Cubic on the Streets, Tetragonal in the Sheets: the Nature of Local Dynamic Order in $CH_3NH_3PbI_3$

Tyler C. Sterling

University of Colorado Boulder

collaborators at University of Colorado Boulder:

Nick Weadock (project leader)
Mike Toney (PI)
Dmitry Reznik (PI and my advisor)

and elsewhere:

Ballal Ahammed & Elif Ertekin (MD simulations)
Julian A Vigil, Aryeh Gold-Parker, Ian C Smith, Matthew Krogstad, Feng Ye, David Voneshen, Peter M Gehring, Hans-Georg Steinrück, Hemamala Karunadasa

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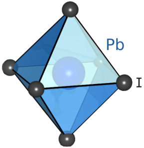
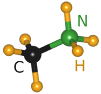
Experiments done on ...

CORELLI at the SNS (Oak Ridge)
Beamline 6-ID-D at the APS (Argonne)
MERLIN at ISIS (Rutherford Appleton)

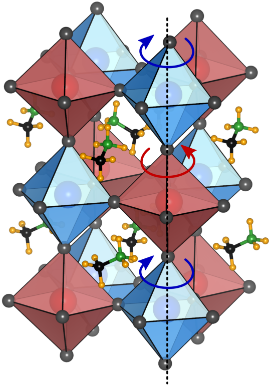
(nominal) structure of $CH_3NH_3PbI_3$ (MAPI)



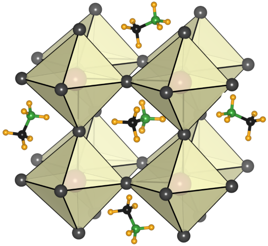
PbI_6 "octahedra"



"methylammonium" (MA)

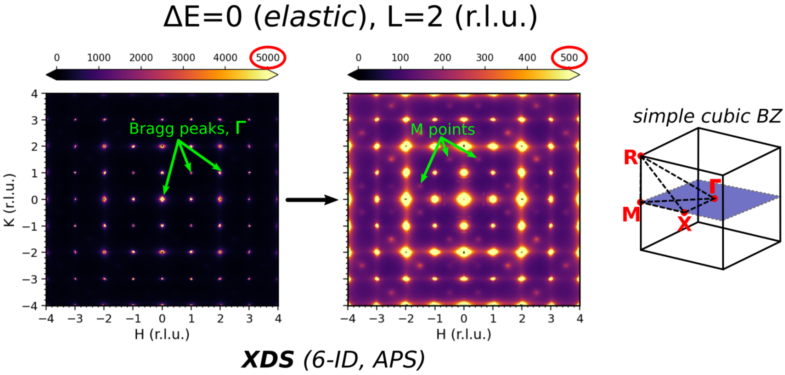


tetragonal **(lowish T)**

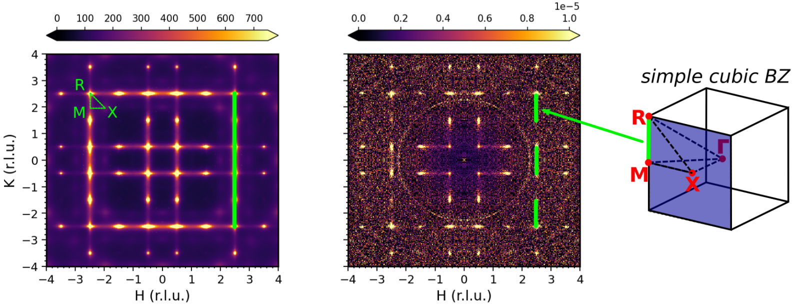


*pseudo*cubic **(room temp.)**

Structure-function relationship in MAPI, MAPB still not known... structure still not known



$\Delta E=0$ (*elastic*), L=1.5 (r.l.u.)



XDS *(6-ID, APS)*　　***NDS*** *(CORELLI, SNS)*

Diffuse scattering shows non-trivial structure ... what is it?!

Classical molecular dynamics (MD) can be used to simulate microscopic dynamics

e.g. spectral energy density in MAPI

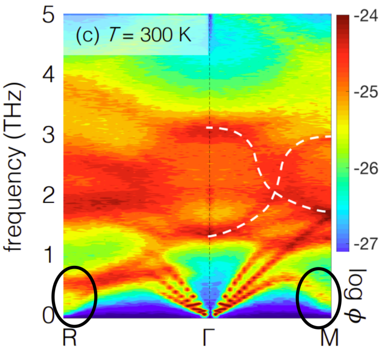


Figure: from *Zhu, Taishan, and Elif Ertekin. Energy & Environmental Science 12.1 (2019): 216-229.*

Standard expression:

$$S(\boldsymbol{Q},\omega) = \int \langle \hat{\rho}(\boldsymbol{r},t)\hat{\rho}(0,0)\rangle \exp(i\boldsymbol{Q}\cdot\boldsymbol{r} - i\omega t)d\boldsymbol{r}dt$$

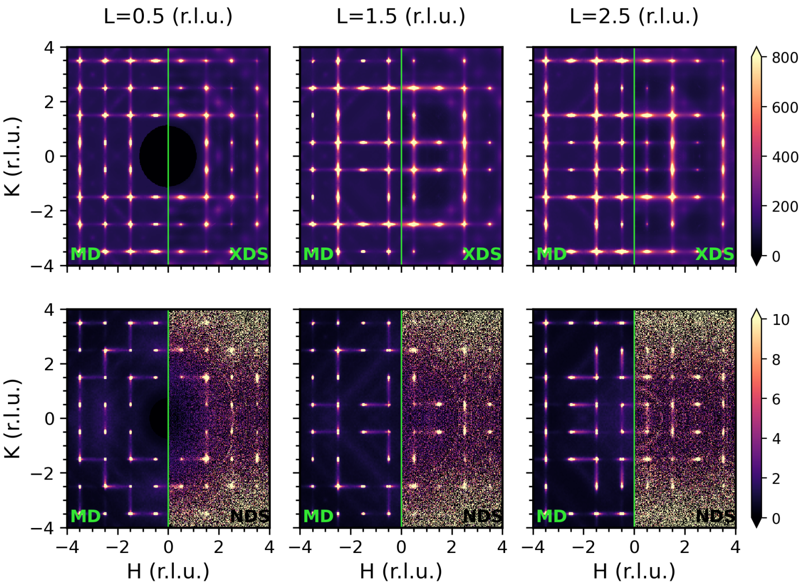
Time development of $\hat{\rho}$ is many-body problem

Approximate $\hat{\rho} \rightarrow \rho$ as classical

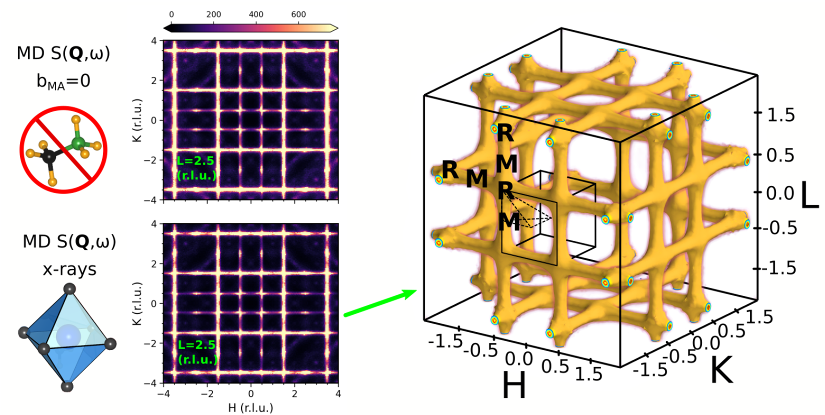
$$S(\boldsymbol{Q},\omega) = \left| \sum_i \underbrace{f_i(Q)}_{\text{"form-factors"}} \int \exp(i\boldsymbol{Q}\cdot \underbrace{\boldsymbol{r}_i(t)}_{\text{trajectories}} - i\omega t)dt \right|^2$$

$\boldsymbol{r}_i(t)$ are straightforwardly calculated by classical MD

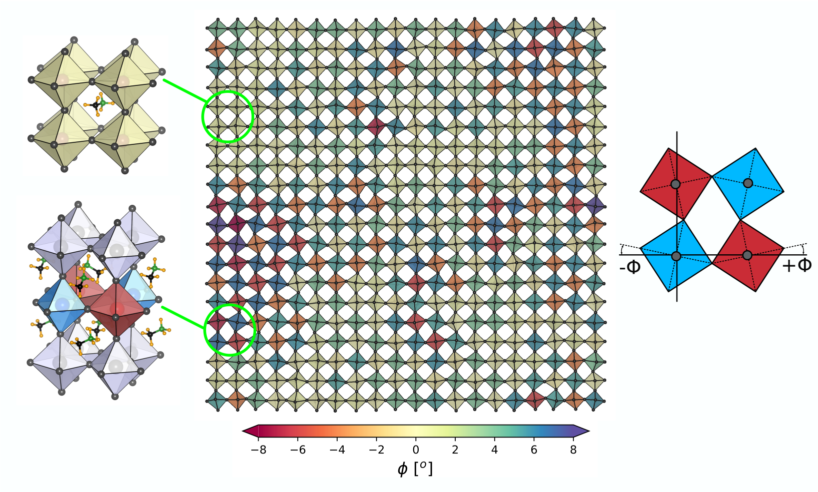
MD vs. experiment



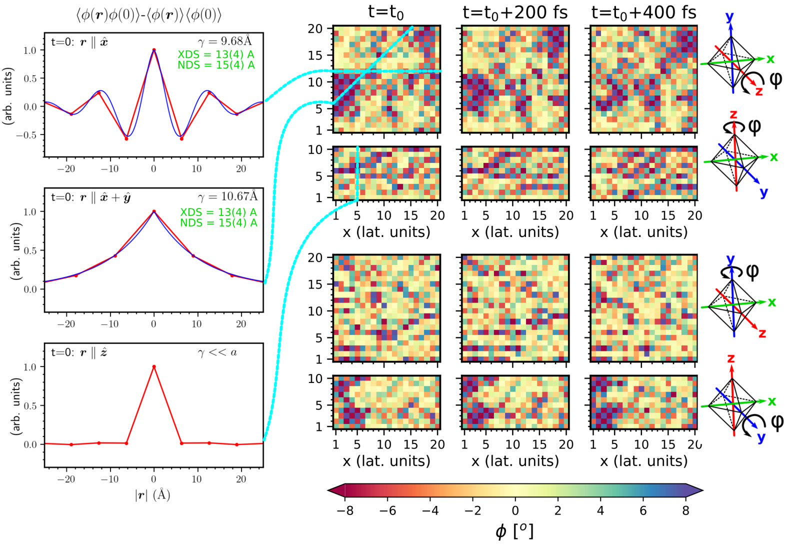
Probing the local order

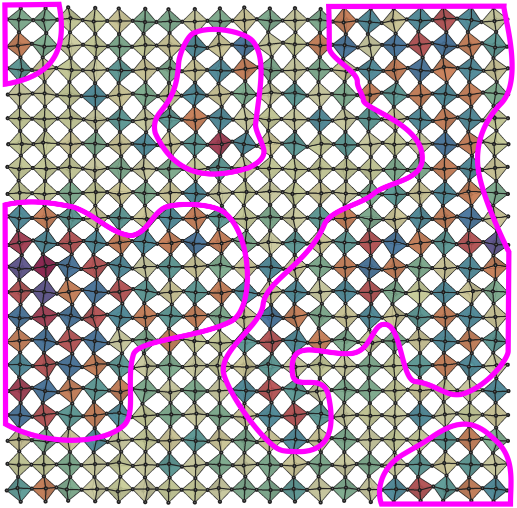


The local order



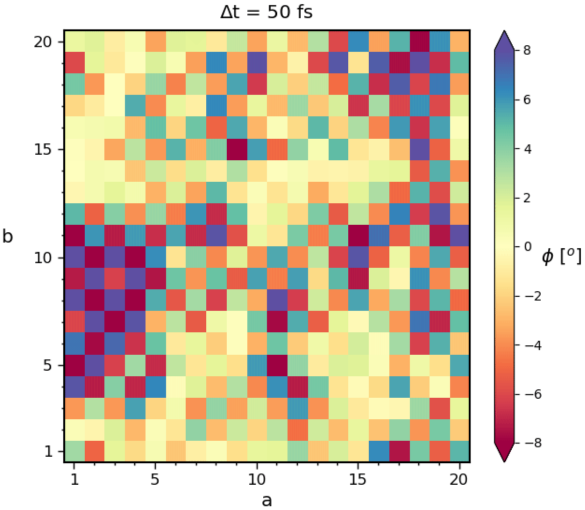
2D nature of local order



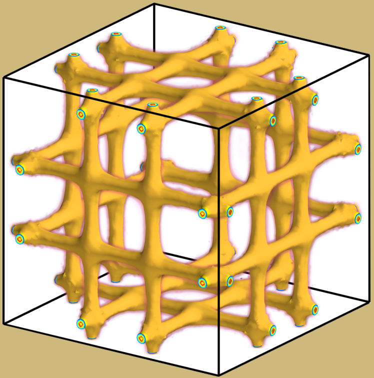


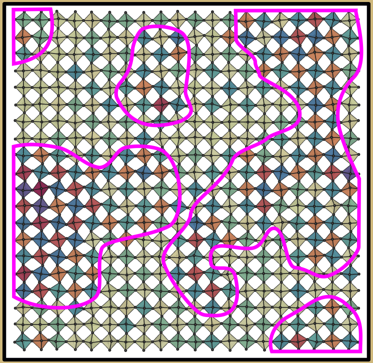
Octahedra form 2D “pancakes” of tetragonal-like domains

Dynamics of pancakes



Non-trivial order in PbI_6 sub-lattice: rods in reciprocal space signal 2D ordering





MD simulations reveal the nature of order: PbI_6 form "pancakes" of fluctuating tetragonal-like 2D domains

Total scattering:

$$S(\boldsymbol{Q},\omega) = \Big| \sum_i f_i(Q) \int \exp(i\boldsymbol{Q}\cdot\boldsymbol{r}_i(t) - i\omega t)dt \Big|^2$$

Sub-lattice contributions:

$$\rho_\alpha(\boldsymbol{Q},\omega) \equiv \sum_{i\in\{\alpha\}} f_i(Q)\exp(i\boldsymbol{Q}\cdot\boldsymbol{r}_i(t) - i\omega t)$$

$$\alpha \equiv \mathrm{PbI}_6 = \{\mathrm{Pb,\ I}\}$$

$$\alpha \equiv \mathrm{MA} = \{\mathrm{C,\ H,\ N}\}$$

"Interference" correlations:

$$S_{\mathrm{int.}}(\boldsymbol{Q},\omega) = S(\boldsymbol{Q},\omega) - (\underbrace{|\rho_{\mathrm{PbI_6}}|^2}_{S_{\mathrm{PbI_6}}(\boldsymbol{Q},\omega)} + \underbrace{|\rho_{\mathrm{MA}}|^2}_{S_{\mathrm{MA}}(\boldsymbol{Q},\omega)})$$

Other sub-lattice contributions