Monitoring Framework for Molecular Manipulation Procedures

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Molecular nanofabrication has the potential to revolutionize fields like quantum information technology since it allows for prototyping functional molecular structures that would not form spontaneously. The key enabler of this advancement is scanning probe microscopy, which allows for precise robotic manipulation at the atomic and molecular scale. A crucial difficulty is that, while manipulating, very few measurements are accessible, and the atomistic structure of the manipulated compound cannot be observed. Hence the manipulation is conducted almost blindly. Having access to the atomistic structure would enhance the interpretability of the manipulation process and thus facilitate the accurate manufacturing of prototypes on the atomic scale. Here, we propose an approach that allows for real-time configuration monitoring based on an machine learning force fields (MLFFs) trained on data obtained from density functional theory (DFT) while the manipulation process is executed by a scanning probe microscope (SPM). We evaluate our approach on synthetic data, and demonstrate its compatibility with experiments in the laboratory. By the use of MLFFs, we tremendously increase the interpretability of molecular manipulation experiments, and therefore, our method holds the potential for significant advancements in molecular scale fabrication.

Scheidt et al. [1] state that the manipulation process can be described as a partially observable Markov decision process (POMDP) [3], where the configurations of the tip-molecule junction represent the hidden states and the force gradient measured in the SPM represents the observable. Exploiting the characteristics of the POMDP, they propose a Bayesian inference-based approach to estimate the most likely atomistic configurations from a manipulation trajectory represented by a sequence of observations from the SPM. To avoid scanning the entire configuration space each time a new configuration is evaluated, they approximate the conditional probability distributions of possible states with a particle filter (PF) approach [4]. The PF utilizes a set of particles that represent estimates of the current configuration. The particles rely on an observation and a transition model, which provide the atomistic structures, the computed force gradients, and the connections between Markov states. To allow for real-time monitoring while operating the SPM, configuration estimates are required on the timescale of seconds. Since the manipulation experiment is conducted at cryogenic temperatures, the particles are associated with equilibrium structures, which are obtained by structure relaxations.

To avoid running hundreds of structure relaxations each time the PF is executed, all possible states are precomputed and stored in the form of a finite state automaton (FSA) [2], which acts as the observation model and the transition model. The FSA can be understood as a directed graph, where the nodes contain the hidden states with the corresponding calculated observables, and the edges describe transitions between the states. The configuration of each hidden state represents the atomistic structure associated with minimum potential energy (obtained by structure relaxations). Scheidt et al. [1] employ a mechanical force field to conduct the structure relaxations.

However, mechanical force fields are rather simple and lack quantum mechanical information and are thus expected to represent an oversimplified model of the molecular structures. Utilizing ab initio electronic structure calculations such as DFT would yield more accurate atomistic structures and observables and, thus, a more precise monitoring of the manipulation process. However, performing structure relaxations based on atomic forces calculated with DFT is not feasible for the vast amount of configurations present in the FSA. An alternative way to obtain configurations close to DFT accuracy in a fast manner is the use of MLFFs, which have revolutionized quantum chemistry by speeding up the computation of physical properties, such as energies and forces, accelerating the exploration of chemical space while maintaining the accuracy of the reference. Deep neural networks allow for precise predictions of various molecular properties, such as for example atomic force fields. By means of the predicted force fields, MD simulations or structure relaxations can be performed on timescales not reachable by simulations based on first principles force field calculations.

In this work, we build a monitoring framework for molecular manipulations based on the POMDP concept described by Scheidt et al. [1]. We employ MLFFs to build the observation model and transition model in the form of an FSA. The FSA contains millions of transitions between states, for each of which a structure relaxation must be performed, leading to billions of model inferences. To reduce the FSA construction time from several months, or even years, to just weeks or a few months, an efficient structure relaxation approach is required. It has been shown that GPUs allow for computationally efficient parallel structure optimizations with the FIRE optimizer [5]. Here, we propose a structure relaxation framework based on the L-BFGS algorithm that allows for parallel calculations and computation of chunks of atomistic structures on several GPUs and CPUs. We demonstrate the working principle of our monitoring

framework for a tip-molecule-surface junction of the 3,4,9,10-perylene-teracarboxylic-dianhydride (PTCDA) molecule between a silver (Ag) tip and an Ag surface, a system, which has been studied extensively [6,]. For a visualization of the PTCDA junction, we refer the reader to Fig. 1.

References

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Figures

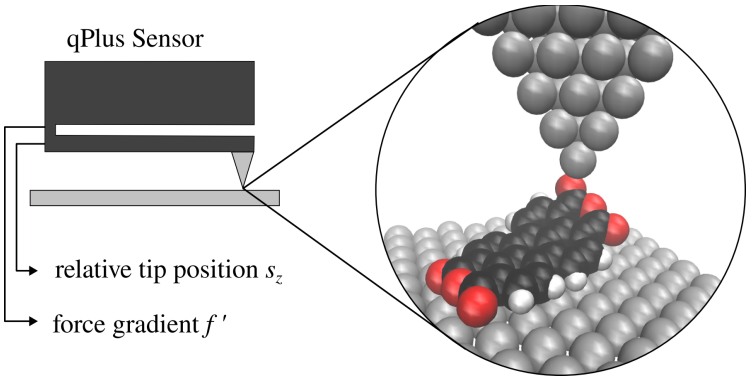

Figure 1. Illustration of the scanning probe microscope (left) and the tip-PTCDA-surface junction (right). The scanning probe microscope allows for measuring the force gradient acting on the tip resulting from the interaction with the PTCDA molecule. Based on the measured force gradient and the relative tip position, we infer the currently observed molecular configuration.