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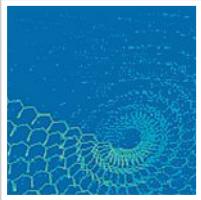

Polymer and Colloid Highlights

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Entanglement Recognition in Polymers

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Transient physical crosslinks, known as entanglements, play an important role in the material behavior of macromolecular systems. It is experimentally established that linear polymers exceeding a specific molecular weight exhibit viscoelastic features that have no counterpart in low-molecular polymers. Those include a pronounced plateau regime in the dynamic moduli, a strong variation of shear viscosity with molecular weight, over- and undershoots in the transient viscosities upon startup of flow. Much work had been devoted to test, approve or disapprove the celebrated reptation[1] and tube models[2] that capture some but not all of the phenomenology of dense polymeric systems. Such theories based on the snake-like motion by which chains of monomers move in the melt are enhancing our understanding of rheology, diffusion, polymer–polymer welding, chemical kinetics and biotechnology.[1] A phase-space formulation for the kinetic theory of polymer melts and concentrated solutions was put forward by Curtiss and Bird[3] We have recently demonstrated that it is readily solvable by Brownian Dynamics simulation,[4] and captures observed aspects of rheological behavior that remained without an interpretation within the original approaches.

A major step forward towards the microscopic interpretation and verification of the reptation and tube concepts is due to Everaers *et al.*[5] They proposed to construct a 'primitive path' for each chain that is obtained by fixing the ends of all chains, and subsequently shrinking the polymer contours subject to the condition of uncrossability between all paths. While the method turned out to successfully connect plateau modulus and entanglement molecular weight, and to determine the lengths of primitive paths, it tends to suffer from the fact that a dynamic, time-consuming, and parameterized annealing procedure was employed to actually minimize the stretching energy of bead-spring chains. The difficulties were overcome by a geometric procedure 'Z1' (Fig. 1) that minimizes the length of the disconnected shortest paths orders of magnitudes more efficiently, and parameter-free.[6] The latter approach further allows to localize entanglement points, and to assign monomers to entanglements. It had been used to extract the dynamical behavior of entanglement networks to high precision, and to map multi-chain simulations onto single-chain mean-field models.[7] Moreover, it had been extended to extract entanglement networks and their statistical and dynamical properties in the presence of flow, of nanoparticles and confinement.[8] Using 'ideal estimators'[9] for the entanglement molecular weight, it became possible to extract this quantity from systems that do not exceed the entanglement molecular weight significantly.

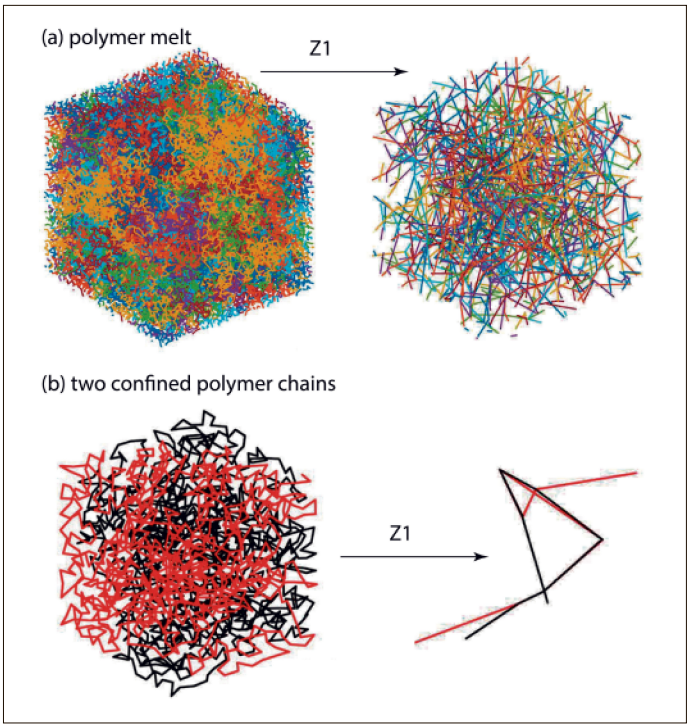

Fig. 1 Examples for the coarse-graining of polymeric systems to their entanglement networks (code online at *www.complexfluids.ethz.ch/Z1*).

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[1] P. G. de Gennes, *Phys. Today* **1983**, *36*, 33.
[2] M. Doi, S. F. Edwards, *J. Chem. Soc. Faraday Trans.* **1978**, *74*, 1789.
[3] C. F. Curtiss, R. B. Bird, *J. Chem. Phys.* **1981**, *74*, 2016.
[4] P. S. Stephanou, T. Schweizer, M. Kröger, *J. Chem. Phys.* **2017**, *146*, 161101.
[5] R. Everaers, S. K. Sukumaran, G. S. Grest, C. Svaneborg, A. Sivasubramanian, K. Kremer, *Science* **2004**, *303*, 823.
[6] M. Kröger, *Comput. Phys. Commun.* **2006**, *168*, 209.
[7] R. J. A. Steenbakkers, C. Tzoumanekas, Y. Li, W. K. Liu, M. Kröger, J. D. Schieber, *New J. Phys.* **2014**, *16*, 015027.
[8] Y. Li, M. Kröger, W. K. Liu, *Phys. Rev. Lett.* **2012**, *109*, 118001.
[9] R. S. Hoy, K. Foteinopoulou, M. Kröger, *Phys. Rev. E* **2009**, *80*, 031803.

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