How does the environment interact with a molecular system? Insights from non-Markovian friction decomposition

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Coarse-graining complex dynamics onto collective variables (CVs) is a central task across many areas of modern science, from protein folding and molecular kinetics to meteorology and finance. In statistical physics, the generalized Langevin equation (GLE) [1] provides a systematic framework for this reduction. Unlike machine-learning approaches, which offer strong empirical performance at the cost of interpretability and training expense, the GLE offers a physics-based alternative.

In practice, however, the non-Markovian effects encoded in the memory kernel and the orthogonal dynamics often remain difficult to interpret physically. Methods have been proposed to decompose the memory kernel according to the different contributions of the bath [2, 3], by analyzing the orthogonal dynamics and linking them to the kernel through the fluctuation–dissipation theorem (FDT). These approaches rely on the Mori projection formalism, which restricts the mean force to a linear function of the CV and the memory kernel to be position-independent. Both restrictions are particularly limiting, as many realistic systems display anharmonic free-energy landscapes and position-dependent friction [4].

We propose an approach to extract the contributions of different components of the environment based on the recent projection framework for position-dependent memory kernels introduced by Vroylandt et al. [5]. This framework captures the spatial variation of the non-Markovian friction and accounts for the associated modification of the FDT. From the total kernel, the orthogonal dynamics are extracted and used to resolve the contributions of different bath components.

The method is applied to all-atom molecular dynamics simulations of the butane dihedral angle and of ion-pair distances in water, with the potential of mean force and the relevant correlation functions obtained by brute-force sampling and memory kernels extracted along the CV. This yields a deeper understanding of bath behavior in position-dependent settings, and quantitative kinetic information is obtained through Grote–Hynes theory [6] using the memory kernel evaluated at the transition state. By resolving which components of the environment dominate friction at the kinetic bottleneck, this approach opens the way to rational strategies for catalysis or inhibition in more complex settings such as protein folding and conformational transitions.

References:

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