

# The Two-Dimensional Nature of Dynamic Disorder in Hybrid Metal-Halide Perovskite Semiconductors

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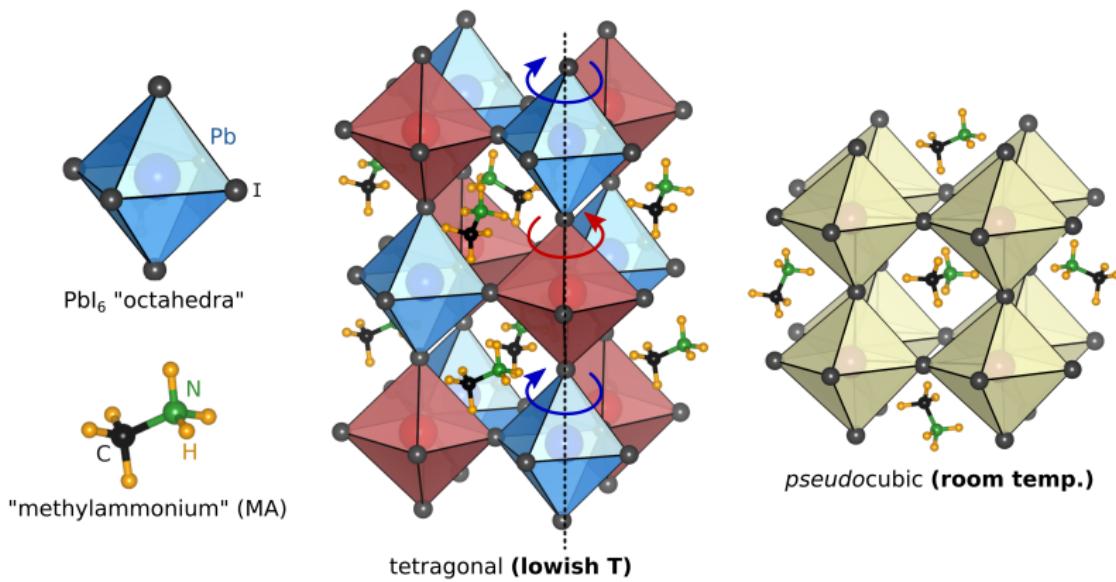


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Neutron Scattering Program

### **Experiments done on ...**

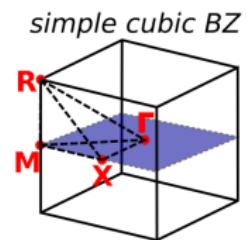
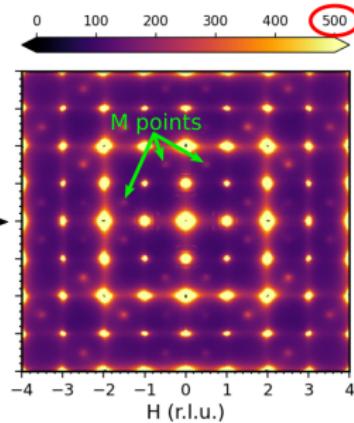
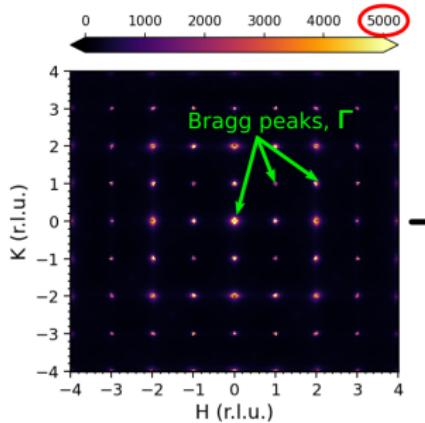
CORELLI at the SNS (Oak Ridge)  
Beamline 6-ID-D at the APS (Argonne)  
MERLIN at ISIS (Rutherford Appleton)

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



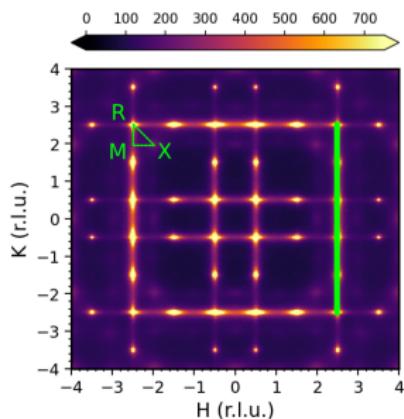
# Structure-function relationship in MAPI, MAPB still not known... structure still not known

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

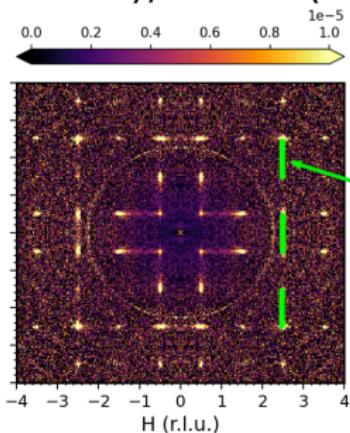


**XDS (6-ID, APS)**

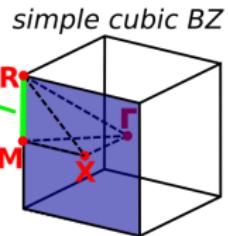
## MAPI, $\Delta E=0$ (elastic), $L=1.5$ (r.l.u.)



**XDS** (6-ID, APS)

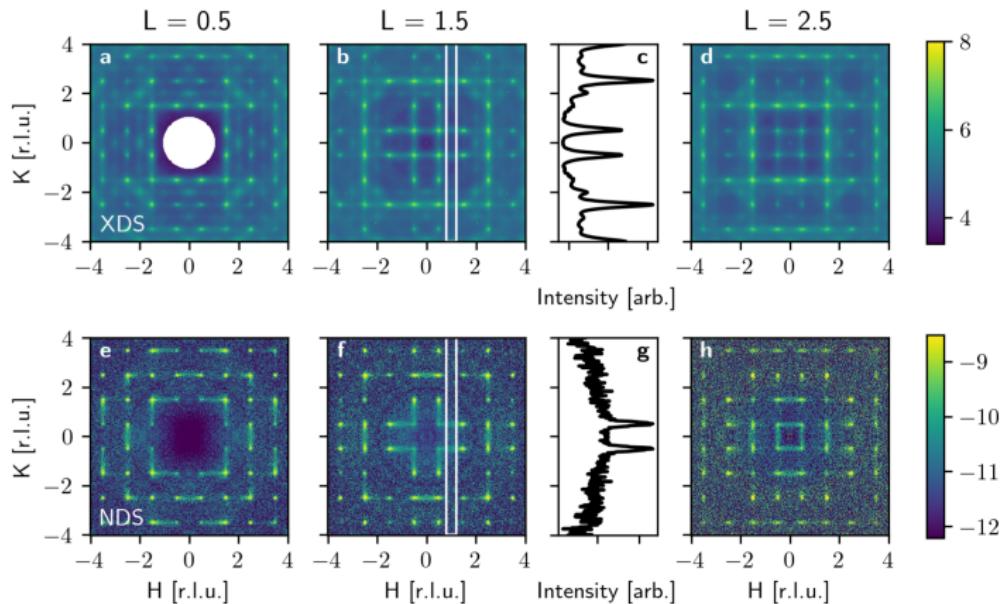


**NDS** (CORELLI, SNS)



Diffuse scattering shows non-trivial structure

## MAPB: $S(\mathbf{Q}, \omega)$ from XDS and NDS



Structure in diffuse scattering present in MAPB too:  
... what is it?!

# Simulating MAPI

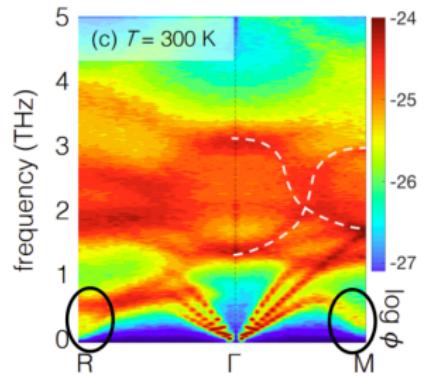
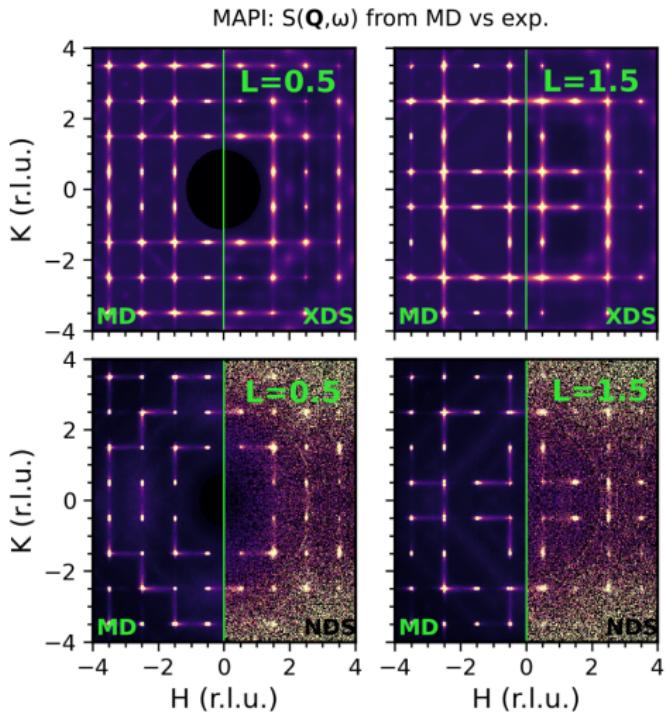
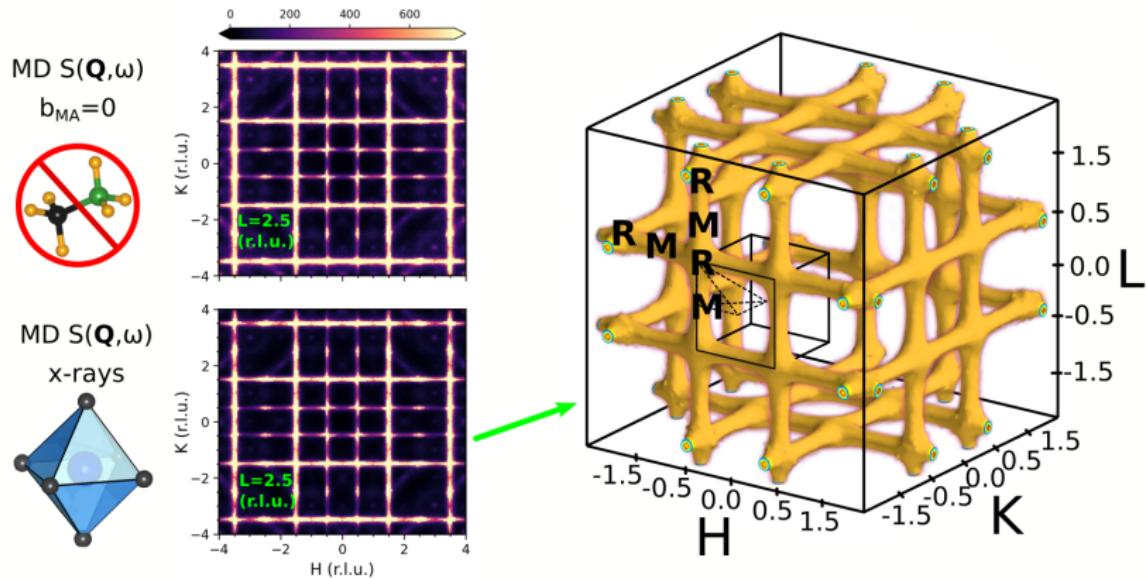


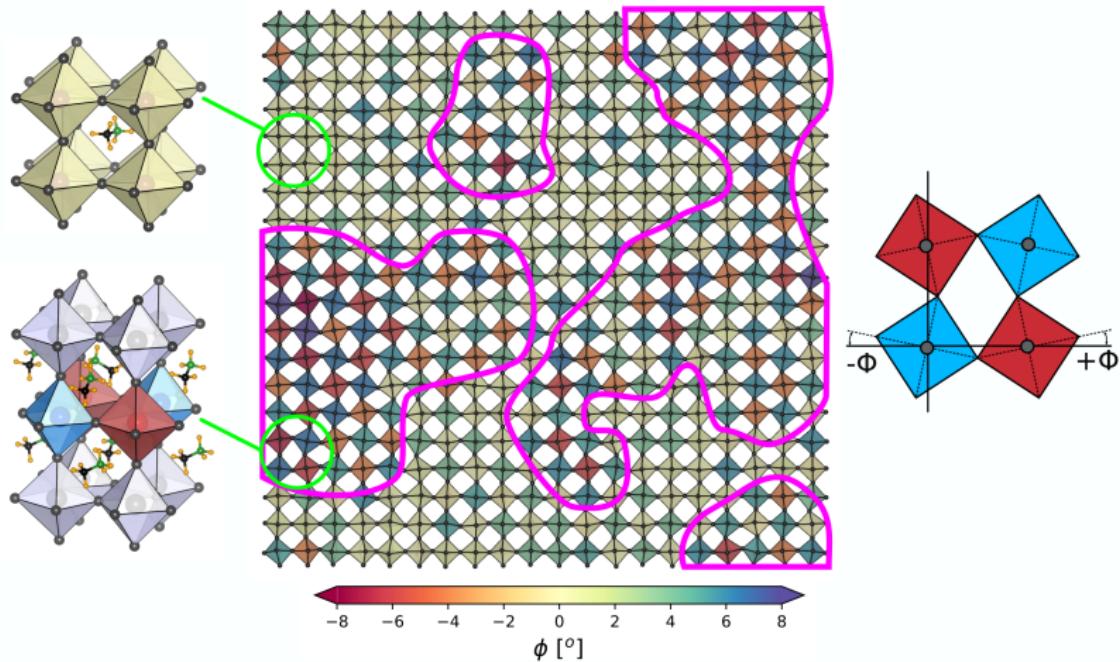
Figure: from Zhu, Taishan, and Elif Ertekin. *Energy & Environmental Science* 12.1 (2019): 216-229.



# What does MD tell us about MAPI?



# The local order



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

HWHM,  $\xi$ , from exp.:

$$S(Q) \sim \frac{(1/\xi)}{(1/\xi)^2 + (Q - Q_0)^2}$$

XDS	MAPB (250K)	MAPI (330K)	MAPI (MD) <sup>1</sup>
$\xi$ (Å)	10(2)	13(4)	10

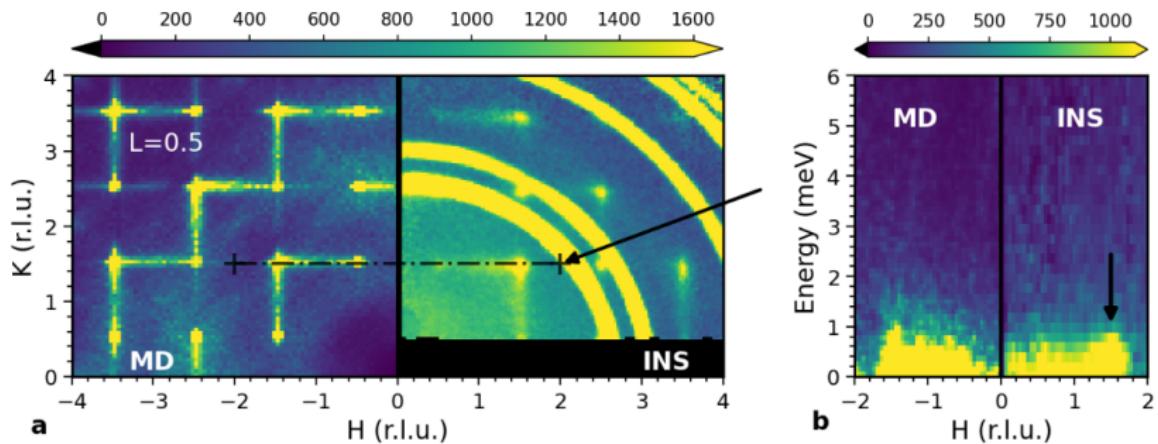
NDS	MAPB (250K)	MAPI (330K)	MAPI (MD) <sup>1</sup>
$\xi$ (Å)	10(2)	15(4)	10

Pancake diameter is  $\sim 4a$   
Pancake thickness is  $\lesssim a$

<sup>1</sup>calculated from realspace correlations:  $\langle \phi(r)\phi(0) \rangle$

# Dynamics of pancakes

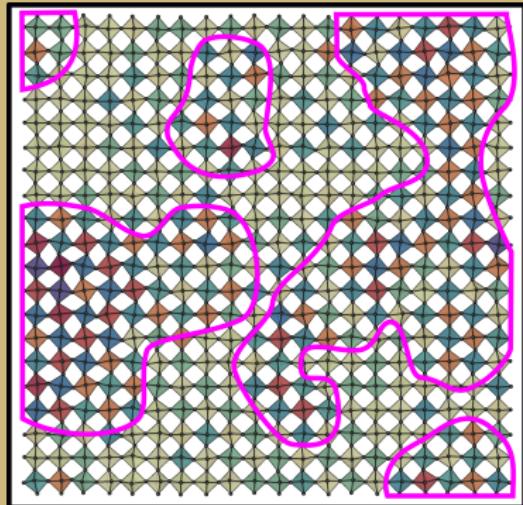
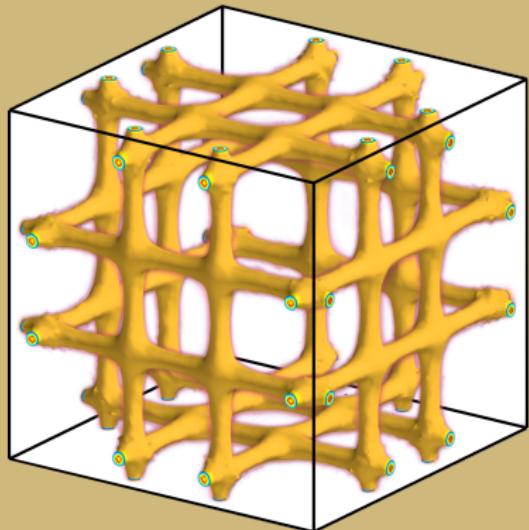
# Lifetime of pancakes



INS	MAPI (330K)	MAPI (MD)
$\tau$ (ps)	$3.25 \pm 0.13^2$	6.58

<sup>2</sup>Resolution limited

**Non-trivial order in  $\text{PbI}_6$**   
**sub-lattice: rods in reciprocal space signal 2D ordering**



**MD simulations reveal the nature of order:  $\text{PbI}_6$  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

