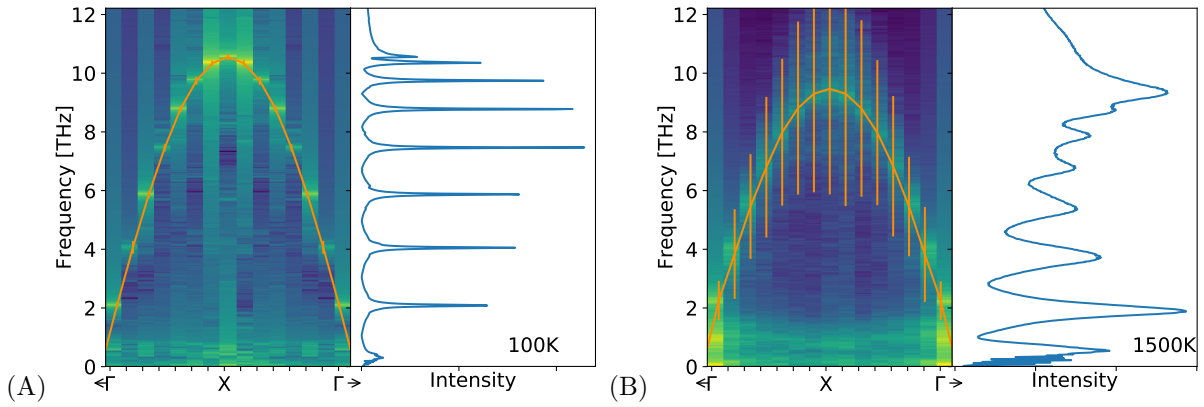


Figure VII.2: **(A)** Morse potential simulation at 100 K **Left:** Logarithmic intensities of the dynamic structure factor. The — line in the heat map is obtained by fitting Lorentzian functions to the intensity maxima. And the error bars are obtained by taking the half height widths of the Lorentzians. **Right:** phonon density of states obtained from velocity autocorrelation function **(B)** Morse potential simulation at 1500 K **Left:** Logarithmic intensities of the dynamic structure factor. The — line in the heat map is obtained by fitting Lorentzian functions to the intensity maxima. And the error bars are obtained by taking the half height widths of the Lorentzians. **Right:** phonon density of states obtained from velocity autocorrelation function

The peaks of the dynamic structure factor and phonon density of states become wider when the temperature is increased. This behavior is shown by comparing figure VII.2 (A) with the dynamic structure factor in figure VII.2 (B) for a 1500 K simulation. The modes of the phonon dispersion experience a red shift, a softening of the modes with increasing temperature. The softening of the modes is caused by the more disordered crystal structure at higher temperatures and the larger mean square displacement of the atoms around their equilibrium positions. When considering the phonon density of states in figure VII.2 (B), it only shows one peak for the high frequency modes, because the highest and the second highest peaks start to overlap. In the dynamic structure factor of figure VII.2 (B) the two high frequency peaks can still be distinguished because of the additional resolution in $\mathbf{k}$ -space.

To study the temperature dependence of the phonon dispersion relation in more detail figure VII.3 shows the positions of the peak maxima along the first Brillouin zone of the dynamic structure factor for several temperatures.

The figure shows that in the lower temperature range ($< 4000\text{K}$) the phonon modes systematically soften. In this regime the line shape predicted by the harmonic approximation is still reasonable, but fails to predict the frequencies of the oscillations. By increasing the temperature further the peaks denoting the maxima get wider. At very high temperatures the data acquires multiple maxima and the Lorentzian fit breaks down. In this regime it does not make sense to approximate the phonon dispersion relation by the maximum intensities of the dynamic structure factor only. The phonon density of states loses its peak pattern and becomes a continuum. In figure VII.3 this temperature regime is shown by the zig-zag lines.

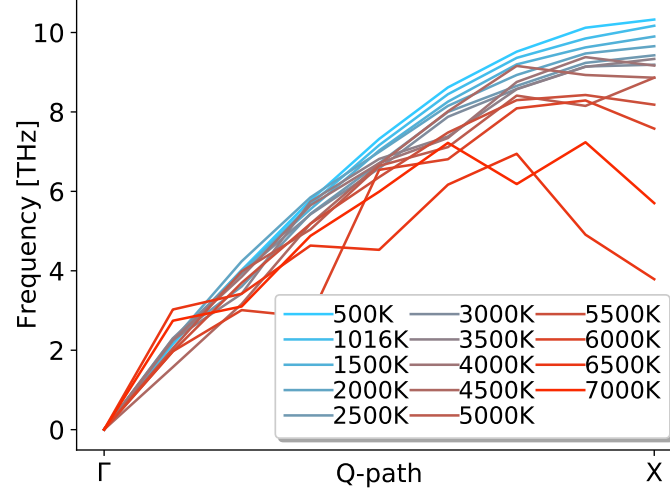


Figure VII.3: Phonon dispersion relations for various temperatures. The curves were obtained by extracting the positions of the maxima from the dynamic structure factor

36 Result Cesium-lead bromide

36.1 Orthorhombic 150K simulation

The analysis of the CsPbBr_3 at 150 K and the harmonic picture is shown in figure VII.1. The harmonic picture can only predict 3 times the number of atoms (20) in the unit cell branches. Since the 60 branches are already used up to populate the states up to frequencies of $\approx 5\text{THz}$, no higher frequency modes can be observed. The dynamic structure factor also shows finite intensities for those frequencies. The population of the phonon modes in the classical limit is inversely proportional to the eigenstate energy and hence this modes will contribute less to a materials properties. For lower frequencies the two approaches are in agreement. This can be seen by the brighter spots in the intensities of the dynamic structure factor along the dispersion lines of the harmonic picture. Also the phonon densities of states on the right hand side of figure VII.1 agree. In the case of the harmonic picture artificial peak broadening (mimicking the effect of temperature) was included to make a comparison to the shape of the molecular dynamics density of states easier. Still the peak positions are in agreement.

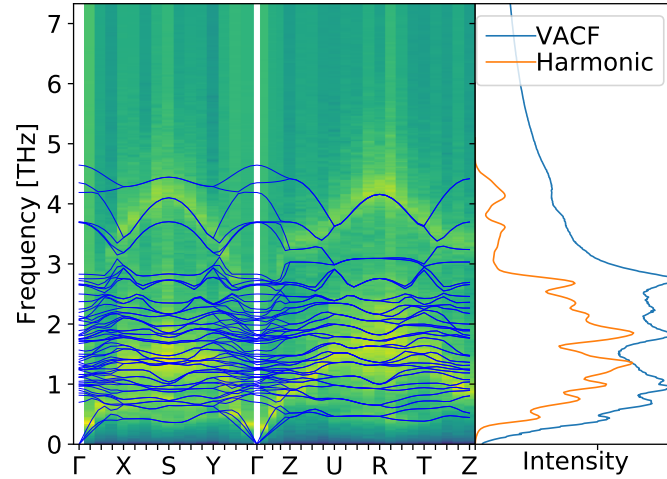


Figure VII.1: **Left:** Dynamic structure factor and harmonic phonon dispersion relation. **Right:** Phonon density of states for orthorhombic CsPbBr_3 at 150K.

For low temperatures it is therefore reasonable to use the harmonic picture. The harmonic approximation is computationally cheaper compared to the molecular dynamics approach. But the molecular dynamics approach gives more insight in the materials behavior since the broadening of the peaks is included what can be used to extract phonon lifetimes. The phonon density of states is decomposed into atomic contributions shown in figure VII.2. According to the masses of the atoms one would expect that the

spectrum is ordered as $\text{Pb} < \text{Cs} < \text{Br}$. With Pb showing the highest intensities at low frequencies.

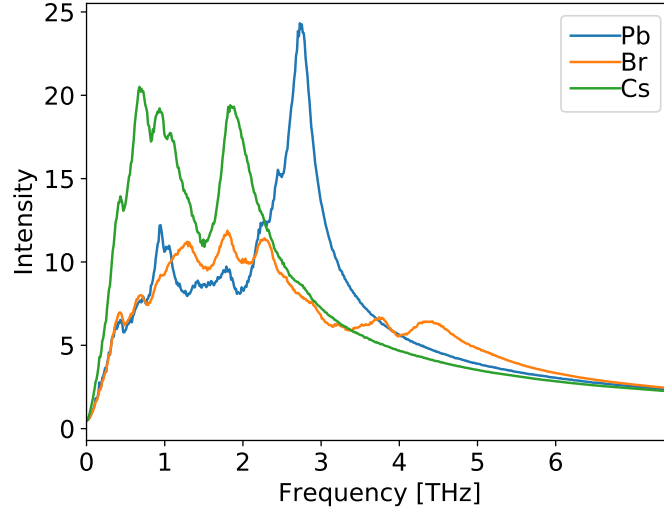


Figure VII.2: Phonon density of states for orthorhombic CsPbBr_3 at 150K decomposed into atomic contributions computed from molecular dynamics simulations

But figure VII.2 shows that the Cs atom has the most dominant contributions in the low frequency range. The reason for this is that Cs is connected to the other constituents of the material by ionic interactions which are weaker than covalent bonds. The bromide and lead atoms are connected via stronger covalent bonds and therefore are contributing in the higher frequency range of the density of states.

36.2 Cubic 400K simulation

By increasing the temperature of the CsPbBr_3 anharmonic effects will get more important. Figure VII.3 shows a comparison of the harmonic picture with the fully anharmonic dynamic structure factor. The first thing that is recognized is that the harmonic picture shows imaginary modes. Therefore the cubic structure can not be described by a harmonic phonon picture or by a single ground state structure. The reason for the imaginary modes is the oscillating (clock-wise counter clock-wise orientations) nature of the Pb-Br octahedra. In the high temperature phase the lead bromide bonds are on average straight, but in a snapshot of a single molecular dynamics structure, the bonds will always be tilted. This indicates that the cubic structure is dynamically stabilized.

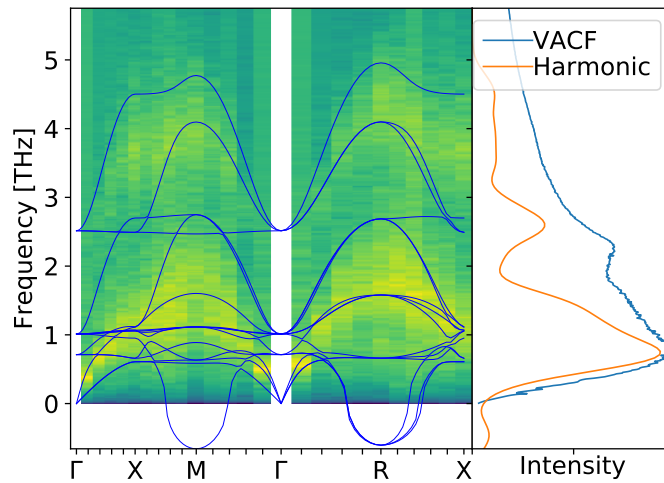


Figure VII.3: **Left:** Dynamic structure factor and harmonic phonon dispersion relation. **Right:** Phonon density of states for cubic CsPbBr_3 at 400 K

This behavior was further analyzed by considering the phonon eigenvectors at the negative frequency sites M and R obtained from the harmonic approach. The eigenvectors at the M point are shown in

Table 11: Phonon eigenvectors at M point for cubic $CsPbBr_3$ unit cell

atom	x	y	z
Pb	0.0	0.0	0.0
Br _x	0.0	-1.0	0.0
Br _y	1.0	0.0	0.0
Br _z	0.0	0.0	0.0
Cs	0.0	0.0	0.0

Table 12: Phonon eigenvectors at R point for cubic unit cell

	branch 1			branch 2			branch 3		
atom	x	y	z	x	y	z	x	y	z
Pb	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Br _x	0.0	-0.7	0.7	0.0	0.7	0.7	-0.7	0.7	0.0
Br _y	0.0	0.0	-1.0	-1.0	0.0	0.0	1.0	0.0	0.0
Br _z	0.0	1.0	0.0	-1.0	0.0	0.0	-1.0	0.0	0.0
Cs	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 11. The subscripts for the bromide atoms denote the direction of the bond formed with the lead atom.

The phonon eigenvectors of Table 11 correspond exactly to the clockwise and counter clockwise tilting of the framework in the xy plane. These modes form a pattern in the xy-plane characteristic for the orthorhombic structure. These oscillating motions are also observed in molecular dynamics simulations giving on average the cubic structure but showing deformed octahedrons at a time instant. The eigenvectors belonging to the imaginary modes at R are collected in Table 12. Once more the eigenvectors show only displacements belonging to the tilting of lead bromide bonds.

The Pb and Cs atoms do not need to be displaced to stabilize the cubic structure. The phonon density of states in figure VII.3 shows good agreement for the peak around 1 THz between the harmonic and the fully anharmonic picture. The peak around 2.5 THz in the harmonic picture has shifted to lower oscillator strength in the molecular dynamics approach. This is caused by the larger mean square displacements of the atoms in the molecular dynamics simulation at high temperature. This is the same effect causing the phonon mode softening in the case of the Morse potential. The decomposition of the phonon density of states into atomic contributions is shown in figure VII.4. The peaks for the lead and bromide atoms are practically the same as in the orthorhombic phase. But the Cs atom shows two peaks at 0.7 THz and 1.8 THz in the orthorhombic phase and only one peak at 0.8 THz in the cubic phase indicating the rearrangement of the lead bromide bonds determining the electrostatic potential in which the Cs atoms are moving.

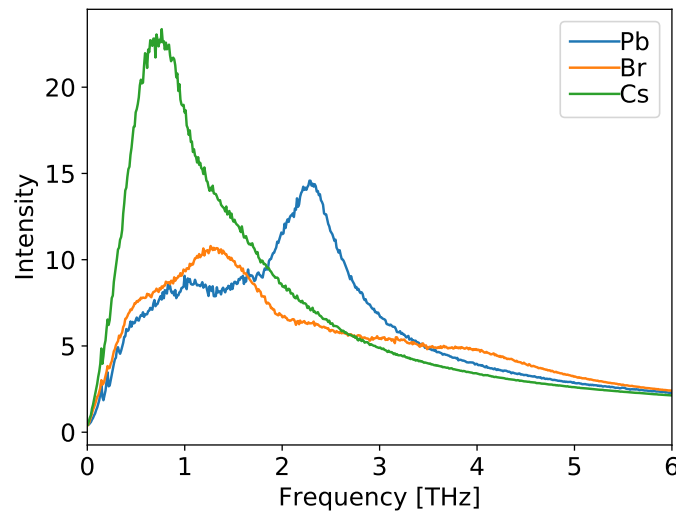


Figure VII.4: Phonon density of states for cubic $CsPbBr_3$ at 400K decomposed into atomic contributions computed from molecular dynamics simulations

37 Discussion

37.1 Morse potential and phonon mode softening

The analysis of the Morse potential showed that phonon dispersion relations are sensitive to temperature. In the case of the Morse potential the phonon frequencies are systematically decreasing. The mean square displacement $\langle x^2 \rangle$ of the atoms increases when the temperature is raised. Therefore the effective force constant sampled during the molecular dynamics simulation within the Morse potential coupling decreases. The relationship between the effective force constant and the mean square displacement for an N dimensional harmonic oscillator is given by

$$k_{eff} = \frac{N}{2} \frac{k_B T}{\langle x^2 \rangle_{MD}} \quad (\text{VII.7})$$

which can be obtained from the partition function of the classical harmonic oscillator. At a higher simulation temperature the atoms are able to sample the wider region of the Morse potential. This is resulting in larger mean square displacements $\langle x^2 \rangle_{MD}$ and therefore in a lower effective coupling constant.

The band representation given by the harmonic picture is a very good way to look at phonon properties in the low temperature regime. But for higher temperatures the band structure picture is only giving a very idealized representation for the true nature of the phononic properties. The peaks of the dynamic structure factor are getting wider with increasing temperature until bands start to overlap. In the temperature region of overlapping bands, talking about discrete bands does not make really sense anymore. The phonon density of states shows all phonon properties for simple materials and low temperatures. It is therefore very useful because of the much faster convergence of the VACF compared to the dynamic structure factor. But for higher temperature the resolution of the phonon density of states might not be good enough to identify all peaks that can be obtained from the dynamic structure factor possessing $\mathbf{k}$ -point resolution.

37.2 Phonon properties of CsPbBr₃

The orthorhombic structure of the CsPbBr₃ at 150K shows only small anharmonicities and is therefore in good agreement with the results computed by the harmonic approximation. For the cubic phase on the other hand the peaks of the dynamic structure factor get too broad for a meaningful description in terms of a discrete band structure. Especially at the M and R point the frequencies computed by the dynamic structure factor show a continuous spectrum between $\approx 1\text{THz}$ and $\approx 2\text{THz}$. Peak broadening in this region will cause the discrete bands computed by the harmonic approximation to overlap. Another difficulty for this temperature is the metastability of the CsPbBr₃ indicated by the imaginary phonon frequencies in the harmonic picture for the ideal cubic structure. The imaginary modes show eigenvectors resulting in a bending and tilting of the lead bromide bonds. This is exactly what is observable from the molecular dynamics simulations. The lead bromide bonds are not straight but form a wiggling pattern that is only straight on average [132]. Therefore the high temperature structure of this perovskite is not a thermodynamically stable structure but a dynamically stabilized material. The comparison of the atom resolved phonon density of states for the cubic and the orthorhombic structure showed a high and low frequency peak for the orthorhombic structure and only the low frequency peak for the cubic structure. The Cs atom is coupled to the Br^- and Pb^{3+} atoms by electrostatic interactions. The stronger tilting of the octahedrons in the orthorhombic phase will cause a stronger Coulomb potential acting on the Cs atoms. In the cubic phase the $\text{Pb} - \text{Br}$ bonds forming the octahedrons are on average straight resulting in a lower potential for the Cs atoms. This effect is therefore responsible for the lower frequencies in the cubic phase. The complete vanishing of the second peak can be understood by the anisotropy of the cubic framework. The orthorhombic phase shows clockwise counter clockwise pattern in the xy plane and a zig-zag pattern in the z direction resulting in a peak splitting in the low frequency region of the Cs atom.

37.3 Summary and outlook

The dynamic structure factor contains all phonon properties without any underlying approximations. To get properly converged results long molecular dynamics runs with different starting structures are needed. The *on-the-fly* machine-learning force field gives the possibility to sample such long trajectories. For dynamically stabilized materials the phonon properties have to be studied from molecular dynamics simulations because a single structure is not sufficient to describe those materials resulting in imaginary phonon modes for static calculations. For the CsPbBr₃ it was shown that the phonon dispersion relation is in good agreement with the harmonic picture at low temperatures. Still it should be noted that the

band broadening observed in molecular dynamics is not included. At higher temperatures this can cause bands to overlap in certain regions of the $\mathbf{k}$ space where the energy difference between the bands is small. For the cubic CsPbBr_3 phase the harmonic picture fails to describe the phonon dispersion relation properly. Nevertheless the eigenvectors of the harmonic approximation in the imaginary frequency range can be used to study the atomic movements responsible for the stabilization of the considered material. The atom resolved phonon density of states shows the rearrangement of the lead-bromide framework determining the potential energy surface of the Cs atoms coupled only by electrostatic interactions.

In an extension to this work it will be interesting to decompose the dynamic structure factor in longitudinal and transversal components. Another possibility would be to project the dynamic structure factor on a set of eigenvectors. From this renormalized frequencies can be obtained. For the eigenvectors one could use those obtained from the harmonic approximation.

Appendices

A Fitting parameters energy surfaces

Table 13: Pearson-correlation coefficients of the raw MD potential energy surface data and fitted model function at a pseudo-cubic volume of $251 \text{ \AA}^3$.

T	PBEsol	LDA	PBE	SCAN	TS	optPBE	PBE-D3	Mattoni	Handley
250 K	0.91	0.93	0.91	0.92	0.93	0.97	0.98	0.93	0.74
300 K	0.92	0.96	0.92	0.91	0.96	0.98	0.97	0.94	0.84
350 K	0.88	0.92	0.87	0.87	0.97	0.97	0.98	0.96	0.80
400 K	0.86	0.94	0.89	0.85	0.96	0.96	0.98	0.97	0.90

Table 14: Pearson-correlation coefficients of the raw MD potential energy surface data and fitted model function at a pseudo-cubic volume of $245 \text{ \AA}^3$.

T	PBEsol	LDA	PBE	SCAN	TS	optPBE	PBE-D3	Mattoni	Handley
350 K	0.85	0.87	0.95	0.94	0.96	0.98	0.97	0.96	0.87

Table 15: Fitted parameters C_1 , C_2 and C_3 (in meV) describing the potential energy surface for the different DFAs and force fields at a pseudo-cubic volume of $251 \text{ \AA}^3$.

T	PBEsol			LDA			PBE			SCAN		
250 K	-68.8	1520.6	17.0	-84.1	1494.5	20.9	-54.7	1620.7	13.5	-44.2	1404.9	10.9
300 K	-72.9	1523.7	18.1	-85.2	1493.1	21.1	-71.9	1616.3	17.8	-45.7	1219.8	18.0
350 K	-72.7	1336.2	18.0	-63.8	1320.7	15.8	-70.4	1435.7	17.4	-38.2	1035.4	9.4
400 K	-71.2	1307.8	17.7	-72.7	1323.4	18.0	-59.4	1343.7	14.7	-44.7	1024.7	11.1

	TS			optPBE			PBE-D3			Mattoni			Handley		
250 K	-48.6	1765.3	12.0	78.6	1108.5	-0.1	224.1	93.4	-0.2	68.9	417.9	-0.1	-74.7	369.1	18.6
300 K	-43.5	1708.1	10.7	79.8	960.2	-0.1	192.2	282.8	-0.2	77.1	211.0	-0.1	-65.3	235.1	16.3
350 K	-40.0	1452.1	9.8	57.5	876.0	-0.1	222.4	44.0	-0.2	92.7	76.3	-0.1	-49.8	147.2	12.5
400 K	-46.8	1380.2	11.5	51.2	735.2	-0.1	196.7	268.3	-0.2	102.2	4.5	-0.1	-50.9	84.1	13.9

	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
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Table 16: Fitted parameters C_1 , C_2 and C_3 (in meV) describing the potential energy surface for the different DFAs and force fields at a pseudo-cubic volume of $245 \text{ \AA}^3$.

T	PBEsol			LDA			PBE			SCAN		
350 K	-60.6	1154.5	15.0	14.0	1091.3	0.0	29.7	1123.4	0.0	100.0	629.6	-0.1

	TS			optPBE			PBE-D3			Mattoni			Handley		
350 K	91.5	1047.6	-0.1	230.3	126.8	-0.2	345.6	-257.0	-0.3	75.6	231.8	-0.1	-51.8	75.0	14.5

	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
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B Real space dielectric function

The Coulomb potential in reciprocal space screened by the model dielectric function ϵ_m as presented in Ref. [56] is given by

$$V(\mathbf{k}) = \left(\frac{4\pi}{\mathbf{k}^2} \right) \epsilon_m^{-1}(|\mathbf{k}|) = \frac{4\pi}{\mathbf{k}^2} \left(1 - (1 - \epsilon_\infty^{-1}) e^{-\frac{|\mathbf{k}|^2}{4\lambda^2}} \right). \quad (.8)$$

The screened Coulomb potential in real space is obtained by the Fourier transform of Eq. (.8),

$$V(\mathbf{r}) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \left[\frac{4\pi}{\mathbf{k}^2} \left(1 - (1 - \epsilon_\infty^{-1}) e^{-\frac{|\mathbf{k}|^2}{4\lambda^2}} \right) \right] e^{i\mathbf{k}\mathbf{r}} d\mathbf{k}. \quad (.9)$$

Switching to spherical coordinates and evaluating the integrals with respect to the spherical angles θ and φ gives,

$$V(r) = \frac{1}{(2\pi)^3} \frac{16\pi^2}{r} \int_0^\infty \left[\frac{1 - (1 - \varepsilon_\infty^{-1})e^{-\frac{k^2}{4\lambda^2}}}{k} \right] \sin(kr) dk. \quad (.10)$$

Hereby, the problem reduces to solving the integrals

$$A(r) = \int_0^\infty \frac{\sin(kr)}{k} dk, \quad (.11)$$

and

$$B(r) = \int_0^\infty \frac{\sin(kr)e^{-\frac{k^2}{4\lambda^2}}}{k} dk. \quad (.12)$$

To solve $A(r)$, a damping function $e^{-\beta k}$ is multiplied to the integrand. Note that in the limit of $\beta \rightarrow 0$ the original function is recovered. The derivative of this integral with respect to β is

$$\frac{dI(\beta, r)}{d\beta} = - \int_0^\infty \sin(kr) e^{-\beta k} dk = - \frac{r}{\beta^2 + r^2}. \quad (.13)$$

The indefinite integral with respect to β results in the inverse tangent function $I(\beta, r) = -\arctan\left(\frac{\beta}{r}\right) + C$. By considering the limit $\beta \rightarrow \infty$,

$$I(\infty, r) = -\frac{\pi}{2} + C = \int_0^\infty \frac{\sin(kr)}{k} e^{-\infty k} dk = 0, \quad (.14)$$

one can determine the integration constant $C = \pi/2$. Thereby Eq. (.11) reduces to

$$A(r) = \frac{\pi}{2}. \quad (.15)$$

To solve $B(r)$, one introduces $D = \frac{1}{4\lambda^2}$ and takes the derivative with respect to r ,

$$\frac{dB(r)}{dr} = \int_0^\infty e^{-Dk^2} \cos(kr) dk = \frac{1}{2} \int_{-\infty}^\infty e^{-Dk^2} e^{ikr} dk. \quad (.16)$$

The integration over k simplifies to a 1-dimensional Fourier transform of a Gaussian function,

$$\frac{dB(r)}{dr} = \frac{1}{2} \sqrt{\frac{\pi}{D}} e^{-\frac{r^2}{4D}}. \quad (.17)$$

Integrating with respect to r results in

$$B(r) = \frac{\pi}{2} \text{erf}(r\lambda). \quad (.18)$$

Combining the Eqs. (.15) and (.18) with Eq. (.10) gives the real space screened Coulomb potential

$$V(r) = \frac{1}{(2\pi)^3} \frac{16\pi^2}{r} \frac{\pi}{2} \varepsilon_m^{-1}(r) = \left(\frac{1}{r}\right) \varepsilon_m^{-1}(r), \quad (.19)$$

where

$$\varepsilon_m^{-1}(r) = 1 - (1 - \varepsilon_\infty^{-1}) \text{erf}(r\lambda). \quad (.20)$$

is the inverse dielectric function in real space. Here λ is expressed in (angular) wavenumbers.

C Peer reviewed articles

- Lahnsteiner, J., Kresse, G., Kumar, A., Sarma, D. D., Franchini, C., Bokdam, M., *Room Temperature Dynamic Correlation between Methylammonium Molecules in Lead-Iodine Based Perovskites: an Ab-initio Molecular Dynamics Perspective*, Phys. Rev. B. 94 214114, 2016.
- Govinda, S., Kore, B. P., Bokdam, M., Mahale, P., Kumar, A., Pal, S., Bhattacharyya, B., Lahnsteiner, J., Kresse, G., Franchini, C., Pandey, A., Sarma, D. D., *Behavior of Methylammonium Dipoles in MAPbX(3) (X = Br and I)*, J. Phys. Chem. Letters, 8, 17, 4113, 2017

- Bokdam, M., Lahnsteiner, J., Ramberger, B., Schfer, T., Kresse, G., *Assessing density functionals using many body theory for hybrid perovskites*, Phys. Rev. Letters, 119, 14, 145501.
- Lahnsteiner, J., Kresse, G., Heinen, J., Bokdam, M., *Finite-temperature structure of the MAPbI(3) perovskite: Comparing density functional approximations and force fields to experiment*, Phys. Rev. Materials 2, 7, 073604.
- Jinnouchi, R., Lahnsteiner, J., Karsai, F., Kresse, G., Bokdam, M., *Phase Transitions of Hybrid Perovskites Simulated by Machine-Learning Force Fields Trained on the Fly with Bayesian Inference*, Phys. Rev. Letters, 122, 22, 225701.
- Lahnsteiner, J., Jinnouchi, R., Bokdam, M., *Long-range order imposed by short-range interactions in methylammonium lead iodide: Comparing point-dipole models to machine-learning force fields*, Phys. Rev. B. 100, 9, 094106.

D Contributed talks

- ETSF Young Researchers' Meeting, June 2017, Tarragona, Spain, Room-temperature dynamic correlation between methylammonium molecules: An ab initio molecular dynamics perspective
- DPG Frhjahrstagung Berlin 2018, March 2018, Berlin, Germany, The Finite Temperature Structure of the MAPbI3 Perovskite: Comparing Exchange-Correlation Potentials, Force Fields and Model Hamiltonians
- Fakultätsöffentliche Präsentation Fakultät für Physik, September 2019, Vienna, Austria, Phase transitions of hybrid perovskites simulated by machine-learning force fields

E Poster presentations

- 2nd ViCoM Young Researchers Meeting, September 2016, Vienna, Austria, Structural arrangement of methyl ammonium molecules in lead iodine perovskites
- 66. Jahrestagung der Österreichischen Physikalischen Gesellschaft (ÖPG 2016), September 2016, Vienna Austria, Structural arrangement of methyl ammonium molecules in lead iodine perovskites
- 3rd International Conference on Perovskite Solar Cells and Optoelectronics, September 2017, Oxford, Great Britain, Advanced Ab-Initio Molecular Dynamics Techniques applied to MAPbI3
- 652. WE-Heraeus-Seminar: Ab initio Electronic Structure Theory for Solids in the 21st Century, November 2017, Bad Honnef, Germany, Advanced Ab-Initio Molecular Dynamics Techniques applied to MAPbI3
- DPG Frühjahrstagung 2019 - Universität Rostock, Regensburg, April 2019, Regensburg, Germany, Finite temperature structure of Hybrid Perovskites from ab-initio and classical MD

References

-
- [1] P. Robert, G. and Y. Weitao, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, 1989).
 - [2] B. Brandsen and J. Joachain, C., *Physics of Atoms and Molecules* (Pearson Education Limited, 2003).
 - [3] H. Weinstein, P. Politzer, and G. Srebrenik, *A misconception concerning the electronic density distribution of an atom*, *Theo. Chem. Acta* **38**, 159 (1975).
 - [4] E. Davidson, *Reduced density Matrices in Quantum Chemistry* (New York Academic Press, 1976).
 - [5] P. Feynman, Richard, *Forces in Molecules*, *Phys. Rev.* **56**, 340 (1939).
 - [6] A. Szabo and S. Ostlund, Neil, *Modern Quantum Chemistry* (Dover Publications, INC, 1989).
 - [7] A. Galindo and P. Pascual, *Quantum Mechanics II* (Springer Verlag, 1989).
 - [8] R. O. M. Born, *Zur Quantentheorie der Molekeln*, *Annalen der Physik* **389**, 457 (1927).
 - [9] A. Galindo and P. Pascual, *Quantum Mechanics I* (Springer Verlag, 1989).
 - [10] P. Ehrenfest, *Bemerkung ber die angenherzte Gltigkeit der klassischen Mechanik innerhalb der Quantenmechanik*, *Zeitschrift fr Physik* **45**, 445 (1927).
 - [11] R. P. Feynman, *Statistical Mechanics* (W. A. Benjamin, INC., 1972).
 - [12] L. Landau and E. Lifschitz, *Statistische Physik Teil 1* (Europa Lehrmittel, 2016).
 - [13] J. Von Neumann, *Mathematische Grundlagen der Quantenmechanik* (Springer Berlin, 1955).
 - [14] R. Kubo, *Statistical Mechanics* (North-Holland, 1965).
 - [15] D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, 1976).
 - [16] J. Kirkwood, *Quantum Statistics of Almost Classical Assemblies*, *Phys. Rev.* **44**, 31 (1933).
 - [17] D. Frenkel and B. Smit, *Understanding Molecular Simulations* (Academic Press INC, 1996).
 - [18] D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, Inc., 1987).
 - [19] T. Arens, F. Hettlich, C. Karpfinger, U. Kockelkorn, K. Lichtenegger, and H. Stachel, *Mathematik* (Spektrum Akademischer Verlag Heidelberg, 2008).
 - [20] L. Fetter, Alexander and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (Dover Publications Inc, 2003).
 - [21] L. van FHove, *Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles*, *Phys. Rev.* **95**, 249 (1954).
 - [22] P. Hopkins, A. Fortini, J. Archer, Andrew, and M. Schmidt, *The Van Hove distribution function for Brownian hard spheres: Dynamical test particle theory and computer simulations for bulk dynamics*, *The Journal of Chemical Physics* **133**, 224505 (2010).
 - [23] P. Hohenberg and W. Kohn, *Inhomogeneous Electron Gas*, *Phys. Rev.* **136**, B864 (1964).
 - [24] W. Kohn and L. J. Sham, *Self-Consistent Equations Including Exchange and Correlation Effects*, *Phys. Rev.* **140**, A1133 (1965).
 - [25] J. Harris, *Adiabatic-connection approach to Kohn-Sham theory*, *Phys. Rev. A* **29**, 1648 (1984).
 - [26] C. A. Hans, *Rattle: A Velocity Version of the Shake algorithm for Molecular Dynamics Calculations*, **52**, 24 (1982).
 - [27] G. Ciccotti and R. J., P., *Molecular Dynamics Simulation of Rigid Molecules*, *Comp. Phys. Reports* **4**, 345 (1986).

- [28] G. Markov and M. C. Payne, *Periodic boundary conditions in ab initio calculations*, [Phys. Rev. B](#) **51**, 4014 (1995).
- [29] W. Leeuw, S., W. Perram, J., and E. Smith, *Simulation of electrostatic systems in periodic boundary conditions. I. Lattice sums and dielectric constants*, [373](#), 27 (1980).
- [30] W. Leeuw, S., W. Perram, J., and E. Smith, *Simulation of electrostatic systems in periodic boundary conditions. II. Equivalence of boundary conditions*, [373](#), 57 (1980).
- [31] W. Leeuw, S., W. Perram, J., and E. Smith, *Simulation of electrostatic systems in periodic boundary conditions. III. Further theory and applications*, [388](#), 57 (1983).
- [32] L. Landau and E. Lifschitz, *Klassische Feldtheorie* (Europa Lehrmittel, 2018).
- [33] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *Equation of State Calculations by Fast Computing Machines*, [The Journal of Chemical Physics](#) **21**, 1087 (1953).
- [34] P. E. Blöchl, *Projector augmented-wave method*, [Phys. Rev. B](#) **50**, 17953 (1994).
- [35] D. Vanderbilt, *Soft self-consistent pseudopotentials in a generalized eigenvalue formalism*, [Phys. Rev. B](#) **41**, 7892 (1990).
- [36] N. R. E. L. (NREL), “Research cell efficiency records,” (2016).
- [37] M. Hirasawa, T. Ishihara, and T. Goto, *Exciton Features in 0-, 2-, and 3-Dimensional Networks of [PbI₆]⁴⁻ Octahedra*, [J. Phys. Soc. Jpn.](#) **63**, 3870 (1994).
- [38] K. Tanaka, T. Takahashi, T. Ban, T. Kondo, K. Uchida, and N. Miura, *Comparative study on the excitons in lead-halide-based perovskite-type crystals {CH₃NH₃PbBr₃} {CH₃NH₃PbI₃}*, [Sol. State Comm.](#) **127**, 619 (2003).
- [39] G. Papavassiliou and I. Koutselas, *Structural, optical and related properties of some natural three- and lower-dimensional semiconductor systems*, [Synthetic Metals](#) **71**, 1713 (1995).
- [40] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, *Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites*, [Science](#) **338**, 643 (2012).
- [41] C. C. Stoumpos, C. D. Malliakas, and M. G. Kanatzidis, *Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties*, [Inorg. Chem.](#) **52**, 9019 (2013).
- [42] W. Shockley and H. J. Queisser, *Detailed Balance Limit of Efficiency of pn Junction Solar Cells*, [J. Appl. Phys.](#) **32**, 510 (1961).
- [43] W.-J. Yin, T. Shi, and Y. Yan, *Unique Properties of Halide Perovskites as Possible Origins of the Superior Solar Cell Performance*, [Adv. Mat.](#) **26**, 4653 (2014).
- [44] C. Li, X. Lu, W. Ding, L. Feng, Y. Gao, and Z. Guo, *Formability of ABX₃ (X = F, Cl, Br, I) halide perovskites*, [Acta. Cryst. Sec. B](#) **64**, 702 (2008).
- [45] R. Wasylshen, O. Knop, and J. Macdonald, *Cation rotation in methylammonium lead halides*, [Sol. State Comm.](#) **56**, 581 (1985).
- [46] T. Baikie, N. S. Barrow, Y. Fang, P. J. Keenan, P. R. Slater, R. O. Piltz, M. Gutmann, S. G. Mhaisalkar, and T. J. White, *A combined single crystal neutron/X-ray diffraction and solid-state nuclear magnetic resonance study of the hybrid perovskites CH₃NH₃PbX₃ (X = I, Br and Cl)*, [J. Mater. Chem. A](#) **3**, 9298 (2015).
- [47] T. Chen, B. J. Foley, B. Ipek, M. Tyagi, J. R. D. Copley, C. M. Brown, J. J. Choi, and S.-H. Lee, *Rotational dynamics of organic cations in the CH₃NH₃PbI₃ perovskite*, [Phys. Chem. Chem. Phys.](#) **17**, 31278 (2015).
- [48] G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar, and T. C. Sum, *Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH₃NH₃PbI₃*, [Science](#) **342**, 344 (2013).

- [49] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, and H. J. Snaith, *Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber*, [*Science* **342**, 341 \(2013\)](#).
- [50] A. Filippetti and A. Mattoni, *Hybrid perovskites for photovoltaics: Insights from first principles*, [*Phys. Rev. B* **89**, 125203 \(2014\)](#).
- [51] P. Umari, E. Mosconi, and F. D. Angelis, *Relativistic GW calculations on $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{SnI}_3$ Perovskites for Solar Cell Applications*, [*Sci. Rep.* **4**, 4467 \(2014\)](#).
- [52] Y. Kutes, L. Ye, Y. Zhou, S. Pang, B. D. Huey, and N. P. Padture, *Direct Observation of Ferroelectric Domains in Solution-Processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Thin Films*, [*J. Phys. Chem. Lett.* **5**, 3335 \(2014\)](#).
- [53] H.-S. Kim, S. K. Kim, B. J. Kim, K.-S. Shin, M. K. Gupta, H. S. Jung, S.-W. Kim, and N.-G. Park, *Ferroelectric Polarization in $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite*, [*J. Phys. Chem. Lett.* **6**, 1729 \(2015\)](#).
- [54] A. Filippetti, P. Delugas, M. I. Saba, and A. Mattoni, *Entropy-Suppressed Ferroelectricity in Hybrid Lead-Iodide Perovskites*, [*J. Phys. Chem. Lett.* **6**, 4909 \(2015\)](#).
- [55] S. G. P. Mahale, B. P. Kore, S. Mukherjee, M. S. Pavan, C. De, S. Ghara, A. Sundaresan, A. Pandey, T. N. G. Row, and D. D. Sarma, *Is $\text{CH}_3\text{NH}_3\text{PbI}_3$ Polar?*, [*J. Phys. Chem. Lett.* **7**, 2412 \(2016\)](#).
- [56] M. Bokdam, T. Sander, A. Stroppa, S. Picozzi, D. D. Sarma, C. Franchini, and G. Kresse, *Role of Polar Phonons in the Photo Excited State of Metal Halide Perovskites*, [*Sci. Rep.* **6**, 28618 \(2016\)](#).
- [57] M. A. Pérez-Osorio, R. L. Milot, M. R. Filip, J. B. Patel, L. M. Herz, M. B. Johnston, and F. Giustino, *Vibrational Properties of the OrganicInorganic Halide Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ from Theory and Experiment: Factor Group Analysis, First-Principles Calculations, and Low-Temperature Infrared Spectra*, [*J. Phys. Chem. C* **119**, 25703 \(2015\)](#).
- [58] F. Brivio, J. M. Frost, J. M. Skelton, A. J. Jackson, O. J. Weber, M. T. Weller, A. R. Goñi, A. M. A. Leguy, P. R. F. Barnes, and A. Walsh, *Lattice dynamics and vibrational spectra of the orthorhombic, tetragonal, and cubic phases of methylammonium lead iodide*, [*Phys. Rev. B* **92**, 144308 \(2015\)](#).
- [59] A. Mattoni, A. Filippetti, M. Saba, C. Caddeo, and P. Delugas, *Temperature Evolution of Methylammonium Trihalide Vibrations at the Atomic Scale*, [*J. Phys. Chem. Lett.* **7**, 529 \(2016\)](#).
- [60] T. Hata, G. Giorgi, and K. Yamashita, *The Effects of the OrganicInorganic Interactions on the Thermal Transport Properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$* , [*Nano Lett.* **16**, 2749 \(2016\)](#).
- [61] S.-Y. Yue, X. Zhang, G. Qin, J. Yang, and M. Hu, *Insight into the collective vibrational modes driving ultralow thermal conductivity of perovskite solar cells*, [*Phys. Rev. B* **94**, 115427 \(2016\)](#).
- [62] A. J. Neukirch, W. Nie, J.-C. Blancon, K. Appavoo, H. Tsai, M. Y. Sfeir, C. Katan, L. Pedesseau, J. Even, J. J. Crochet, G. Gupta, A. D. Mohite, and S. Tretiak, *Polaron Stabilization by Cooperative Lattice Distortion and Cation Rotations in Hybrid Perovskite Materials*, [*Nano Lett.* **16**, 3809 \(2016\)](#).
- [63] A. Poglitsch and D. Weber, *Dynamic disorder in methylammoniumtrihalogenoplumbates (II) observed by millimeterwave spectroscopy*, [*J. Chem. Phys.* **87**, 6373 \(1987\)](#).
- [64] N. Onoda-Yamamuro, T. Matsuo, and H. Suga, *Calorimetric and IR spectroscopic studies of phase transitions in methylammonium trihalogenoplumbates (II)*, [*J. Phys. Chem. Solids* **51**, 1383 \(1990\)](#).
- [65] A. A. Bakulin, O. Selig, H. J. Bakker, Y. L. Rezus, C. Mller, T. Glaser, R. Lovrincic, Z. Sun, Z. Chen, A. Walsh, J. M. Frost, and T. L. C. Jansen, *Real-Time Observation of Organic Cation Reorientation in Methylammonium Lead Iodide Perovskites*, [*J. Phys. Chem. Lett.* **6**, 3663 \(2015\)](#).
- [66] A. M. A. Leguy, J. M. Frost, A. P. McMahon, V. G. Sakai, W. Kockelmann, C. Law, X. Li, F. Foglia, A. Walsh, B. C. O'Regan, J. Nelson, J. T. Cabral, and P. R. F. Barnes, *The dynamics of methylammonium ions in hybrid organic-inorganic perovskite solar cells*, [*Nature Comm.* **6**, 7124 \(2015\)](#).
- [67] E. Mosconi, C. Quarti, T. Ivanovska, G. Ruani, and F. De Angelis, *Structural and electronic properties of organo-halide lead perovskites: a combined IR-spectroscopy and ab initio molecular dynamics investigation*, [*Phys. Chem. Chem. Phys.* **16**, 16137 \(2014\)](#).

- [68] J. M. Frost, K. T. Butler, and A. Walsh, *Molecular ferroelectric contributions to anomalous hysteresis in hybrid perovskite solar cells*, [APL Materials](#) **2**, 081506 (2014).
- [69] M. A. Carignano, A. Kachmar, and J. Hutter, *Thermal Effects on CH₃NH₃PbI₃ Perovskite from Ab Initio Molecular Dynamics Simulations*, [J. Phys. Chem. C](#) **119**, 8991 (2015).
- [70] C. Goehry, G. A. Nemnes, and A. Manolescu, *Collective Behavior of Molecular Dipoles in CH₃NH₃PbI₃*, [J. Phys. Chem. C](#) **119**, 19674 (2015).
- [71] S. Meloni, T. Moehl, W. Tress, M. Franckevicius, M. Saliba, Y. H. Lee, P. Gao, M. K. Nazeeruddin, S. M. Zakeeruddin, U. Rothlisberger, and M. Graetzel, *Ionic polarization-induced current-voltage hysteresis in CH₃NH₃PbX₃ perovskite solar cells*, [Nature Comm.](#) **7**, 10334 (2016).
- [72] J. Even, M. Carignano, and C. Katan, *Molecular disorder and translation/rotation coupling in the plastic crystal phase of hybrid perovskites*, [Nanoscale](#) **8**, 6222 (2016).
- [73] A. Mattoni, A. Filippetti, M. I. Saba, and P. Delugas, *Methylammonium Rotational Dynamics in Lead Halide Perovskite by Classical Molecular Dynamics: The Role of Temperature*, [J. Phys. Chem. C](#) **119**, 17421 (2015).
- [74] J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. van Schilfgaarde, and A. Walsh, *Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells*, [Nano Lett.](#) **14**, 2584 (2014).
- [75] I. Swainson, R. Hammond, C. Soullire, O. Knop, and W. Massa, *Phase transitions in the perovskite methylammonium lead bromide, {CH₃ND₃PbBr₃}*, [J. Solid State Chem.](#) **176**, 97 (2003).
- [76] L. Chi, I. Swainson, L. Cranswick, J.-H. Her, P. Stephens, and O. Knop, *The ordered phase of methylammonium lead chloride {CH₃ND₃PbCl₃}*, [J. Solid State Chem.](#) **178**, 1376 (2005).
- [77] T. Baikie, Y. Fang, J. M. Kadro, M. Schreyer, F. Wei, S. G. Mhaisalkar, M. Graetzel, and T. J. White, *Synthesis and crystal chemistry of the hybrid perovskite (CH₃NH₃)PbI₃ for solid-state sensitised solar cell applications*, [J. Mater. Chem. A](#) **1**, 5628 (2013).
- [78] G. Kresse and J. Hafner, *Ab-initio Molecular-Dynamics for Liquid-Metals*, [Phys. Rev. B](#) **47**, 558 (1993).
- [79] G. Kresse and J. Furthmüller, *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set*, [Phys. Rev. B](#) **54**, 11169 (1996).
- [80] G. Kresse and D. Joubert, *From ultrasoft pseudopotentials to the projector augmented-wave method*, [Phys. Rev. B](#) **59**, 1758 (1999).
- [81] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces*, [Phys. Rev. Lett.](#) **100**, 136406 (2008).
- [82] M. P. Allen and D. J. Tildesley, *Computer simulation of liquids* (Oxford university press, 1991).
- [83] E. Menéndez-Proupin, P. Palacios, P. Wahnón, and J. C. Conesa, *Self-consistent relativistic band structure of the CH₃NH₃PbI₃ perovskite*, [Phys. Rev. B](#) **90**, 045207 (2014).
- [84] M. R. Filip, G. E. Eperon, H. J. Snaith, and F. Giustino, *Steric engineering of metal-halide perovskites with tunable optical band gaps*, [Nature Comm.](#) **5**, 5757 (2014).
- [85] M. R. Filip and F. Giustino, *GW quasiparticle band gap of the hybrid organic-inorganic perovskite CH₃NH₃PbI₃: Effect of spin-orbit interaction, semicore electrons, and self-consistency*, [Phys. Rev. B](#) **90**, 245145 (2014).
- [86] C. Quarti, E. Mosconi, and F. D. Angelis, *Interplay of Orientational Order and Electronic Structure in Methylammonium Lead Iodide: Implications for Solar Cell Operation*, [Chem. Mat.](#) **26**, 6557 (2014).
- [87] A. Amat, E. Mosconi, E. Ronca, C. Quarti, P. Umari, M. K. Nazeeruddin, M. Grätzel, and F. De Angelis, *Cation-Induced Band-Gap Tuning in Organohalide Perovskites: Interplay of Spin-Orbit Coupling and Octahedra Tilting*, [Nano Lett.](#) **14**, 3608 (2014).

- [88] J.-H. Lee, N. C. Bristowe, P. D. Bristowe, and A. K. Cheetham, *Role of hydrogen-bonding and its interplay with octahedral tilting in $\text{CH}_3\text{NH}_3\text{PbI}_3$* , *Chem. Commun.* **51**, 6434 (2015).
- [89] J. H. Lee, J.-H. Lee, E.-H. Kong, and H. M. Jang, *The nature of hydrogen-bonding interaction in the prototypic hybrid halide perovskite, tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$* , *Sci. Rep.* **6**, 21687 (2016).
- [90] C. Quarti, E. Mosconi, and F. De Angelis, *Structural and electronic properties of organo-halide hybrid perovskites from ab initio molecular dynamics*, *Phys. Chem. Chem. Phys.* **17**, 9394 (2015).
- [91] C. Quarti, E. Mosconi, J. M. Ball, V. D’Innocenzo, C. Tao, S. Pathak, H. J. Snaith, A. Petrozza, and F. De Angelis, *Structural and optical properties of methylammonium lead iodide across the tetragonal to cubic phase transition: implications for perovskite solar cells*, *Energy Environ. Sci.* **9**, 155 (2016).
- [92] C. Motta, F. El-Mellouhi, and S. Sanvito, *Exploring the cation dynamics in lead-bromide hybrid perovskites*, *Phys. Rev. B* **93**, 235412 (2016).
- [93] J. Li and P. Rinke, *Atomic structure of metal-halide perovskites from first principles: The chicken-and-egg paradox of the organic-inorganic interaction*, *Phys. Rev. B* **94**, 045201 (2016).
- [94] M. T. Weller, O. J. Weber, P. F. Henry, A. M. Di Pumpo, and T. C. Hansen, *Complete structure and cation orientation in the perovskite photovoltaic methylammonium lead iodide between 100 and 352 K*, *Chem. Commun.* **51**, 4180 (2015).
- [95] P. Whitfield, N. Herron, W. E. Guise, K. Page, Y. Q. Cheng, I. Milas, and M. K. Crawford, *Structures, Phase Transitions and Tricritical Behavior of the Hybrid Perovskite Methyl Ammonium Lead Iodide*, *Sci. Rep.* **6**, 35685 (2016).
- [96] A. Franz, D. M. Többsen, and S. Schorr, *Interaction between cation orientation, octahedra tilting and hydrogen bonding in methylammonium lead triiodide*, *Crystal Research and Technology* **51**, 534 (2016).
- [97] N. Onoda-Yamamuro, T. Matsuo, and H. Suga, *Dielectric study of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{Cl}, \text{Br}, \text{I}$)*, *J. Phys. Chem. Solids* **53**, 935 (1992).
- [98] S. Govinda, B. P. Kore, M. Bokdam, P. Mahale, A. Kumar, S. Pal, B. Bhattacharyya, J. Lahnsteiner, G. Kresse, C. Franchini, A. Pandey, and D. D. Sarma, *Behavior of Methylammonium Dipoles in MAPbX_3 ($X = \text{Br}$ and I)*, *J. Phys. Chem. Lett.* **8**, 4113 (2017).
- [99] W. M. J. Franssen, S. G. D. van Es, R. Derviolu, G. A. de Wijs, and A. P. M. Kentgens, *Symmetry, Dynamics, and Defects in Methylammonium Lead Halide Perovskites*, *J. Phys. Chem. Lett.* **8**, 61 (2017).
- [100] E. Mosconi, J. M. Azpiroz, and F. De Angelis, *Ab Initio Molecular Dynamics Simulations of Methylammonium Lead Iodide Perovskite Degradation by Water*, *Chem. Mat.* **27**, 4885 (2015).
- [101] J. Lahnsteiner, G. Kresse, A. Kumar, D. D. Sarma, C. Franchini, and M. Bokdam, *Room-temperature dynamic correlation between methylammonium molecules in lead-iodine based perovskites: An ab initio molecular dynamics perspective*, *Phys. Rev. B* **94**, 214114 (2016).
- [102] K. Druzbicki, R. S. Pinna, S. Rudi, M. Jura, G. Gorini, and F. Fernandez-Alonso, *Unexpected Cation Dynamics in the Low-Temperature Phase of Methylammonium Lead Iodide: The Need for Improved Models*, *J. Phys. Chem. Lett.* **7**, 4701 (2016).
- [103] M. A. Carignano, S. A. Aravindh, I. S. Roqan, J. Even, and C. Katan, *Critical Fluctuations and Anharmonicity in Lead Iodide Perovskites from Molecular Dynamics Supercell Simulations*, *J. Phys. Chem. C* **121**, 20729 (2017).
- [104] A. Mattoni, A. Filippetti, and C. Caddeo, *Modeling hybrid perovskites by molecular dynamics*, *J. Phys.: Condens. Matter* **29**, 043001 (2017).
- [105] C. M. Handley and C. L. Freeman, *A new potential for methylammonium lead iodide*, *Phys. Chem. Chem. Phys.* **19**, 2313 (2017).
- [106] M. Šimėnas, S. Balciunas, M. Maczka, J. Banys, and E. E. Törnau, *Exploring Antipolar Nature of Methylammonium Lead Halides: a Monte Carlo and Pyrocurrent Study*, *J. Phys. Chem. Lett.* **8**, 4906 (2017).

- [107] L. Z. Tan, F. Zheng, and A. M. Rappe, *Intermolecular Interactions in Hybrid Perovskites Understood from a Combined Density Functional Theory and Effective Hamiltonian Approach*, *ACS Energy Letters* **2**, 937 (2017).
- [108] Q. Xu, T. Eguchi, H. Nakayama, N. Nakamura, and M. Kishita, *Molecular Motions and Phase Transitions in Solid $CH_3NH_3PbX_3$ ($X = Cl, Br, I$) as Studied by NMR and NQR**, *Zeitschrift für Naturforschung - Section A Journal of Physical Sciences* **46**, 240 (1991).
- [109] M. Bokdam, J. Lahnsteiner, B. Ramberger, T. Schäfer, and G. Kresse, *Assessing Density Functionals Using Many Body Theory for Hybrid Perovskites*, *Phys. Rev. Lett.* **119**, 145501 (2017).
- [110] G. Kresse and J. Furthmüller, *Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set*, *Comp. Mat. Sci.* **6**, 15 (1996).
- [111] J. P. Perdew, K. Burke, and M. Ernzerhof, *Generalized Gradient Approximation Made Simple*, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [112] J. Klimeš, D. R. Bowler, and A. Michaelides, *Van der Waals density functionals applied to solids*, *Phys. Rev. B* **83**, 195131 (2011).
- [113] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu*, *J. Chem. Phys.* **132**, 154104 (2010).
- [114] A. Tkatchenko and M. Scheffler, *Accurate molecular van der Waals interactions from ground-state electron density and free-atom reference data*, *Phys. Rev. Lett.* **102**, 073005 (2009).
- [115] J. Sun, A. Ruzsinszky, and J. P. Perdew, *Strongly Constrained and Appropriately Normed Semilocal Density Functional*, *Phys. Rev. Lett.* **115**, 036402 (2015).
- [116] M. A. Pérez-Osorio, A. Champagne, M. Zacharias, G.-M. Rignanese, and F. Giustino, *Van der Waals Interactions and Anharmonicity in the Lattice Vibrations, Dielectric Constants, Effective Charges, and Infrared Spectra of the Organic-Inorganic Halide Perovskite $CH_3NH_3PbI_3$* , *J. Phys. Chem. C* **121**, 18459 (2017).
- [117] G. Bussi and M. Parrinello, *Accurate sampling using Langevin dynamics*, *Phys. Rev. E* **75**, 1 (2007).
- [118] T. Bucko, J. Hafner, and G. Angyan, Janos, *Geometry optimization of periodic systems using internal coordinates*, *J. Chem. Phys.* **122** (2005), 10.1063/1.1864932.
- [119] J. Baker, D. Kinghorn, and P. Pulay, *Geometry optimization in delocalized internal coordinates: An efficient quadratically scaling algorithm for large molecules*, *J. Chem. Phys.* **110**, 4986 (1999).
- [120] R. Wahl, D. Vogtenhuber, and G. Kresse, *$SrTiO_3$ and $BaTiO_3$ revisited using the projector augmented wave method: Performance of hybrid and semilocal functionals*, *Phys. Rev. B* **78**, 104116 (2008).
- [121] D. Dubbeldam, S. Calero, D. E. Ellis, and R. Q. Snurr, *RASPA: molecular simulation software for adsorption and diffusion in flexible nanoporous materials*, *Molecular Simulation* **42**, 81 (2016).
- [122] E. Anderson, Z. Bai, C. Bischof, S. Blackford, J. Demmel, J. Dongarra, J. Du Croz, A. Greenbaum, S. Hammarling, A. McKenney, and D. Sorensen, *LAPACK Users' Guide*, 3rd ed. (Society for Industrial and Applied Mathematics, Philadelphia, PA, 1999).
- [123] D. A. Egger and L. Kronik, *Role of Dispersive Interactions in Determining Structural Properties of Organic-Inorganic Halide Perovskites: Insights from First-Principles Calculations*, *J. Phys. Chem. Lett.* **5**, 2728 (2014).
- [124] Y. Kawamura, H. Mashiyama, and K. Hasebe, *Structural Study on Cubic-Tetragonal Transition of $CH_3NH_3PbI_3$* , *J. Phys. Soc. Jpn.* **71**, 1694 (2002).
- [125] J. Behler and M. Parrinello, *Generalized Neural-Network Representation of High-Dimensional Potential-Energy Surfaces*, *Phys. Rev. Lett.* **98**, 146401 (2007).
- [126] A. P. Bartók, M. C. Payne, R. Kondor, and G. Csányi, *Gaussian Approximation Potentials: The Accuracy of Quantum Mechanics, without the Electrons*, *Phys. Rev. Lett.* **104**, 136403 (2010).

- [127] Z. Li, J. Kernmode, and A. De Vita, *Molecular Dynamics with On-the-Fly Machine Learning of Quantum-Mechanical Forces*, *Phys. Rev. Lett.* **114**, 096405 (2015).
- [128] L. Jacobsen, T. Jørgensen, M., and B. Hammer, *On-the-Fly Machine Learning of Atomic Potential in Density Functional Theory Structure Optimization*, *Phys. Rev. Lett.* **120**, 026102 (2018).
- [129] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, *Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells*, *Journal of the American Chemical Society* **131**, 60506051 (2009).
- [130] “Best research-cell efficiencies, national renewable energylaboratory,” <https://www.nrel.gov/pv/assets/images/efficiency-chart.png>, accessed: 2020-01-27.
- [131] D. Weber, *CH₃NH₃PbX₃, ein Pb(II)-System mit kubischer Perowskitstruktur / CH₃NH₃PbX₃, a Pb(II)-System with Cubic Perovskite Structure*, *Zeitschrift für Naturforschung B* **33**, 1443 (1978).
- [132] J. Lahnsteiner, G. Kresse, J. Heinen, and M. Bokdam, *The Finite Temperature Structure of the MAPbI₃ Perovskite: Comparing Density Functional Approximations and Force Fields to Experiment*, *Phys. Rev. Mat.* **2**, 073604.
- [133] A. P. Bartók, R. Kondor, and G. Csányi, *On representing chemical environments*, *Phys. Rev. B* **87**, 184115 (2013).
- [134] “See supplemental material at,” <http://link.aps.org/supplemental/10.1103/PhysRevLett.122.225701>, accessed: 2020-01-27.
- [135] M. Bishop, Christopher, *Pattern Recognition and Machine Learning* (Springer, 2011).
- [136] J. Kästner, *Umbrella sampling*, *Comp. Mol. Sci.* **1**, 932 (2011).
- [137] A. Marronier, G. Roma, S. Boyer-Richard, L. Pedesseau, J.-M. Jancu, Y. Bonnassieux, S.-C. C. Katan, C., G. Kanatzidis, M., and J. Even, *Anharmonicity and Disorder in the Black Phases of Cesium Lead Iodide Used for Stable Inorganic Perovskite Solar Cells*, *ACS Nano* **12**, 3477 (2018).
- [138] R. J. Sutton, M. R. Filip, A. A. Haghighirad, N. Sakai, B. Wenger, F. Giustino, and H. J. Snaith, *Cubic or Orthorhombic? Revealing the Crystal Structure of Metastable Black-Phase CsPbI₃ by Theory and Experiment*, *ACS Energy Letters* **3**, 1787 (2018).
- [139] J. Ma and L.-W. Wang, *Nanoscale Charge Localization Induced by Random Orientations of Organic Molecules in Hybrid Perovskite CH₃NH₃PbI₃*, *Nano Lett.* **15**, 248 (2015).
- [140] F. Zheng, L. Z. Tan, S. Liu, and A. M. Rappe, *Rashba SpinOrbit Coupling Enhanced Carrier Lifetime in CH₃NH₃PbI₃*, *Nano Lett.* **15**, 7794 (2015).
- [141] C. Motta, F. El-Mellouhi, S. Kais, N. Tabet, F. Alharbi, and S. Sanvito, *Revealing the role of organic cations in hybrid halide perovskite CH₃NH₃PbI₃*, *Nature Comm.* **6**, 7026 (2015).
- [142] T. Etienne, E. Mosconi, and F. De Angelis, *Dynamical Origin of the Rashba Effect in Organohalide Lead Perovskites: A Key to Suppressed Carrier Recombination in Perovskite Solar Cells?*, *J. Phys. Chem. Lett.* **7**, 1638 (2016).
- [143] J. Gong, M. Yang, X. Ma, R. D. Schaller, G. Liu, L. Kong, Y. Yang, M. C. Beard, M. Lesslie, Y. Dai, B. Huang, K. Zhu, and T. Xu, *ElectronRotor Interaction in OrganicInorganic Lead Iodide Perovskites Discovered by Isotope Effects*, *J. Phys. Chem. Lett.* **7**, 2879 (2016).
- [144] S. Hu, H. Gao, Y. Qi, Y. Tao, Y. Li, J. R. Reimers, M. Bokdam, C. Franchini, D. Di Sante, A. Stroppa, and W. Ren, *Dipole Order in Halide Perovskites: Polarization and Rashba Band Splittings*, *J. Phys. Chem. C* **121**, 23045 (2017).
- [145] B. Kang and K. Biswas, *Preferential CH₃NH₃⁺ Alignment and Octahedral Tilting Affect Charge Localization in Cubic Phase CH₃NH₃PbI₃*, *J. Phys. Chem. C* **121**, 8319 (2017).
- [146] M. Šiménas, J. Banys, and E. E. Törnau, *Screening of point defects in methylammonium lead halides: a Monte Carlo study*, *J. Mater. Chem. C* **6**, 1487 (2018).
- [147] S. Ashhab, M. Carignano, and M. E. Madjet, *Domain boundaries in Luttinger-Tisza ordered dipole lattices*, *J. Appl. Phys.* **125**, 163103 (2019).

- [148] W. Zhong, D. Vanderbilt, and K. M. Rabe, *First-principles theory of ferroelectric phase transitions for perovskites: The case of BaTiO₃*, [*Phys. Rev. B* **52**, 6301 \(1995\)](#).
- [149] A. Pecchia, D. Gentilini, D. Rossi, M. Auf der Maur, and A. Di Carlo, *Role of Ferroelectric Nanodomains in the Transport Properties of Perovskite Solar Cells*, [*Nano Lett.* **16**, 988 \(2016\)](#).
- [150] J. Li, J. Järvi, and P. Rinke, *Multiscale model for disordered hybrid perovskites: The concept of organic cation pair modes*, [*Phys. Rev. B* **98**, 045201 \(2018\)](#).
- [151] J. Järvi, J. Li, and P. Rinke, *Multi-scale model for the structure of hybrid perovskites: analysis of charge migration in disordered MAPbI₃ structures*, [*New J. Phys.* **20**, 103013 \(2018\)](#).
- [152] J. C. Thomas, J. S. Bechtel, and A. Van der Ven, *Hamiltonians and order parameters for crystals of orientable molecules*, [*Phys. Rev. B* **98**, 094105 \(2018\)](#).
- [153] A. M. A. Leguy, A. R. Goi, J. M. Frost, J. Skelton, F. Brivio, X. Rodriguez-Martnez, O. J. Weber, A. Pallipurath, M. I. Alonso, M. Campoy-Quiles, M. T. Weller, J. Nelson, A. Walsh, and P. R. F. Barnes, *Dynamic disorder, phonon lifetimes, and the assignment of modes to the vibrational spectra of methylammonium lead halide perovskites*, [*Phys. Chem. Chem. Phys.* **18**, 27051 \(2016\)](#).
- [154] J. Ryosuke, L. Jonathan, K. Ferenc, K. Georg, and B. Menno, *Phase Transitions of Hybrid Perovskites Simulated by Machine-Learning Force Fields Trained on the Fly with Bayesian Inference*, [*Phys. Rev. Lett.* **122**, 225701 \(2019\)](#).
- [155] S. Chen and A. Bongiorno, *Boundary conditions in periodic density functional calculations of insulating materials*, [*Phys. Rev. B* **83**, 165125 \(2011\)](#).
- [156] P. Liu, C. Franchini, M. Marsman, and G. Kresse, *Assessing model-dielectric-dependent hybrid functionals on the antiferromagnetic transition-metal monoxides MnO, FeO, CoO, and NiO*, (2019), [arXiv:1902.05025](#).
- [157] A. Vallés, P. Derlet, and E. Crespo, D. Pineda, *Molecular dynamics computation of the dynamical structure factor of a LennardJones glass: Propagation of acoustic modes at the nm-scale*, [*J. Alloys Compd.* **586**, S250 \(2014\)](#).
- [158] A. Togo and I. Tanaka, *First principles phonon calculations in materials science*, *Scr. Mater.* **108**, 1 (2015).