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Discussion: Theoretical Horizons and Calculation

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1. Inexpensive Evaluation of the Quantum Kinetic Energy and Particle Momentum Distribution by First-Principles Simulations (Michele Ceriotti, EPFL, Switzerland)

Dr Walewski opened the discussion of the lecture by Prof Ceriotti: While calculating the anisotropic kinetic energy tensor by running the sliding window average, one loses the rigorous canonical ensemble average property. Would it be possible to perform the average in a microscopic internal coordinate system relative to the molecular frame?

Prof Ceriotti replied: Yes, it can be done, either by defining a physically-motivated reference frame or by aligning molecules to a fixed reference and rotating the kinetic energy tensor estimator accordingly before averaging. The problem with these approaches is that they require one to have well-defined and relatively rigid molecular entities. For instance, this would not work in the presence of excess protons. As shown in Romanelli, G., Ceriotti, M., Manolopoulos, D. E., Pantalei, C., Senesi, R., and Andreani, C. (2013). ‘Direct Measurement of Competing Quantum Effects on the Kinetic Energy of Heavy Water upon Melting’ *J. Phys. Chem. Lett.* **4**(19), 3251-3256., there is only a 1% difference between the result obtained with a moving average and that obtained by aligning the molecules to a fixed reference.



Prof Greaves communicated: Is it possible for you to simulate the amorphization of hexagonal ice to high-density water?

Prof Ceriotti communicated in response: We have considered this, however it is always hard to build reliable computational models of meta-stable phases, requiring a complex preparation protocol that cannot be precisely mimicked in simulations. In particular, given the time scales involved, one would have to generate the model using an empirical water model and then run an ab initio simulation to extract PMD data for that configuration. It is tricky, but it would certainly be an interesting problem to study theoretically.

Dr Krzystyniak queried: There's a relation between the coefficients of Gram-Charlier expansion and multivariate $n(p)$. Why choosing the multivariate Gaussian model?

Prof Ceriotti replied: It is easy to approximate $n(p)$ as a multi-variate Gaussian distribution because one can compute the second moments of $n(p)$ from a conventional path integral simulation. To obtain the actual PMD one needs to perform an open-path simulation, which is much more demanding.

2. Collective Proton Tunneling in Ordinary Ice (Christoph Drechsel-Grau, Bochum, Germany)

Dr Salzmann opened the discussion of the lecture by Dr Drechsel-Grau: Statistically speaking, the chance of defect migration along a six-membered ring is very small. From your results, would you argue that this is still preferred over migrations over larger rings or even chains?

Dr Drechsel-Grau replied: We used constraints that prevent protons from exiting the six-membered ring.

Dr Sturniolo communicated: Is there any estimate about the relationship between single-proton and collective-proton tunneling probabilities?

Dr Drechsel-Grau communicated in response: No, since single jumps do not occur in a stable system.

3. Simulation Studies of Hydrogen Bonded Ferroelectrics (Thor Wikfeldt, Reykjavik/Stockholm)

Dr Ceriotti opened the discussion of the lecture by Dr Wikfeldt: The gyration radius of a ring polymer is not a physical observable. How could we describe delocalization in a more physically motivated way? For instance, in Parrinello, M., and Rahman, A., 'Study of an F center in molten KCl' *J. Chem. Phys.*, **80**(2), 860-867 (1984) they define an estimator for the spread of the density associated with a single particle.

Dr Wikfeldt replied: It is true that an increase in a particle's radius of gyration in PIMD simulations is not direct proof that quantum tunnelling is at play. However, a strong delocalization of the ring-polymer along a reaction coordinate, where the spread resembles an instanton path, is a strong indicator of tunnelling. This is what we observe in our work on squaric acid (*J. Chem. Phys.*, **140**, 041103 (2014)).

4. Interaction Induced Localization of Protons: Temperature and Superfluid Helium Solvation Effects (Lukasz Walewski, Bochum, Germany)

Prof Fernandez-Alonso opened the discussion of the lecture by Dr Walewski: What is the correlation between localization index in the gas phase and intermolecular He-H, He-O, He-Cl interactions?

Dr Walewski replied: This still needs to be investigated.

Prof Fernandez-Alonso communicated: Can H₂ be treated by your computational method?

Dr Walewski communicated in response: Yes, for some specific systems .

Dr Senesi commented: Is there any estimate of the excess kinetic energy due to the interaction induced by the localization of protons?

Dr Walewski replied: This will be calculated in the near future.

5. Nuclear Quantum Effects in Enzyme Catalysis from Momentum Distributions (Dan Major, BIU, Israel)

Prof Ceriotti opened the discussion of the lecture by Prof Major: Was any bias added on ring polymer centroids or the individual beads?

Prof Major replied: There was no added bias.