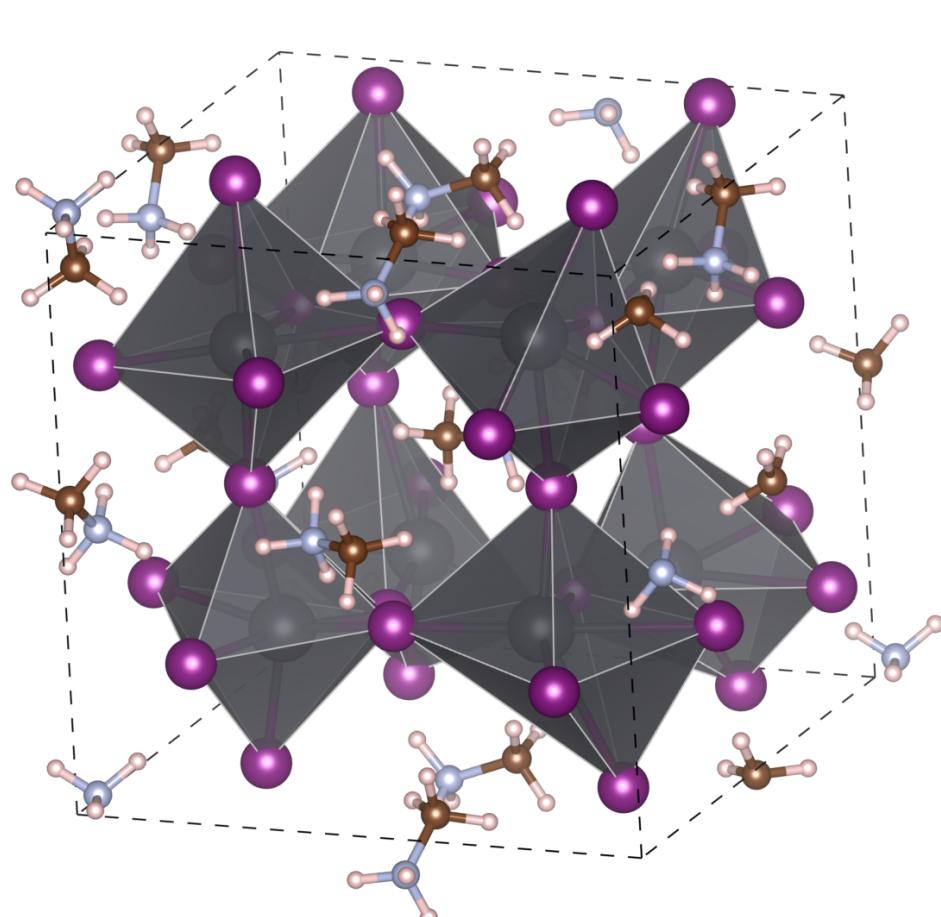


Crystal kinematics of hybrid-halide perovskites

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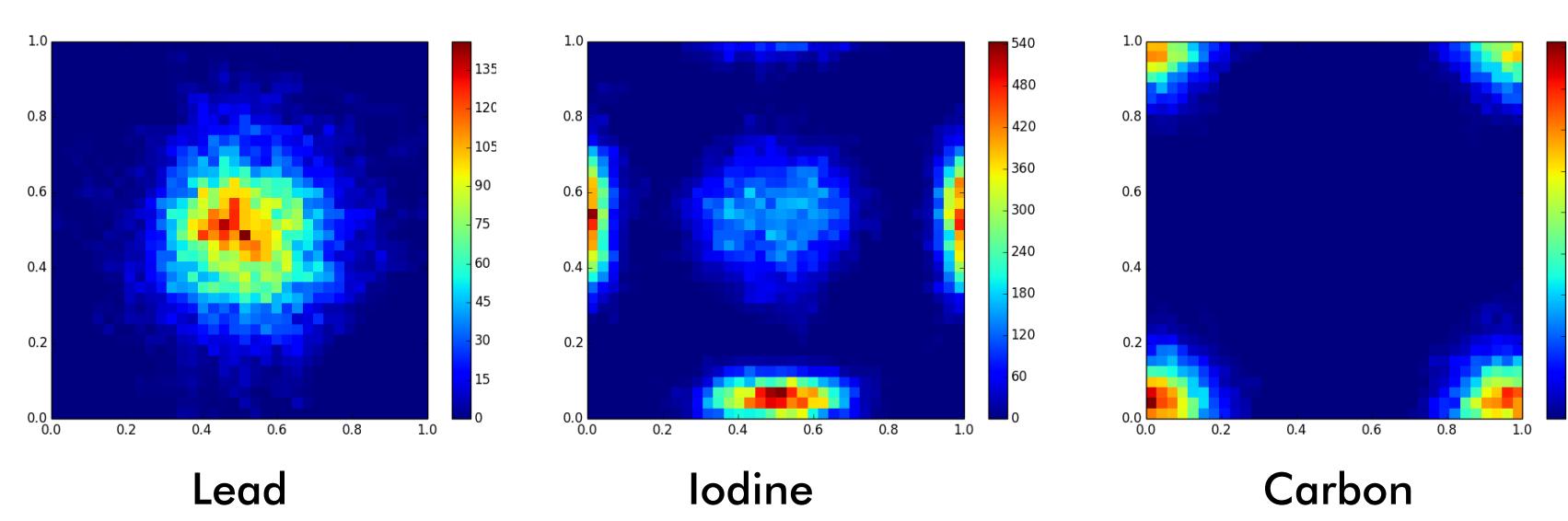
Ab-initio Molecular Dynamics

Hybrid halide perovskite (here, methyl-ammonium lead iodide - $\text{CH}_3\text{NH}_3\text{PbI}_3$) is a promising new solution processible solar cell material. Its genre mixing material properties present new challenges for computation.

Most DFT studies are on static representations of the average crystal structure. The large open cage structure of PbI_6 octahedra, and the electrostatically held organic molecule suggests that rich kinetic behaviour may be observed.

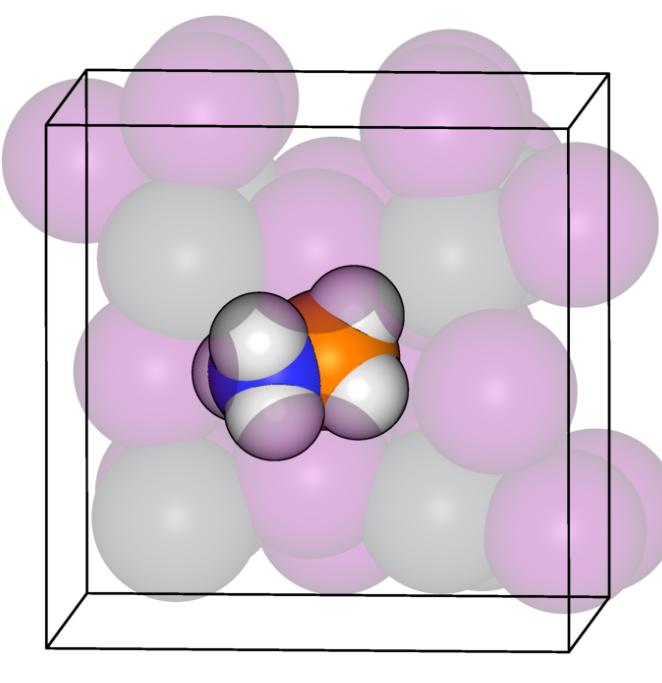
Ab-initio molecular dynamics show that this material is extremely soft at room temperature. A major motion is the octahedra tilting; we can see this in the highly anisotropic distribution of iodine location versus time.

Our 'pseudo-cubic' structure is an average structure, produced by dynamic tilting. These same soft modes are responsible for the phase transitions (and associated changes in crystal structure) going to tetragonal and finally orthorhombic at cryogenic temperatures.

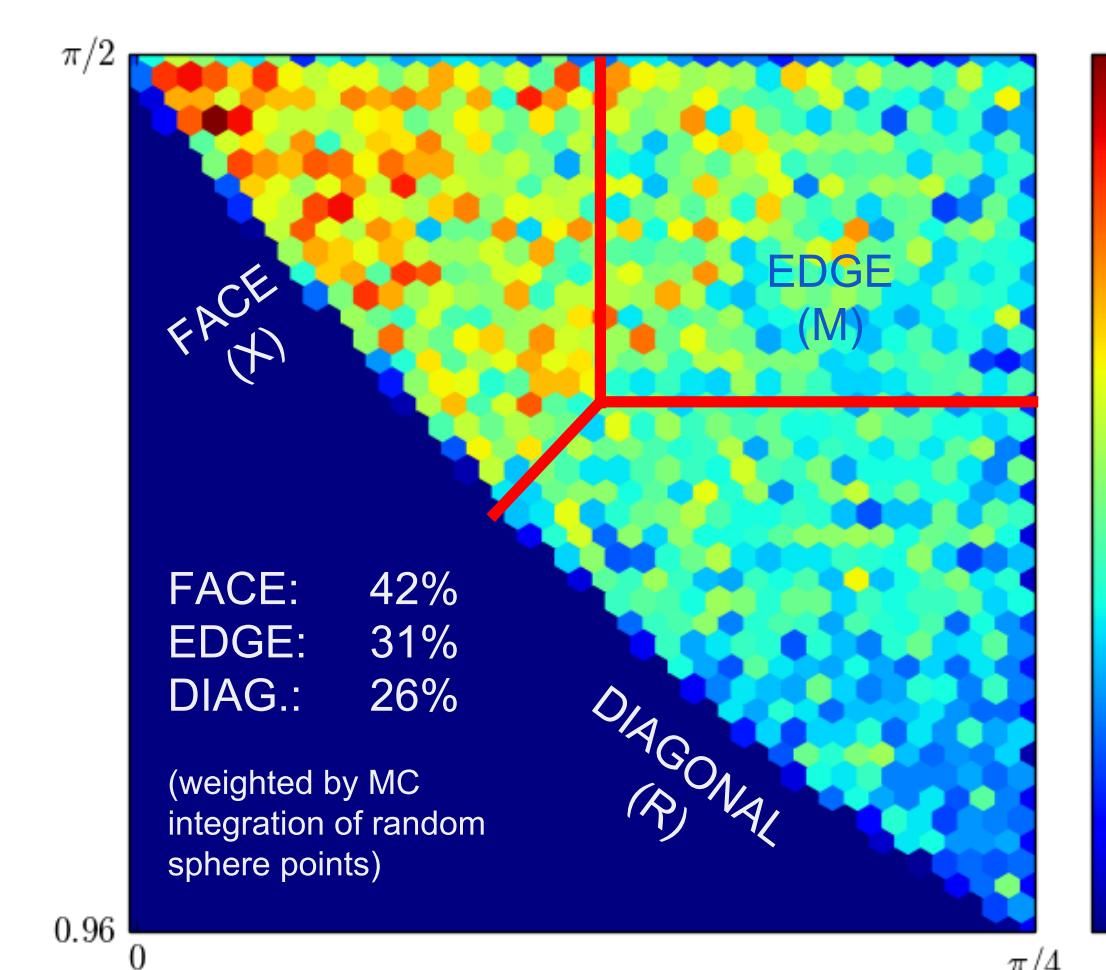
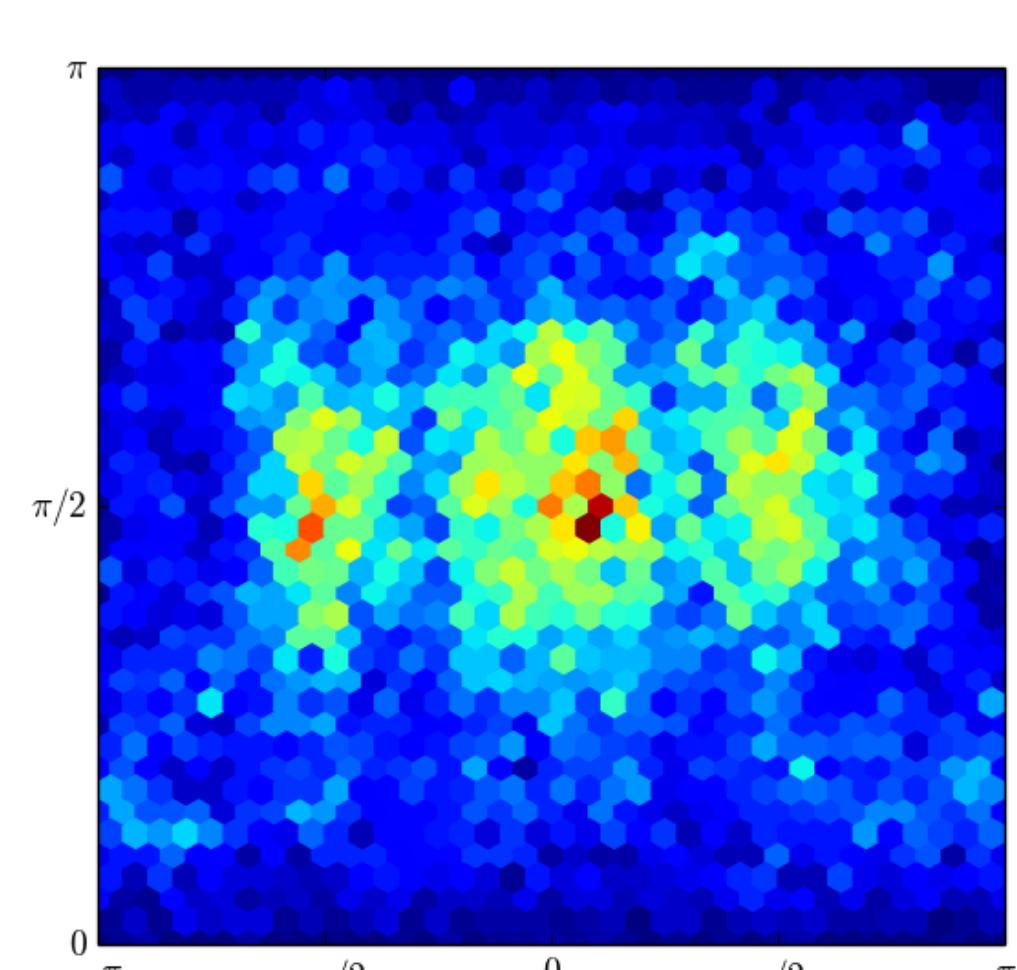


The fluctuation of band gap versus time calculated to exist in this material will have repercussions for optoelectronic properties.

Ab-initial molecular dynamics is not difficult to carry out - the challenge is in devising analysis methods which make sense of the data and provide understanding. Here we initially concentrated on studying the alignment of the organic cation, to model its motion and understand how it contributes to the dielectric response of the material.



<http://youtu.be/Rr2DDiYUoNA>



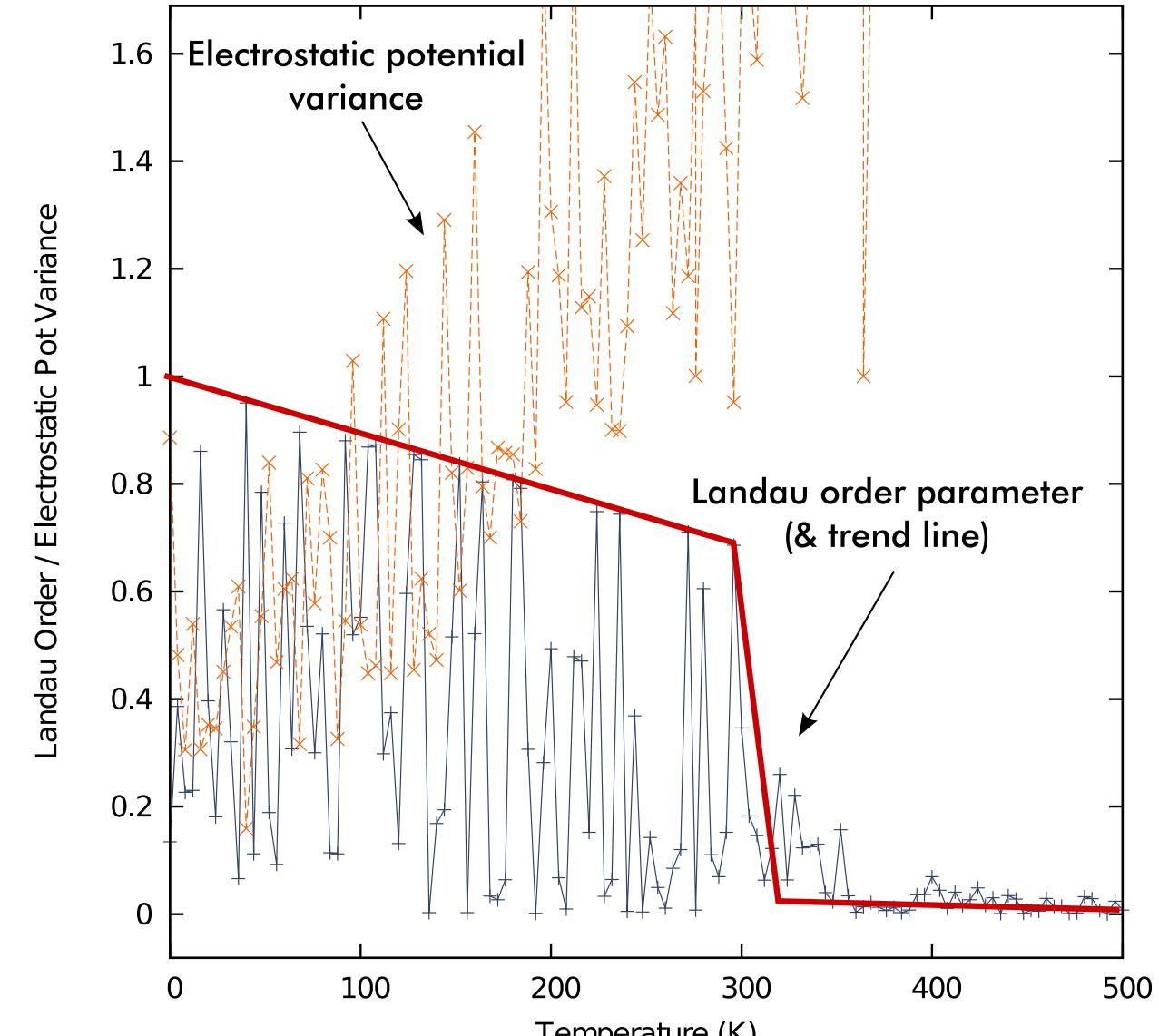
Histogramming the polar angles traced by the 8 MA ions can tell us limited information. Exploiting the octahedral symmetry at the analysis level gives us a 48 fold increase in signal-to-noise, enabling quantiation.

VASP plane wave DFT code, BOMD, PBESol functional. Gamma point & low (350 eV) plane-wave cut-off, 2x2x2 Pseudo-cubic super cell; 0.5 fs integration step.

Cage strain & Landau order

By introducing an additional, local, strain term into our Hamiltonian (parameterised from a 4x4x4 supercell periodic DFT calculation of aligned MA domains, where we flip a single MA ion), we can induce the formation of fully ferroelectric domains.

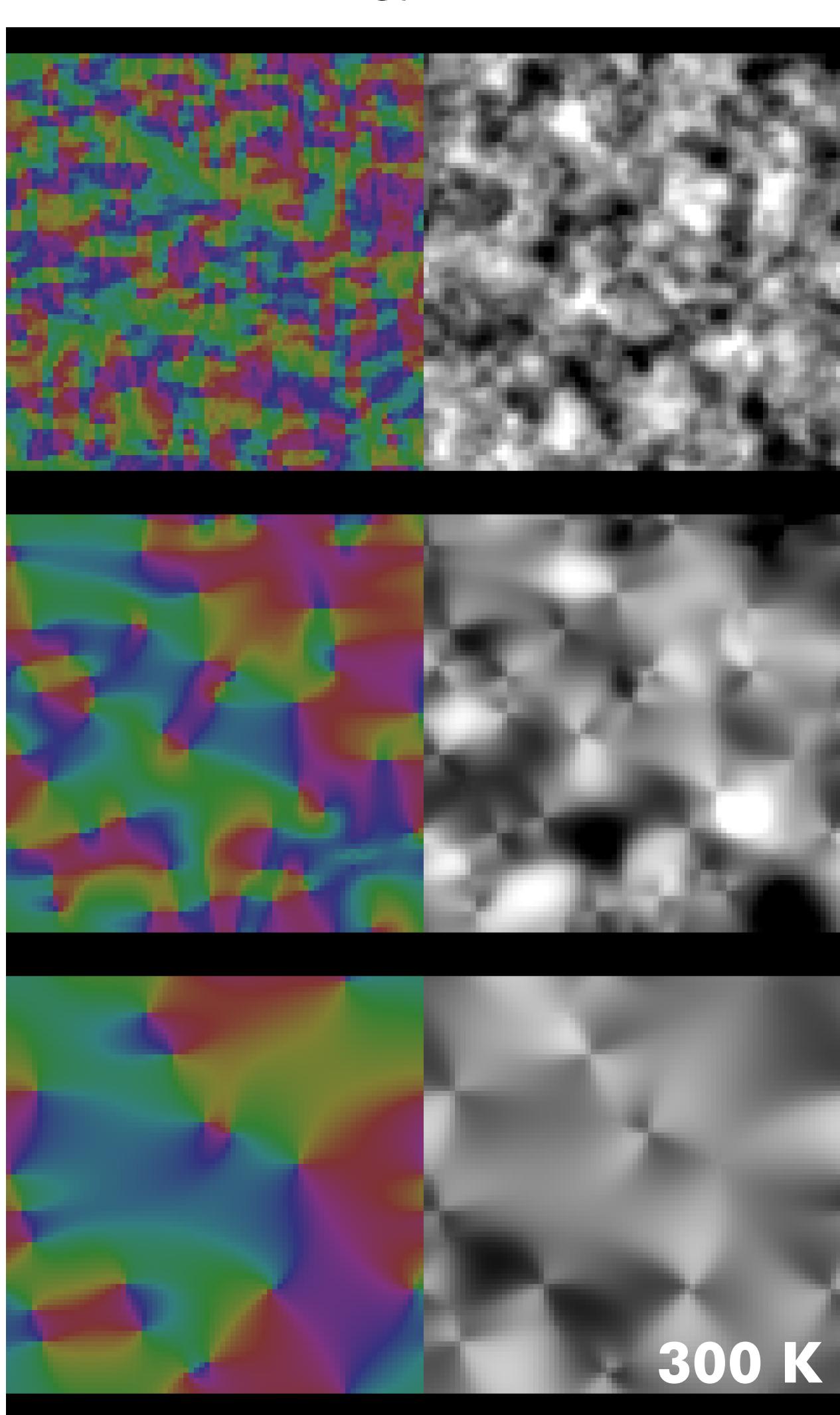
The degree of overall alignment of the simulation volume can be easily tracked by defining a Landau order parameter, the most simple of which is simply the vector average of the MA alignments. For a fully aligned domain, the length of this vector is 1, otherwise ~0.



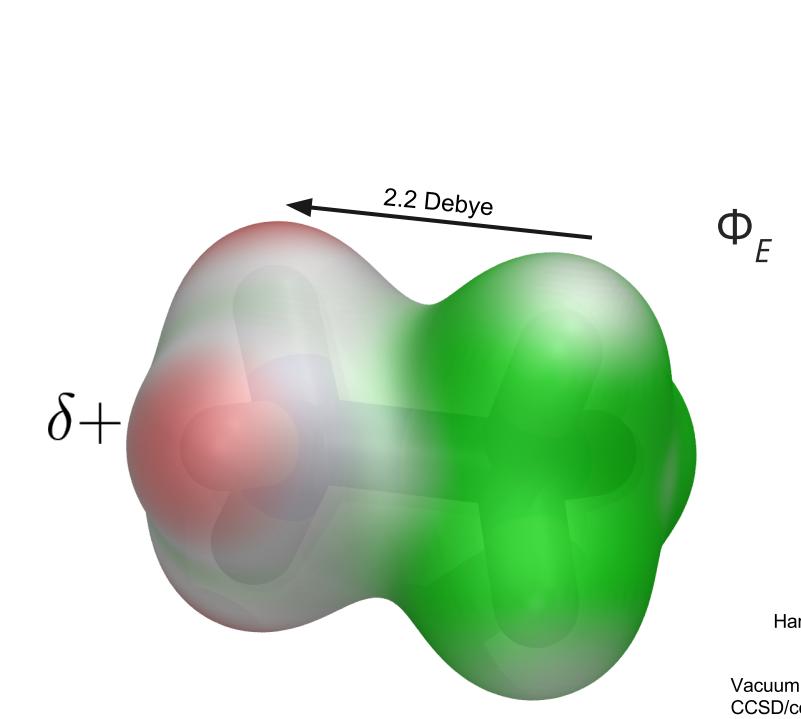
Our initial value for this interaction energy is ~25 meV per nearest-neighbour site, the total DFT energy for flipping one dipole in a fully aligned system, shared between the six co-facial unit cells.

The Landau parameter defined naively is extremely noisy, yet the trend is that it decays slowly before undergoing an abrupt transition near 300 K, at which point the electrostatic potential variance also diverges.

$$H = \sum_i \sum_{j,local} K \cdot p_i \cdot p_j$$

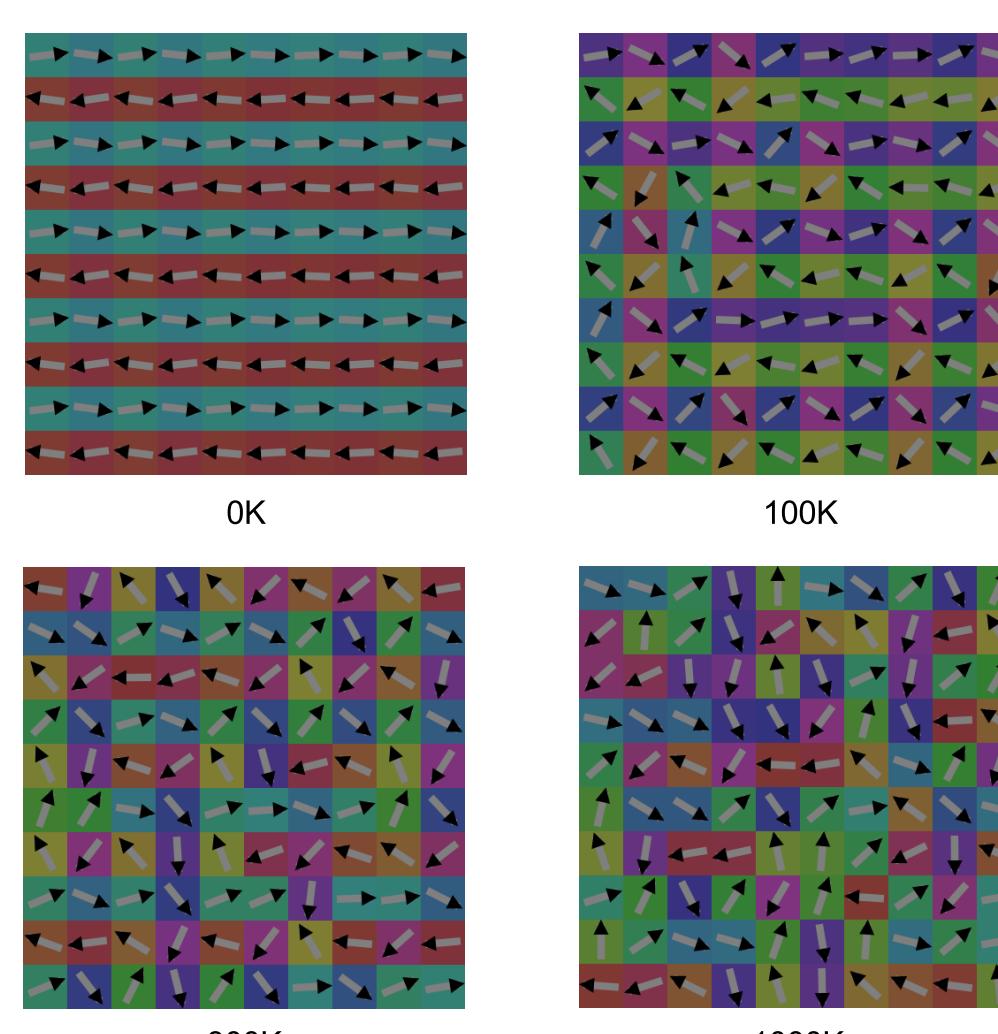


Dipole order (left) and electrostatic potential (right), showing the slow ripening of ferroelectric domains.



$$H = \sum_{dipole,E-field}^n (p_i \cdot E) + \sum_{dipole,dipole}^{n,m} \frac{1}{4\pi\epsilon_0} \left(\frac{p_i \cdot p_j}{r^3} - \frac{3(\hat{n} \cdot p_i)(\hat{n} \cdot p_j)}{r^3} \right) + \sum_{dipole,strain}^n K \cdot |p_i \cdot \hat{x}|$$

The simple classical Hamiltonian is extremely computationally efficient to evaluate, with a cut-off for dipole:dipole interactions (here 3 unit cells).



With no strain term, the low temperature state is anti-ferroelectric with fully twinned domains. Increasing temperature induces disorder, transitioning to a full paraelectric phase at high temperature.

Table 2. Calculated properties of four hybrid lead halide perovskites from density functional theory. The molecular dipole (D) is given in Debye; the pseudo-cubic lattice constant ($a = \sqrt[3]{V}$) in Å; the electronic polarisation (ΔP) in $\mu\text{C}/\text{cm}^2$; and the rotation barrier (E_{rot}) and dipole interaction (E_{dip}) in kJ/mol .

Cation	D	a	ΔP	E_{rot}	E_{dip}
NH_4^+	0.00	6.21	8	0.3	0.00
CH_3NH_3^+	2.29	6.29	38	1.3	4.60
CF_3NH_3^+	6.58	6.35	48	-	42.00
$\text{NH}_2\text{CH}_2\text{NH}_2^+$	0.21	6.34	63	13.9	0.03

Nano Lett., 2014, 14 (5), pp 2584–2590

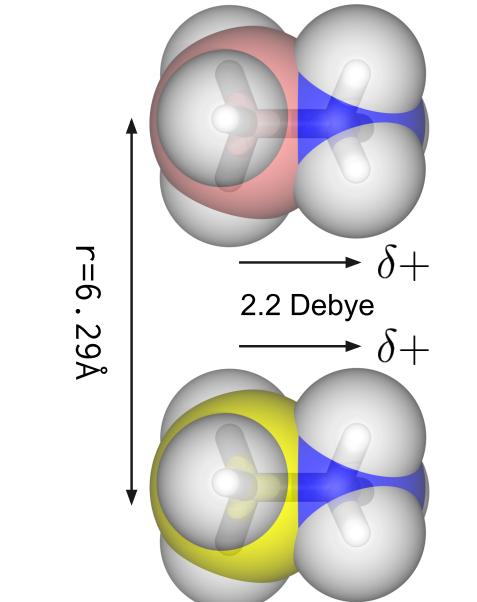
The same model and codes could also be used to simulate other organic cation-substitutions in hybrid halide perovskites.

Tilting and distorting of the octahedra would also experience similar interactions - and could be studied with a reparameterisation of the same model.

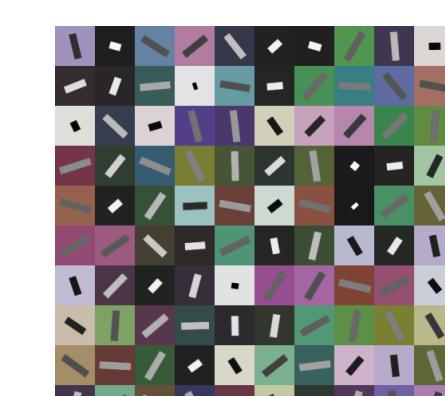
Monte Carlo model

Methyl-ammonium has a dipole of ~2.2 Debye. With its ability, as shown by molecular dynamics, to rotate within the octahedra cage, we construct codes to simulate the electrostatic interaction of rotating dipoles. The pseudo-cubic structure of high temperature MAPbI₃ leads itself naturally to a simple on-lattice presentation of rotating dipoles.

The rotational motion of the dipoles is updated with a Metropolis algorithm.

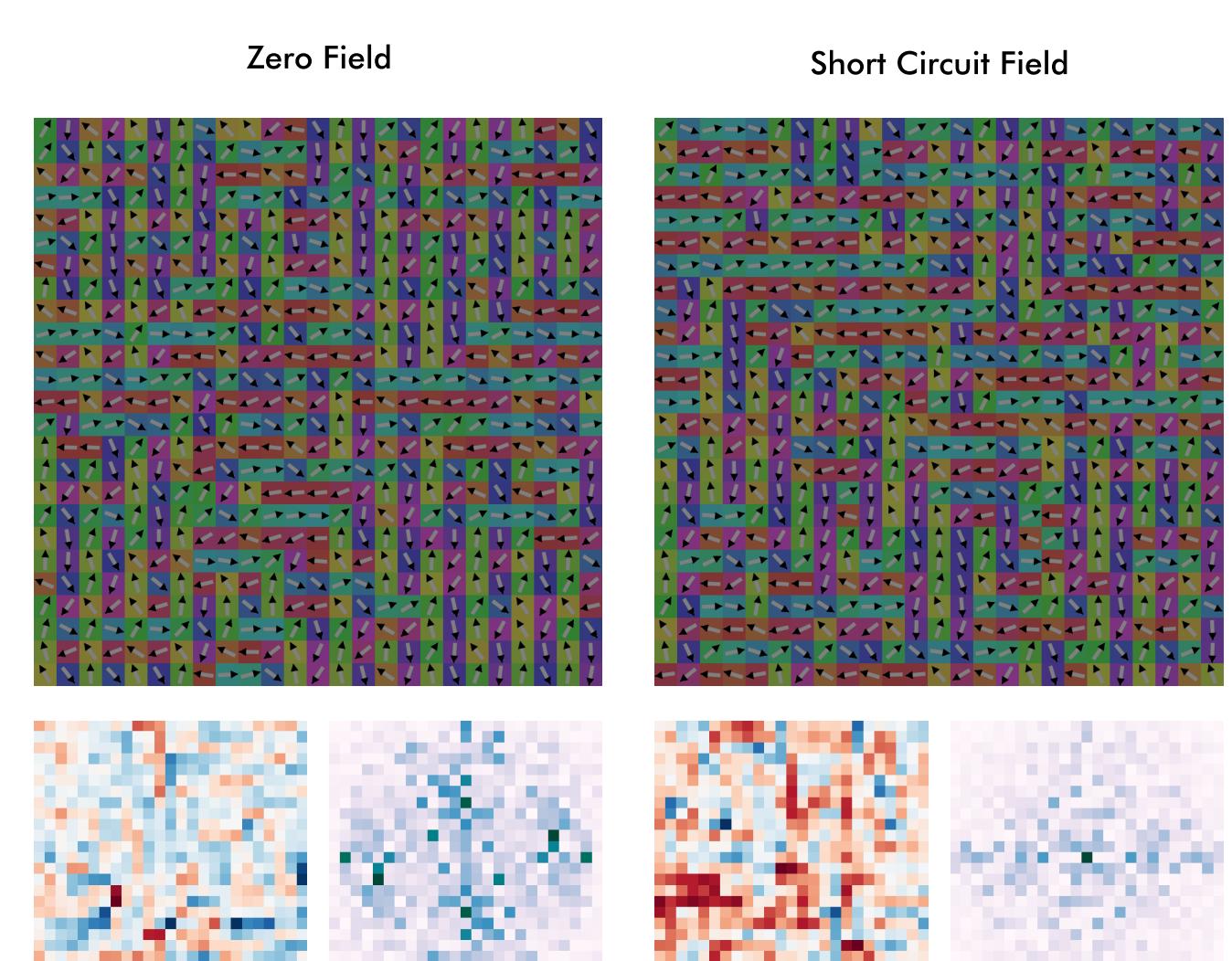


The main model parameterisation is the strength of the dipole-dipole interaction, which we calculate in the limit of using a vacuum dielectric, due to the open nature of the perovskite cage structure.



Here we display the alignment of the dipoles by projecting their polar direction in X and Y onto a colourwheel, and describing the Z component as a tone / saturation.

The code is full 3D, here we show clearer 2D data.



From the equilibrium orientations of the dipoles, we calculate the electrostatic potential as a result of the dipole alignment (bottom left), and also the Fourier transform of this data (bottom right). At short circuit in a solar cell, there is a field across the active region; at open circuit the field is ~zero. This field transitions the electrostatic landscape of the device from a configuration where there are ordered ridges & valleys of electrostatic potential, to regions of deeper and larger trapping basins of potential.

Conclusion & further work

The MAPbI₃ octahedra continuous tilt, distort and displace, this makes it conceptually difficult to define their motion, as our rigid unit model is no longer applicable..

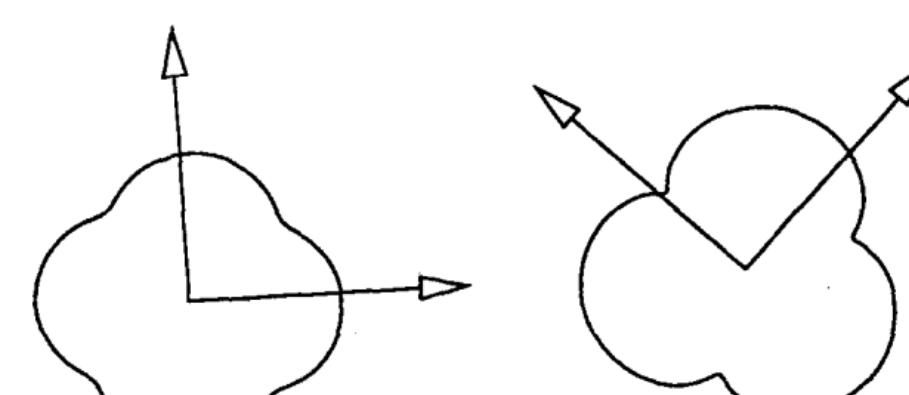


Fig. 1. In order to measure the relative orientation of two different shapes, a choice of axes for each shape must be made.

"Gauge kinematics of deformable bodies" Shapere, Wilczek Am. J. Phys. 57, 514 (1989); DOI: 10.1119/1.15986

We are writing codes (SMASH) which analyse the kinematics of these distortions, in order to provide a dynamic (time dependent) description of the tilting.

By also tracking the distortion of the octahedra, we can relate the displacement motion of the PbI_6 constituent ions to variations in the electrostatic potentials.

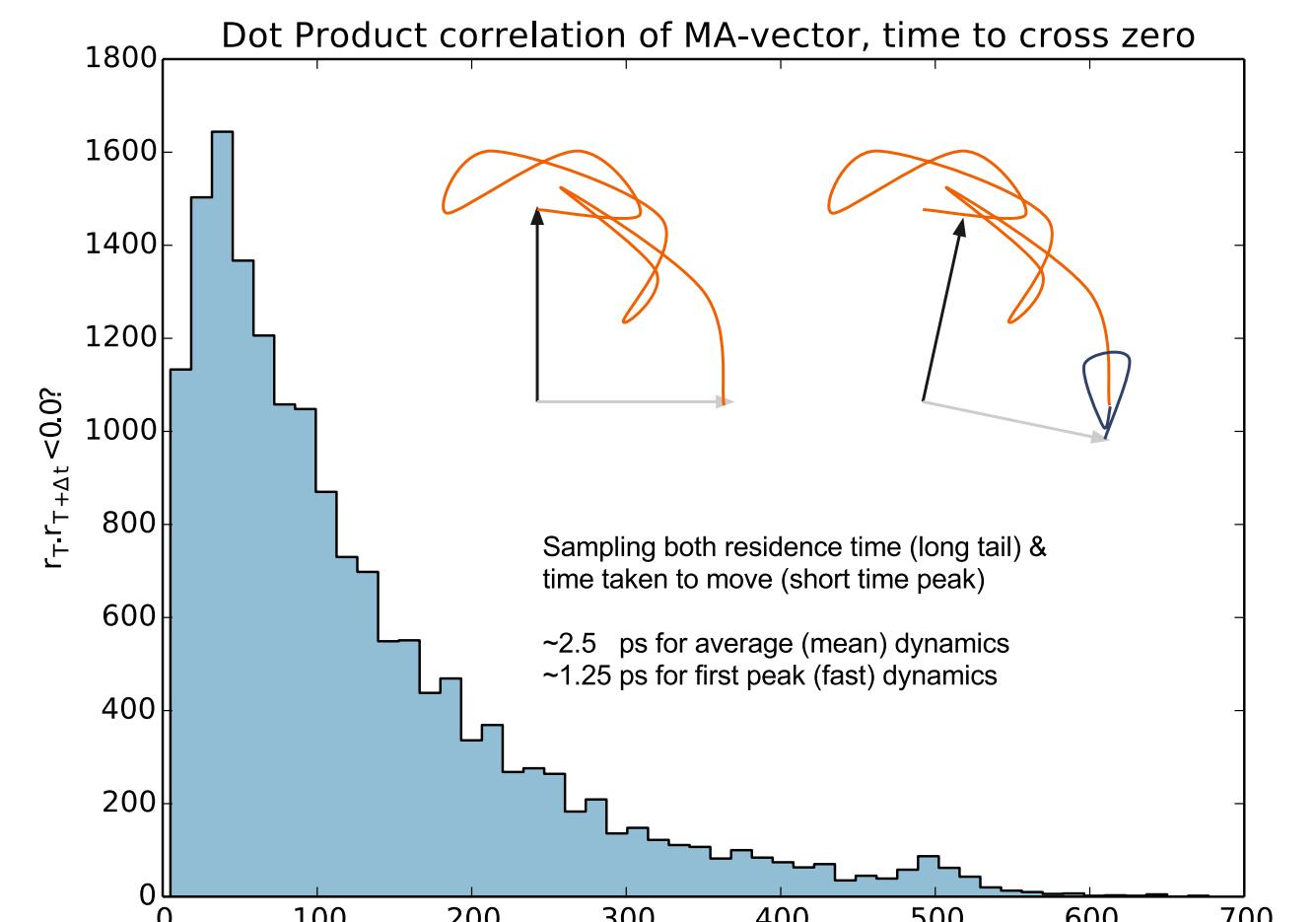
We intend to simulate the electrical properties of these materials - both to understand how polarons will move within the crystal field generated by the hybrid perovskite, and to understand to what degree free charges in the system modify the kinetic behaviour of the material. Certainly these materials offer an interesting computational modelling challenge.

We are grateful to fruitful discussions with Piers Barnes and Aurelien Leguy; the molecular dynamics in this work was originally started in order to explain their (unpublished) quasi-inelastic neutron scattering data.

Some, partial, experimental validation of the observed kinetic behaviour has come through quasi-inelastic neutron scattering of Piers Barnes and Aurelien Leguy. Direct measurement of the methyl-ammonium precession has been achieved by Artem Bakulin et al. through 2D photon echo (IR pump-probe).

Further work will involve collaborating with data analysis to prove or disprove the motion we calculate.

We have extended our molecular dynamics to more demanding 4x4x4 unit cell expansions, to sample more collective rotations than will be represented in 2x2x2.



Supporting information to this poster (most notably videos of the dynamic data presented here) are available at an accompanying website. Scan the QR code to the right, or use the URL below.



<http://jarist.github.io/PerovskiteKinematics>