Looking for the Mechanism of Anisotropic Surface Self-diffusion on Ice Crystals Using Molecular Dynamics

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1. Background

An understanding of the mechanism of self-diffusion on the surface of ice crystals is important to our understanding of the factors that influence the shape of atmospheric ice crystals, which in turn has implications for climate[1,2]. Many aspects of surface self-diffusion have been investigated. Findings suggest that surface diffusion occurs through the forming and breaking of single hydrogen bonds[3]. Recent research has also found diffusive anisotropy on prismatic facets at 230 K[4]. We are using molecular dynamics[5] simulations to determine the mechanism of water molecules diffusing on the surface of ice and to understand the cause of this anisotropy.

**Figure 1.** Prismatic facet of a hexagonal ice crystal

Figure 2. Cross sectional view of simulated prismatic surface
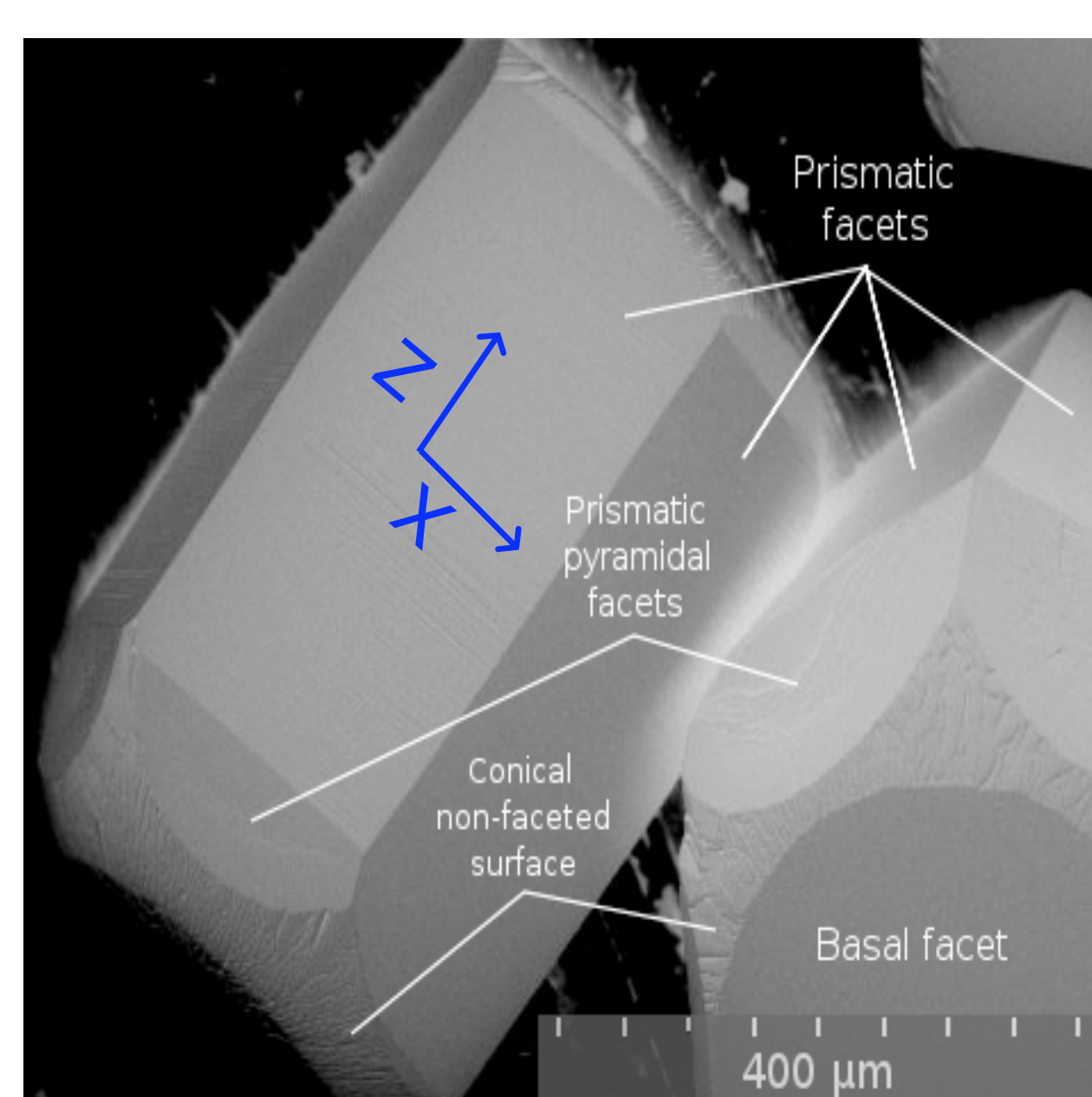
1) Diffusive anisotropy in the prismatic plane has been found in simulations of hexagonal ice crystals, such as the one pictured.
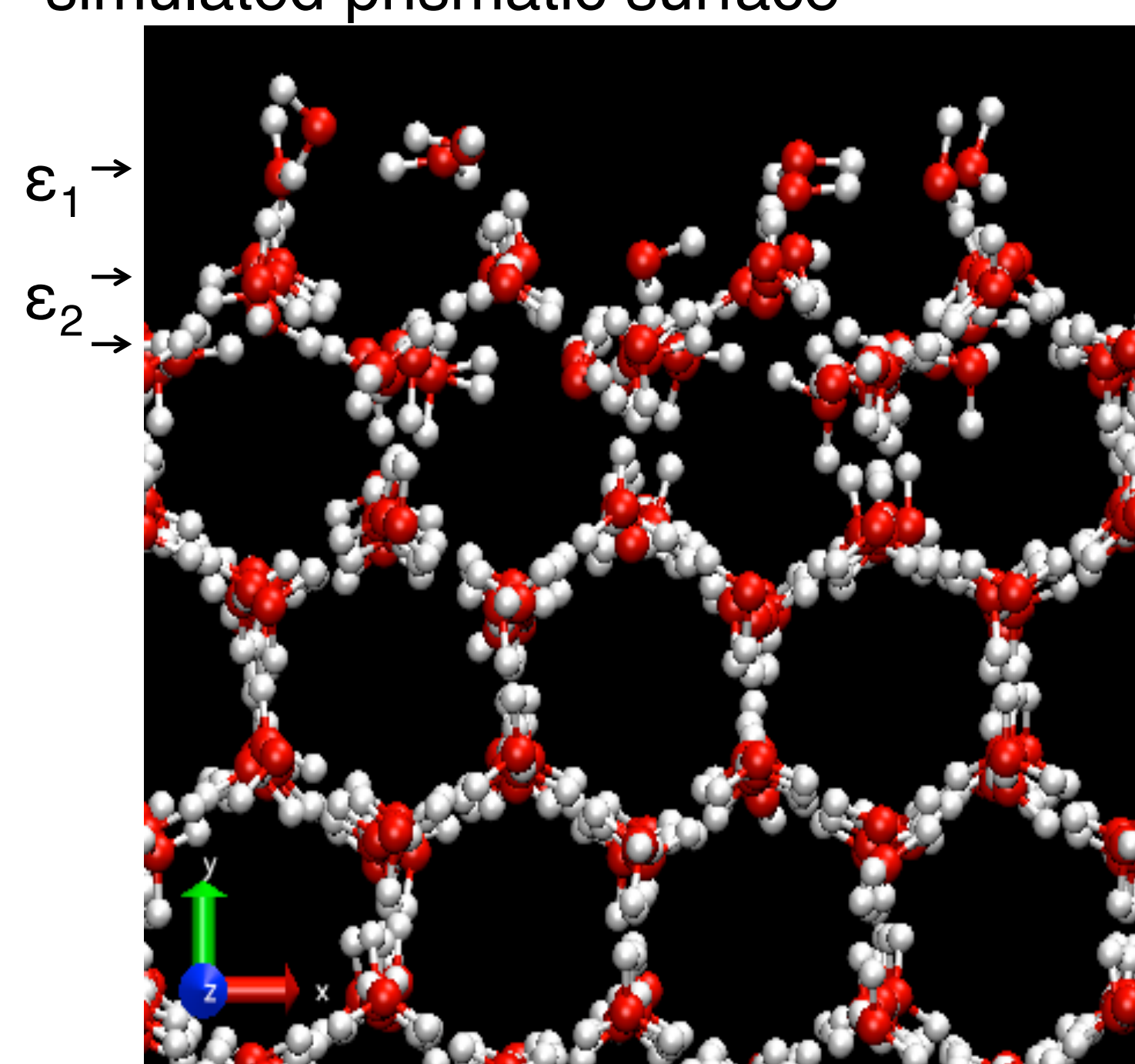
2) Structured hexagons make up the inner lattice of the crystal. The less ordered molecules at the top of the figure make up the quasi liquid layer (QLL) where diffusion occurs. This bilayer is separated into ε_1 and ε_2.

Figure 3. Density profile along the Y axis
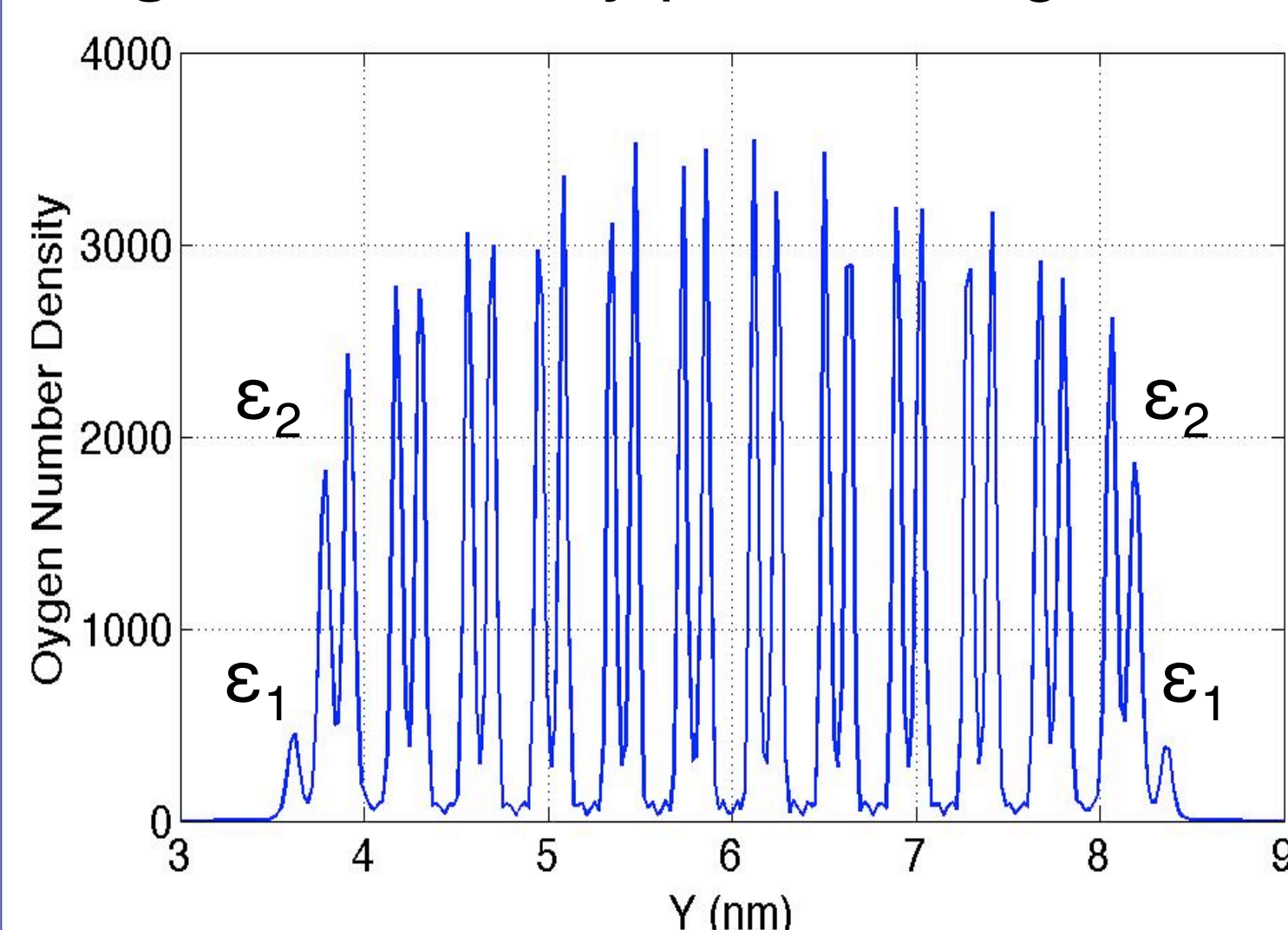
3) Peaks show the density of oxygen molecules. Large peaks in the middle are the solid crystal structure. Small, single peaks on the left and right side are the ε_1 layer. The two slightly diminished doublets beside the ε_1 peaks are the ε_2 bilayers.

**Figure 4.** Mean squared displacement at -60°C for different potentials
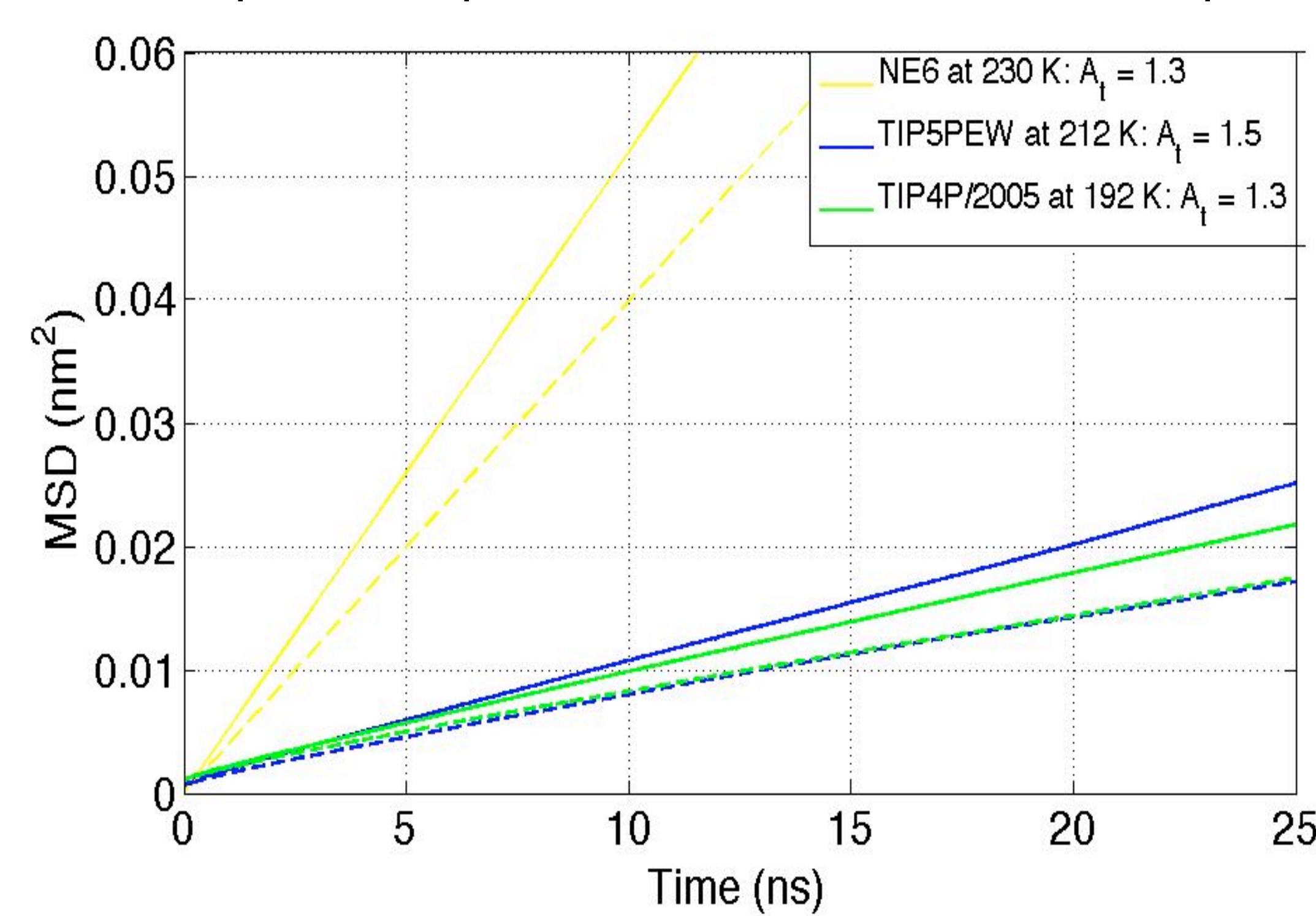
4) The time-averaged mean squared displacement in the X direction (solid line) and the Z direction (dashed line) were calculated for the model used in this investigation (NE6[6]) and two other intermolecular potentials to determine whether the anisotropy is model independent. A_t is a measure of time-averaged diffusive anisotropy.

$$A_t = \frac{D_X}{D_Z}$$

Where D_X and D_Z are diffusion coefficients in the X and Z directions respectively. These results show that diffusive anisotropy is model independent.
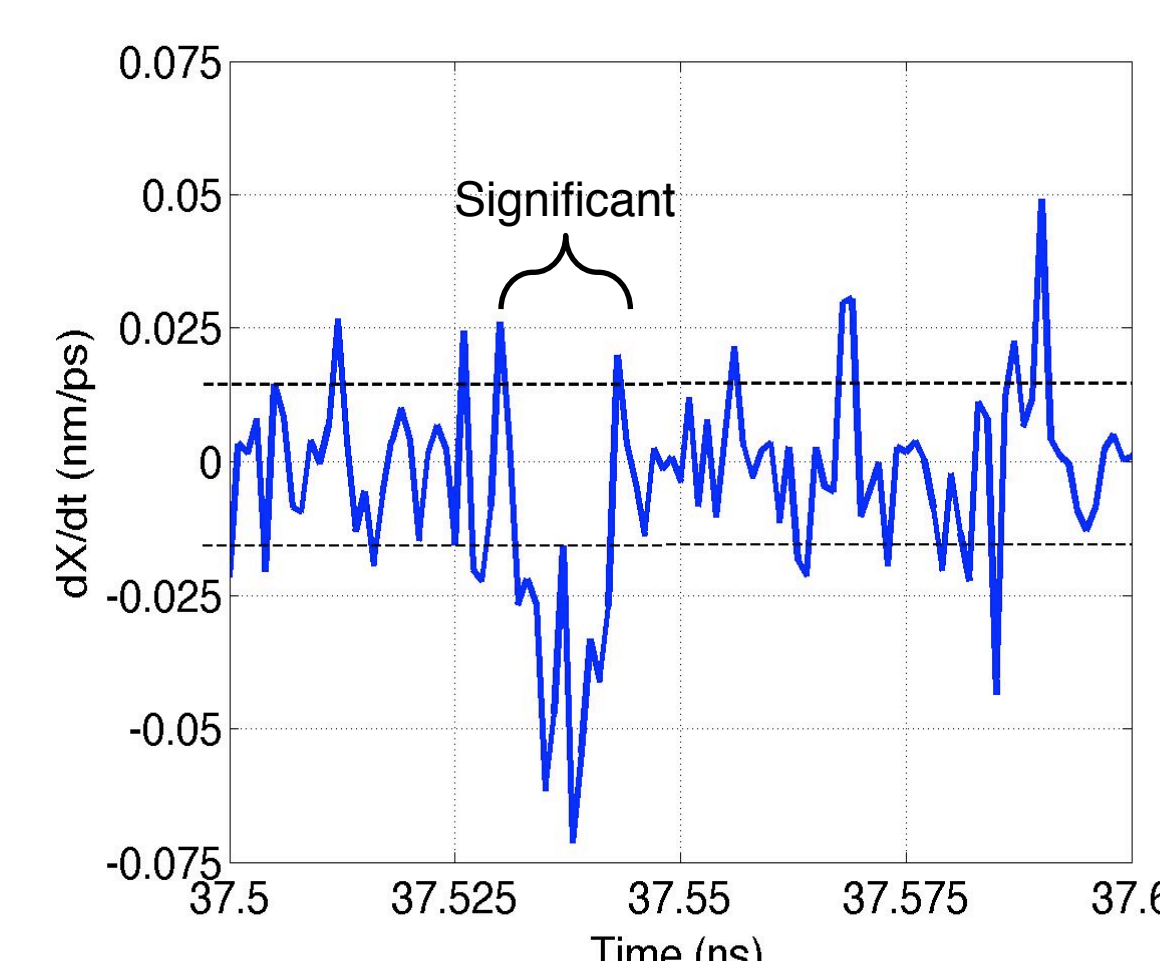
2. Significant Events

Figure 5. Running mean of a molecule's trajectory in the X direction
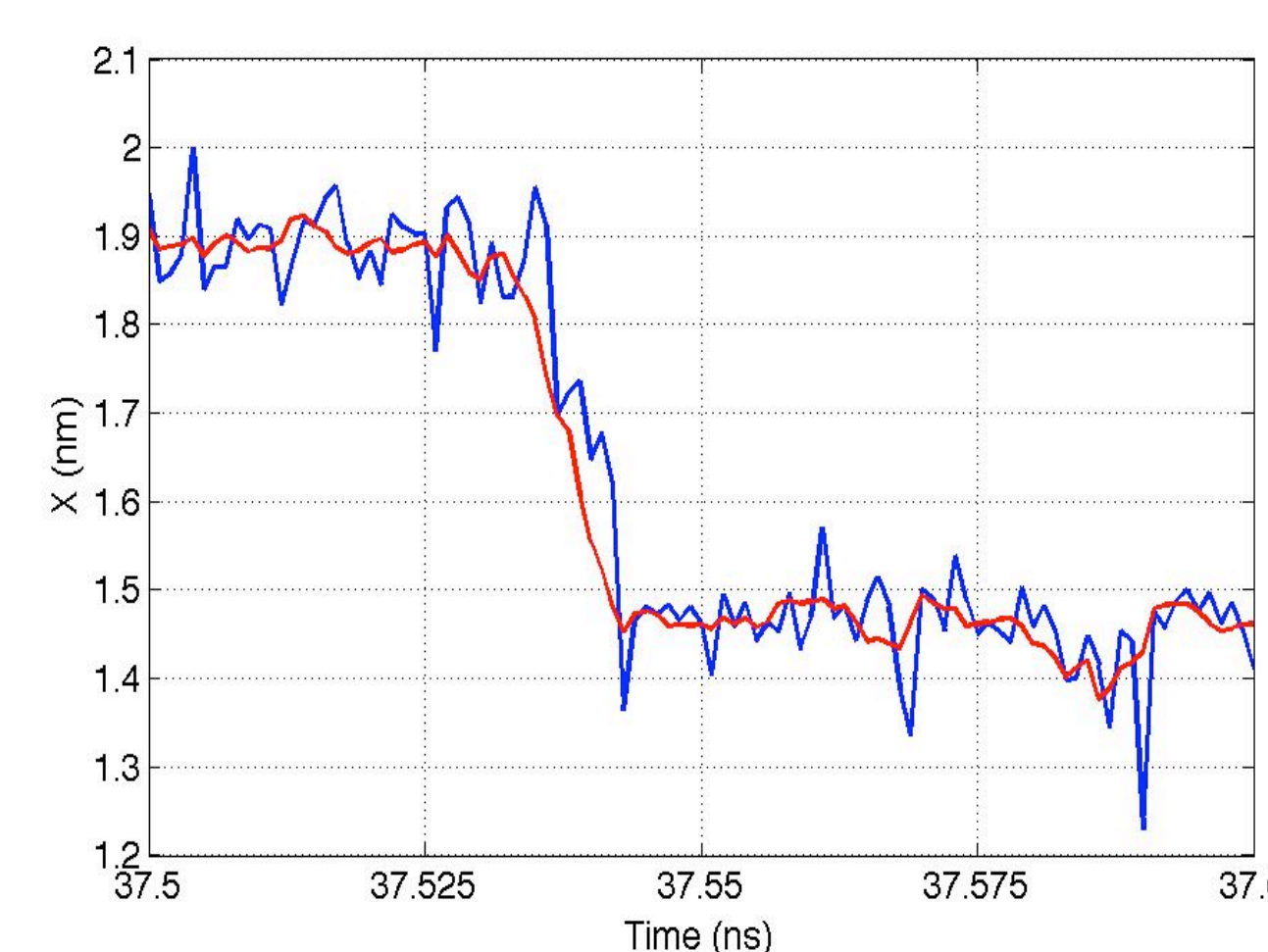
5) In order to reduce noise, a 5 ps running mean of the trajectory data was calculated.

Figure 6. Derivative of running mean

6) Instances where the molecule's speed surpasses the threshold of .015 nm/ps (dashed line) were used to identify significant events which were then checked for lasting displacement over a 3 ps window.

3. Calculating Event Averaged Anisotropy

We used an event-averaged measure of anisotropy, A_e.

$$A_e = \frac{\langle \Delta X^2 \rangle}{\langle \Delta Z^2 \rangle}$$

Where ΔX and ΔZ are the displacements in the X and Z directions respectively.

Table 1. Calculated A_e by location

Location	A_e	% Total Events
Both ε_1 and ε_2 (Total)	1.29	100%
Starts in ε_1, ends in ε_2	1.23	2%
Starts in ε_2, ends in ε_1	1.10	2%
Starts in ε_1, ends in ε_1	1.90	21%
Starts in ε_2, ends in ε_2	0.98	75%

Table 1) There were 21,784 total events. Most of these events occurred in ε_2, where the anisotropy disappears. However, the events that occurred in ε_1 were hugely anisotropic, and overall, the A_e was equal to the A_t suggesting that these significant events are representative of overall diffusion.

4. Findings

- Individual events can be strongly anisotropic in both directions
- In ε_1, these individual events average out to produce overall anisotropy in the X direction
- In ε_2, these individual anisotropic events average out to overall isotropic diffusion
- Significant events occur through the breaking and forming of single hydrogen bonds

Figure 7. Trajectory and energy data for a single molecule
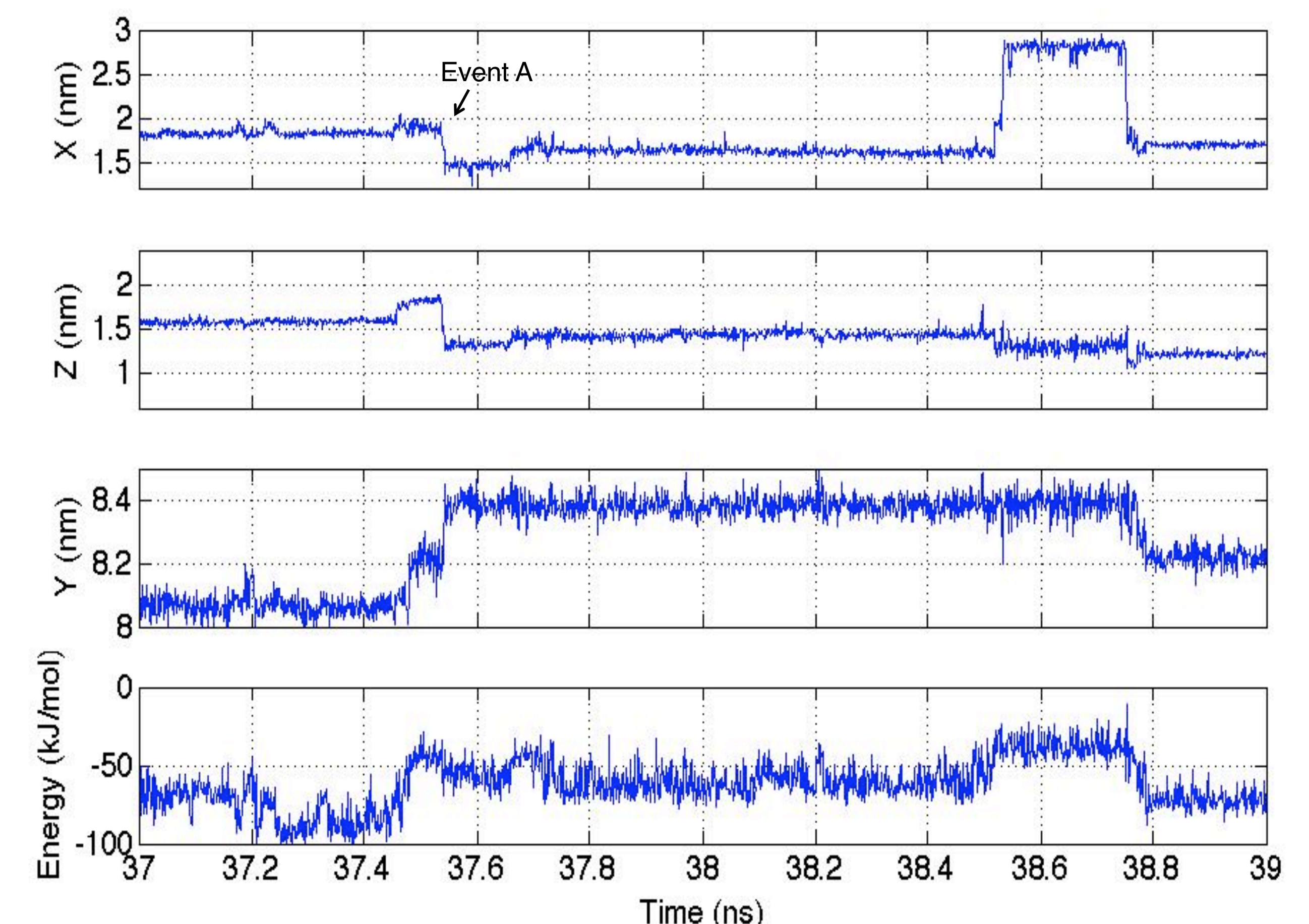
8) In the trajectory shown, the molecule moves from ε_2 to ε_1. We confirmed that these significant events occur through the breaking and reforming of a single hydrogen bond. We also found that molecules in ε_1 had about half a hydrogen bond less on average than molecules in ε_2.

Figure 8. Density profiles along the X and Z axes
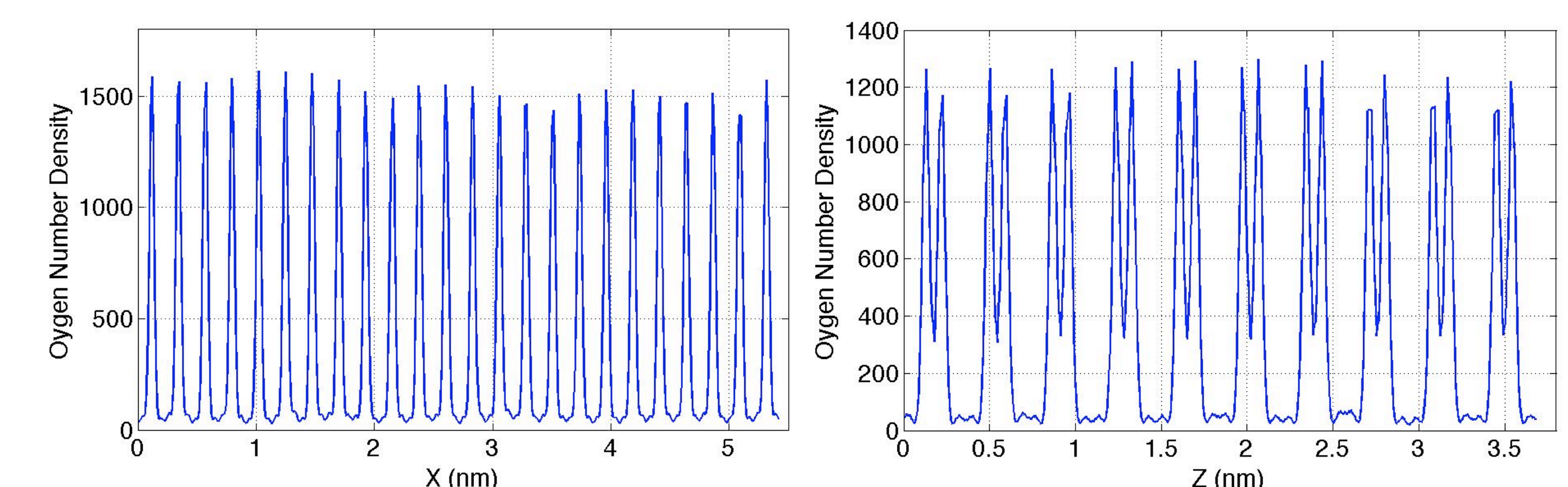
8) Structural differences in the X and Z directions contribute to diffusive anisotropy

5. Conclusions

- Diffusive anisotropy is model independent

- The anisotropy appears to be restricted to the ε_1 layer

7. References

1. Yang, P.; Liou, K.N. *Contr. Atmos. Phys.* **1998**, 71, 223-248.
2. Stephens, G.L.; Tsay, S.; Stackhouse, P.W.; Flatau, P.J. *Journal of Atmospheric Science*, **1990**, 47, 1742-1753
3. Bolton, K.; Petterson, J.B.C. *J. Phys. Chem.* **2000**, 104, 1590-1595
4. Gladich, I.; Pfalzgraff, W.; Marsalek, O.; Jungwirth, P.; Roselova, M.; Neshyba, S. Phys. Chem. Chem. Phys. **2011**
5. Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, J. J. Chem. Theory Comput. **2008**, 4, 435-437
6. Nada, H.; van der Eerden, J.P.J.M. *Journal of Chemical Physics.* **2003**, 118, 7401-7413