Chaotic and thermodynamic interplay in nanocavities

Vassilios Gavriil, Alkiviadis-Constantinos Cefalas, Zoe Kollia and Evangelia Sarantopoulou.
Theoretical & Physical Chemistry Institute, National Hellenic Research Foundation, 11635, Athens, Greece

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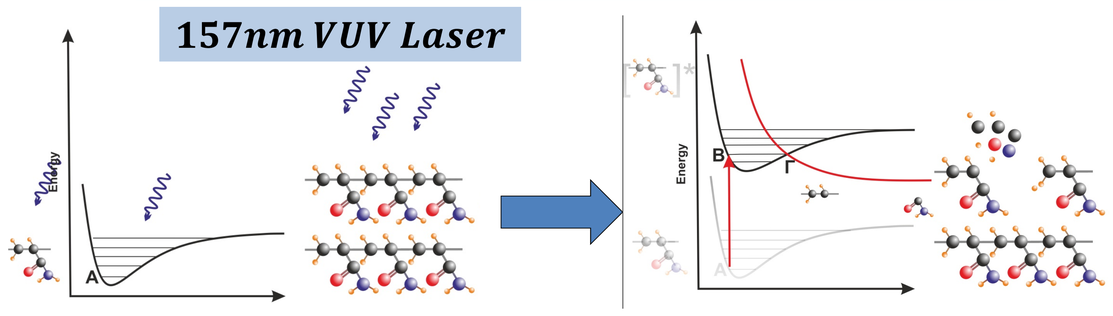
Abstract

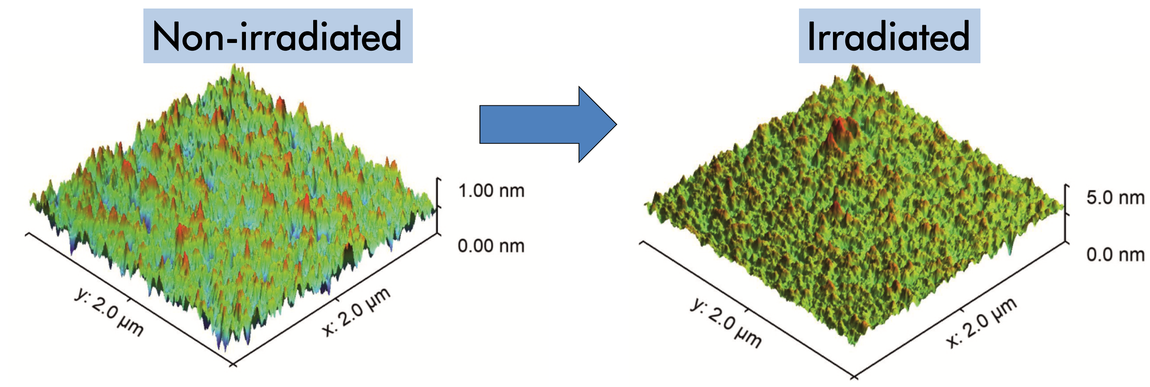
Molecular confinement in nanocavity networks implies interplay between thermodynamic and chaotic response leading to surface entropic variations. Molecules, especially water molecules near surfaces are successively trapped and escape from nanocavities. The time scale of physical interactions inside the 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 (vapour domain) and the chaotic state (nanocavity domain), leading to a variation of the number of available microstates. 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.

2D-Surface Nanocavity Networks

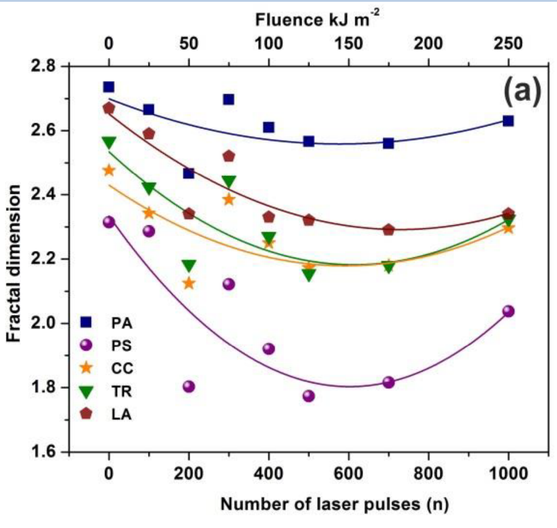
157nm VUV Laser



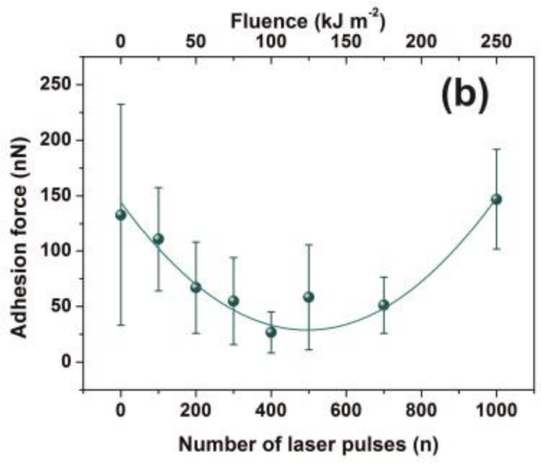
Laser photons disassemble polymeric chains creating nanocavity networks.



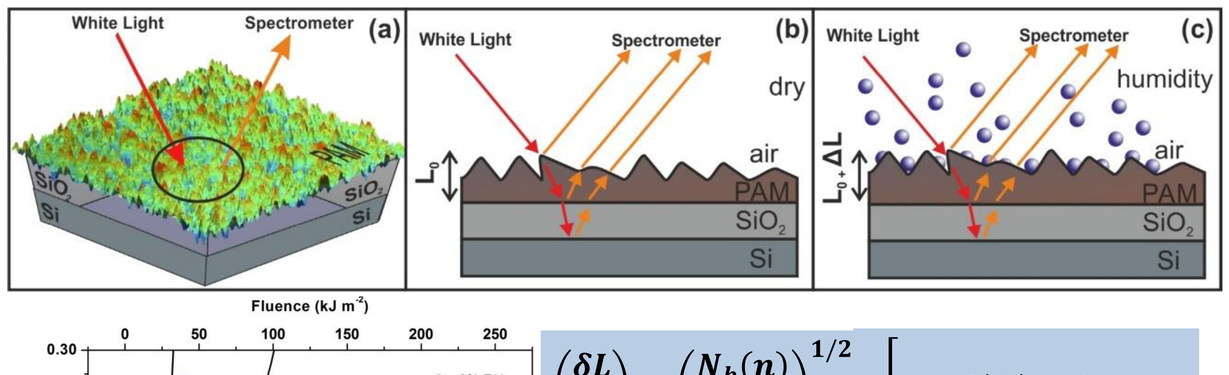
Surface Fractality *vs* Laser pulses



Adhesion Force *vs* Laser pulses



Molecular Confinement in Nanocavities

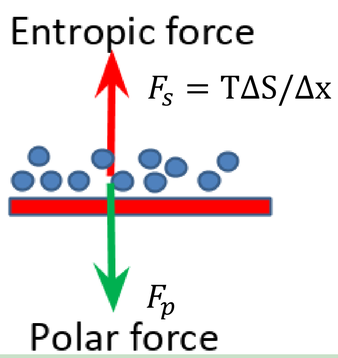


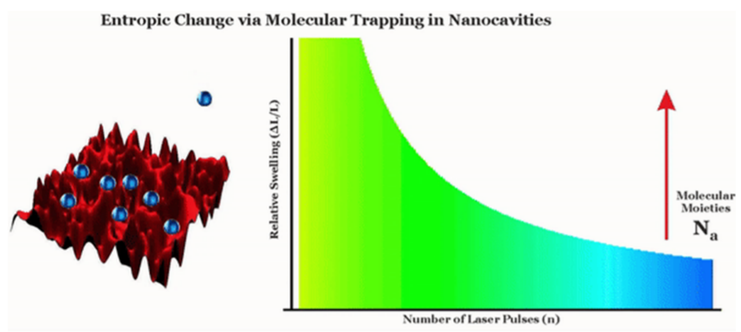
$$\left(\frac{\delta L}{L}\right) = \left(\frac{N_b(n)}{E(n)V}\right)^{1/2} \left[-\lambda l\langle\Phi\rangle + (1 + \beta(n)) \left[\ln\frac{x(n)}{1-x(n)} \pm \frac{1}{x(n)}\ln\left(1-x(n)\right)\right]\right]^2$$

$-\lambda l$ electric dipole interactions contribution

$\beta(n)$ entropy variation contribution

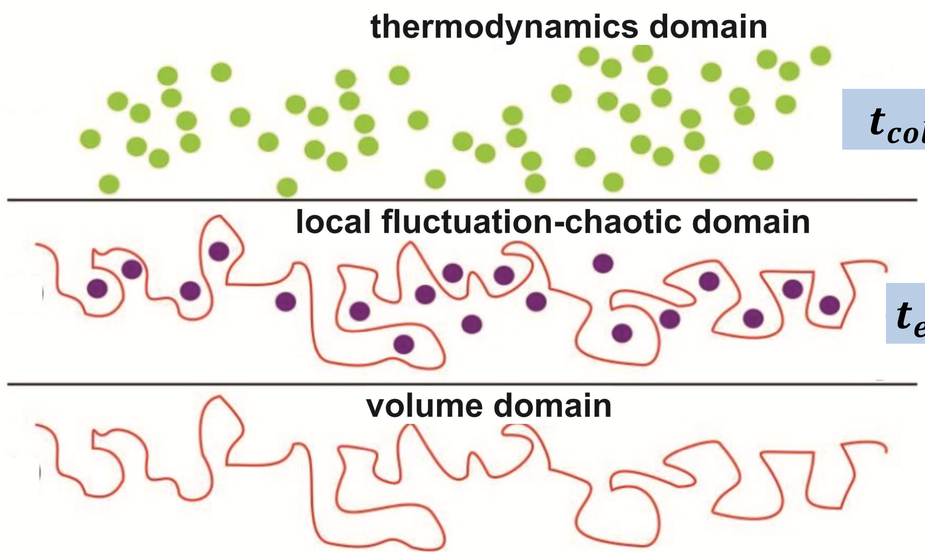
Entropy Deviation





Entropic force: Particles immobilization , restriction of translational and rotational degrees of freedom.
Polar force : Electric charge.

Time scale divergence



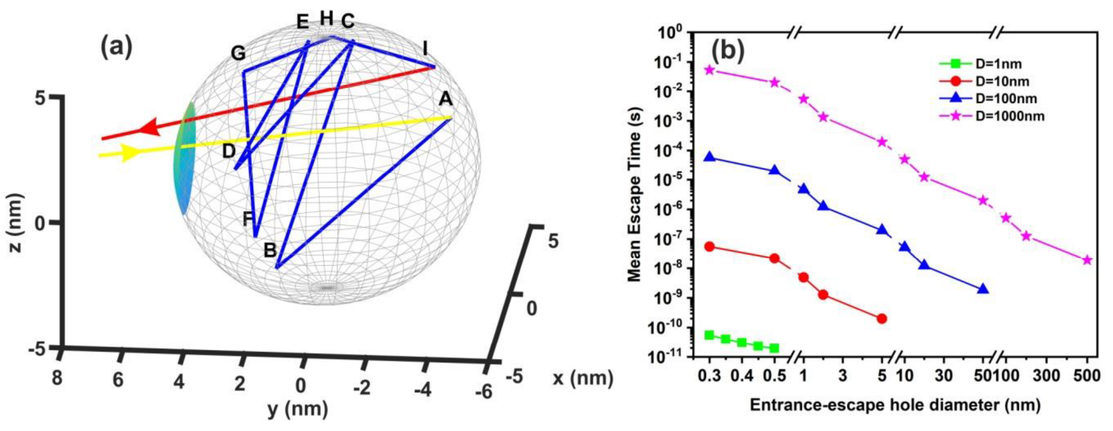
$t_{col} = 7 \times 10^{-8} s$

$\gg$

$t_{esc} = 10^{-10} s$

Molecular confinement is responsible for a non-thermodynamic equilibrium local fluctuating–domain of trapped molecules characterised by chaotic behaviour at the boundary of 2D interphase.

Random walk simulations



The time differentiation inside and outside nanocavities adds a state of ordered arrangements, thus introducing an interplay between the thermodynamic (external domain) and the chaotic state (2D surface-domain).

References

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Entropy and Random Walk Trails Water Confinement and Non-Thermal Equilibrium in Photon-Induced Nanocavities , Nanomaterials ***2020***, *10(6), 1101*