

Abstract Submitted
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Multidimensional Correlation-Function Analysis of Single-Molecule Data: Heterogeneity in a Polymer near the Glass Transition¹

SACHIN DEV VERMA, University of South Carolina, Columbia, DAVID VANDEN BOUT, University of Texas, Austin, MARK BERG, University of South Carolina, Columbia — Nonexponential decays, i.e. rate dispersion, are common in the relaxation of complex materials. Single-molecule measurements should determine whether such rate dispersion is due to heterogeneity. Current methods of analysis are based on averaging molecule-by-molecule. They are inconsistent with ergodicity and are ambiguous in practice. A new definition of heterogeneity based on multidimensional correlation-functions is proposed. Averages are taken over both time and the entire ensemble of molecules, ensuring consistency with ergodic behavior. An efficient algorithm has been developed to calculate multidimensional correlation-functions. The effectiveness of the new method is demonstrated on linear-dichroism data in poly(cyclohexyl acrylate) near its glass transition ($T_g + 2K$) [J. Chem. Phys. 125, 124701 (2006)]. Molecule-by-molecule averaging of this data fails to provide useful conclusions. Multidimensional analysis gives clear and quantitative results: $95 \pm 5\%$ of rotational-rate dispersion is due to heterogeneous local environments, and the rate exchange is at least 11 times longer than the mean rotation time.

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