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Computational X-ray Photon Correlation Spectroscopy to analyze Dynamic Polymer Networks

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Dynamic polymer networks (DPNs) are quickly emerging as attractive materials for future applications due to their robustness, flexibility, and reconfigurable characteristics. Reversible bonding and de-bonding in DPNs can be leveraged broadly for performance advantages, and also give rise to the stress relaxation phenomenon that can be measured experimentally. The goal of this study is to quantify the dependence of the observed macroscopic behavior of stress relaxation on the microscale scale dynamics of the reversible bonds.

Experimentally, the X-ray Photon Correlation Spectroscopy (XPCS) and X-ray Speckle Visibility Spectroscopy (XSVS) experiments are used to probe the internal dynamics of materials at different length and time scales. However, it is very difficult to isolate the contributions from individual bonds or polymer chain segments. The scattering signal comprises interactions from multiple compositional components, which makes it non-trivial to deconvolve the signal obtained from the experimental data. To overcome these difficulties, we present a computational framework to model these experiments by computing the intensity speckles from the atomic positions obtained from molecular dynamics (MD) and coarse-grained molecular dynamics (CGMD) simulations. The interpretation of the dynamics through CGMD enables us to connect the measureable XPCS/XSVS signals with the dynamics of individual crosslinks.

We discuss a fast Fourier transform-based (FFT-based) method that can rapidly compute the XPCS/XSVS signals from MD/CGMD simulations. The FFT-based method has the advantage of being able to compute the speckle intensity simultaneously over all points in the $\mathbf{q}$-space. We present the convergence of the FFT-based method to the direct method that computes the speckle intensity at one $\mathbf{q}$-point at a time. We show that the computational XPCS/XSVS signals satisfy the known relations (e.g. Siegert relation) in experimental XPCS/XSVS through the test case of liquid Argon.

The efficiency and accuracy of our computational XPCS/XSVS model enable us to analyze the dynamics of DPNs during in-situ stress relaxation. We present the change in material dynamics with the chain length, crosslink density, and crosslink distribution along the polymer backbone. We discuss the crosslinks bonding/de-bonding rates in the presence of a polymer melt, reversible crosslinks and permanent crosslinks, and their effect on the XPCS/XSVS signals. The work is a first step toward connecting the macroscopic stress-relaxation behavior of DPNs, the microscopic bond dynamics, and the XPCS/XSVS signals, through the use of CGMD simulations.

Primary author: MOHANTY, Shaswat (Stanford University)

Co-authors: COOPER, Christopher (Stanford University); WANG, Hui; LIANG, Mengning (SLAC); CAI, Wei (SLAC)

Presenter: MOHANTY, Shaswat (Stanford University)

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