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## Limits of the phonon quasi-particle picture at the cubic-to-tetragonal phase transition in halide perovskites

Erik Fransson<sup>1</sup>, Petter Rosander<sup>1</sup>, Fredrik Eriksson<sup>1</sup>, J. Magnus Rahm<sup>1</sup>, Terumasa Tadano<sup>2</sup>  & Paul Erhart<sup>1</sup>  

The soft modes associated with continuous-order phase transitions are associated with strong anharmonicity. This leads to the overdamped limit where the phonon quasi-particle picture can break down. However, this limit is commonly restricted to a narrow temperature range, making it difficult to observe its signature feature, namely the breakdown of the inverse relationship between the relaxation time and damping. Here we present a physically intuitive picture based on the relaxation times of the mode coordinate and its conjugate momentum, which at the instability approach infinity and the inverse damping factor, respectively. We demonstrate this behavior for the cubic-to-tetragonal phase transition of the inorganic halide perovskite CsPbBr<sub>3</sub> via molecular dynamics simulations, and show that the overdamped region extends almost 200 K above the transition temperature. Further, we investigate how the dynamics of these soft phonon modes change when crossing the phase transition.

<sup>1</sup>Department of Physics, Chalmers University of Technology, SE-41296 Gothenburg, Sweden. <sup>2</sup>Research Center for Magnetic and Spintronic Materials, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan. ✉email: [erhart@chalmers.se](mailto:erhart@chalmers.se)

The vibrational properties of solids are pivotal for many physical phenomena, including but not limited to phase stability and thermal conduction. In crystalline solids, the vibrational spectrum is commonly described in terms of phonons as quasi-particle representations of the lattice vibrations. The phonon frequency  $\omega_0$  is typically much larger than the damping  $\Gamma$ , and the phonon relaxation time  $\tau = 2/\Gamma$  is thus much longer than the oscillation period, such that the quasi-particle picture is well motivated<sup>1–6</sup>. In this so-called underdamped limit, the relaxation time *decreases* as the damping  $\Gamma$  increases.

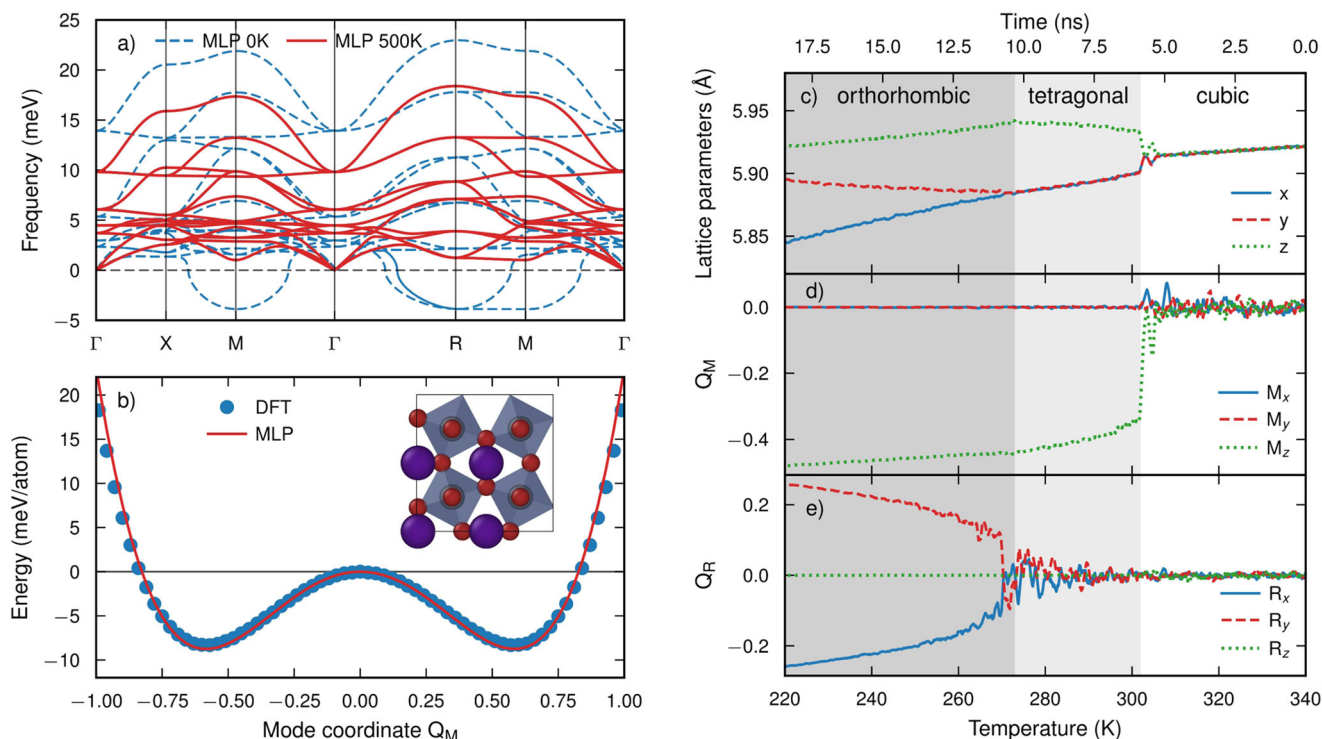
By comparison, there are far fewer cases when phonon modes become overdamped, i.e.,  $\omega_0\tau < 1$ <sup>7,8</sup>. This can occur either due to large damping or for very soft modes, usually in the immediate vicinity of a phase transition, for example, in the case of body-centered cubic Ti<sup>9–11</sup>, rotationally disordered 2D materials<sup>12</sup>, in ferroelectrics such as BaTiO<sub>3</sub><sup>13–17</sup> or in halide perovskites<sup>18,19</sup>. In the overdamped limit, the relaxation time *increases* with increasing damping  $\Gamma$ , which calls into question the picture of a well-defined phonon mode with a frequency and relaxation time. Overdamped phonon dynamics is, however, usually limited to a rather narrow temperature window, and under these circumstances, the inversion of the relationship between relaxation time and damping cannot be readily observed. Here, we demonstrate that the soft phonons modes associated with the phase transitions in the prototypical halide perovskite CsPbBr<sub>3</sub> are, however, outstanding manifestations of this exact behavior as the overdamped region extends almost 200 K above the tetragonal-cubic phase transition.

Halide perovskites are promising materials for photovoltaic and optoelectronic applications. Specifically, CsPbBr<sub>3</sub> has received a lot of attention in recent years<sup>20</sup>. With increasing

temperature, it undergoes phase transitions from an orthorhombic (Pnma) to a tetragonal (P4/mbm) and eventually a cubic phase (Pm3m)<sup>21–25</sup>. These phase transitions are connected to specific phonon modes and arise due to the tilting of the PbBr<sub>6</sub> octahedra, corresponding to phonon modes at the R and M points (Fig. 1a)<sup>26–30</sup>. Experimentally, these modes have been shown to exhibit overdamped characteristics in the vicinity of the phase transitions<sup>18,19,31</sup>. The phase transitions have also been studied from first-principles and via molecular dynamics (MD) simulations; see, e.g., refs. 32–35.

Here, we reveal the dynamics of the octahedral tilt modes in CsPbBr<sub>3</sub> over a wide temperature range via MD simulations based on a machine-learned potential (MLP) that achieves close to density functional theory (DFT) accuracy (Supplementary Note S2, Fig. S1)<sup>36,37</sup>. To obtain access to mode-specific dynamics, we project the MD trajectories onto normal modes that are associated with phase transitions in this material. As shown below, this requires both large systems (comprising at least several 10000 atoms) and sufficiently long times scales (~50–100 ns) in order to achieve converged results (see Supplementary Note S7, Fig. S9, and Fig. S8). The DFT data and the MLP models are provided as a Zenodo dataset<sup>38</sup>.

Reference data for the construction of the MLP was generated by DFT calculations<sup>39–41</sup> using the strongly constrained and appropriately normed (SCAN) exchange-correlation functional<sup>42</sup> (Supplementary Note S1). Simulations and atomic structures were handled via the ASE<sup>43</sup> and CALORINE packages<sup>44</sup>. The phonon frequencies and relaxation times obtained with the MLP are in good agreement with experimental work for multiple phonon modes (see Fig. S5). In addition, we consider several different self-consistent phonons (SCP) methods<sup>45</sup> as well as



**Fig. 1 Phonons and phase transitions in CsPbBr<sub>3</sub>.** **a** Phonon dispersion for the cubic phases of CsPbBr<sub>3</sub> obtained using the machine-learned potential (MLP) in the harmonic approximation, 0 K (dashed lines) and from an effective harmonic model (EHM) at 500 K (solid lines). **b** Potential energy landscape along the unstable M-tilt mode calculated with MLP and density functional theory (DFT). The inset shows the CsPbBr<sub>3</sub> crystal structure (Cs purple, Pb gray, Br red) in the energy minima, for which the PbBr<sub>6</sub> octahedra have been tilted in-phase (visualization made with OVITO<sup>75</sup>). **c–e** Lattice parameters and mode coordinates obtained from a cooling run based on the isothermal-isobaric ( $NpT$ ) ensemble with phase transitions at approximately 300 K and 275 K. In **c–e** Solid, dashed, and dotted lines refer to the Cartesian directions  $x$ ,  $y$ , and  $z$ , respectively.

effective harmonic models (EHMs)<sup>46–49</sup> using the HIPHIVE<sup>50</sup>, ALAMODE<sup>51</sup>, and SSCHA packages<sup>52</sup>.

## Results and discussion

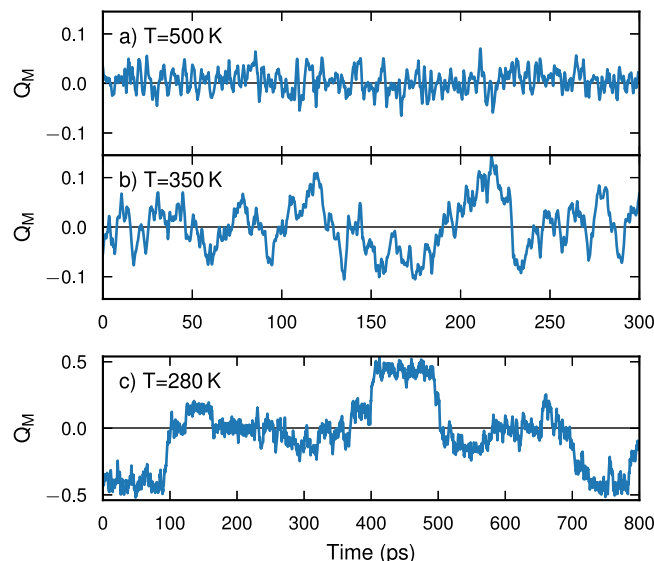
**Tilt modes and phase transitions.** The phase transitions in CsPbBr<sub>3</sub>, and similarly in many other perovskites, are driven by modes that correspond to tilting of the PbBr<sub>6</sub> octahedra. These modes are located at the M (in-phase tilting) and R-points (out-of-phase tilting) in the phonon dispersion for the cubic structure (Fig. 1a). They are threefold degenerate, corresponding to tilting around the three Cartesian directions. These tilt modes exhibit a double-well potential energy surface (PES), which the MLP reproduces perfectly compared to DFT (Fig. 1b).

The MLP predicts temperatures of 300 K and 275 K for the cubic-tetragonal,  $T_{c \leftrightarrow t}$ , and tetragonal-orthorhombic,  $T_{t \leftrightarrow o}$ , transitions, respectively (Fig. 1c). This is lower than the experimental values of 400 K and 360 K<sup>20,22,23,25</sup>, a discrepancy that can be primarily attributed to the underlying exchange-correlation functional<sup>53</sup>.

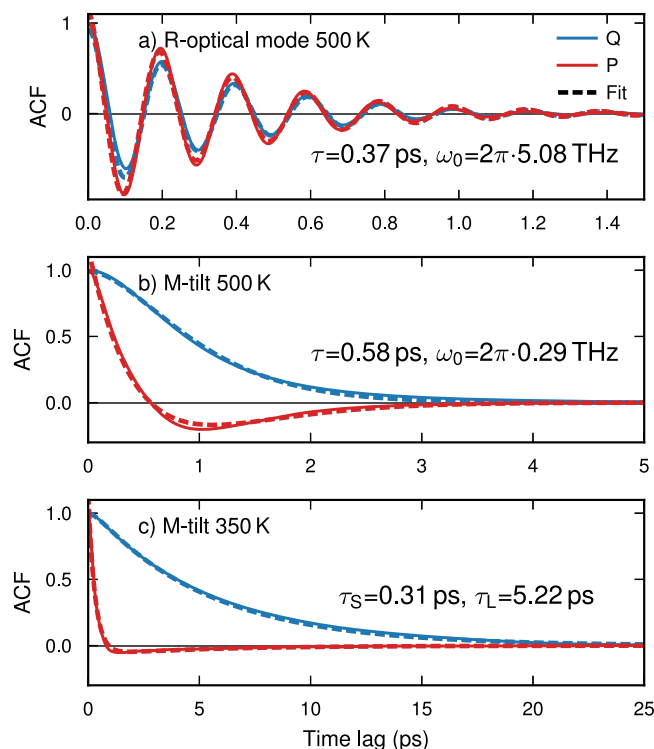
The mode coordinates of the tilt modes are useful order parameters for analyzing the phase transitions (Fig. 1d, e). At 300 K, the system transitions from the cubic to the tetragonal phase, as seen in both the lattice parameters and in the freezing in of one of the three M-tilt modes ( $M_z$ ). For the tetragonal phase, two R-modes ( $R_x$  and  $R_y$ ) start to show larger fluctuations, and at 265 K, the system transitions to the orthorhombic phase. Here, we also note the slight difference in character between these two phase transitions. For the cubic-tetragonal transition, the order parameter ( $Q_M$ ) and lattice parameter change sharply at the transition temperature  $T_{c \leftrightarrow t}$  (closer in character to a first-order transition), whereas for the tetragonal-orthorhombic transition, the order parameter and lattice parameter change more gradually around  $T_{t \leftrightarrow o}$  (exhibiting continuous character) in agreement with experimental observations of the transition character<sup>20,21</sup>. We note here that the mode coordinate is a global order parameter for the system. In the cubic phase, even though the mode coordinate is on average zero, there still exists a strong local correlation between the neighboring octahedra. This connects to previous work on perovskites regarding the local atomic structure deviating from the cubic structure while globally still appearing cubic<sup>28,29,54–58</sup>.

**Mode coordinate dynamics.** The mode coordinates exhibit interesting dynamical behavior already in the cubic phase far above the transition to the tetragonal phase, which can be conveniently observed in the time domain (Fig. 2a, b). At 500 K, regular (phonon) oscillator behavior is observed, whereas, at 350 K (closer but still above  $T_C$ ), a slower dynamic component becomes evident. Finally, at 280 K and thus below the phase transition, one observes the common oscillatory motion superimposed on a long timescale hopping motion between the two minima, corresponding to the (degenerate) tetragonal phase (Fig. 1b). We note here that the hopping frequency depends strongly on system size, and is thus not a good thermodynamic observable on its own.

The mode coordinate can be analyzed by fitting the respective autocorrelation functions (ACFs) to a damped harmonic oscillator (DHO) model (Fig. 3). The ACF for a regular (underdamped) mode shows a clear oscillatory pattern, as illustrated here by the highest optical mode at the R-point with a typical relaxation time of about 0.37 ps, which is longer than the mode period of about 0.2 ps (Fig. 3a). The M-tilt mode at 500 K has similar damping but is much softer (yet still underdamped), and the ACF decays with a relaxation time of about 0.58 ps (Fig. 3b). At 350 K (Fig. 3c), however, the same mode is

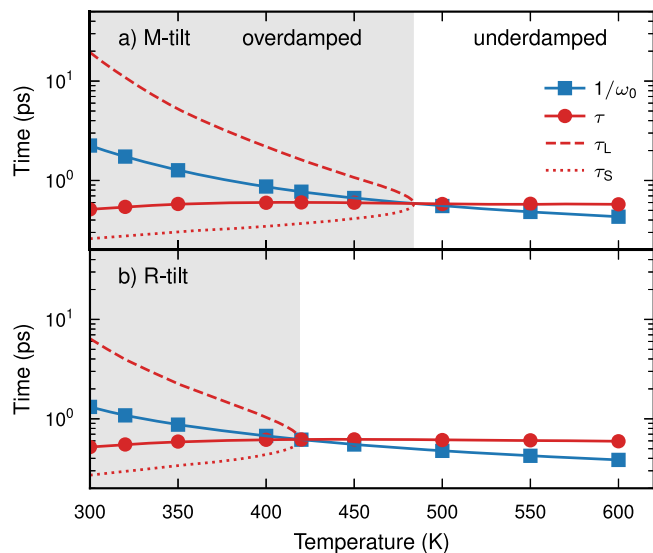


**Fig. 2 Phonon mode coordinates.** Mode coordinate  $Q(t)$  for the M-tilt mode, **a** at 500 K (well above  $T_{c \leftrightarrow t}$ ), **b** at 350 K (close to  $T_{c \leftrightarrow t}$ ), and **c** at 280 K (below above  $T_{c \leftrightarrow t}$ ). The M-tilt mode is three-fold degenerate ( $x, y, z$ ), but here only the  $M_z$  mode is shown. Also note that for 280 K, the system switches the tilt axis at irregular intervals.



**Fig. 3 Phonon mode auto-correlation functions (ACFs).** ACFs (solid lines) of **a** the highest optical mode at the R-point as well as the M-tilt mode at **b** 500 K and **c** 350 K, along with fits to a damped harmonic oscillator (DHO) model (dashed lines). Note the large difference in time scale between **b** and **c**.

overdamped, and in this case, the DHO model becomes the sum of two exponential decays, see Eq. (3), with relaxation times  $\tau_L = 5.22$  ps and  $\tau_S = 0.31$  ps. It is interesting to note that the decay time of the ACF at 350 K is about ten times longer than at 500 K. The DHO fits still match the data very well for both the



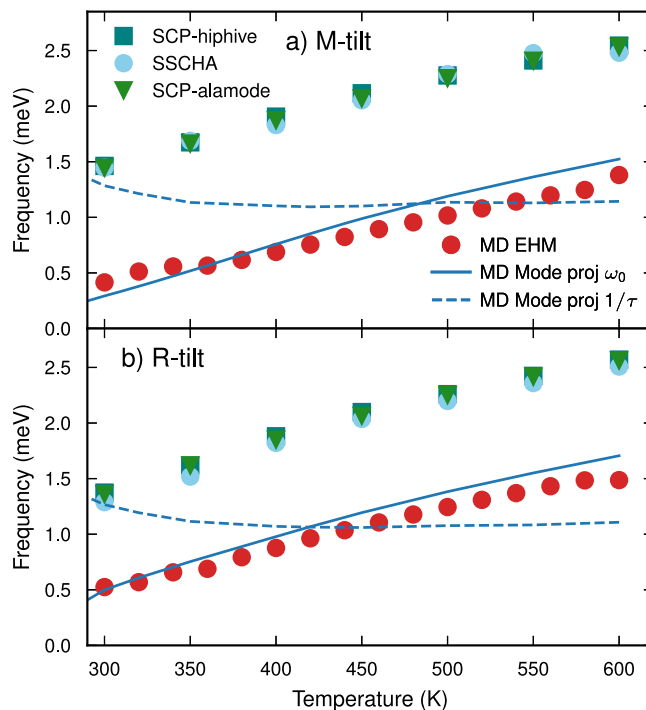
**Fig. 4 Phonon frequencies and relaxation times.** Frequencies and relaxation times were obtained from auto-correlation functions of **a** M-tilt and **b** R-tilt modes as a function of temperature. The shaded region indicates the overdamped regime. Note that the M-tilt mode is overdamped already about 200 K above the phase transition temperature. Here, markers are data points, and lines are interpolations to guide the eye.

underdamped and overdamped cases (see Fig. S11 for how the two exponential decays behave for  $Q$  and  $P$  in the overdamped case).

When  $\Gamma/\omega_0$  increases, and the system becomes overdamped, the dynamics of the modes are moving towards the diffusive Brownian motion regime. For overdamped modes, the relaxation time of the ACF increases as  $\Gamma/\omega_0$  increases, opposite to the underdamped behavior. While this is a well-known feature of a simple one-dimensional DHO, here, one observes this behavior for phonon modes in a complex atomistic system. This phenomenon arises due to the *free* energy landscape being very flat close to the transition, resembling a bathtub. As a result of the high friction and weak restoring force, it, therefore, takes a long time for the DHO to move back and forth around zero (Fig. 2c; see Fig. S12 for the power spectra)<sup>59</sup>.

**Frequency and relaxation times vs. temperature.** The frequencies and relaxation times of the M-tilt and R-tilt modes are summarized as a function of temperature in Fig. 4. The frequency  $\omega_0$  softens significantly with decreasing temperature for both modes, whereas the relaxation time  $\tau$  is more or less constant. The softening of the frequency thus drives the modes to the overdamped limit with decreasing temperature. The M-tilt and R-tilt modes only become underdamped above 480 K and 410 K, respectively, well above the transition temperature to the tetragonal phase at 300 K. This indicates that we expect the phonon quasi-particle for these modes to work better at high temperatures, which interestingly is the opposite behavior compared to most phonon modes which become more damped and anharmonic with increasing temperature. At the cross-over from the underdamped to the overdamped regime, the two-time scales  $\tau_S$  and  $\tau_L$  emerge. When approaching  $T_{c \rightarrow b}$  we see that  $\tau_L$  increases exponentially, whereas  $\tau_S \rightarrow \tau/2$ .

**SCPs and effective harmonic models.** Next, we analyze the representation of these strongly anharmonic modes by commonly used phonon renormalization techniques, specifically different SCP schemes and EHMs (Fig. 5) (see Supplementary Note S5 and

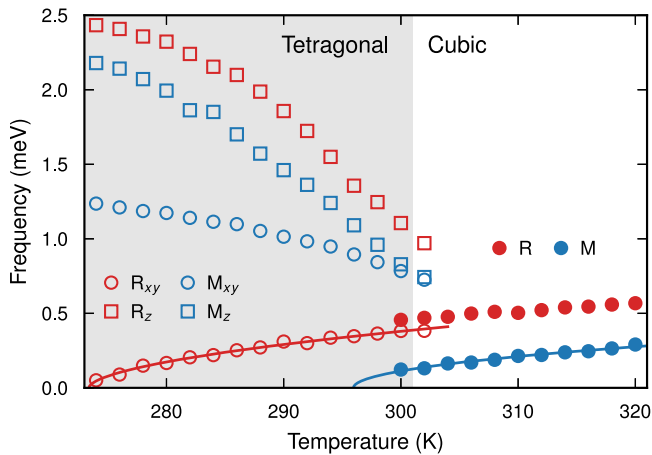


**Fig. 5 Phonon frequencies comparison with SCP.** Frequencies of **a** M-tilt and **b** R-tilt modes as a function of temperature from several self-consistent phonons (SCP) schemes, effective harmonic models (EHMs) based on molecular dynamics (MD), and damped harmonic oscillator (DHO) frequencies fitted to auto-correlation functions.

Supplementary Note S6 for a more detailed description of the methods). To this end, we constructed 4th-order force constant potentials (FCPs) at each temperature which were used as input to all SCP methods; see Supplementary Note S4 and Fig. S6 for more details. There are several SCPs variants<sup>45</sup>. In SCP-alamode, the Green's function approach is employed as implemented in the ALAMODE package<sup>51</sup>. In the stochastic self-consistent harmonic approximation (SSCHA) scheme, the harmonic free energy is minimized using gradient methods, as implemented in the SSCHA package<sup>52</sup>. In SCP-hiphive second-order force-constants are obtained by iterative fitting to forces from displacements sampled from the harmonic model and forces obtained from the MLP as implemented in the HIPHIVE package<sup>50</sup>. Here, we employ the “bare” SCP implementations in ALAMODE and SSCHA. We note, however, that there are computationally more demanding corrections for both methods<sup>35,60</sup>, the analysis of which is, however, beyond the scope of the present work. The EHMs (in this field also referred to as temperature-dependent potentials) are constructed from fitting second-order force constants to displacement and force data obtained from MD simulations with the MLP (see Supplementary Note S6 for details).

Here, we find very similar behavior for both M-tilt and R-tilt modes. The three SCP methods (SCP-hiphive, SSCHA, SCP-alamode) employed here are in excellent agreement with each other, given the differences in theory and implementation between them. The SCP frequencies systematically overestimate the frequency  $\omega_0$  obtained from the ACFs by about 1 meV (see Supplementary Note S5 for a more detailed description of the SCP methods). The EHMs constructed by fitting the forces from MD trajectories, on the other hand, show good agreement with the mode projection results. We note here that the trend for SCPs and EHMs to over and underestimate frequencies, respectively, appears to hold for all modes in the system, which is in line with previous studies<sup>35,61–63</sup>. However, while EHMs from MD yield a





**Fig. 6 Phonon frequencies across the phase transition.** M and R-tilt mode frequencies from auto-correlation functions and damped harmonic oscillator fits as a function of temperature in the tetragonal and cubic phases. Here, filled symbols correspond to the frequencies in the cubic phase, and open symbols to the frequencies in the tetragonal phase. Solid lines show Curie-Weiss fits of the form,  $\omega_0(T) \propto (T - T_C)^p$ . For the M-mode in the cubic phase we obtain  $T_C = 295$  K (with fixed  $p = 0.5$ ), while for the  $R_{xy}$  mode in the tetragonal phase we obtain  $T_C = 273$  K and  $p = 0.55$ . The cubic and tetragonal frequencies overlap in temperature, which is possible due to the first-order character of the transition and the fact that simulations are carried out in the microcanonical (NVE) ensemble, which does not allow for the cell shape to change between cubic and tetragonal.

better frequency for the tilt modes compared to SCP, this is not in general true (see Fig. S7 for details).

**Behavior near phase transitions.** Next, we look at how these modes behave as the system goes through the transition from the cubic to the tetragonal phase. While in the cubic phase, the three M (and R) modes (denoted with subscripts  $x$ ,  $y$ , and  $z$  to indicate the Cartesian direction) are degenerate, the degeneracy is broken in the tetragonal phase, and the  $z$ -direction becomes symmetrically distinct from the other two (Fig. 1c, d). Therefore, in order to distinguish these modes, we will denote them by  $M_{xy}$  and  $M_z$  (analogously for R-modes) in the tetragonal phase. In the tetragonal phase, there exist multiple global minima for the M-mode coordinate, as can be seen in Fig. 2c, where the system jumps between these minima. To avoid capturing this (system-size dependent) hopping time in the ACFs, we employ very large system sizes of up to 400,000 atoms, for which the system remains in the same tetragonal orientation throughout the entire simulation. Furthermore, we extrapolate the frequencies to the infinite system-size limit (Fig. S10).

The resulting frequencies are shown in Fig. 6. For the cubic-to-tetragonal transition, the M-frequency does not go to zero at the transition temperature, which is in agreement with the character of the transition being first order, as observed experimentally<sup>20,21,23</sup>. For the tetragonal-to-orthorhombic phase transition, on the other hand, the  $R_{xy}$  frequency does go to zero at the transition temperature, in agreement with a continuous transition as observed experimentally<sup>21</sup>. This leads to the long timescale in the DHO trending to infinity,  $\tau_L \rightarrow \infty$ , as the temperature approaches  $T_C$ . Additionally, the  $R_{xy}$  mode exhibits a strong size dependence close to the transition temperature (see Fig. S10).

The Curie-Weiss law,  $\omega_0(T) \propto (T - T_C)^p$ , provides very good fits for the temperature dependence of the modes driving the

phase transitions. For the tetragonal-to-orthorhombic transition, the fitted critical temperature,  $T_C = 273$  K, agrees very well with the observed transition temperature of 274(1) K, which is consistent with this transition being a continuous transition<sup>21</sup>. Furthermore, the fitted critical exponent of 0.55 is very close to the value of 1/2 suggested by Landau theory observed in many continuous phase transitions driven by soft modes<sup>15,64–66</sup>. The cubic-to-tetragonal transition has a first-order character, as evident from the finite frequency of the M mode at the transition temperature. As a result, fitting both the critical temperature and the critical exponent is ambiguous (due to the absence of data at temperatures for which the frequency goes to zero). We, therefore, fix the critical exponent to 1/2, which yields a critical temperature of 295 K, about 7 K lower than the transition temperature. Here, the critical temperature corresponds to the temperature at which the cubic phase becomes dynamically unstable, i.e., the point at which the free energy barrier between the two phases disappears.

The parameter  $\tau$  remains fairly constant in the tetragonal phase across its entire temperature range for all four modes (Fig. S13). Interestingly, once the  $M_z$  mode freezes in (and the tetragonal phase is formed), both the  $M_z$  and  $R_z$  modes stiffen significantly with temperature. This results in the  $R_z$  mode becoming underdamped again with decreasing temperature at around 290 K and both M-modes approaching the underdamped limit as the system approaches the orthorhombic transition.

## Conclusions

We have carried out a detailed computational analysis of the dynamics in CsPbBr<sub>3</sub>, focusing in particular on the tilt modes. We observe overdamped modes for the cubic phase almost 200 K above the cubic-to-tetragonal transition temperature. These overdamped tilt-modes exhibit correlation on very long time scales ( $\tau_L$ ) compared to the typical relaxation time ( $\tau$ ) or period ( $1/\omega_0$ ) of the mode. This is in line with the dynamics of the modes transitioning toward Brownian motion due to the frequency approaching zero. What we find here is that these modes can, however, still be mathematically well described as DHOs, which allows one to formally obtain a phonon frequency and relaxation time compliant with a quasi-particle picture. A physically more intuitive description is, however, obtained if the DHO model is described by two relaxation times, which can be approximately associated with mode coordinate and momentum, respectively. As a result of the soft character of these modes, the respective amplitudes can be large already at moderate temperatures. This implies that even for relatively modest electron-phonon coupling strengths, these modes should have a notable impact on the optoelectronic properties of these materials<sup>56,67–70</sup>. A systematic investigation of these effects on a per-mode basis would be an interesting topic of further study.

In addition, we demonstrated that commonly used computational phonon renormalization methods agree very well with each other but, without extensive correction schemes, exhibit systematic errors in describing the frequencies of the anharmonic tilt modes considered here. Understanding the single-point frequencies obtained from such methods and their relation to the full dynamical spectra is thus very important when, e.g., comparing to experimental measurements.

## Methods

To analyze phonon modes directly from MD simulations, we employed phonon mode projection<sup>3,71,72</sup>. The MD simulations were carried out using the GPUMD package<sup>37,73</sup>. For more details on the MD simulations, see Supplementary Note S3. The atomic displacements  $\mathbf{u}(t)$  and velocities  $\mathbf{v}(t)$  can be projected on a mode  $\lambda$ , with the supercell eigenvector  $\mathbf{e}_\lambda$  via

$$Q_\lambda(t) = \mathbf{u}(t) \cdot \mathbf{e}_\lambda \quad \text{and} \quad P_\lambda(t) = \mathbf{v}(t) \cdot \mathbf{e}_\lambda.$$

Here, the phonon supercell eigenvector of the tilt modes were obtained with PHONOPY<sup>74</sup>, and symmetrized such that each of the three degenerate modes corresponds to tilting around the  $x$ ,  $y$ , and  $z$  direction respectively. The ACFs of  $Q$  and  $P$  were calculated in order to analyze the dynamics of the modes of interest as

$$C_Q(t) = \langle Q_A(t')Q_A(t+t') \rangle, \quad (1)$$

which can be modeled as the ACF of a DHO. The DHO is driven by a stochastic force and has a natural frequency  $\omega_0$  and a damping  $\Gamma$ . The ACF of the DHO splits into an underdamped regime ( $\omega_0 > \Gamma/2$ ) and an overdamped regime ( $\omega_0 < \Gamma/2$ ). In the underdamped regime, the solution of the DHO is

$$C_Q^{\text{DHO}}(t) = Ae^{-t/\tau} \left( \cos \omega_c t + \frac{\Gamma}{2\omega_c} \sin \omega_c t \right), \quad (2)$$

where  $\omega_c = \sqrt{\omega_0^2 - \frac{\Gamma^2}{4}}$ , the relaxation time is  $\tau = 2/\Gamma$ , and  $A$  is the amplitude<sup>11</sup>. In the overdamped limit, the solution becomes the sum of two exponential decays as

$$C_Q^{\text{DHO}}(t) = \frac{A}{\tau_L - \tau_S} \left( \tau_L e^{-t/\tau_L} - \tau_S e^{-t/\tau_S} \right) \quad (3)$$

where

$$\tau_{S,L} = \frac{\tau}{1 \pm \sqrt{1 - (\omega_0 \tau)^2}}.$$

Here,  $\tau_S$  and  $\tau_L$  denote the short and long timescales, respectively. If the natural frequency approaches zero (e.g., for continuous phase transitions driven by a soft mode), we thus expect  $\tau_L \rightarrow \infty$  and  $\tau_S \rightarrow \tau/2$ . In this limit, the resulting ACF,  $C_Q^{\text{DHO}}(t)$ , would only consist of a single exponential decay, with a decay time approaching infinity, which corresponds to the behavior seen in Brownian motion.

Similar expressions are obtained for the ACF of the phonon velocity, which is  $C_P^{\text{DHO}}(t) = -\frac{d}{dt} C_Q^{\text{DHO}}(t)$ . For the overdamped case, it becomes

$$C_P^{\text{DHO}}(t) = \frac{A}{\tau_L - \tau_S} \left( \frac{1}{\tau_S} e^{-t/\tau_S} - \frac{1}{\tau_L} e^{-t/\tau_L} \right)$$

The ACFs for  $Q$  and  $P$  were fitted simultaneously to the DHO model in order to extract  $\omega_0$  and  $\Gamma$ .

## Data availability

The DFT data and the MLP models are provided in a Zenodo dataset<sup>38</sup>.

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## Author contributions

E.F. carried out the analysis based on MD simulations and wrote the first draft of the paper. P.R. constructed the 4th-order FCPs and carried out the SCP analysis with HIPHIVE and SSCHA, as well as some of the DFT calculations. J.M.R. and P.E. carried out the DFT calculations and J.M.R. trained the neuroevolution potential (NEP) model. F.E. analyzed the DHO expressions. T.T. constructed an interface between HIPHIVE and ALAMODE and carried out the SCP calculations with ALAMODE. P.E. supervised the project. All authors reviewed and edited the paper.

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## Competing interests

The authors declare no competing interests.

## Additional information

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**Correspondence** and requests for materials should be addressed to Paul Erhart.

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