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Exploring the Importance of Dynamics in Materials from the Atomic to the Supramolecular Scale Using Advanced Computational Methods

By

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Declaration

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2024

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Understanding the dynamic behavior of materials at the microscopic level is essential for explaining their macroscopic properties and behaviors, from hard to soft matter. However, capturing complex atomic/molecular dynamics and translating them into a comprehensive understanding of material properties and functionalities is often challenging. This thesis aims to address this issue by focusing on metals, exploring in detail the non-trivial atomic dynamics within them.

We begin with metal surfaces, concentrating on copper face-centered cubic slabs, and extend our studies to metal clusters and nanoparticles. We employed neural network (NN) potentials trained on DFT data to run NN-molecular dynamics simulations that allow us to model large metallic surfaces for long enough to observe the interesting atomic dynamics that can be present within them even well below the melting temperature. We used advanced and abstract descriptors - such as, e.g., high-dimensional Smooth Overlap of Atomic Positions (SOAP) and/or Local Environment and Neighbor Shuffling (LENS) dynamic descriptors - to distinguish and characterize atomic environments (AEs) based on their structural and dynamical similarity/diversity.

Extending our methodology to gold nanoparticles, we demonstrate the transferability and generality of our approach. Observing rich dynamic behaviors even at room temperature in various NPs, allowed us to characterize many AEs and their continuous dynamic exchange in relevant conditions. This progress led to a collaboration with experimental groups, combining advanced computational and experimental techniques to characterize these systems under relevant conditions with unprecedented resolution, overcoming the limitations of each method when used separately.

In the realm of all these comprehensive analyses on metals, we introduce the concept of "*statistical identity*". This concept captures the unique dynamic behavior of these systems, which partially preserves and transforms under relevant conditions, showing a dynamic equilibrium where AEs continuously emerge and disappear. This

principle suggests that to accurately infer the material properties, it is essential to fully account for these dynamic behaviors.

In the final study presented in this thesis, we examined how intrinsic guest/product exchange dynamics may control reactivity in a dynamic supramolecular host-guest system. We focused on amide hydrolysis within a coordination cage. Similar to our findings on metals, our approach revealed that dynamic processes are crucial for comprehending the global properties of the system, providing a thorough insight into the interplay between structural features and dynamic behaviors.

Altogether, these research efforts demonstrate the potential of examining the microscopic dynamics present in complex and innately dynamic molecular systems, and how this leads to a more accurate comprehension of their macroscopic properties. The versatility of the methods used in the works presented herein enables their application to a wide range of systems across various scales. This broad applicability opens new perspectives for revisiting traditional classification methods for condensed matter systems, providing stimulating evidence of how, e.g., metals may exhibit complex internal atomic dynamics reminiscent of those observed in supramolecular systems. This thesis offers a new perspective, effectively moving the focus from static structures and energy to microscopic dynamics. This is a general paradigm shift, which has the potential of advancing our understanding of complex dynamical systems, from metals to soft self-assembled materials, offering insights that cannot be reached relying solely on traditional structural and energy-based analyses.