Probing the limits of the phonon quasi-particle picture: The transition from underdamped to overdamped dynamics in CsPbBr₃

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The soft modes associated with continuous-order phase transitions are commonly associated with particularly strong anharmonicity. Here, we show that this can lead to overdamped behavior already far above the actual transition temperature using molecular dynamics simulations and a machine-learned potential. While in the overdamped limit the interpretation of lattice vibrations as phonon quasi-particles with a specified frequency and relaxation time becomes physically questionable the mathematical description in terms of damped oscillators still holds. A physically more intuitive picture can be obtained by considering 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 quantitatively for the prototypical case of the cubic-to-tetragonal phase transition of the inorganic halide perovskite CsPbBr₃, and show that the overdamped region extends almost 200 K (or about 60%) above the transition temperature.

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, \( \omega \), is typically much larger than the damping \( \Gamma \); the phonon relaxation time \( \tau = 2/\Gamma \) is thus much longer than the oscillation period, such that the quasi-particle picture is well motivated [1–6]. 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., \( \omega \tau < 1 \) [7, 8]. This can occur either due to large damping or for very soft modes, usually in the immediate vicinity of a phase transition, as for example in the case of body-centered cubic Ti [9–11], rotationally disordered 2D materials [12], in ferroelectrics such as BaTiO₃ [13–16] or in halide perovskites [17, 18]. Notably, 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 relation 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 CsPbBr₃ 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, CsPbBr₃ has received a lot of attention in recent years [19]. With increasing temperature it undergoes phase transitions from an orthorhombic (Pnma) to a tetragonal (P4/mbm) and eventually a cubic phase (Pm3m) [20–24].

These phase transitions are connected to specific phonon modes and arise due to tilting of the PbBr₆ octahedra, corresponding to phonon modes at the R and M points (Fig. 1a) [25–28]. Experimentally, these modes have been shown to exhibit overdamped characteristics in the vicinity of the phase transitions [17, 18, 29]. The phase transitions have also been studied from first-principles and via molecular dynamics (MD) simulations, see, e.g., Refs. 30–32.

Here, we reveal the dynamics of the octahedral tilt modes in CsPbBr₃ over a wide temperature range, which as shown below requires both large large systems (comprising at least several 10,000 atoms) and sufficiently long times scales (\( \sim 50 \text{ ns to } 100 \text{ ns} \)) in order to achieve converged results (Fig. S7 and Fig. S6) [34]. To this end, we employ a MLP that achieves close to DFT accuracy (Note S2) [35, 36] and extensive MD simulations enabled by an efficient implementation on graphical processing units (GPUs) [37]. Reference data for the construction of the MLP was generated by DFT calculations [38–40] using the strongly constrained and appropriately normed (SCAN) exchange-correlation functional [41] (Note S1). Simulations and atomic structures were handled via the ASE [42] and CALORINE packages [43]. The dynamics were analyzed directly from MD simulations via normal mode projections. The obtained phonon frequencies and relaxation times with the MLP are in good agreement with experimental work for multiple phonon modes (see Fig. S11). In addition, we consider several different self-consistent phonon (SCP) renormalization methods [44] as well as EHMs [45–48] using the Hiphive [49], AlamoDE [50], and SSCHA packages [51].

To analyze phonon modes directly from MD simulations we employ phonon mode projection [3, 52, 53]. The atomic displacements \( \mathbf{u}(t) \) and velocities \( \mathbf{v}(t) \) can be pro-
FIG. 1. (a) Phonon dispersion for the cubic phases of CsPbBr$_3$ obtained using the MLP in the harmonic approximation (0 K) and from an EHM at 500 K. (b) Potential energy landscape along the unstable M-mode calculated with MLP and DFT. The inset shows the CsPbBr$_3$ crystal structure (Cs purple, Pb gray, Br red) in the energy minima, for which the PbBr$_6$ have been tilted in-phase (visualization made with ovito [33]). (c, d, 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 265 K.

JECTED on a mode $\lambda$, with the supercell eigenvector $e_\lambda$ via

$$Q_\lambda(t) = u(t) \cdot e_\lambda$$

and $P_\lambda(t) = v(t) \cdot e_\lambda$.

The autocorrelation functions (ACFs) of $Q$ and $P$ are calculated in order to analyze the dynamics of the modes of interest as

$$C_Q(t) = \langle Q_\lambda(t')Q_\lambda(t + t') \rangle,$$

which can be modeled as the ACF of a damped harmonic oscillator (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

$$C^DHO_Q(t) = A e^{-t/\tau} \left( \cos \omega_c t + \frac{\Gamma}{2\omega_c} \sin \omega_c t \right),$$

where

$$\omega_c = \sqrt{\omega_0^2 - \frac{\Gamma^2}{4}},$$

$\tau$ is the relaxation time is $\tau = 2/\Gamma$, and $A$ is the amplitude [11]. In the overdamped limit the solution becomes the sum of two exponential decays as

$$C^DHO_Q(t) = \frac{A}{\tau_L - \tau_S} \left( \tau_L e^{-t/\tau_L} - \tau_S e^{-t/\tau_S} \right),$$

where

$$\tau_{S,L} = \frac{\tau}{1 \pm \sqrt{1 - \omega_0^2 \tau^2}}.$$
cubic structure (Fig. 1a). They are three-fold 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 the cubic-tetragonal and tetragonal-orthorhombic transitions at 300 K and 265 K, respectively (Fig. 1c), which is lower than the experimental values of 400 K and 360 K [19, 21, 22, 24], a discrepancy that can be primarily attributed to the underlying exchange-correlation functional.

The mode coordinates of the tilt-modes are very 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 and lattice parameter changes rather sharply at the transition temperature $T_C$ (closer in character to a displacive transition), whereas for the tetragonal-orthorhombic transition the order parameter and lattice parameter change more gradually around $T_C$ (exhibiting more order-disorder character) in agreement with experimental observations of the transition character [19].

The mode coordinates exhibit interesting dynamical behavior already in the cubic phase, which can be conveniently observed in the time domain (Fig. 2). At 500 K regular (phonon) oscillator behavior is observed, whereas for 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) [54].

The mode coordinate can be analyzed by fitting the respective ACFs to a 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 (Fig. 3a). For the M-tilt mode at 500 K the mode is quite strongly damped (yet underdamped) and the ACF decays quickly with a relaxation time of about 0.58 ps (Fig. 3b). At 350 K, however, the same mode is overdamped and in this case the DHO model becomes the sum of two exponential decays, see Eq. 3, with relaxation times $\tau_S = 5.22$ ps and $\tau_L = 0.31$ ps. It is noteworthy that the relaxation time of the ACF at 350 K is about ten-times longer than at 500 K. The DHO fits still match the data surprisingly well for both the underdamped and overdamped cases (see Fig. S8 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 is 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 we demonstrate this behavior for phonon modes in a complex system. This phenomenon arises due to the free energy landscape being very flat close to the transition. As a result of the high friction it therefore takes a long time for the DHO to move back and forth around zero (Fig. 2c; also see Fig. S10 for the power spectra) [55].

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 times \( \tau \) is more or less constant. We note that the frequency \( \omega_0 \) decreases almost linearly across the entire temperature range and does not follow \( \omega_0^2 \sim (T - T_C) \) as sometimes seen for displacive phase transitions [7, 56, 57]. The softening of the frequency thus drives the modes to the overdamped limit with decreasing temperature. Remarkably, 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. At the cross-over from the underdamped to the overdamped regime, the two time scales \( \tau_S \) and \( \tau_L \) emerge. When approaching \( T_C \), we see that \( \tau_L \) increases exponentially, whereas \( \tau_S \to \tau/2 \).

Lastly, we analyze the representation of these strongly anharmonic modes by commonly used phonon renormalization techniques, specifically different SCP schemes and EHMs (Fig. 5) (see Note S5 and Note S6 for a more detailed description of the methods). There are several variations of SCPs [44], and here we employ three different ones SCP-alamode, stochastic self-consistent harmonic approximation (SSCHA), SCP-hiphive. In SCP-alamode the Green’s functions approach is employed as implemented in the alamode software [50]. In SSCHA the harmonic free energy is minimized using gradient methods, as implemented in the software package sscha [51]. In SCP-hiphive second order force-constants are obtained from fitting with displacement sampled from the harmonic model and forces obtained from the MLP as implemented in the HIPHIVE package [49]. 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 with the MLP.

Here, we find a very similar behavior for both M-tilt and R-tilt modes. The three SCP (SCP-hiphive, SSCHA, SCP-alamode) methods employed here are in remarkable 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 almost a factor of two (see Note S5 for
a more detailed description of the SCP methods). The EHMIs constructed by fitting the forces from MD trajectories show good agreement with the mode projection results. We note here that the trend for SCPs and EHMIs to over and underestimate frequencies, respectively, appears to hold for all modes in the system, which is in line with previous studies [32, 58–60]. However, while EHMIs from MD yield a better frequency for the tilt mode compared to SCP, this is not in general true (see Fig. S9 for details).

To conclude, we have carried out a detailed computational analysis of the tilt-modes in CsPbBr$_3$. Most strikingly, we observe overdamped modes for the cubic phase almost 200 K above the phase transition temperatures. These overdamped modes exhibit correlation on very long time scales, much longer than the typical relaxation time period of the mode. This is in line with the dynamics transitioning toward Brownian motion behavior. What we find here is that these modes can, however, still be mathematically well described by a DHO, from which one can 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.

In addition, we demonstrated that commonly used computational phonon renormalization methods agree very well with each other but exhibit systematic errors in describing the frequency of anharmonic modes. Understanding the single-point frequency obtained from such methods and its relation to the full dynamical spectra is thus very important when, e.g., comparing with experimental measurements.

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[1] J. M. Ziman, Electrons and Phonons (Oxford University Press, London, 1960).
[2] T. Sun and P. B. Allen, Phys. Rev. B 82, 224305 (2010).
[3] T. Sun, X. Shen, and P. B. Allen, Phys. Rev. B 82, 224304 (2010).
[4] D.-B. Zhang, T. Sun, and R. M. Wentzcovitch, Phys. Rev. Lett. 112, 058501 (2014).
[5] W. Lv and A. Henry, Scientific Reports 6, 10.1038/srep37675 (2016).
[6] L. Isaeva, G. Barbalinardo, D. Donadio, and S. Baroni, Nature Communications 10, 10.1038/s41467-019-11572-4 (2019).
[7] B. D. Silverman, Phys. Rev. B 9, 203 (1974).
[8] T. Schneider and E. Stoll, Phys. Rev. B 17, 1302 (1978).
[9] W. Petry, A. Heimming, J. Trampenau, M. Alba, C. Herzig, H. R. Schober, and G. Vogl, Physical Review B 43, 10933 (1991).
[10] E. Fransson and P. Erhart, Acta Materialia 196, 770 (2020).
[11] E. Fransson, M. Slabanja, P. Erhart, and G. Wahnström, Advanced Theory and Simulations 4, 2000240 (2021).
[12] S. E. Kim, F. Mujid, A. Rai, F. Eriksson, J. Stuh, P. Poddar, A. Ray, C. Park, E. Fransson, Y. Zhong, D. A. Muller, P. Erhart, D. G. Cahill, and J. Park, Nature 597, 660 (2021).
[13] T. Nakamura, Ferroelectrics 9, 159 (1975).
[14] T. Nakamura, Ferroelectrics 137, 65 (1992).
[15] M. T. Dove, American Mineralogist 82, 213 (1997).
[16] S. Ehsan, M. Arrigoni, G. K. H. Madsen, P. Blaha, and A. Tröster, Physical Review B 103, 10.1038/physrevb.103.094108 (2021).
[17] M. Songvilay, N. Giles-Donovan, M. Bari, Z.-G. Ye, J. L. Minns, M. A. Green, G. Xu, P. M. Gehring, K. Schmalzl, W. D. Ratcliff, C. M. Brown, D. Chernyshev, W. van Beek, S. Cochran, and C. Stock, Phys. Rev. Materials 3, 093602 (2019).
[18] T. Lanigan-Atkins, X. He, M. Krogsdad, D. Pajerowski, D. Abernathy, G. N. Xu, Z. Xu, D.-Y. Chung, M. Kanatzidis, S. Rosenkranz, R. Osborn, and O. Delaire, Nature Materials 20, 977 (2021).
[19] C. C. Stoumpos, C. D. Malliakas, J. A. Peters, Z. Liu, M. Sebastian, J. Im, T. C. Chasapis, A. C. Wibowo, D. Y. Chung, A. J. Freeman, B. W. Wessels, and M. G. Kanatzidis, Crystal Growth & Design 13, 2722 (2013).
[20] S. Hirotsu, J. Harada, M. Iizumi, and K. Gesi, Journal of the Physical Society of Japan 37, 1393 (1974).
[21] S. Sharma, N. Weiden, and A. Weiss, Zeitschrift für Naturforschung A 46, 329 (1991).
[22] M. Rodová, J. Brožek, K. Kužek, and K. Nitsch, Journal of Thermal Analysis and Calorimetry 71, 667 (2003).
[23] C. A. López, C. Abia, M. C. Alvarez-Galván, B.-K. Hong, M. V. Martínez-Huerta, F. Serrano-Sánchez, F. Carrasco, A. Castellanos-Gómez, M. T. Fernández-Díaz, and J. A. Alonso, ACS Omega 5, 5931 (2020).
[24] D. Malyskin, V. Sereda, I. Ivanov, M. Mazzurin, A. Sednev-Lugovets, D. Tsvetkov, and A. Zuev, Materials Letters 278, 128458 (2020).
[25] L.-y. Huang and W. R. L. Lambrecht, Phys. Rev. B 90, 195201 (2014).
[26] E. L. da Silva, J. M. Skelton, S. C. Parker, and A. Walsh, Physical Review B 91, 10.1103/physrevb.91.144107 (2015).
[27] R. X. Yang, J. M. Skelton, E. L. da Silva, J. M. Frost, and A. Walsh, The Journal of Physical Chemistry Letters 8, 4720 (2017).
[28] R. X. Yang, J. M. Skelton, E. L. da Silva, J. M. Frost, and A. Walsh, The Journal of Chemical Physics 152, 024703 (2020).
[29] A. Cohen, T. M. Brenner, J. Klarbring, R. Sharma, D. H. Fabini, R. Korobko, P. K. Nayak, O. Hellman, and O. Yaffe, Advanced Materials 34, 2107932 (2022).
[30] X. Zhu, S. Caicedo-Dávila, C. Gehrmann, and D. A.
Egger, ACS Applied Materials & Interfaces 14, 22973 (2022).
[31] J. Lahnsteiner and M. Bokdam, Phys. Rev. B 105, 024302 (2022).
[32] T. Tadano and W. A. Saidi, Phys. Rev. Lett. 129, 185901 (2022).
[33] A. Stukowski, Modelling and Simulation in Materials Science and Engineering 18, 015012 (2009).
[34] See Supplemental Material at [URL will be inserted by publisher] for additional figures and further details.
[35] Z. Fan, Z. Zeng, C. Zhang, Y. Wang, K. Song, H. Dong, Y. Chen, and T. Ala-Nissila, Physical Review B 104, 104309 (2021).
[36] Z. Fan, Y. Wang, P. Ying, K. Song, J. Wang, Y. Wang, Z. Zeng, K. Xu, E. Lindgren, J. M. Rahm, A. J. Gabourie, J. Liu, H. Dong, J. Wu, Y. Chen, Z. Zhong, J. Sun, P. Erhart, Y. Su, and T. Ala-Nissila, Journal of Chemical Physics 157, 114801 (2022).
[37] The DFT data and the MLP models are provided in a zenodo dataset [61].
[38] G. Kresse and J. Hafner, Physical Review B 47, 558 (1993).
[39] P. E. Blöchl, Physical Review B 50, 17953 (1994).
[40] G. Kresse and J. Furthmüller, Computational Materials Science 6, 15 (1996).
[41] J. Sun, A. Ruzzinszky, and J. P. Perdew, Physical Review Letters 115, 036402 (2015).
[42] A. H. Larsen, J. J. Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dulak, J. Friis, M. N. Groves, B. Hammer, C. Hargus, E. D. Hermes, P. C. Jennings, P. B. Jensen, J. Kernode, J. R. Kitchin, E. L. Kolshbjerg, J. Kubal, K. Kaasbjerg, S. Lysgaard, J. B. Maronsson, T. Maxson, T. Olsen, L. Pastewka, A. Peterson, C. Rostgaard, J. Schiotz, O. Schütt, M. Strange, K. S. Thygesen, T. Vegge, L. Vilhelmsen, M. Walter, Z. Zeng, and K. W. Jacobsen, Journal of Physics: Condensed Matter 29, 273002 (2017).
[43] CALORINE, https://gitlab.com/materials-modeling/calorine (2022), accessed: 2022-10-31.
[44] K. Esfarjani and Y. Liang, in Nanoscale Energy Trans-