

# On the anomalous diffusion of proton in Y-doped BaZrO<sub>3</sub> perovskite oxide

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## ARTICLE INFO

### Keywords:

Anomalous diffusion  
Perovskite oxide  
Machine-learning molecular dynamics  
Theoretical model  
Proton

## ABSTRACT

Proton transport in perovskite oxides (ABO<sub>3</sub>) is a complex dynamical process involving hydroxide ion rotation and proton transfer. Combining ab initio molecular dynamics (AIMD) and machine-learning molecular dynamics (MLMD) simulations of proton dynamics in Y-doped BaZrO<sub>3</sub> perovskite oxide, we systematically illustrate the anomalous characteristics of proton motion. At short times, proton performs superdiffusion through the O—H wag and proton transfer. At intermediate times, the larger rotation angle results in the larger plateau value. At longer times, proton diffusion first becomes subdiffusive due to the hydroxide ion rotations then gradually turns to normal diffusion. A theoretical model is also offered to quantitatively describe this abnormal proton diffusion. In all, this work provides a more complete understanding of proton dynamics in perovskite oxides.

Proton transport in solids plays a significant role in many different fields of physics [1], chemistry [2], and biology [3,4]. Perovskite oxide (ABO<sub>3</sub>) [5] exhibits high proton conductivity at high temperatures and is one of the most promising electrolytes for solid oxide fuel cells (SOFCs) and electrolysis cells (SOEC). Proton transport in perovskite oxides is generally characterized by a Grotthuss mechanism [6] consisting of proton transfer between two neighboring oxide ions and hydroxide ion rotation [7,8]. As a long-range mobile cation, proton has a delocalized nature in perovskite oxides. However, hydroxide ion rotation at oxide ion sites leads to a local dynamics, and thus slows down the dynamics of proton. In BaCeO<sub>3</sub>, the proton has been found to be confined around an oxide ion during the first-principles molecular dynamics simulation [9]. In the meanwhile, the behavior of proton rapid rotational diffusion around the oxygen has been observed indirectly from quasi-elastic neutron scattering and  $\mu$ -SR experiments [10–12]. In this local dynamics, two high frequency vibration modes are involved: O—H stretching and O—H wag (reorientation) vibration [13,25]. The back and forth bouncing of proton within these two modes indicates that proton is strongly localized by the oxygen although the orientation of

the hydroxide ion is stochastically changing. Apart from the above two high frequency vibration modes in the local dynamics, hydroxide ion rotation as one of Grotthuss-type diffusion steps requires comparable energy barriers to proton transfer [30,31] and exhibits a localized behavior of proton as well. Therefore, the raised question is what the proton diffusion behavior is when combining two high frequency motions: O—H stretching and O—H wag vibration and two relatively low frequency motions with large energy barriers: proton transfer and hydroxide ion rotation. Furthermore, whether the proton diffusion can be effectively described by a normal motion? Despite the dynamics of proton in Y-doped BaZrO<sub>3</sub> (BZY) —one of the most promising proton-conducting perovskites has been investigated based on first-principles molecular dynamics simulations [13,14], normal diffusion is assumed to interpret experimental data. Unfortunately, more insights into the proton dynamics in BZY in a whole time range have not yet been advanced. In particular, the relevance of the local dynamics such as hydroxide ion rotation to proton diffusion in perovskite oxides has to be addressed. Thus, the dynamics of isolated proton in perovskite oxides is needed to be fully characterized. Detailed theoretical model for the

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dynamics of proton diffusion is also needed to understand the proton diffusion behavior.

The dynamical properties of particle transport are generally characterized by the power-law formulation of the mean-square displacement (MSD) over time [15],

$$\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle \simeq K_\alpha t^\alpha \quad (1)$$

Here  $\vec{r}(t)$  is the position of proton at time  $t$ , brackets  $\langle \dots \rangle$  represents the ensemble average, and  $\alpha$  is used to distinguish the diffusion behavior ( $\alpha > 1$ ,  $\alpha = 1$ , and  $\alpha < 1$  correspond to the superdiffusion, normal diffusion, and subdiffusion, respectively).

Due to a limited number of trajectories, the time series  $\vec{r}(t)$  are alternatively calculated in terms of the time-averaged mean-square displacement (TAMSD) as a function of the lag time [15],

$$\overline{\delta^2(\Delta, T)} = \frac{1}{T - \Delta} \int_0^{T-\Delta} |\vec{r}(t + \Delta) - \vec{r}(t)|^2 dt \quad (2)$$

where  $\Delta$  and  $T$  are the lag time and the total measurement time, respectively. In addition to the individual TAMSDs, the corresponding average over the set of  $N$  trajectories is obtained by [16],

$$\langle \overline{\delta^2(\Delta)} \rangle = \frac{1}{N} \sum_{i=1}^N \overline{\delta_i^2(\Delta)} \quad (3)$$

All first-principles calculations are performed using the Vienna Ab initio simulation package (VASP) [17–19] with the projector augmented wave (PAW) method [19]. The Perdew-Burke-Ernzerhof (PBE) [20] exchange-correlation functional is used. The cutoff energy for the plane wave basis set for all calculations is 500 eV which has been used for proton conducting perovskites [21,22]. The cubic BZY system with  $3 \times 3 \times 3$  cubic unit cells is constructed. Four distant Y dopants (the corresponding dopant level of 14.8%) in the system are considered and four protons are induced to achieve the dynamics of proton. The initial BZY system is relaxed using first-principles calculations. To investigate proton dynamics in BZY, we performed AIMD calculations, where the NVT ensemble (constant number of particles, volume, and temperature) was adopted with a time step of 0.5 fs. The temperature was controlled at 1000 K by employing the Nosé-Hoover thermostat [28,29]. The system volume was increased from the relaxation of first-principles calculation at 0 K to that of the temperature at 1000 K based on the thermal expansion parameter in experiment [23]. After a relaxation of structure for 5 ps at 1000 K, we continued to simulate the system for another 55 ps to obtain the trajectory of proton diffusion. The calculated TAMSDs are given in Fig. 1a. In this time window, one can distinguish three different regimes for the motion of the proton:

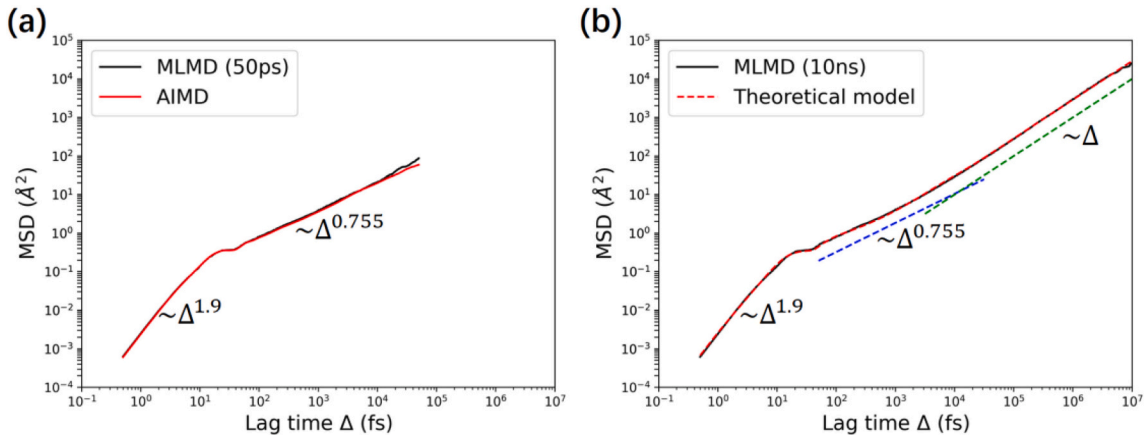
- at short times (from zero to about 20 fs), the dynamics is superdiffusive;
- at intermediate times (from about 20 fs to about 40 fs), the MSD remains constant for a given time interval, and the protons seem to be “trapped” to certain oxygen donors;
- at longer times (from about 40 fs to up to 50 ps), the motion becomes diffusive again but exhibits subdiffusive motion.

Given the complexity of this anomalous diffusion behavior, 50 ps of AIMD run may not be sufficient to elucidate all physics for longer times. One remaining question is whether proton will manifest normal diffusion behavior at even longer times, as suggested in other computational works [2,13,14]. To overcome the timescale limitation, we trained a machine-learning potential (MLP) with first-principles data using DeePMD [32,35] artificial neural network architecture and performed MLMD simulation for 10 ns, which is 200 times of the AIMD run. The cutoff radius of the MLP is set to 6.0 Angstrom and a deep neural network that contains three hidden layers with 240, 240 and 240 nodes is employed to map the local atomic environment to the atomic energy contributions. The dataset includes more than 200,000 configurations from AIMD simulations.

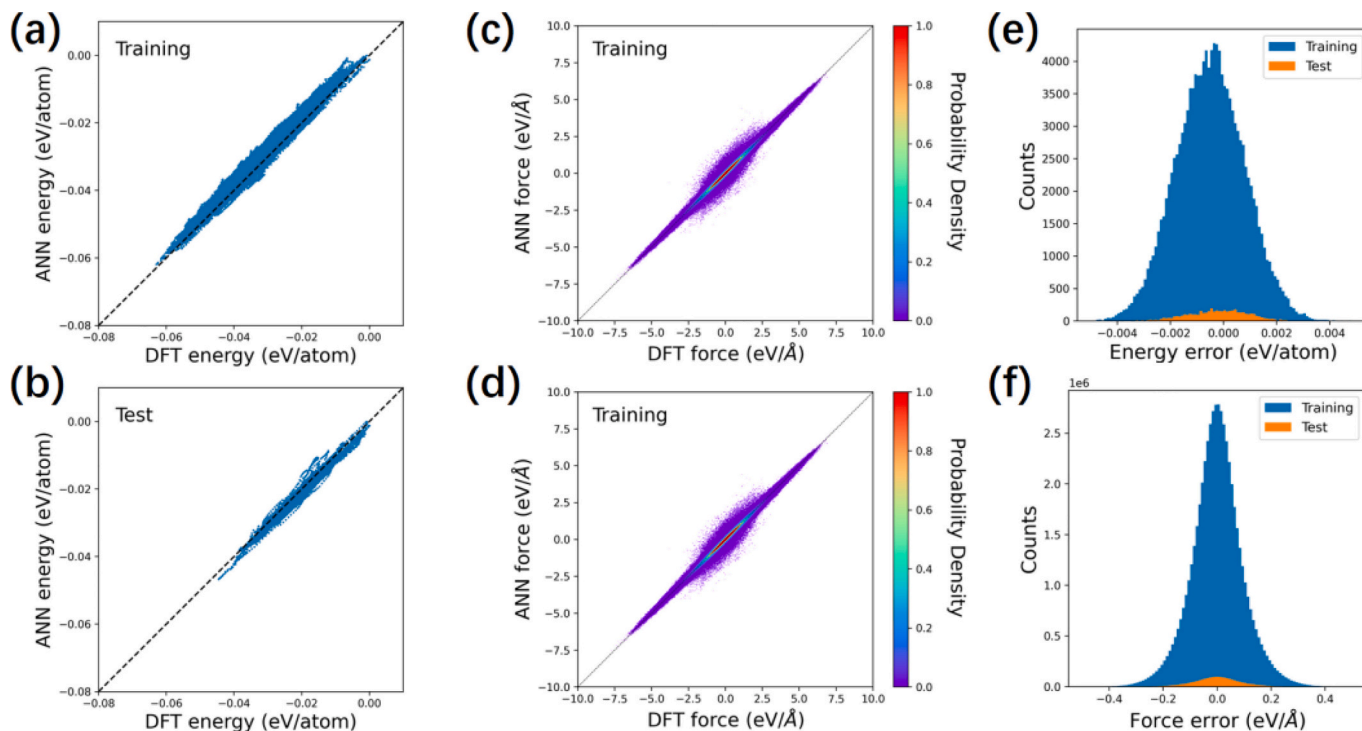
Comparisons between the DFT and deep neural network results on energy and force are plotted in Fig. 2. The resulting root mean-square errors (RMSE) of the energies are 1.38 and 1.33 meV/atom for training and test sets, respectively. As for forces, the RMSE are 107.1 and 139.6 meV/Angstrom for training and test sets, respectively. The RMSE values are consistent with the typical RMSE values for machine learning model [33]. We then performed a MLMD run using the same settings of AIMD simulation (same initial structure/timestep/ensemble) and calculated the TAMSDs for a 50 ps trajectory and a 10 ns trajectory, as shown in Fig. 1a and b. We can see that:

- MLMD gives TAMSD results that are very close to that of the AIMD run for the first 50 ps trajectory as shown in Fig. 1a. The error at lag time  $\Delta$  larger than  $10^4$  fs is due to the limited samples at the larger lag time.
- at longer times (from about 40 fs to up to 10 ns), the motion first becomes subdiffusive then gradually turns to normal diffusion as shown in Fig. 1b.

In order to understand the physics of proton transport at different time scales, vibrational motions of the proton precursory to elementary processes of hydroxide ion rotation and proton transfer are explored. The normalized vibrational density of states (VDOS) via a Fourier transform of the atomic velocity autocorrelation function (VACF) of

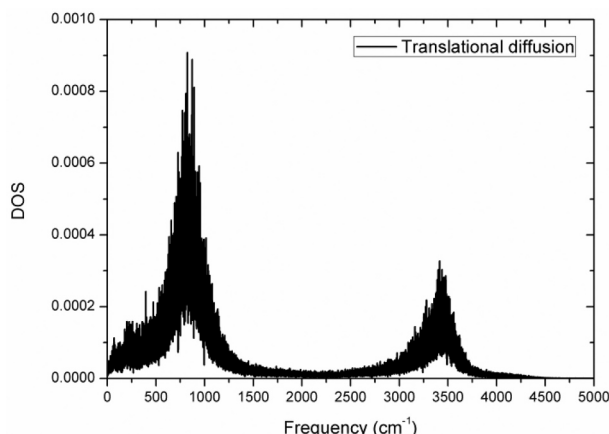


**Fig. 1.** (a) TAMSDs  $\langle \overline{\delta^2(\Delta)} \rangle$  of proton in BZY for 50 ps trajectory. (b) TAMSDs  $\langle \overline{\delta^2(\Delta)} \rangle$  of proton in BZY for 10 ns trajectory. Orange solid line represents the fit to the MSD of the theoretical model based on fractional Brown motions (Eq. 4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Comparisons of the deep neural network results with respect to the references of DFT data. (a) and (b) show the comparisons of energies per atom for training and test set, respectively. (c) and (d) exhibit force comparisons for training and test set. 2D histogram plots are used to show the density distribution of errors, respectively. (e) and (f) display the error distributions for energies and forces for training and test set, respectively.

proton are calculated as shown in Fig. 3. We can see that there are two broad peaks in the DOS of normal region, one is located at around 839.5  $\text{cm}^{-1}$  (low-frequency peak) and the other is located at around 3445  $\text{cm}^{-1}$  (high-frequency peak). In proton conducting oxides, the high-frequency vibration generally corresponds to stretching modes of the hydroxide ion [25,26], while the lower-frequency peak at around 839.5  $\text{cm}^{-1}$  represents the reorientation of the O—H bond (assigned as O—H wag modes) [26]. Due to the presence of hydrogen bonds, O—H bond length is increased and O—H stretching frequency is decreased. Hence, the broad band is associated with a wide range of hydrogen bond distribution [27]. It can be noted that O—H wag frequency of 839.5  $\text{cm}^{-1}$  matches well with the MSD inflection point of 40 fs at the transition from the intermediate to longer time scale shown in Fig. 1a. The MSD reaches a maximum at 20 fs because of the dominant O—H wag motion, while the plateau rather than a reduction in MSD from 20 to 40 fs is observed, which indicates that relative hydroxide ion rotations with larger

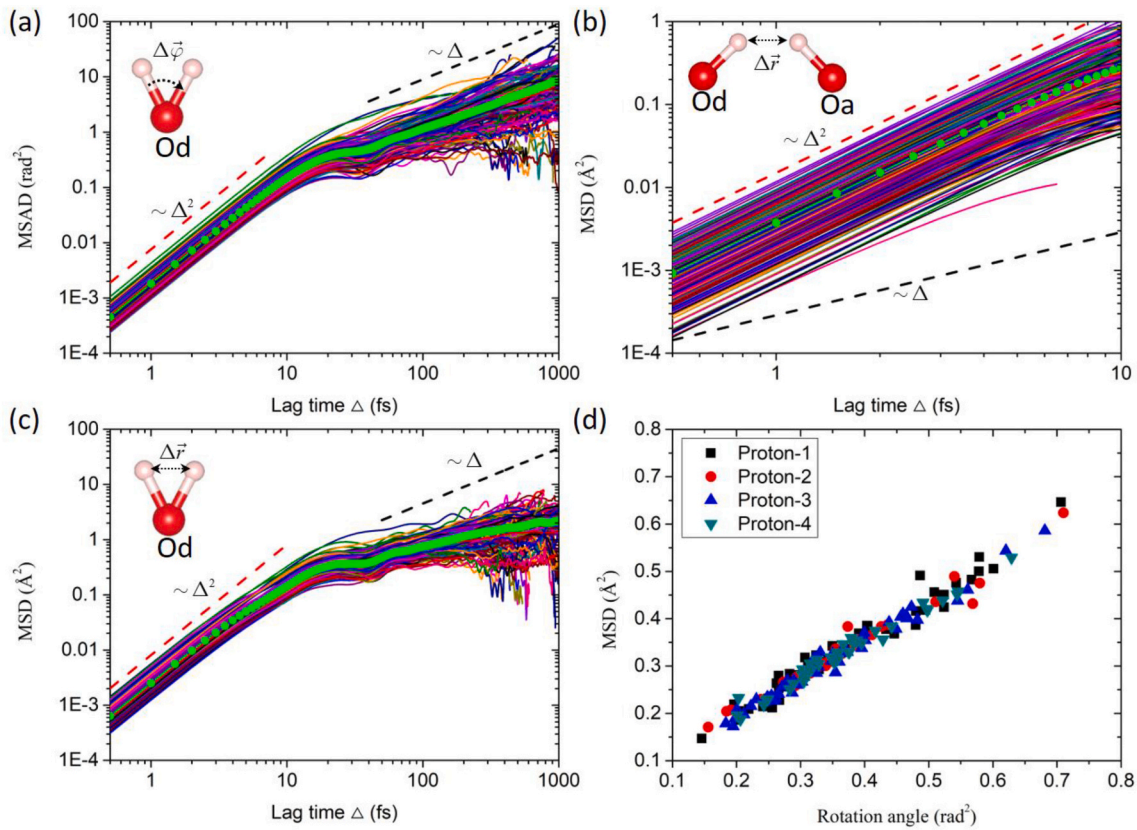


**Fig. 3.** Power spectra of translational VACF.

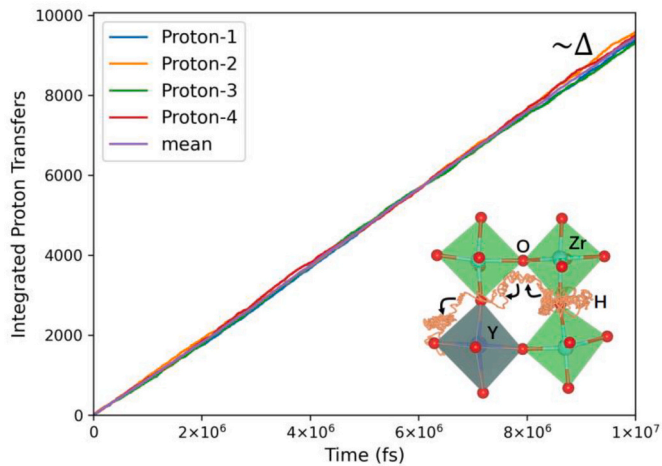
rotation angle are present as well during proton dynamics. The proton trapping event is not observed in current AIMD simulations.

Since O—H wag motion plays an important role in proton motion especially at short times, the angular motion of hydroxide ion is analyzed. The time-averaged mean-square angular displacement (MSAD) of hydroxide ion rotations between proton transfers are calculated as shown in Fig. 4a using  $\overline{\delta^2(\Delta, T)} = \frac{1}{T-\Delta} \int_0^{T-\Delta} |\vec{\varphi}(t+\Delta) - \vec{\varphi}(t)|^2 dt$  where  $\Delta$  and  $T$  are the lag time and the total measurement time,  $\vec{\varphi}(t)$  is the total angular displacement of hydroxide ion. A detailed calculation of the  $\vec{\varphi}(t)$  is given in Ref. 34. It is noted that hydroxide ion rotation displays superrotation with power near 2 at short times, while displays subrotation at longer times. In addition, MSDs related to proton transfers are calculated shown in Fig. 4b, which display superdiffusion. In order to gain further insight into proton translational motion, the corresponding translational MSDs of proton during the hydroxide ion rotations are obtained as well shown in Fig. 4c. Although proton transfer and hydroxide ion rotation are fundamentally different in nature, they exhibit superdiffusive characteristics at short times, which results in superdiffusive characteristics in proton diffusion shown in Fig. 1a at short times. In the meanwhile, we can see that the plateau values in both MSAD shown in Fig. 4a and MSD shown in Fig. 4c are different for different hydroxide ion rotations. The relevance of MSD to the rotation angle at lag time of 20 fs is shown in Fig. 4d. It can be noted that the value of plateau is significantly dependent on the rotation angles. The larger angle, the larger plateau value, which means that hydroxide ion rotation properties determine the starting point of MSD for longer times. However, at relatively long times, hydroxide ion rotations show subdiffusive characteristics, which characterizes its local dynamics. While combining the superdiffusive proton transfers, the overall normal diffusion at longer times shown in Fig. 1a is present.

In order to confirm the normal characteristics of proton motion at longer times shown in Fig. 1b, the integrated proton transfers are calculated for each proton shown in Fig. 5. We can see that the integrated proton transfers for each proton increases linearly as the



**Fig. 4.** (a) Time-averaged MSADs of the hydroxide ion rotations. The green line with circle symbols is the mean data of all lines. (b) Time-averaged MSDs of proton transfers. The green line with circle symbols is the mean data of all lines. (c) Time-averaged MSDs of proton during the hydroxide ion rotations. The green line with circle symbols is the mean data of all lines. (d) The relevance of MSD to the rotation angle at lag time of 20 fs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 5.** Integrated proton transfers as a function of simulation time.

simulation time increases. The motion of proton transfer exhibits converged superdiffusive characteristics. Combining with the subdiffusive hydroxide ion rotations at longer times, the proton motion gradually turns from subdiffusive FBM to normal diffusion, which is consistent with Fig. 1b.

To generalize the explanation of the anomalous dynamics, an analytical model combining above two fractional Brownian motions (FBMs) is proposed based on the modified Richard expression [24]:

$$MSD(\Delta) = \frac{D_{st}\Delta^{\alpha_s}}{\left[1 + \left|\frac{D_{st}\Delta^{\alpha_s}}{M_{st}}\right|^{n_1}\right]^{1/n_1}} + \frac{(D_{st} + D_{ll})\Delta^{\alpha_{ll}}}{\left[1 + \left|\frac{(D_{st} + D_{ll})\Delta^{\alpha_{ll}}}{M_{ll}}\right|^{n_2}\right]^{1/n_2}} + D_{l2}\Delta \quad (4)$$

where the relevant parameters are defined as follows:

$$D_{st} = D_s + (D_{s0} - D_s)\tau_1 \quad (5a)$$

$$M_{st} = M_s + (M_{s0} - M_s)\tau_1 \quad (5b)$$

$$n_{l1} = n_s + (n_{s0} - n_s)\tau_1 \quad (5c)$$

$$D_{ll} = D_{l1} + (D_{l10} - D_{l1})\tau_1 \quad (5d)$$

$$M_{ll} = M_{l1} + (M_{l10} - M_{l1})\tau_2 \quad (5e)$$

$$n_{l2} = n_{l1} + (n_{l10} - n_{l1})\tau_2 \quad (5f)$$

$$D_{l2} = D_{l2} + (D_{l20} - D_{l2})\tau_2 \quad (5g)$$

where parameters  $D_s$ ,  $D_{s0}$ ,  $M_s$ ,  $M_{s0}$ ,  $n_s$ ,  $n_{s0}$  are defined for the short-time superdiffusion,  $D_{l1}$ ,  $D_{l10}$ ,  $M_{l1}$ ,  $M_{l10}$ ,  $n_{l1}$ ,  $n_{l10}$  are defined for the long-time subdiffusion,  $D_{l2}$ ,  $D_{l20}$  are defined for long-time normal diffusion. In particular,  $M_s$  and  $M_{l1}$  account for the MSD near the transition from short-time superdiffusion to the long-time subdiffusion and long-time subdiffusion to long-time normal diffusion,  $D_s$  and  $\alpha_s$  correspond to the diffusion parameters for short-times superdiffusion (shown in Fig. S1a),  $D_{l10}$  and  $\alpha_{l1}$  correspond to the diffusion parameters for long-time subdiffusion (shown in Fig. S1b) and  $D_{l20}$  corresponds to the diffusion parameters for long-time normal diffusion (shown in Fig. S1c). The parameter  $\tau_1$  and  $\tau_2$  describe the transition from short-time superdiffusion to the long-time subdiffusion and long-time subdiffusion to long-time normal diffusion are given by:

$$\tau_1 = \left[ \frac{(\Delta/T_{tr1})^{t_{11}}}{(\Delta/T_{tr1})^{t_{11}} + 1} \right]^{t_{21}} \quad (6a)$$

$$\tau_2 = \left[ \frac{(\Delta/T_{tr2})^{t_{12}}}{(\Delta/T_{tr2})^{t_{12}} + 1} \right]^{t_{22}} \quad (6b)$$

where  $T_{tr1}$  and  $T_{tr2}$  account for the lag time near the transition from short-time superdiffusion to the long-time subdiffusion and long-time subdiffusion to long-time normal diffusion. All parameters of this theoretical model are listed in Table S1.

As we can see (Fig. 1b) that theoretical model can reproduce the entire MSD curve very well including intermediate time scale. For short times, the increase of the MSD is different from a ballistic  $\Delta^2$  scaling and fitted exponent  $\alpha$  is 1.9. For relatively long times, the fitted exponent  $\alpha$  is 0.755 less than 1 corresponding to subdiffusion. For the longer times, the fitted exponent  $\alpha$  is 1 corresponding to normal diffusion. Thus, theoretical model quantitatively confirms the anomalous dynamics of proton.

In this paper, we performed AIMD calculations to study the proton dynamics in Y-doped BaZrO<sub>3</sub> perovskite oxide. We found that the motion of proton exhibits the anomalous behavior. There are three different regimes in proton diffusion MSD – specifically, superdiffusion at short times, emergence of a plateau in the MSD at intermediate times, from subdiffusion gradually turning to normal diffusion at longer times. The anomalous dynamics of proton is quantitatively analyzed by a theoretical model based on FBMs.

By analyzing the normalized vibrational density of states (VDOS), the O–H wag mode frequency of 839.5 cm<sup>-1</sup> corresponds to the inflection point of 40 fs in the MSD, which indicates that the O–H wag motion dominates the proton motion at short times. The translational MSDs of both hydroxide ion rotation and proton transfer exhibit superdiffusive characteristics resulting in the superdiffusion at short times. At intermediate times, the plateau in MSD means the relative hydroxide ion rotation with larger rotation angles (longer time) are present, while the proton trapping event is not observed. The value of plateau is significantly dependent on hydroxide ion rotation angles: the larger angle, the larger plateau height. At longer times, hydroxide ion rotations show subdiffusive characteristics. Coupling with superdiffusive proton transfer, the overall proton motion is normal diffusion. In all, this work provides a more complete understanding of proton dynamics in perovskite oxides.

## Author statement

**H. Niu:** Investigation, Writing - Original Draft **Y. Jing:** Conceptualization, Investigation, Writing - Original Draft, Writing - Review & Editing **Y. Sun:** Formal analysis **L. Guo:** Formal analysis **N. R. Aluru:** Conceptualization, Writing - Original Draft, Writing - Review & Editing **W. Li:** Investigation **J. Yang:** Investigation **X. Li:** Investigation

## Data availability

The raw/processed data required to reproduce these findings are available to download from [https://github.com/hongweiniu/proton\\_diffusion\\_in\\_BZY](https://github.com/hongweiniu/proton_diffusion_in_BZY).

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

This work is supported by the National Science Foundation under grant # 1545907, the National Center for Supercomputing Applications

(NCSA), the NSF of China under Grant No. 12172112, 11932005 and 11974091, and the International Postdoctoral Exchange Fellowship Program of China under Grants No. 20140016.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ssi.2022.115859>.

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