

Atomistic and coarse grained simulations reveal increased ice nucleation activity on silver iodide surfaces in slit and wedge geometries – Response to RC2

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General comment:

This is an interesting paper that illustrates some of the complexities of heterogeneous ice nucleation on AgI by showing how the rate of nucleation in slits and wedges depends on the slit width and wedge angle. In a similar way to how AgI can enhance nucleation by providing a local matching template for ice growth, slits and wedges that provide a good match (e.g. by having a slit width that matches an integer number of ice bilayers) to the structure of the resulting ice crystal also enhance nucleation. I am happy to recommend publication once consideration has been given to the technical issues mentioned below.

Response: We thank the referee for the very positive review of our work.

Specific comments:

Comment 1: polar surfaces such as the AgI (0001) surface are well-known to be unstable in the absence of a polarity compensation mechanism. By keeping the ions in the AgI crystal fixed, this instability is avoided (albeit perhaps artificially), but it is important to consider how the electrostatic boundary conditions might affect the observed properties. Some discussion of these questions would be appreciated. The Sayer and Cox paper already referenced and *J. Chem. Phys.* 153, 164709 (2020) are interesting in this regard.

Response: We thank the referee for the good comment. In the absence of trustworthy *ab initio* MD data or experimental atomic resolution images of the interface, the stability of the polar (0001) surface of AgI remains somewhat of a mystery. The available empirical force fields [e.g. Rains et al., *PRB* 44, 17, 9228 (1991)] cannot be used to model bulk-terminated AgI(0001) in periodic boundary conditions without constraining the surface and compensating the dipole field. The approach employed by Sayer and Cox, while both elegant and physically sound, does not lend itself to the present study, where we need to investigate a large number of systems with different symmetries. However, in the slit systems the dipoles cancel out, and even in the asymmetric wedge systems, the dipole field components perpendicular to the surface are at least reduced. We have added a short paragraph in the methods section to discuss this problem:

Lines 80-86 (in the revised manuscript): “An artificial constraint is usually necessary as the polar

surface is unstable using conventional force fields fitted to reproduce properties of bulk systems, and rigid surfaces have been employed in the majority of computational studies of silver iodide (Fraux and Doye, 2014; Zielke et al., 2014; Zielke et al., 2015; Glatz et al., 2016; Roudsari et al., 2020). Stable interfaces with unconstrained surface ions in flat polar surfaces could only be achieved by introducing counter ions in the solution and imposing electrostatic boundary conditions on the simulation box (Sayer et al. 2019, 2020).”

Comment 2: by keeping the ions in the AgI crystal fixed rather than allowing them to exhibit thermal vibrations around their lattice positions provides a more perfect template for ice nucleation than would be expected if vibrations were allowed. Some discussion of how this potentially affects the results would be appreciated.

Response: We agree with the referee’s comment and have added the following sentence to the methods section. However, as stated in the response to Comment 1, we believe that there is no easy solution to avoid this problem, and while it affects the results quantitatively, we are quite confident that the qualitative differences between the systems that we have reported would not be affected by this.

Lines 85-86: “We note that suppressing the thermal motion of surface ions enhances the ordering of water at the interface and thereby affects ice nucleation rates (Fraux and Doye, 2014).”