

Capillary condensation revisited: two Kelvin equations

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It is well known that a vapour, confined between two identical infinite parallel walls (with contact angle $\theta < \pi/2$), condenses to liquid, at a pressure below that of bulk saturation. This shift in the location of the first-order phase boundary, referred to as capillary condensation, is described by the macroscopic Kelvin equation, and has been extensively tested using microscopic DFT and simulation methods. In this talk we show that when one caps the capillary (so that the geometry is that of a long groove), the order of capillary condensation may be dramatically altered and is determined by the wetting properties of the capped end. If this is partially wet, capillary condensation remains first order while if it is completely wet, the condensation is continuous. The change in order of the condensation brings together several key ideas in the theory of wetting and corner filling transitions and is neatly summarised by a companion equation to the Kelvin equation, which determines the size of the metastable region.