Mixed phononic and non-phononic transport in hybrid lead halide perovskites: glass-crystal duality, dynamical disorder, and anharmonicity

Supplementary Information

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S1. Ultrashort mean free path

The line broadening of the SED as the temperature increases reveals that some acoustic modes retain a well-defined wave nature, while the wave nature of the higher frequency optical modes is lost. Evidence for this is shown in Figure 2(d) by comparison of the modal mean free time to the wave period. In Figure S1 we further compare the modal mean free path to the modal wavelength for TA modes. For these modes, the mean free paths are similar to, and in some cases smaller than, the corresponding wavelengths.



Figure S1. The mean free path of TA modes obtained by fitting SED results, in comparison to recent experimental measurements (Ref. 24) and corresponding wavelengths. These modes along $\Gamma \to X$ exhibit mean free paths similar to or even shorter than their wavelengths.

S2. Origins of low acoustic mode group velocities

The low group velocities exhibited by the acoustic modes in MAPbI₃ compared to silicon in principle can arise from soft bonding and/or heavy atomic masses, both of which play a role here. For instance, near Γ the group velocity can be related to the elastic constants and mass density. For cubic crystals, from the continuum perspective the simplest cases for longitudinal modes are $v_{[010]} = \sqrt{C_{11}/\rho}$, $v_{[110]} = \sqrt{(C_{11} + C_{12} + 2C_{44})/\rho}$, and $v_{[111]} = \sqrt{(C_{11} + 2C_{12} + 4C_{44})/\rho}$. Thus lower *p*-wave speeds might suggest greater mass density ρ and/or smaller elastic constants C_{ij} . The calculated mass densities for these these cubic materials are 6187.0 kg/m³, 7194.1 kg/m³, 2235.7 kg/m³, so the contribution of the mass density differences to the low group velocities is around $\sqrt{\rho_{perovskite}/\rho_{silicon}} \sim 1.7$. Meanwhile the elastic constants computed using density functional theory are shown in Table S1. The contribution of the elastic constant differences to the low group velocities for the [110] direction is around $\sqrt{(C_{11} + C_{12} + 2C_{44})_{silicon}/(C_{11} + C_{12} + 2C_{44})_{perovskites}} \sim 3.5$. The two effects combined together give estimated differences in group velocity of $\sim 1.7 \times 3.5 \approx 6$, with the small elastic constants appearing to show a somewhat larger influence here.

Table S1. Lattice constants and elastic constants $(C_{11}, C_{12} \text{ and } C_{44})$ calculated by density functional theory.

material systems	lattice constant (Å)	elastic constants (GPa)		
	a_0	C_{11}	C_{12}	C_{44}
Si	5.43	159.21	62.59	75.69
$CsPbI_3$	6.62	21.56	4.02	3.46
$MAPbI_3$	6.60	24.84	6.48	3.99

S3. Perturbation of electronic charge distribution due to Pb/Si displacement



Figure S2. The change in electron density due to displacement of a lead (silicon) atom in (a) MAPb₃, (b) CsPb₃ and (c) silicon. The displacement is 5% of corresponding lattice constant. The disturbance of electron distribution due to such lattice perturbation is long range in perovskites (a-b) but localized in silicon (c).

The main text considers the perturbation to the electronic charge distribution due to the displacement of one Pb atom in MAPbI₃ and CsPbI₃ by 5% of the lattice constant, and shows that it is long ranged. For comparison, the perturbations in the charge density for the two perovskites and for silicon is compared in Figure S2. In contrast to disturbances in perovskites that span several unit cells, for silicon the perturbations are localized to within one cubic (8 atom) unit cell.

Table S2. Born effective charges for Si, PbTe, $CsPbI_3$ and $MAPbI_3$. The results for Si and PbTe compare well with the published results in Refs. 1 and 2.

	Born effective charge		
material systems	Z^{*} (e)		
Si	0.0 (Si)		
PbTe	5.74 (Pb) -5.74 (Te)		
CsPbI_3	4.76 (Pb) -0.77 (I)		
$MAPbI_3$	4.95 (Pb) -0.75 (I)		

The long-range interactions in the halide perovskites result from the long-tail character

of coulombic interactions, and are universal to all heteropolar materials (*e.g.*, Refs. 52-56). Common to such materials, these interactions lead to high electronic polarizability, dielectric constants, and Born effective charges. In Table S2, we present our calculated Born effective charges based on density functional perturbation theory, for the two halide perovskites compared to Si and PbTe. The unit cells for these materials are cubic, so the diagonal components of the Born effective charge tensor are all equivalent and the offdiagonal components are zero. In the two halide perovskites, the Born effective charges of Pb are comparable to that of PbTe, indicated of the similar chemistry of resonance bonding in these ionic compounds.

S4. Bonding nature in perovskites



Figure S3. Total and projected band structure for MAPbI₃. The top valence bands are formed by Pb- $6s^2$, Pb- $6p^2$ and I- $5p^6$ orbitals.



Figure S4. (a-c) Projected density of states to s and p orbitals of each atom. The bands around valence band maximum in perovskites are composed of Pb-s and dominantly I-p orbital electrons.

Figure S3 shows the electronic band structure for MAPbI₃. The size of each data point indicates the magnitude of the projection of the Kohn-Sham eigenfunctions onto specified atomic orbitals, with orange demoting *p*-orbitals and blue *s*-orbitals. Based on the band structure, the topmost valence bands are dominated by I p states mixed in with Pb s and Pb p states. Within the valence bands, the Pb 6s bands shown in blue and the Pb 6p bands shown in orange are separated by around 4–5 eV, indicating a weak sp-hybridization in the PbI₆ octahedral framework. The flat, non-dispersive MA orbitals overlap energetically only with the deeper inorganic PbI₆ framework orbitals, which can also be observed from the projected density of states in Figure S4 (a-c).

S5. Softening of optical modes on diatomic chains with second-nearest-neighbor interactions

Here we use a diatomic chain model to theoretically demonstrate the softening of optical modes due to the presence of long-range interactions as discussed in the main manuscript. The chain model, as illustrated in Figure S5(a), includes two types of atoms, with masses m_1 and m_2 respectively. The interactions between atoms of differing types (m_1 and m_2) in *i*-th neighboring cell are represented by force constants α_i . We only consider α_1 and α_2 here. The interactions between atoms of the same type m_1 in the second-nearest-neighbor cell are denoted by β_1 ; similarly interactions between atoms of the same type m_2 in the second-nearest-neighbor cell are denoted by β_2 .



Figure S5. (a) The diatomic chain model taking into account second-nearest-neighbor interactions. (b) Dispersion relation for varying combinations of interactions. The softening of Γ -optical mode relates only to the interactions between different atoms (α_1, α_2), while the long-range interactions between atoms of the same type (β_1, β_2) are absent.

We start from the equation of motion for m_1 and m_2 in the *n*-th unit cell. Let the lattice constant be *a*, and the displacements for m_1 and m_2 be *u* and *v*, then

$$m_1 \frac{d^2 u_n}{dt^2} = \alpha_1 (v_n + v_{n+1} - 2u_n) + \beta_1 (u_{n+1} + v_{n-1} - 2u_n) + \alpha_2 (v_{n+1} + v_{n-2} - 2u_n) \quad , (1)$$

$$m_2 \frac{d^2 v_n}{dt^2} = \alpha_1 (u_n + u_{n+1} - 2v_n) + \beta_2 (v_{n+1} + v_{n-1} - 2v_n) + \alpha_2 (u_{n+2} + u_{n-1} - 2v_n) \quad . \tag{2}$$

Assume the harmonic solution

$$u_n = u_0 \exp[i(kna - \omega t)] \quad , \tag{3}$$

$$v_n = v_0 \exp[i(kna - \omega t)] \quad , \tag{4}$$

we arrive at AU = 0, where

$$A_{11} = m_1 \omega^2 - A'_{11} \quad , \tag{5}$$

$$A_{22} = m_2 \omega^2 - A'_{22} \quad , \tag{6}$$

$$A_{12} = A_{21}^* = \alpha_1 \left[1 + \exp(-ika) \right] + \alpha_2 \left[\exp(ika) + \exp(-ik2a) \right] \quad , \tag{7}$$

$$A'_{11} = -2(\alpha_1 + 2\sin^2\frac{ka}{2}\beta_1 + \alpha_2) \quad , \tag{8}$$

$$A'_{22} = -2(\alpha_1 + 2\sin^2\frac{ka}{2}\beta_2 + \alpha_2) \quad , \tag{9}$$

and $\mathbf{U} = (u_0, v_0)^T$. To obtain nontrivial solutions, the determinant |A| should vanish,

$$0 = |A| = m_1 m_2 \omega^4 + (A'_{11} m_2 + A'_{22} m_1) \omega^2 + (A'_{11} A'_{22} - |A_{22}|^2) \quad .$$
(10)

This leads to the dispersion relations

$$\omega = \left(\frac{1}{2m_1m_2}\left[-(A'_{11}m_2 + A'_{22}m_1)\right. \\ \pm \sqrt{(A'_{11}m_2 + A'_{22}m_1)^2 - 8m_1m_2(A'_{11}A'_{22} - |A_{22}|^2)}\right]\right)^{1/2} ,$$
(11)

which plotted in Figure S5 (b) for three sets of parameters adopted in Ref. 51. Interestingly, the center softening can be explicitly written as

$$\omega(k=0) = \left(\frac{2(\alpha_1 + \alpha_2)}{\mu}\right)^{1/2} , \qquad (12)$$

where $\mu = m_1 m_2/(m_1 + m_2)$ is the reduced mass. Note that the softening of Γ optical modes is neutral to the interactions between atoms of the same types denoted by β_1 and β_2 . In the case of perovskites studied in the main text, this implies the important long-range interactions between Pb and I p orbitals.

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- ² U. Waghmare, N. Spaldin, H. Kandpal and R. Seshadri, *Physical Review B*, 2003, **67**, 125111.