Untying of complex knots on stretched polymers in elongational fields

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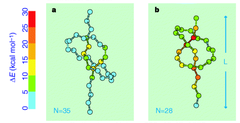
Motivation

Knots are common in our everyday lives on both macroscopic and microscopic scales. From a polymer physics standpoint, the presence of knots has important consequences for overall polymer properties. It is important to study not only how molecules with knots behave, but also how the knot untying process changes polymer properties.

Influence of a knot on the strength of a polymer strand

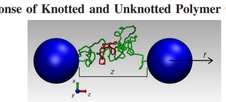
A. Marco Saitta*, Paul D. Soper†, E. Wasserman† & Michael L. Klein*



Saitta et al., *Nature*, **399**, 46-48, 1985.

Stretching Response of Knotted and Unknotted Polymer Chains

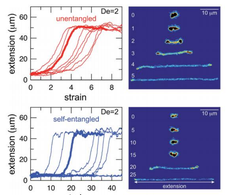
Michele Caraglio*, Cristian Micheletti‡, Enzo Orlandini‡



Caraglio et al., *Physical Review Letters*, **115**, 188301, 2015.

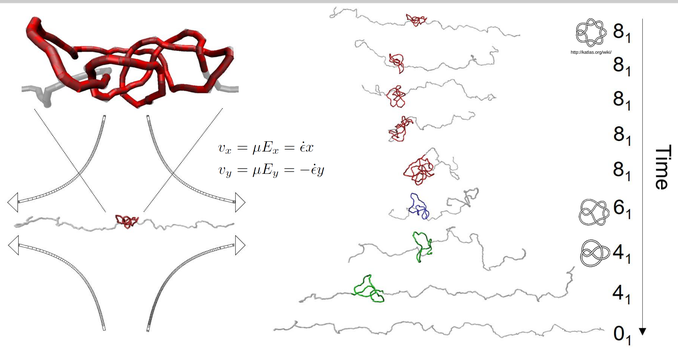
Stretching self-entangled DNA molecules in elongational fields†

C. Benjamin Renner and Patrick S. Doyle*



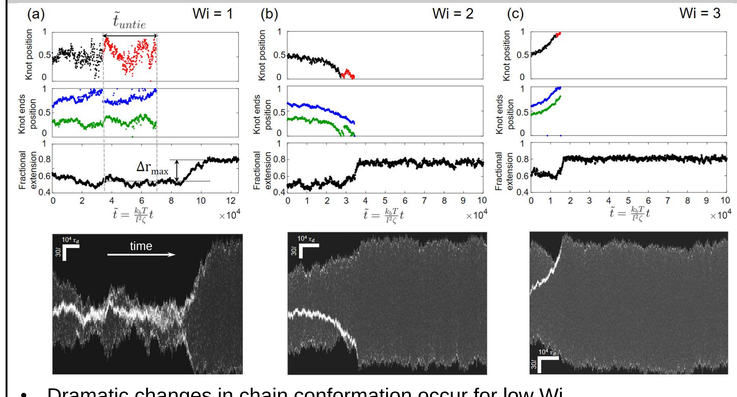
Renner and Doyle, *Soft Matter*, **11**, 3085-3288, 2015.

Simulation setup



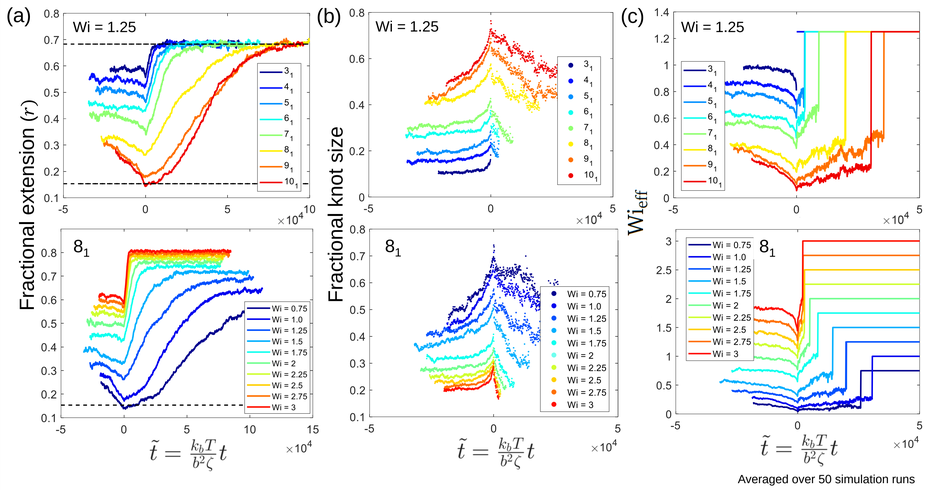
- Brownian dynamics simulation of knotted DNA in elongational fields
- Molecule behavior characterized by Weissenberg number, $Wi \equiv \dot{\epsilon}\tau$

Individual unknotting trajectories



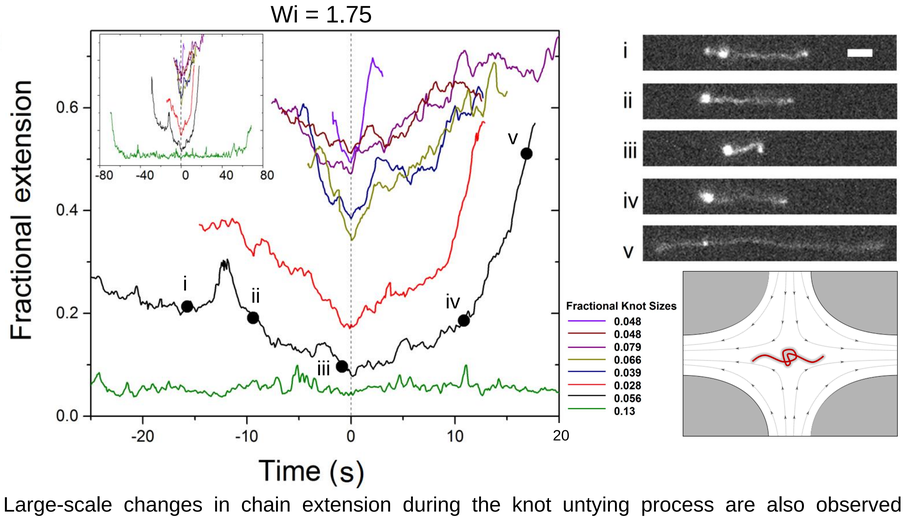
- Dramatic changes in chain conformation occur for low Wi
- Knot motion appears to be more directed at high Wi

Knot untying process



As a knot moves off the chain in an elongational field ($\tilde{t} < 0$), the knot swells due to varying tension along the chain and $\mathrm{Wi}_{\mathrm{eff}} = \mathrm{Wi}\left(1 - \frac{L_{\mathrm{knot}}}{L_{\mathrm{chain}}}\right)^{1+2\nu}$ decreases, leading to a decrease in chain extension. After the knot reaches the chain end and begins to untie ($\tilde{t} \geq 0$), the knot size decreases and $\mathrm{Wi}_{\mathrm{eff}}$ increases, resulting in an increase in chain extension.

Experimental results

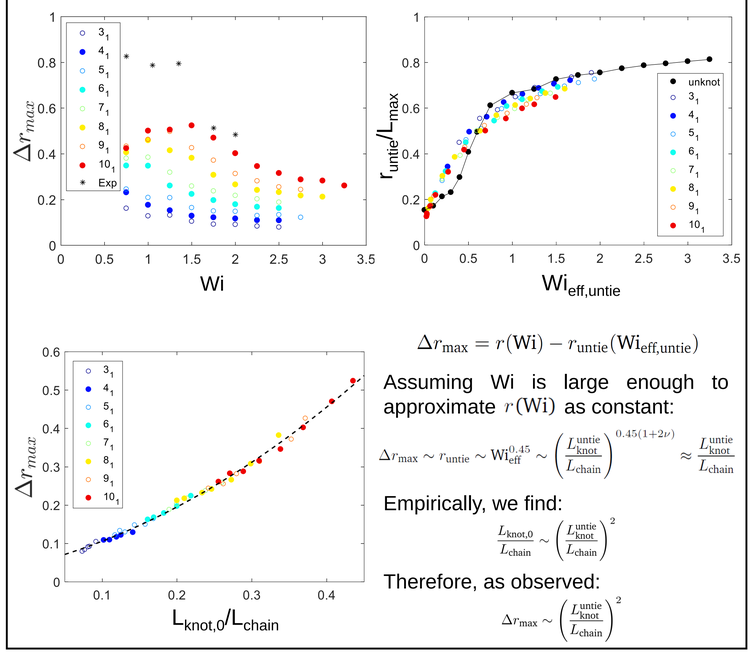


Large-scale changes in chain extension during the knot untying process are also observed experimentally. The knots observed experimentally can remain in a partially untied, coiled state for long periods of time ($\sim 80\tau$ for green trace, $\tau = 2.1$ s).

Further reading

1. Soh et al. "Untying of complex knots on stretched polymers in elongational fields" *Macromolecules*, **51**, 9562-9571, 2018.
2. Soh et al. "Knots modify the coil-stretch transition in linear DNA polymers" *Soft Matter,* **14**, 1689-1698, 2018.
3. Klotz et al. "Motion of knots in DNA stretched by elongational fields" *Physical Review Letters*, **120**, 188003, 2018.
4. Narsimhan et al. "Steady-state and transient behavior of knotted chains in extensional fields" *ACS Macro Letters*, **6**, 1285-1289, 2017.

Untying-induced change in extension



$$\Delta r_{\max} = r(\mathrm{Wi}) - r_{\mathrm{untie}}(\mathrm{Wi}_{\mathrm{eff,untie}})$$

Assuming Wi is large enough to approximate $r(\mathrm{Wi})$ as constant:

$$\Delta r_{\max} \sim r_{\mathrm{untie}} \sim \mathrm{Wi}_{\mathrm{eff}}^{0.45} \sim \left(\frac{L_{\mathrm{knot}}^{\mathrm{untie}}}{L_{\mathrm{chain}}}\right)^{0.45(1+2\nu)} \approx \frac{L_{\mathrm{knot}}^{\mathrm{untie}}}{L_{\mathrm{chain}}}$$

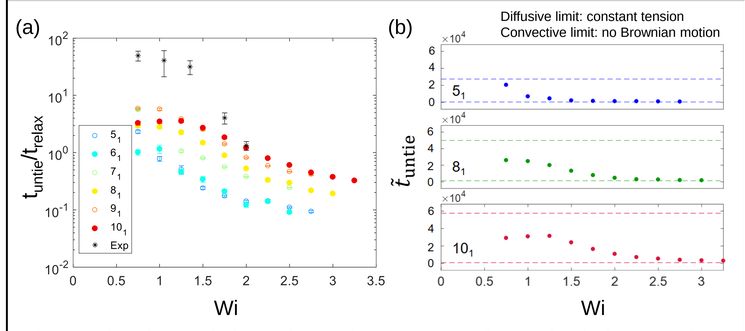
Empirically, we find:

$$\frac{L_{\mathrm{knot},0}}{L_{\mathrm{chain}}} \sim \left(\frac{L_{\mathrm{knot}}^{\mathrm{untie}}}{L_{\mathrm{chain}}}\right)^2$$

Therefore, as observed:

$$\Delta r_{\max} \sim \left(\frac{L_{\mathrm{knot}}^{\mathrm{untie}}}{L_{\mathrm{chain}}}\right)^2$$

Knot untying time



Due to the change in knot size and consequent change in chain extension as a knot unties, the untying process can be diffusion- or convection-driven.

Summary

- Varying tension along a chain in an elongational field leads to a dynamic change in knot size as the knot moves off the chain, which results in a change in $\mathrm{Wi}_{\mathrm{eff}}$ and chain extension
- Flow kinematics strongly influence the knot untying process

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