Study of molecular recognition of supercooled benzoic acid with MiCMoS

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The importance of crystal nucleation is immense. Yet, nucleation is still far from being fully understood. Despite its merits, the Classical Nucleation Theory (CNT) is being increasingly superseded by evidences that a multi-step mechanism should be explicitly considered. Unfortunately, the experimental observation of individual molecular recognition events that lead to nucleation is challenging. Accurately calibrated molecular dynamics simulations [1-4] could help to figure what is going on at the atomic level, providing a physical framework to interpret the experimental outcomes.

Here, we report on the study of pre-nucleation clusters of supercooled liquid benzoic acid (BZA) with the free Milano Chemistry Molecular Simulation (MiCMoS) platform [5,6]. The molecular recognition of BZA is governed by strong hydrogen bonds, which promote the formation of supramolecular aggregates. These aggregates vary in size, ranging from simple cyclic dimers to clusters consisting of dozens of molecules (Figure 1), with different degrees of stability. We propose a simple energy criterion to distinguish between transient aggregates and true sub-critical clusters, the latter likely lying on the path to nucleation. The influence of confinement on the clustering of BZA is also investigated: confinement increases the liquid viscosity and hampers the molecular rotational reorientation, extending the lifetime of hydrogen bonds. Polarization effects in the vicinity of barriers are also detected, with possible implications on the development of long-range order.

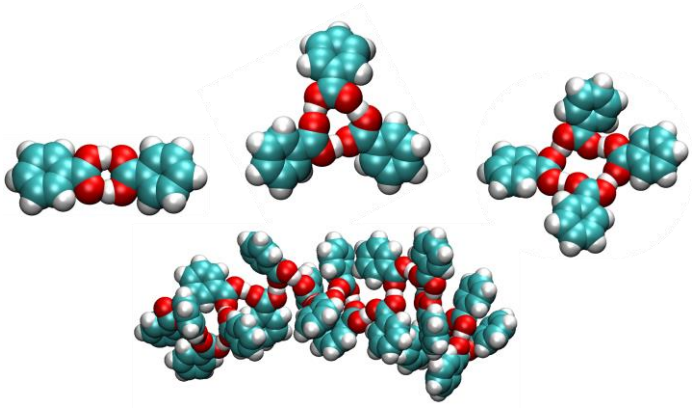

Figure 1. Selection of hydrogen-bonded clusters of benzoic acid.

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