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The most likely nucleation pathways in multiphase fluctuating hydrodynamics

Mirko Gallo[*], Filippo Occhioni [*], Riccardo Daniele[*], Carlo Massimo Casciola[*]

The precise identification of thermodynamic conditions for liquid vapour phase change inception is extremely complex. Liquids can be held in metastable states (stretched or superheated) for a long time without phase transitions. The incipit of phase change is nucleation, a process driven by stochastic events of free-energy barrier crossing, which corresponds to the formation of nanobubbles. Here, the granular nature of matter begins to play a significant role. Through a complex mechanism—still not fully understood—molecules tend to aggregate or disperse with a certain probability, forming clusters of the new phase. Occasionally, a rare event occurs where a sufficiently large cluster, referred to as a *critical cluster*, forms. This cluster can overcome an activation energy barrier (the nucleation barrier), triggering the phase transition.

Although this is a simplified depiction, it underscores that the key observables of a phase transition must inherently be characterised within the framework of statistical mechanics. Therefore, understanding the stochastic nature of nucleation is essential to obtain quantitative insights into phase changes.

An additional layer of complexity arises from the broad range of time scales involved in nucleation. The characteristic time required for the formation of the new phase $\langle\tau\rangle$ is linked to the nucleation barrier, scaling as $\langle\tau\rangle \sim \exp(\Delta F^{\dagger}/k_B T)$, where $\Delta F^{\dagger}$ is the barrier and $k_B T$ is the thermal energy. This timescale can vary dramatically, from nanoseconds near spinodals (under strong metastability) to geological timescales near saturation (under weak metastability) [1]. Molecular Dynamics (MD) is a powerful tool for investigating thermally activated processes. However, its application to real fluids is complex. Furthermore, MD computational cost limits its application to small systems and short times, preventing the study of hydrodynamics and thermal transport processes [2]. Fluctuating hydrodynamics coupled with diffuse interface thermodynamics can describe the boiling and cavitation from nucleation up to macroscopic hydrodynamics. Still, only when the energy barrier is low, and nucleation is not so rare to be sampled with brute force simulations [3], [4], [5], [6], [7]. This talk will describe how rare event techniques based on the Large Deviation Theory identify the most likely nucleation pathways and their probability in multiphase fluctuating hydrodynamics. In accordance with experimental data, this novel framework precisely identifies the phase change mechanisms and by-products of the boiling temperature and cavitation pressure of several real fluids.

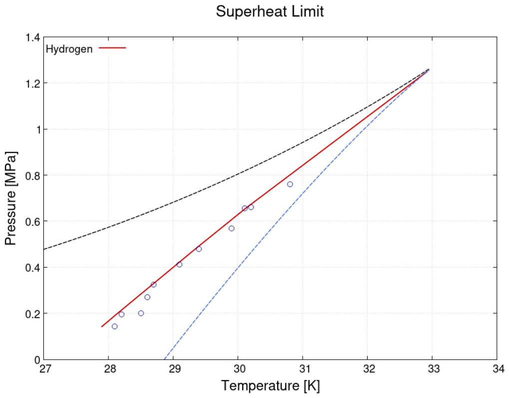

Figure 1: Boiling temperature vs pressure of liquid hydrogen. The solid lines correspond to our theoretical prediction, the empty circles are experimental measures, and the black and blue dashed lines refer to binodal and spinodal curves.

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[*] Department of Mechanical and Aerospace Engineering Sapienza University of Rome

[1] Magaletti et al., *Scientific Reports* 2021

[2] Menzl et al., *PNAS* 2016

[3] Gallo et al., *PRF* 2018

[4] Gallo et al., *JFM* 2020

[5] Gallo et al., *JFM* 2021

[6] Gallo et al., *Nature Comm.* 2023

[7] Gallo et al., *Int.J.Mult.Phase.Flows* 2024