

# Physical Aspects of Polymer Science

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## (FP2) Thermalisation kinetics of self-assembling semi-flexible polymers

C F Lee

Imperial College London, UK

All polymerisations are in principle reversible – thermal fluctuations will inevitably break the polymers apart and the ends of two polymers can join up to form a longer polymer upon encountering. Breakage of synthetic polymers due to thermal fluctuations is typically rare. Nevertheless, some synthetic and many bio-polymers do remodel themselves by breakage and recombination at an experimentally accessible time scale. Held at fixed temperature, these re-modelling systems will eventually reach thermal equilibrium. For a dilute system of semi-flexible polymers, the length distribution at thermal equilibrium is exponential [1]. To model the thermalisation kinetics, a classic paper by Hill employed the Smoluchowski (diffusion-limited) theory to calculate the recombination rate of two polymers [2]. In order for the polymerising system to approach the equilibrium length distribution, Hill concluded that a long polymer has a higher tendency to break in the middle than close to the ends. However, this prediction contradicts with recent analytical calculations of the breakage profile of a semi-flexible polymer under thermal perturbations [3, 4], which predicts that the breakage profile is uniform along the length of the polymer. To reconcile this discrepancy, I demonstrate here why the Smoluchowski theory cannot apply to a polymerising system where every polymer serves as a source as well as a sink of other polymers (Fig. 1). In particular, I show with analytical and numerical arguments that the recombination rate of any two polymers is identical irrespective of the pair's lengths.

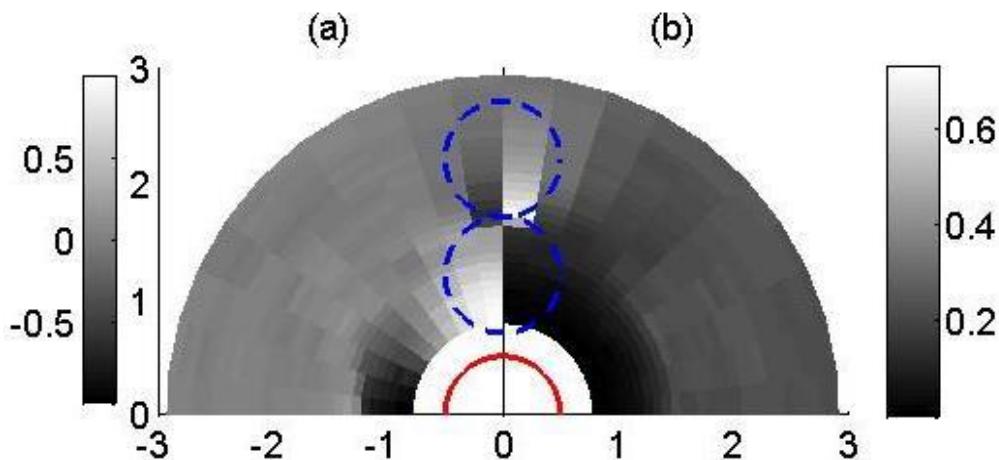


Fig. 1: The equilibrium two-point correlation functions of a dimer (blue dashed line) and a trimer (red solid line). The trimer is held fixed with one of the end monomers located at the origin. a) The mean nematic order parameter of the dimer showing its orientation around the trimer. b) The distribution of the dimer's centre of mass showing a peak due to breakage at around (0, 1.7).

- [1] C.F. Lee, Length distribution of stiff, self-assembled polymers at thermal equilibrium, *Journal of Physics: Condensed Matter* 24 (2012) 415101-415101
- [2] T.L. Hill, Length dependence of rate constants for end-to-end association and dissociation of equilibrium linear aggregates, *Biophysical Journal* 44 (1983) 285-288
- [3] C.F. Lee, Thermal breakage of a discrete one-dimensional string, *Physical Review E* 80 (2009) 031134-031134
- [4] C.F. Lee, Thermal breakage of a semiflexible polymer: Breakage profile and rate, arXiv:1410.1498 (2014)