

# Supplemental material for momentum distribution, vibrational dynamics and the potential of mean force in ice

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## ANALYSIS OF THE ANHARMONICITY ALONG THE HYDROGEN BOND DIRECTION

The hypothesis that the potential of mean force of the proton in ice Ih is quasi-harmonic can be verified directly by analyzing the quantile function [1] of the end-to-end distribution. For a one-dimensional probability distribution  $p(x)$ , the quantile function  $Q(p)$  characterizes the inverse of the cumulative probability distribution  $F(x)$

$$Q(p) = \inf\{x \in R : p \leq F(x)\}. \quad (1)$$

The quantile function can be used to compare two probability distributions by plotting the corresponding quantile functions against each other. This is called the quantile-quantile plot. The quantile-quantile plot between the end-to-end distribution collected from the PICPMD simulation along the hydrogen bond direction and the normal distribution that best fits this data is shown in the left panel of Fig. 1 alongside a plot of each distribution (right panel). The end-to-end distribution along the bond direction is very close to a normal distribution, thereby showing that the potential of mean force along this direction can be well described by a quasi-harmonic form. The quantile-quantile plot also exhibits small deviations at the tails indicating the presence of some degree of additional anharmonicity.

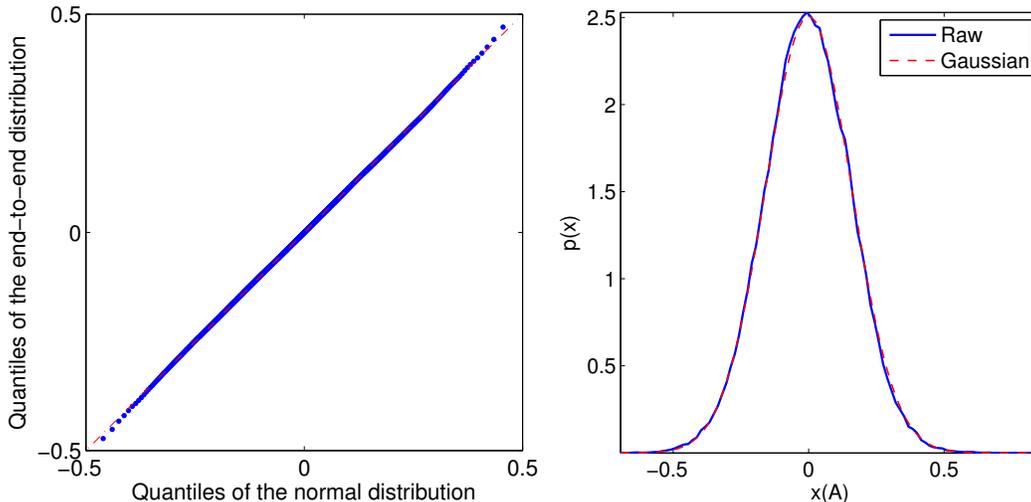


FIG. 1: The Quantile-quantile plot between the end-to-end distribution along the bond direction and the normal distribution is depicted in the left panel. The distributions are shown in the right panel. The end-to-end distribution along the bond direction is very close to a normal distribution, but with small deviation at the tail. The quantile-quantile plot indicates that the potential of the mean force along the bond direction is well modeled by a quasi-harmonic potential.

In order to gain better insight on the anharmonicity in the bonding direction, we perform the following analysis. The potential energy surface is obtained by moving one proton along the hydrogen bond direction while the positions of all other atoms are fixed at their equilibrium positions. The resultant potential energy surface is depicted in Fig. 2, and the deviation from a harmonic potential can be readily seen. The ground state wavefunction  $|\Psi^2|$  is also plotted in Fig. 2 in order to show the extent of the quantum delocalization of the proton ( $-0.2\text{\AA} \sim +0.3\text{\AA}$ ). The potential energy surface about  $x = 0$  is asymmetric, indicating a cubic dependence on displacement in the first anharmonic

correction (black dashed line in Fig. 2). Higher order corrections set in at displacements larger than  $\approx 0.3\text{\AA}$ , which is clearly beyond the range of the ground state wavefunction. The harmonic frequency at the minimum of this potential is  $3065\text{cm}^{-1}$ , close to the value of  $\bar{\omega}_1$  garnered from the phonon calculation (see Table I in the manuscript). The size of the anharmonicity can be gauged upon comparison of this harmonic value with the effective frequency of  $2847\text{cm}^{-1}$  obtained from the end-to-end distribution associated with the potential in Fig. 2 at  $T = 269\text{K}$ . As expected, the anharmonicity lowers the value of the frequency and the shift is close to that between the PICPMD and the phonon derived results. The anharmonicity is a consequence of quantum delocalization which causes the proton to sample the potential energy surface over an extended range in the bond direction. It should be noted that the potential in Fig. 2 differs from the potential of mean force that the proton experiences in the simulation. We expect however that along the bond direction the two potentials should behave qualitatively similarly as suggested by the close similarity of their respective harmonic frequencies and anharmonic shifts. The delocalization along the bond that we find is comparable to the one observed in other ice phases with intact water molecules (see e.g. [2, 3]).

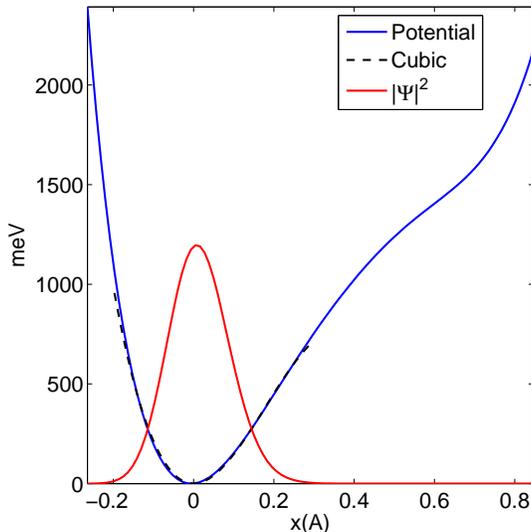


FIG. 2: The potential energy surface of the proton in ice Ih along the bond direction (blue solid line), the cubic fitting potential (black dashed line) and the corresponding ground state wavefunction  $|\Psi^2|$  (red solid line).

## QUANTUM EFFECTS ON THE OXYGEN NUCLEI

The phonon calculation reported in the main text also yields an estimate of the quantum effects on the oxygen nuclei. The corresponding principal frequencies are  $\bar{\omega}_1 = 640.1 \pm 16.6\text{cm}^{-1}$ ,  $\bar{\omega}_2 = 585.1 \pm 9.8\text{cm}^{-1}$ , and  $\bar{\omega}_3 = 351.9 \pm 30.7\text{cm}^{-1}$ . The frequencies mostly arise from the network modes, but are blue-shifted due to oxygen participation in stretching, bending and libration. The kinetic energy estimate for oxygen is  $56.4 \pm 0.4\text{meV}$ , and is approximately 35% in excess of the classical result (35meV at 269K). The magnitude of this effect is consistent with earlier predictions [4] and with that found for fluorine nuclei in recent calculations on hydrogen fluoride [5].

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