Water drops on ice

Luis G. MacDowell[1], David Sibley[2], Pablo Llombart[1,3], Eva G. Noya[3], and A. Archer[2]
[1]Departamento de Química Física, Universidad Complutense de Madrid, 28040 Madrid, Spain
[2]Department of Mathematical Sciences, University of Loughborough, Leicestershire LE11 3TU, Reino Unido
[3]Instituto de Química Física Rocasolano, Consejo Superior de Investigaciones Científicas, 28006 Madrid, Spain

Does water wet ice? As the triple point is approached, the surface disorder grows steadily at the ice-air interface, and a liquid film of *premelted* water is formed. Whether this film attains a finite thickness or diverges at the triple point has remained a controversial issue for a long time. However, recent confocal microscopy experiments confirm early observations of water droplets standing on the surface of ice very close to the triple point, while ice crystal terraces grow and spread below the droplet [2, 3]. Whereas the appearence of an incomplete wetting state of very low energy has been predicted theoretically on the basis of the Lifshitz theory of van der Waals interactions [1], still a great number of open questions remain to be solved.

Indeed, in the experiments by Murata *et al.* [3], the droplets are formed only significantly above saturation, and likewise, disappear reversibly above saturation as the vapor pressure is decreased. Furthermore, a second wetting state seems to appear in this systems at higher saturation, since a thick film appears to emerge below the droplets. More strikingly, the authors observe the formation of distinct droplets well below the vapor-liquid coexistence line. How can we explain this unexpected phenomenology from current knowledge on wetting?

Clearly, one expects here a rather complicated phenomenology, as both vapor condensation, freezing, evaporation and sublimation come into play simultaneously, together with Young-Laplace effects, crystal growth, ice nucleation and terrace spreading. Can this complicated situation be explained from equilibrium thermodynamics at all? What happens on the solid surface right below the wetting film?

In this communication we will pursue previous computer simulations studies [4] and new mesoscopic models to describe and rationalize the puzzling physics of water droplets on ice. The modeling requires to address simultaneously the properties of vapor-liquid and ice-liquid interfaces, as well as the terraced structure of the disordered solid interface. Furthermore, because of the occurrence of premelting on this surface, one needs to take into consideration the interaction of such surfaces via the interface potential, which is dominated in the nanometer scale by retarded interactions. A successful explanation of these experiments thus requires understanding the physics of the problem from the tenth of a nanometer to the micrometer scale. From atomistic simulations of the premelting film and its surface fluctuations to the mesoscopic modeling of spreading droplets.

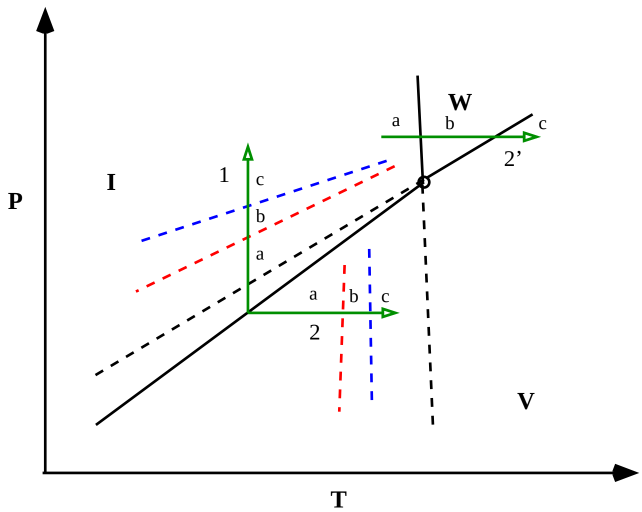

Fig. 1. Wetting phase diagram of water on ice. The phase coexistence lines (black) have to be supplemented with the metastable prolongation of liquid-vapor coexistence in the freezing state. As pressure is increased at constant temperature (path 1), droplets emerge only above the red line; a second change occurs above the blue line when thick films spread from the droplet. Such behavior was reported to occur also at subsaturation along line 2, but likely impurities could shift the triple point making the system to heat above the triple point as in path 2'.

[1] M. Elbaum, S. G. Lipson, and J. G. Dash, J. Cryst. Growth **129**, 491 (1993).

[2] G. Sazaki, S. Zepeda, S. Nakatsubo, M. Yokomine, and Y. Furukawa, Proc. Natl. Acad. Sci. USA **109**, 1052 (2012).

[3] K. Murata, H. Asakawa, K. Nagashima, Y. Furukawa, and G. Sazaki, Proc. Natl. Acad. Sci. USA **113**, E6741 (2016).

[4] J. Benet, P. Llombart, E. Sanz, and L. G. MacDowell, Phys. Rev. Lett. **117**, 096101 (2016).