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Clusters, Nanodroplets, and Fluid Cavities in Hydrothermal Water

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Probing the molecular-scale structure and reactivity of water along the two phase boundary and near the critical point is crucial for understanding the onset of boiling. This phenomenon is driven by the emergence of vacuum cavities in the liquid phase and involves the aggregation of water into clusters and nanodroplets in the vapor. In this study, we integrate LAMMPS MD simulations up to 500 ns with 50-100 ps period CP2K *ab initio* MD simulations [1] to probe the structure and reactivity of hydrothermal water, with a focus on proton and hydroxide generation at droplet surfaces and within fluid pore spaces. Preliminary results from our MD simulations along the saturated vapor line demonstrate that the largest water clusters progress from $(H_2O)_5$ at 100°C, to $(H_2O)_{12}$ at 200°C, to $(H_2O)_{22}$ at 250°C and $(H_2O)_{114}$ at 300°C. By 350°C, these aggregates reach up to $(H_2O)_{400}$ sized moieties, indicating a transition from smaller clusters to nanodroplet type phases near critical conditions. In the denser fluid, consistent with work by Maxim et al [2] and Zahn [3], we observe a progressive increase in fluid pore space with temperature, starting from approximately 43% at 25°C to 65% at 350°C (see Fig.1). These short-lived (10-50 ps) vacuum cavities merge into larger voids or nanobubbles that drive the onset of boiling, and their formation is preceded by the disruption of the local hydrogen-bond network. At higher temperatures, this disruption becomes more frequent, reflecting a weakened hydrogen-bond network that initiates rapid nanocavity and bubble growth. Finally, it is worth noting that the organization of water molecules in nanodroplets and fluid cavities gives rise to markedly different ionization behaviour than bulk water at comparable temperatures, with important implications for pK_w and pH in these confined environments. Our ongoing CP2K calculations are exploring these droplet and cavity ionization processes, and we will present preliminary results on how droplet surfaces and liquid-vacuum interfaces control proton and hydroxide formation. [1] Hutter, J. et al. (2014), WIREs Comput. Mol. Sci. 4, 15-25; [2] Zahn, D. (2004), Phys. Rev. Lett. 93, 227801; [3] Maxim, F. et al. (2021), Adv. Sci. 8, 2002312.

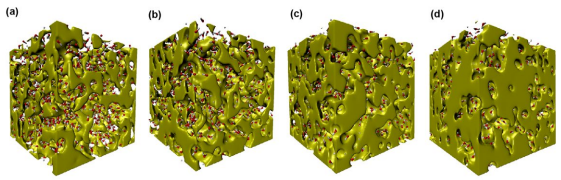

Figure 1. Snapshots from LAMMPS MD simulations of a 1000 water supercell at 4 different thermodynamic conditions: (a) 100°C (0.96 g/cm³, 45.2% void space), (b) 200°C (0.86 g/cm³, 49.9% void space), (c) 300°C (0.71 g/cm³, 57.9% void space), and (d) 350°C (0.57 g/cm³, 65.3% void space). The green surfaces depict an isosurface of the void space, while individual water molecules are sandwiched between pore regions. As temperature increases, the interconnected cavities grow more extensive, showcasing the progressive formation of a porous fluid network in near-critical water.