

The Nature of Local Dynamic Order in $\text{CH}_3\text{NH}_3\text{PbI}_3$

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collaborators at University of Colorado Boulder:

Nick Weadock (4:15 PM Today)

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

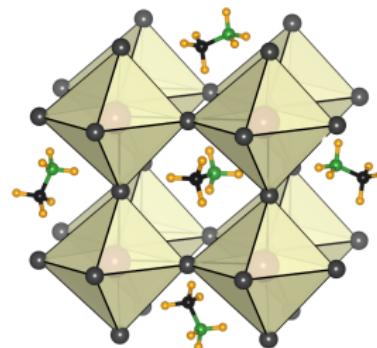
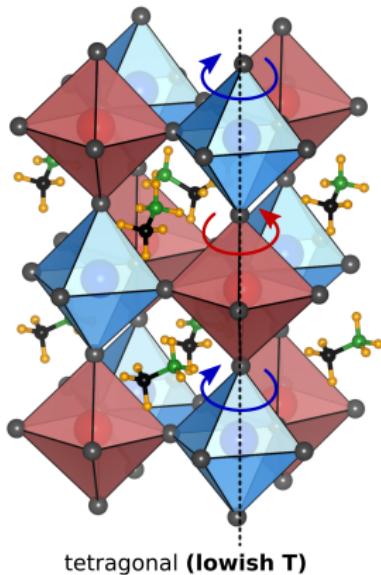
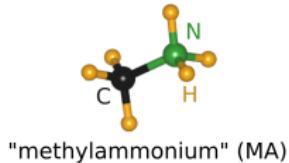
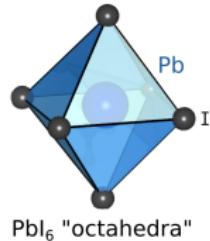


Work at CU used funding from DOE, Office of Science,
Neutron Scattering Program

Experiments done on ...

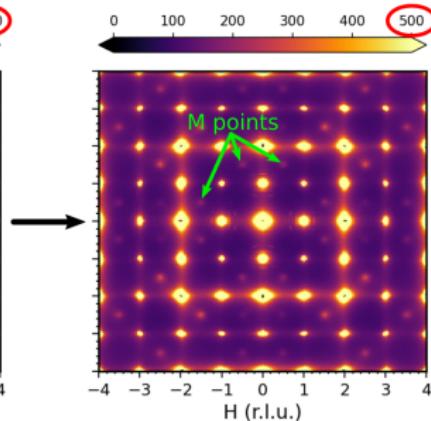
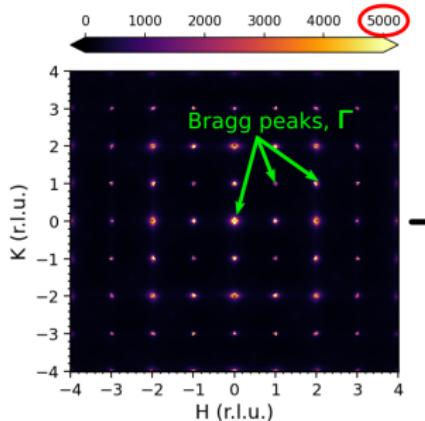
CORELLI at the SNS (Oak Ridge)
Beamline 6-ID-D at the APS (Argonne)
MERLIN at ISIS (Rutherford Appleton)

(nominal) structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPI)

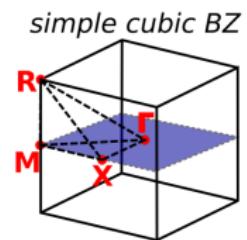


Structure-function relationship in MAPI, MAPB still not known... structure still not known

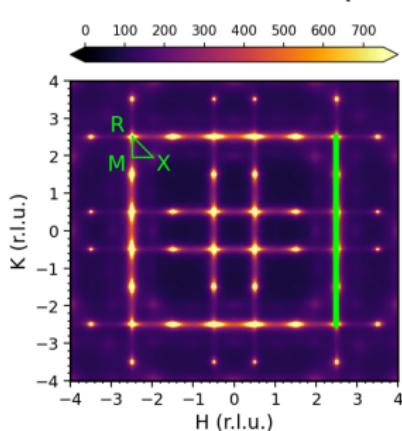
$\Delta E=0$ (elastic), $L=2$ (r.l.u.)



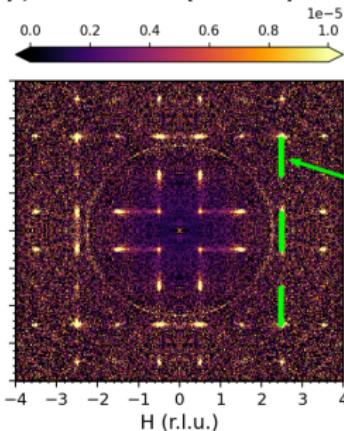
XDS (6-ID, APS)



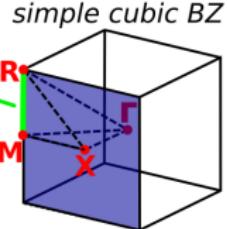
$\Delta E = 0$ (elastic), $L = 1.5$ (r.l.u.)



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

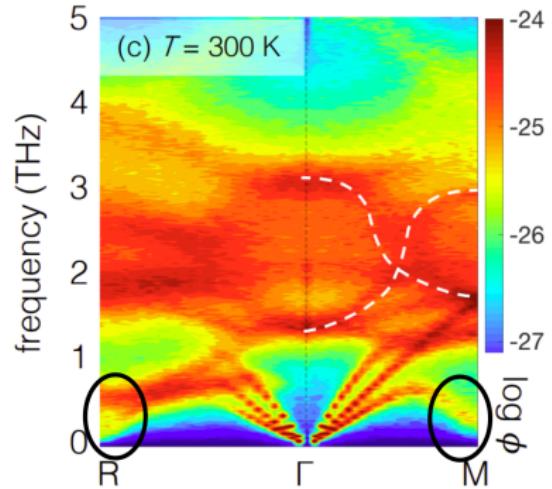


Figure: from *Zhu, Taishan, and Elif Ertekin. Energy & Environmental Science 12.1 (2019): 216-229.*

Standard expression:

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

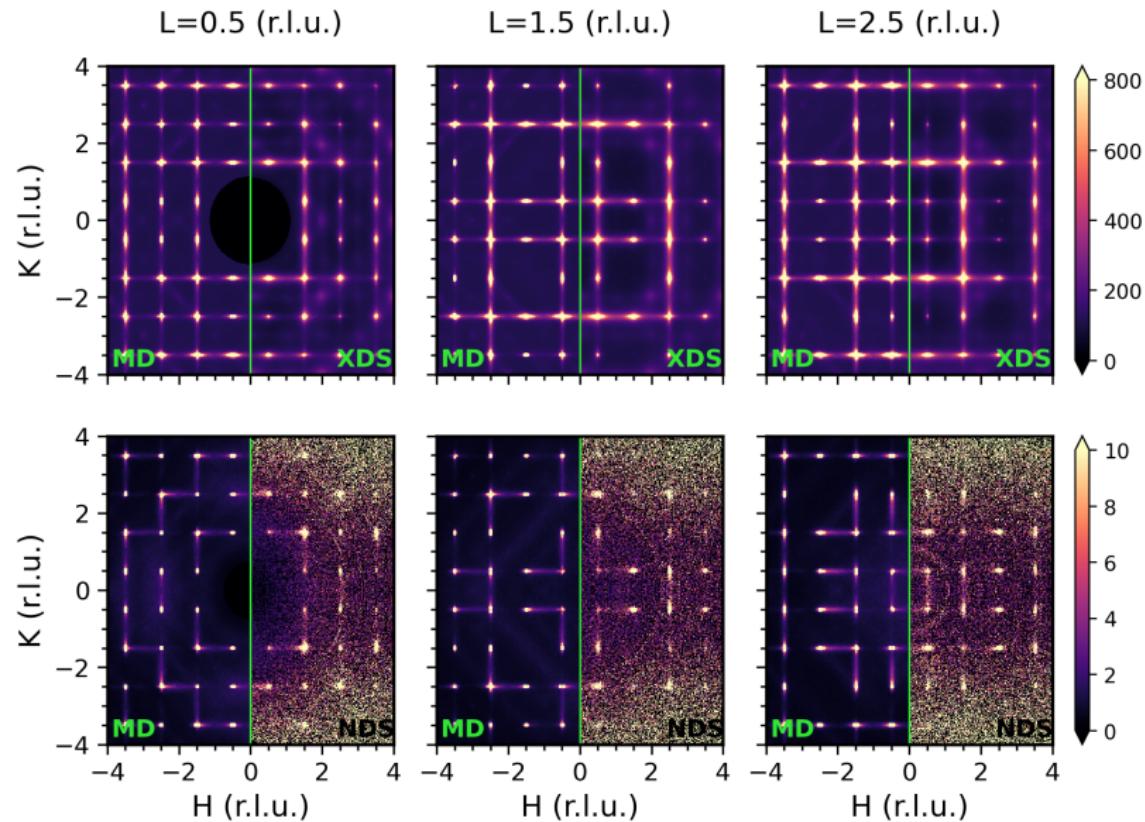
Time development of $\hat{\rho}$ is **many-body problem**

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

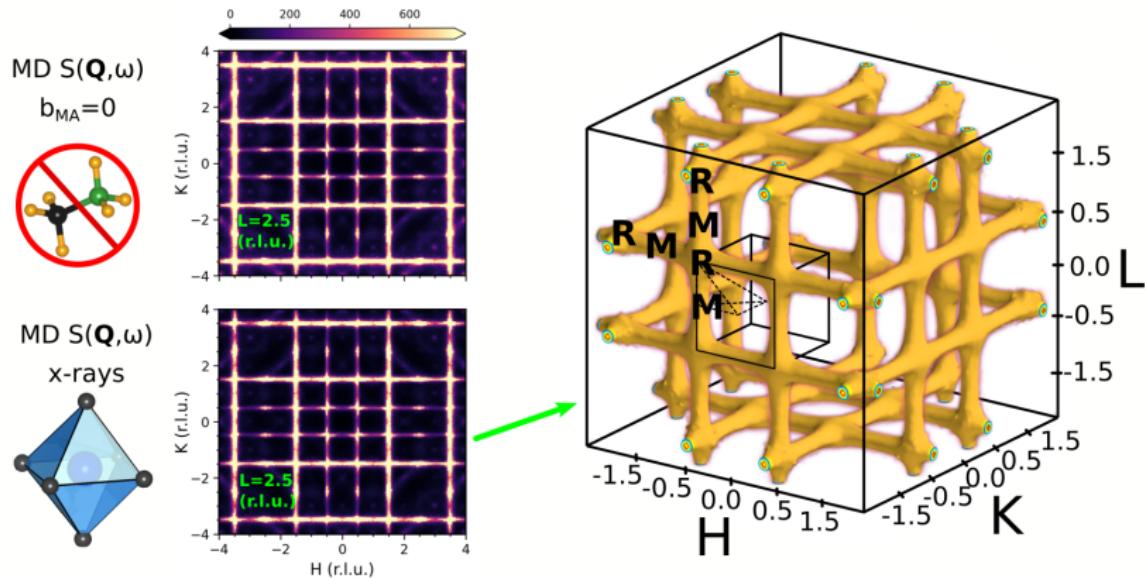
$$S(\mathbf{Q}, \omega) = \left| \sum_i \underbrace{f_i(Q)}_{\text{"form-factors"}} \int \exp(i\mathbf{Q} \cdot \underbrace{\mathbf{r}_i(t)}_{\text{trajectories}} - i\omega t) dt \right|^2$$

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

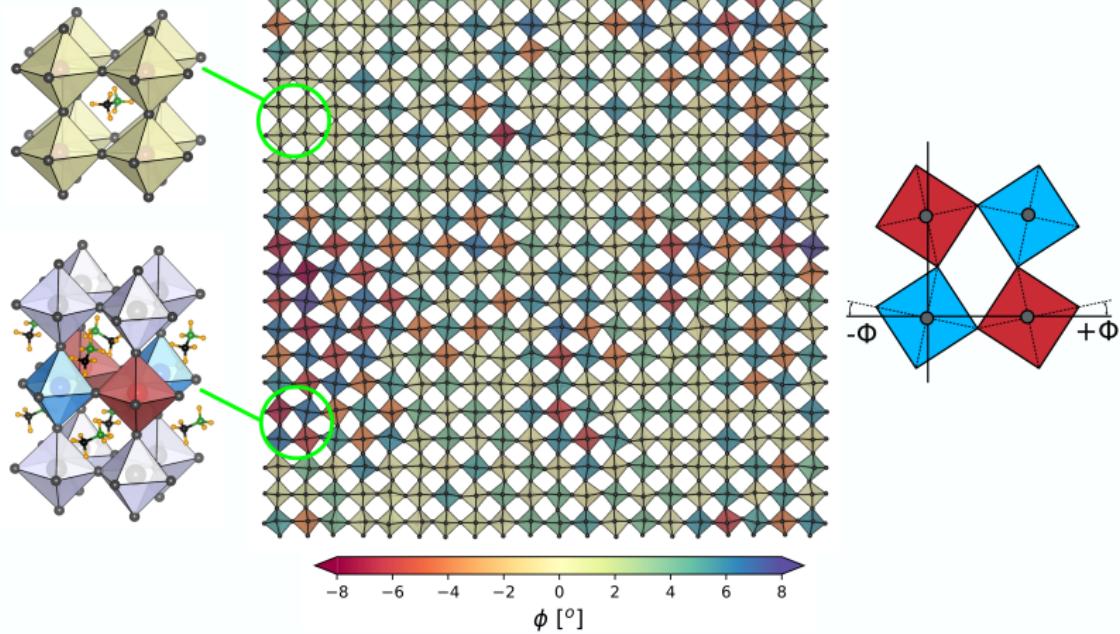
MD vs. experiment

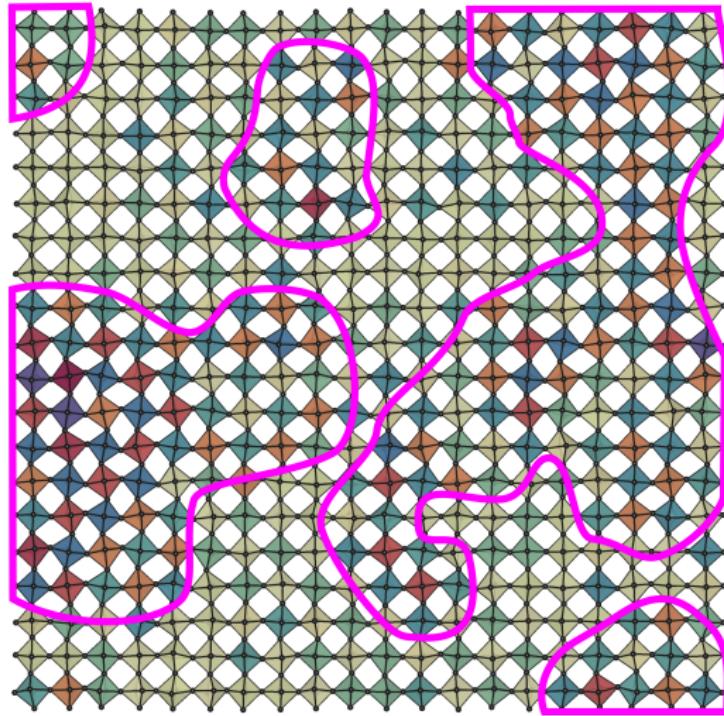


Probing the local order



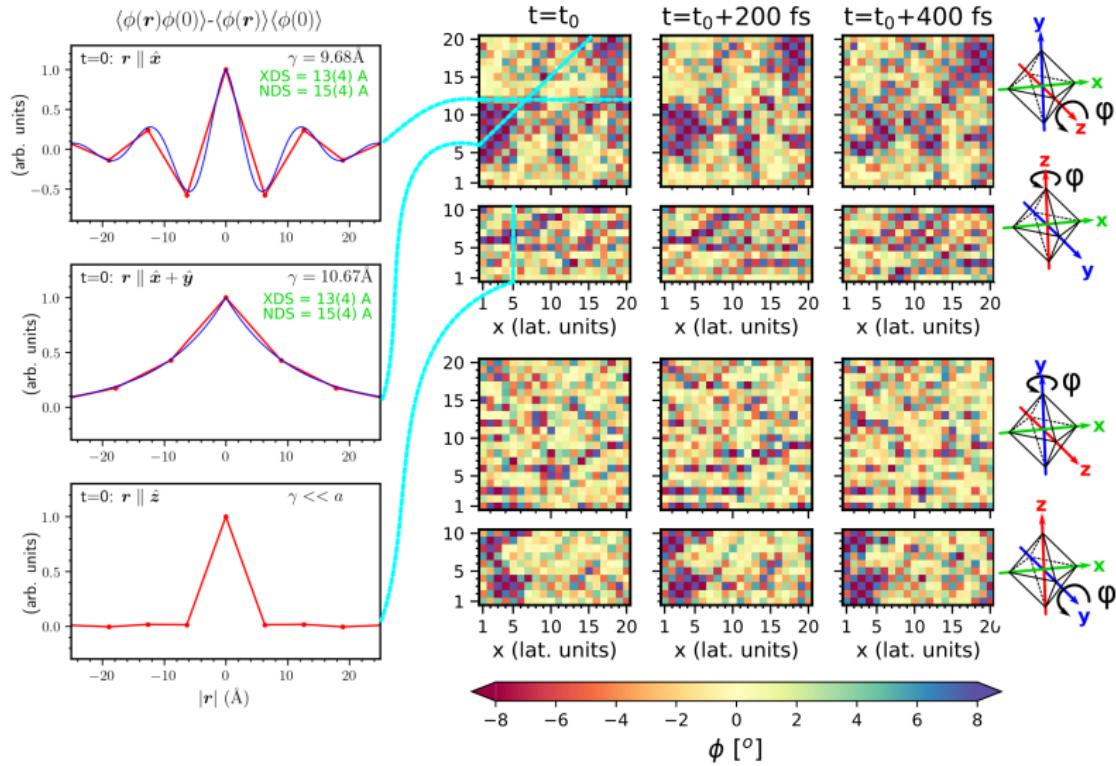
The local order





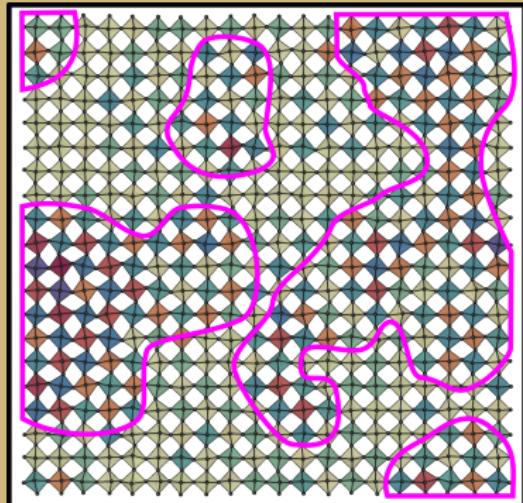
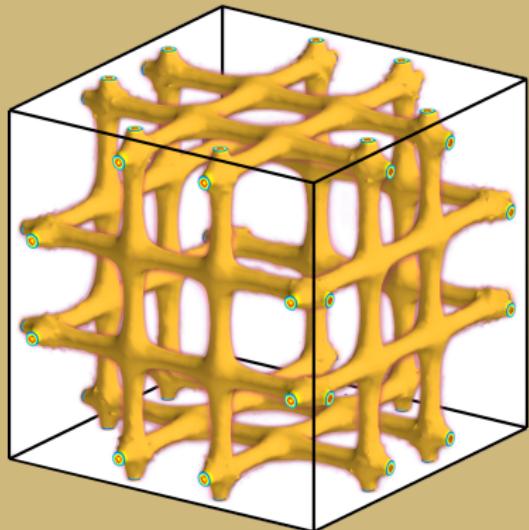
Octahedra form 2D “pancakes” of tetragonal-like domains

2D nature of local order



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:

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

Sub-lattice contributions:

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

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

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

“Interference” correlations:

$$S_{\text{int.}}(\mathbf{Q}, \omega) = S(\mathbf{Q}, \omega) - \left(\underbrace{|\rho_{\text{PbI}_6}|^2}_{S_{\text{PbI}_6}(\mathbf{Q}, \omega)} + \underbrace{|\rho_{\text{MA}}|^2}_{S_{\text{MA}}(\mathbf{Q}, \omega)} \right)$$

Other sub-lattice contributions

