Nuclear quantum effects in a 1-D model of hydrogen bonded ferroelectrics

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Abstract. A one dimensional model of a coupled hydrogen (H) bonding chain is developed and parametrized to density functional theory (DFT) calculations on squaric acid, a prototypical H-bonded antiferroelectric crystal. The energetics of single and collective proton jumps and its dependence on H-bond length, as obtained by DFT, is reproduced quite well in the model despite its simplicity where only hydrogen and oxygen atom positions in (O-H...O) H-bonds and nearest-neighbor coupling between H positions are explicitly included. Classical and path-integral molecular dynamics simulations are performed to shed light on nuclear quantum effects and how they influence the paraelectric phase transition. A large H/D isotope shift in the transition temperature $T_C$ as well as a geometric isotope effect is obtained in good agreement with experiment. Fixing the O-O bond length results in shifts of $T_C$ to higher temperature but a pronounced isotope shift of $T_C$ remains, highlighting the importance of quantum effects beyond the geometrical changes in H-bonds accompanying isotopic substitution. Intermediate between fully atomistic models and simpler Ising-type models, the proposed H-bond chain model is a useful toy model for investigating microscopic mechanisms behind phase transitions in H-bonded ferroelectrics and the detailed role of quantum fluctuations.

1. Introduction

One dimensional (1D) chains of molecules connected by hydrogen (H) bonds play a key role in a range of important phenomena in nature. Bridges consisting of several water molecules are fundamental to proton transfer processes in enzyme catalysis [1] and in membrane water channels [2] and the mechanisms of such concerted proton transfers are thus of great biological interest [3]. Water molecules confined inside carbon nanotubes have been investigated as an ideal model system of proton conduction along water wires [4, 5], and the presence of tunneling-assisted concerted proton jumps between molecules in cyclic water hexamers in ice has recently been demonstrated both experimentally [6] and theoretically [7].

Directional H-bond chains also lead to ferroelectric properties in a range of H-bonded crystals [8, 9]. These H-bonded ferroelectrics have been actively investigated since the discovery of ferroelectricity in rochelle salt in 1921 [10], both due to their many possible uses in technological applications [11] and because their fundamental properties are unusual and not yet fully understood. In particular the prototypical KDP system, composed of H-bonded KH$_2$PO$_4$ molecules, has been intensively investigated [12, 13]. Organic H-bonded ferroelectrics constitute another class of materials that have been proposed [14] as flexible low-cost, environmentally friendly alternative components of electronic devices, especially after the discovery of room-temperature ferroelectricity in the croconic acid crystal [15, 16, 17]. Croconic acid is a
cyclic oxocarbon (C₅O₅H₂) in which two inequivalent chains of H-bonds determine the overall polarization. A related but simpler organic ferroelectric is squaric acid, H₂SQ, which is composed of stacked planar sheets of C₄O₂H₂ molecules with opposite polarization in neighboring planes, leading to antiferroelectric properties. Both experimental [18] and theoretical [19] studies have shown that the two orthogonal interpenetrating H-bonding chains in H₂SQ are effectively decoupled, suggesting that a 1D picture may be able to capture fundamental properties of this system.

A key aspect of most H-bonded ferroelectrics that determines their ferroelectric behavior is the motion of H atoms in correlated double well potentials. This correlation consists in H atom positions in neighboring H-bonds being strongly coupled due to the energetic requirement of satisfying the ice rules: in the case of squaric acid each molecule participates in 4 H-bonds, two donating and two accepting. An intriguing property of these systems is the giant isotope shift on Tc. In squaric acid Tc shifts from 373 K in the hydrogenated crystal to 520 K in the deuterated crystal. An early explanation for this behavior was based on quantum tunneling of protons in double-well potentials as proposed by Blinc [20]. After the experimental observation of large geometrical isotope effects (often called Ubbelohde effects [21]), where O–O bond lengths increase significantly upon deuteration, it was argued that quantum tunneling is not necessary to explain this large shift of Tc since H and D atoms experience different double-well potentials that lead to different values of Tc [22]. However, more recent work has again emphasized the involvement of tunneling in H-bonded ferroelectrics. An experimental measurement of the proton momentum distribution in KDP indicated the presence of tunneling above Tc [23], and a first-principles computational investigation suggested tunneling in clusters of correlated protons and heavy atom displacements as the underlying mechanism behind the geometric isotope effect and shift of Tc [13, 24]. A comprehensive understanding of H-bonded ferroelectrics, in particular the role of nuclear quantum effects, is thus yet to be developed.

In recent work we used ab initio path integral molecular dynamics (PIMD) simulations, employing density functional theory (DFT), to investigate nuclear quantum effects on the structure and ordering behavior of squaric acid [25]. We first compared the proton transfer barrier obtained by various density functionals to more accurate methods, i.e. the explicitly correlated MP2 and RPA methods, and found that vdW-DF2 [26] gave the best agreement although it slightly underestimated the barrier. The vdW-DF2 functional was subsequently used in PIMD simulations, revealing a very large influence of nuclear quantum effects. Concerted proton jumps along H-bonding chains were found to be facilitated by synchronous quantum tunneling of several protons. Although accurate in terms of the full-dimensional quantum mechanical description of both electronic and nuclear degrees of freedom, this previous study was limited to a small system size and short simulation times due to the significant computational cost. Simpler models are required to investigate in more detail the paraelectric phase transition, cooperative effects along H-bonding chains and the influence of nuclear quantum effects.

In this work a simple model for a coupled 1D H-bonding chain is presented. It has been parametrized to DFT calculations on squaric acid, a system where a 1D description can be expected to be a good approximation. The structure of the planar building blocks of squaric acid is shown in Fig. 1(a) while the H-bond chain model is illustrated in Fig. 1(b). For more complex materials the model can be generalized to higher dimensions but one might expect that physical insights derived here will be useful for other similar systems.

Extensive molecular dynamics (MD) simulations have been performed on the model to investigate its disordering phase transition, and PIMD simulations have been used to study nuclear quantum effects. In the next section details of the model and the DFT calculations used to parametrize it will be described. Results will be discussed in section 3 and conclusions summarized in section 4.
Figure 1. (a) Crystal structure in one plane of squaric acid showing a 3×2 supercell. The primitive unit cell is composed of two molecules in neighboring parallel planes. A collective transfer of three protons (H₁, H₂ and H₃) along one H-bonding chain is shown by dashed arrows. (b) Schematic of the 1D H-bond chain model. Protons in neighboring H-bonds (illustrated vertically) are harmonically coupled by springs $k_{HH}$, the bond length $R$ is coupled by springs $k_{OO}$ around an equilibrium value $R_{eq}$, and the protons experience a potential that depends on the distance $R$ (see text). The left panel shows the equilibrium structure and (top) a double-well potential for a synchronous jump of all protons, while the right panel shows the jump of one proton across the H-bond and (top) the corresponding single-well potential.

2. Methods

2.1. The HBC model

The proposed H-bond chain (HBC) model contains three terms in the Hamiltonian: (i) an adiabatic ground state energy surface based on two diabatic states suggested by McKenzie [27] for the motion of protons in H-bonds, (ii) a harmonic potential for the oxygen-oxygen distance and (iii) a harmonic potential between protons in nearest-neighbor H-bonds. The Hamiltonian for $N$ H-bonds is thus written as

$$\mathcal{H} = \sum_{i=1}^{N} \left( V(r_i, R_i) + V_{OO}(R_i) + V_{HH}(r_i, r_{i+1}) \right)$$

(1)

where $r$ and $R$ denote hydrogen position and oxygen-oxygen distance, respectively (to be denoted by $d_{OH}$ and $d_{OO}$ in following sections). Periodic boundary conditions are assumed, implying $r_{N+1} \equiv r_1$. The kinetic energy has not been included here. The adiabatic ground state potential of the two diabatic state Hamiltonian is [27]

$$V(r, R) = \frac{1}{2} (V_M(r) + V_M(R - r)) - \frac{1}{2} \sqrt{(V_M(r) - V_M(R - r))^2 + 4\Delta(R)^2}$$

(2)

with $\Delta(R) = \Delta_1 e^{-b(R - R_1)}$, $R_1 = 2r_0 + 1/a$ and $V_M(r)$ are Morse functions. The double-well potential experienced by a proton thus depends on the H-bond length $R$. Conversely, displacements of the proton from its equilibrium position exert a force on the oxygen atoms, providing a description of the coupling between proton positions and H-bond geometry characteristic for H-bonded ferroelectrics.

One Morse function is written as

$$V_M(r) = D \left( e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right)$$

(3)
where $r_0$ is the equilibrium OH distance. The harmonic coupling for the oxygen-oxygen distance and between neighboring protons are written, respectively, as $V_{\text{OO}}(R) = \frac{1}{2} k_{\text{OO}} (R - R_{\text{eq}})^2$ and $V_{\text{HH}}(r_i, r_{i+1}) = \frac{1}{2} k_{\text{HH}} (r_i - r_{i+1})^2$. The parameters $a$, $D$, $\Delta_1$, $r_0$, $R_{\text{eq}}$, $k_{\text{OO}}$ and $k_{\text{HH}}$ were fit to DFT calculations employing the vdW-DF2 functional, which was shown to describe squaric acid well in terms of H-bond geometry and proton transfer barrier [25]. The parameter $b$ was set equal to the value of $a$, as suggested by McKenzie [27].

It should be noted that a similar model has been developed before to investigate the effect of quantum fluctuations on lattice constants at zero temperature [28], and McKenzie has investigated [29] isotope effects in the two diabatic state potential $V(r, R)$ used here.

2.2. DFT calculations

To fit the parameters, potential energy surfaces for proton transfer between neighboring molecules were calculated at various intermolecular O-O distances $d_{\text{OO}}$ using DFT. Simply moving the O atoms on the neighboring squaric acid molecules closer to each other leads to unphysical structures. Instead, structures from the minimum energy path (MEP) were used since along this path $d_{\text{OO}}$ varies from 2.590 Å (initial, geometry optimized structure) to 2.456 Å (transition state for proton transfer). The MEP was obtained from the nudged elastic band method [30]. For each (frozen) configuration of the $C_2$H$_4$ molecule along the MEP the potential energy surface for proton transfer was mapped out by transferring the proton along the O-O bond vector and performing DFT single-point calculations. The molecular frame distorts asymmetrically along the MEP when the proton is transferred from one oxygen to the next, but here symmetry is imposed by averaging the molecular structures on either side of the transition state (at fixed $d_{\text{OO}}$). Since the MEP involves a rotation of the $C_2$H$_4$ squaric unit, parametrizing the HBC model to the potential energy surface obtained in this manner will implicitly include this heavy-atom mode that couples to the proton transfer.

All DFT calculations were performed using the vdW-DF2 functional [26] in the plane-wave based VASP code [31, 32] with PAW potentials [33], an energy cutoff of 500 eV and a $4 \times 1 \times 4$ k-point mesh. A simplified unit cell with only one $C_4$O$_4$ molecule was used since interlayer interactions affect the proton-transfer barrier only slightly (less that 0.01 eV) [25].

2.3. Simulation methods

To investigate the ordering behavior of the HBC model it was implemented into the i-PI code [34] for MD and PIMD simulations. The PIMD simulations were run in the NVT ensemble using a white noise Langevin thermostat [35] in the normal mode representation and a local Langevin thermostat for the centroid coordinates, while a simple Langevin thermostat was used in MD. The required number of beads $P$ was determined by increasing $P$ until convergence was reached for quantum effects on geometrical distributions at a few temperatures. The number of beads to use at other temperatures was then determined by keeping the ratio $\beta/P$ roughly constant, where $\beta = 1/k_B T$. For PIMD simulation of hydrogen the number of beads ranged from 240 at 50 K to 12 at 1000 K, and for deuterium $P$ ranged from 84 at 100 K to 8 at 1000 K. A chain length of 300 H-bonds was used in all simulations.

3. Results

3.1. Parametrizing the HBC model

The right panel of Fig. 2(a) shows the symmetrized DFT-calculated double-well potentials for proton motion between the two oxygens in the H-bond, for different values of $d_{\text{OO}}$. The variable $\delta$ gives the position of the proton along the H-bond as $2\delta = d_{\text{OO}} - 2d_{\text{OH}}$ ($\delta = 0$ thus corresponds to the symmetric transition state). A single unit cell was used in the DFT calculations, with the potential energy surfaces thus corresponding to a collective transfer of all protons along a H-bonding chain. Figure 2(a), left panel, shows the best-fit model prediction obtained by
Table 1. Best-fit values of the parameters of the HBC model.

| Parameter | Value   |
|-----------|---------|
| $a$ (Å$^{-1}$) | 2.7465  |
| $D$ (eV)    | 0.87558 |
| $\Delta_1$ (eV) | 0.18516 |
| $r_0$ (Å)   | 1.0613  |
| $R_{eq}$ (Å) | 2.650   |
| $k_{OO}$ (eV/Å$^2$) | 8.00    |
| $k_{HH}$ (eV/Å$^2$) | 3.40    |

a non-linear least-squares fit. Qualitatively the agreement with the DFT calculations is quite good, with the barrier height decreasing at smaller separations $R$.

Figure 2(b) shows DFT calculations and the model prediction for asynchronous proton transfer, i.e. where only one proton jumps in a 1x1x3 supercell. Introducing the harmonic coupling between protons in neighboring H-bonds, and thereby enforcing the ice rules, is seen to result in good agreement with DFT. The best-fit values of all parameters are given in Table 1. The parameters of the two-state diabatic potential determining the relevant energy scales for proton motion, $D$ and $\Delta_1$, are significantly smaller than the original parameters proposed by McKenzie [27], reflecting the small barrier for proton transfer in squaric acid as obtained by DFT/vdW-DF2.

Figure 2. (a) Comparison of potential energy surfaces for synchronous jumps at different O-O distances $d_{OO}$ with HBC model energy surfaces on the left and DFT energy surfaces on the right. (b) Potential energy surfaces for synchronous and asynchronous jumps for the HBC model compared to DFT energies for an asynchronous jump of one proton in a 1x1x3 supercell.

3.2. MD and PIMD simulations
In the following, results from an extensive series of simulations will be discussed. PIMD simulations have been performed using both hydrogen and deuterium masses (denoted by PIMD-H and PIMD-D) and MD simulations serve as classical reference points. Simulations are performed both using a fully flexible oxygen-oxygen distance $d_{OO}$ and with a fixed value of $d_{OO}$, chosen here to be 2.6 Å.

3.2.1. Geometrical isotope effects The coupling between H motion and the H-bond length is built into the HBC model and one can thus use the PIMD simulations to investigate how the quantum delocalization of different H isotopes influences the H-bond geometry, i.e. the geometrical isotope effects. In our previous work [25] where squaric acid was simulated using ab initio PIMD we found these effects to be accurately reproduced with a lengthening of $d_{OO}$...
by around 0.02 Å upon deuteration at room temperature. Figure 3 shows average $d_{OO}$ for the flexible HBC simulations as function of temperature. A first key observation is the very large H/D isotope effect on $d_{OO}$ which is largest at low temperatures and decreases at higher temperatures. A similarly large difference is seen between PIMD-D and classical MD (effectively infinite mass PIMD) simulations. These observations agree well with both experiments [36, 37] and our previous ab initio PIMD simulations [25], showing that the main physical mechanisms behind the geometrical isotope effect are captured by this simple model. Kinks can also be seen in the temperature dependence of $d_{OO}$, although the effect is hardly seen in PIMD-H simulations.

As will be discussed below, these kinks indicate the presence of phase transitions related to the onset of proton disordering.

![Figure 3. Average O-O distances $d_{OO}$ as function of temperature where a linear correlation between $T$ and $d_{OO}$ is shown with a solid line.](image)

### 3.2.2. Proton ordering in flexible-$d_{OO}$ simulations

I now turn to the analysis of proton ordering and begin by discussing the flexible-$d_{OO}$ simulations. Figure 4 shows the average off-centering coordinate $\bar{\delta}$ and the value of the probability density $P(\delta)$ at the symmetric position $\delta = 0$, $P(\delta = 0)$, as function of temperature. $\bar{\delta}(T)$ values are extracted from the normalized probability densities $P(\delta)$ at each temperature. Similarly to the observation in Fig. 3, kinks are observed in the $\bar{\delta}(T)$ and $P(\delta = 0, T)$ curves. An inspection of the $P(\delta)$ probability densities confirms that these kinks are associated with the phase transition temperatures $T_C$ above which collective jumps of H atoms become possible; $P(\delta)$ is unimodal below $T_C$ and bimodal above $T_C$ due to collective proton jumps. $T_C$ is thus found at around 100 K, 250 K and 375 K for PIMD-H, PIMD-D and MD, respectively. The experimentally determined H/D isotope shift of $T_C$ by 147 K is thus accurately reproduced, but the phase transitions occur at temperatures roughly 250 K below the experimental values, $T_C$ (H) = 373 K and $T_C$ (D) = 520 K. This is likely due to the proton transfer barrier, which may be underestimated in the DFT/vdW-DF2 calculations used to parametrize the HBC model. Indeed, the same downward shift of $T_C$ was observed in our previous vdW-DF2 PIMD simulations [25] which explicitly accounted for all atomic degrees of freedom, where $T_C$ (H) was located between 100 and 200 K and $T_C$ (D) between 300 and 400 K.

Figure 4 demonstrates that neither the $\bar{\delta}$ coordinate nor the $P(\delta = 0)$ value alone determine the phase transition temperature, since their values differ significantly between PIMD-H, PIMD-D and MD at their respective transition temperatures of 100 K, 250 K and 375 K. On the other hand, nearly linear correlations are seen between $T_C$ and both $\bar{\delta}$ and $P(\delta = 0)$.

A direct visualization of the ordering behavior is shown in Fig. 5 where the polarization of the H-bonded chains is plotted as function of simulation time. Each individual bond is represented on the vertical axis and pixels along horizontal lines are colored either gray or red according to the directionality of the bond, defined by which oxygen atom the H atom is closer to (for PIMD simulations the centroids of the ring-polymers are used). The top panels show the lowest
Figure 4. PIMD-H, PIMD-D and MD simulations with flexible-$d_{OO}$. (a) Mean value of the $\delta$ parameter as function of temperature. (b) Values of the $P(\delta)$ probability densities at $\delta=0$ as function of temperature.

Figure 5. Maps of the polarization of the coupled H-bond chains as function of simulation time (horizontal axis) for each individual H-bond (vertical axis). Panel (a) shows PIMD-H simulations at 100 and 175 K, panel (b) shows PIMD-D at 275 and 350 K, and panel (c) shows MD simulations at 375 and 450 K.

temperatures, for PIMD-H, PIMD-D and MD simulations, below which ferroelectric ordering is observed and the lower panels show 75 K higher temperatures. Similar behavior is seen for the fixed-$d_{OO}$ simulations. The large polarized regions in the upper panels of Fig. 5, i.e. just above the disordering phase transitions, reflect long-ranged spatial correlations along the H-bonding chains, in agreement with neutron scattering experiments on squaric acid [38] that indicated correlation lengths of at least 25 molecular units above $T_C$. At 75 K higher temperatures these correlations are of significantly shorter range. An isotope effect is clearly present in that the correlation length (size of polarized regions) is smaller for PIMD-H compared to PIMD-D at
$T_C+75$ K, and smaller also for PIMD-D compared to classical MD. The sizes of correlated polarized regions and the dynamics and properties of domain walls will be investigated in future work.

3.2.3. Proton ordering in fixed-$d_{OO}$ simulations

Further insights into the nature of the phase transition can be obtained from the fixed-$d_{OO}$ simulations, the results of which are shown in Fig. 6. As can be seen, $T_C$ shifts to higher temperatures for both MD and PIMD simulations, the kinks in $\bar{\delta}(T)$ and $P(\delta = 0, T)$ are now observed at around 200 K, 375 K and 425 K, for PIMD-H, PIMD-D and MD, respectively. A large isotope shift of $T_C$ thus remains even though PIMD-H and PIMD-D simulations are performed at the same bond distance $d_{OO}=2.6$ Å. As discussed in the introduction, the exact role of quantum fluctuations in determining $T_C$ has been debated since Blinc proposed [20] the proton-tunneling model for H-bonded ferroelectrics. One school of thought implicated the geometrical isotope effect as the major mechanism behind the $T_C$ shift [37, 22]. However, the geometrical effect is inactive in the fixed-$d_{OO}$ simulations and the observed shift of $T_C$ must thus be directly related to the stronger quantum fluctuations of H compared to D atoms.

![Figure 6. PIMD-H, PIMD-D and MD simulations with fixed-$d_{OO}$. (a) Mean value of the $\delta$ parameter as function of temperature. (b) Values of the $P(\delta)$ probability densities at $\delta=0$ as function of temperature.](image)

One difference between the fixed and flexible simulations concerns the extent of quantum delocalization of the two hydrogen isotopes. A standard measure of quantum delocalization is the radius of gyration, defined as $R_g^2 = \frac{1}{P} \sum_{i=1}^{P} (x_i - \bar{x})^2$ where $P$ is the number of beads and $\bar{x}$ is the centroid coordinate of the ring-polymer. Figure 7 shows the average $R_g$ as function of temperature for H and D atoms in PIMD where a comparison is made between the fixed and flexible-$d_{OO}$ simulations. First, as expected, the H atoms are significantly more delocalized compared to D atoms with $R_g(H)$ around 35% larger than $R_g(D)$. On the other hand, while $R_g$ in fixed and flexible simulations coincides at higher temperature, the increasing deviation of $R_g$ between flexible and fixed-$d_{OO}$ simulations at lower temperatures is interesting. An average flexible bond length shorter than a fixed bond length can be expected to correlate with larger quantum fluctuations since the H/D atom can more easily delocalize over the barrier, and this may partly explain why the flexible-$d_{OO}$ PIMD-H simulations show larger $R_g$ than the corresponding fixed-$d_{OO}$ simulations. However, the increasing deviation in $R_g$ at lower temperature contrasts with the decreasing difference between average $d_{OO}$ in flexible PIMD-H and the frozen bond length $d_{OO}=2.6$ Å in the fixed-$d_{OO}$ simulations (see Fig. 3). Furthermore, the average $d_{OO}$ in the flexible PIMD-D simulations at low temperatures is larger than 2.6 Å,
and yet $R_g$ for flexible PIMD-D is larger than for the fixed PIMD-D at low temperatures. This behaviour is thus not simply a consequence of different average bond lengths. Instead, it can be understood as an effect where the O-O vibrational mode induces quantum delocalization of H/D atoms when the bond distance contracts, where quantum tunneling through a reduced energy barrier is the likely underlying mechanism. This effect has been called vibrationally enhanced tunneling [39].

4. Conclusions
In this work a simple potential model of a coupled H-bonded chain has been developed and parametrized to DFT calculations on squaric acid, a prototypical organic H-bonded ferroelectric. Through an extensive series of classical MD and quantum PIMD simulations I have illustrated that the model exhibits interesting properties that resemble the behavior of H-bonded ferroelectrics. The geometrical isotope effect at room temperature is reproduced in the simulations as an expansion by about 0.02 Å of H-bond distances upon deuteration. A proton-disordering ferroelectric-paraelectric phase transition occurs when collective jumps of protons across H-bonds become possible, and the transition temperature $T_C$ is strongly dependent on the H atom mass; an H/D isotope shift of $T_C$ of roughly 150 K is observed in good agreement with experiments on squaric acid. However, the transition temperatures for H and D are significantly lower than the corresponding experimental temperatures, which is likely due to an underestimated proton transfer energy barrier. Moreover, the simulated transition appears to be continuous while in experiments it is found to be of first order. This is likely because of the simplistic description in the model of the coupling to heavy atom degrees of freedom and the neglect of thermal expansion. Indeed, experiments indicate a mixed order-disorder and displacive character of the phase transition in squaric acid [40]. When fixing the O-O bond length $d_{OO}$ in the model the phase transition temperature is shifted to roughly 100 K higher temperatures, even though the chosen value of $d_{OO}=2.6$ Å is smaller than the average $d_{OO}$ at lower temperatures for PIMD-D simulations, and the H/D isotope shift of $T_C$ remains. The latter observation shows that the geometrical isotope effect is not sufficient to explain the shift of $T_C$ and, indeed, the quantum effects related to the different masses of H and D are crucial. The upwards shift of $T_C$ after fixing $d_{OO}$ can be understood from the enhanced quantum fluctuations of H and D atoms due to thermal vibrations of the H-bond distance, where shorter bond distances induce quantum delocalization and tunneling of the H/D atoms.

The initial simulation results reported here suggest that the H-bond chain model may prove useful for investigating in further detail the interplay between collective and quantum effects, the coupling between proton motion and lattice vibrational modes, and mechanisms behind disordering phase transitions in H-bonded ferroelectrics. Future work to improve the model will
include refining the potential parameters to reproduce the correct $T_C$ values, extending the model to include interchain correlations (both for parallel and perpendicular chains in the molecular planes and interplane interactions) and incorporating lattice thermal expansion. Interesting future applications will include investigating the properties of domain walls, determining critical exponents to compare with both experiments and Ising-type models, and to further elucidate quantum effects such as proton tunneling by computing momentum distributions and comparing to experimental deep inelastic neutron scattering measurements [41].

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