Macromolecules in nanoconfinement: insights in mobility and partitioning for the engineering of molecules separation and delivery systems.

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Integration of nano-engineered materials into useful bioactive devices has been hampered by the lack of understanding of the mechanisms of molecular trafficking occurring in nanoconfined spaces**.** Deviations from classic laws for neutral molecules diffusion through nanopores were already reported more than 20 years ago, but still the mechanism of intrapore diffusion and partitioning in confined structures has not been fully clarified yet.

In particular, the influence of slit-like confinement on the molecular motion of neutral PEO chains will be discussed. Fluorescence Correlation Spectroscopy analysis of the macromolecules fluctuations related to their diffusion in nanochannels having only one dimension, the height, close to the bulk size of the molecule, unravels that mobility is affected by polymer confinement extent and by surface interactions.

The talk will focus, then, on some applicative aspects related to mobility in nanoconfinement.

The possibility of manipulating uncharged single molecules confined in nanochannels by affecting molecule partitioning through temperature changes will be shown. The partitioning decreases with temperature and the trend is size dependent, thus a size separation mechanism for confined molecules is demonstrated. The mechanism mainly exploits the fine energetic balance of confined flexible macromolecules, where rather small changes in temperature unbalance the sensitive thermodynamic equilibrium, affecting confined molecules concentration.

Molecules confined in nanocavities can also present interesting delivery rates; in particular, single molecule passage is achievable when the nanocavity size is precisely modulated to that of the molecule to deliver.