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Deformation and Kinetics of Scission in Polymer Chains under Tension

Jie Zhu[1], Laurence Brassart[2]

[1] University of Oxford, United Kingdom. jiezhu0617@gmail.com
[2] University of Oxford, United Kingdom. laurence.brassart@eng.ox.ac.uk

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Extended Abstract

Abstract

Polymer networks derive their macroscopic elasticity and failure from the mechanics of their constituent polymer chains. At small to moderate deformations, the chain response is largely entropic, arising from conformational rearrangements. Under extreme deformations, such as during fracture, cavitation, or rapid loading, some chains can become highly aligned and eventually rupture. In this regime, energetic backbone deformation becomes dominant, including bond stretching and bond-angle deformation. However, many widely used single-chain models are primarily entropic (e.g., freely jointed and freely rotating chain descriptions) and therefore lose accuracy at large forces. Extensible variants introduce uniform segment extensibility with a fitted stiffness, which can improve force-extension predictions but obscures the underlying bond-level mechanisms. On the failure side, chain scission is often estimated from a 1D uniform-tension assumption with statistically identical and independent failure sites, which neglects how 3D conformations redistribute the effective loading along the backbone and thereby shape the rupture kinetics. In this talk, I will present two complementary single-chain developments that address these limitations. First, I will introduce an equilibrium framework for chain stretching with deformable bond lengths and bond angles. We develop a statistical-mechanics model that treats these deformations explicitly and predicts the full force-extension response. Guided by this model, we propose a semi-analytical deformable freely rotating chain (dFRC) approximation, in which the effective bond length and bond angle evolve with chain stretch through

free-energy minimisation. Using molecular-mechanics-derived parameters without fitting, both the statistical and dFRC models accurately reproduce the stretching response of carbon chains across all force regimes. Second, I will introduce a transition-state-theory framework for chain scission under tension that resolves rupture at the level of individual backbone bonds. 3D conformational effects enter through bond-level potentials of mean force, i.e. effective free-energy profiles versus bond extension, which quantify how the applied load is redistributed along the chain. The resulting scission kinetics is spatially heterogeneous, with enhanced rupture near the ends and a well-defined interior response for long chains. Relative to uniform-tension 1D descriptions, these conformational effects can strongly alter the predicted scission rate, especially at intermediate forces. Together, these developments provide physically grounded ingredients for multiscale models of polymer network elasticity and fracture.

Keywords:

Rubber elasticity Single-chain mechanics Statistical mechanics Transition state theory