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A theory for metastabilities in bubble nucleation: can it help explaining nanobubbles?¹

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The stability and the very existence of nanobubbles on a solid-liquid interface is a conundrum that has been puzzling the community of researchers working in the field since their discovery through AFM measurements in the late nineties. Nanobubbles are typically flat, with height on the order of 5-10 nm and lateral size order 100 nm or less. Pinning of the contact line presumably plays a crucial role and, based on classical estimates, they should dissolve almost immediately while they are instead reported to persist for days. Recently we developed a novel theoretical approach that is able to predict the heterogeneous nucleation path, and to explain the catalytic effect of geometrical defects in lowering the associated free-energy barrier (Giacomello et al., PRL 2012). The theory bridges the scales from nanometer to micron, and is then suitable for dealing with nanobubbles, as shown by comparison with advanced rare-event techniques used to evaluate the metastability in the atomistic context (Giacomello et al., Langmuir 2012). The interest of the approach is that it can provide an estimate for the transition frequency, i.e. the average lifetime of a metastable configuration. As will be discussed, the model can in principle be enriched to account for the interaction of the gas phase with the solid, indicated as responsible for the almost universal contact angle observed in the nanobubbles (Weijs et al., PRL 2012). If nanobubbles can be explained in the context of equilibrium statistical ensembles, as long-lived metastable states associated with a complex free-energy landscape, the work under way could shed new light on the elusive subject of their persistence. At present we cannot however exclude substantial non-equilibrium effects, outside the concept of metastability in the strict statistical-mechanics sense and associated, e.g., with thermal gradients.

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