

# Chaotic and Thermodynamic Interplay in Nanocavities <sup>†</sup>

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Molecular confinement in nanocavity networks implies interplay between thermodynamic and chaotic response leading to surface entropic variations. Molecules, especially water molecules near surfaces are successively trapped and escape from nanocavities [1]. The time scale of physical interactions inside the nanocavities is governed by the molecular mean escape time from the nanocavities, pointing to a non-thermal equilibrium state inside the cavity. On the contrary, the external water vapour domain is in a thermal equilibrium state and the time scale is specified by the mean trapping time—the time a molecules travels in the outside domain before being trapped. Random walk simulations inside and outside different size nanocavities reveal the differentiation of time scales inside and outside nanocavities, pointing to an interplay between the thermodynamic state (vapor domain) and the chaotic state (nanocavity domain), leading to a variation of the number of available microstates [2]. Increment of microstates is responsible for entropy deviation during molecular water confinement, experimentally measured in complex nanocavity networks, crafted on polymeric matrixes by 157 nm vacuum ultraviolet laser light. The methodology is used for quantifying entropic variations caused by confined water or other molecules on surfaces.

## References

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