Simulations of homopolymer collapse kinetics in dilute solution

A. Byrne, E.G. Timoshenko, K.A. Dawson

Theory Group, Centre for Soft Condensed Matter and Biomaterials, Department of Chemistry, University College Dublin, Dublin 4, Ireland

Summary

Using the Monte Carlo lattice model for homopolymers we have studied some equilibrium and kinetic properties at the collapse transition of a homopolymer. The simulation reproduced the correct scaling for the Flory coil, Gaussian coil and collapse globule states. Reptative movements were required to obtain compact globular structures.

The diffusion of polymer clusters are also quenched during in the coarsening stage of homopolymer collapse. This is an artifact of the lattice system used. A direct consequence is that cluster growth from the accretion of monomers cannot proceed due to the diffusion of polymer clusters.

There seems to be a number of processes involved in multi-chain collapse at low concentrations. Firstly, inter-molecular polymer collisions prior to full single polymer collapse lead to mesoglobule structures of a few polymers inter-mingled with each other.
The size of these mesoglobules is determined by a careful balance between the intra-molecular characteristic collapse time c and the diffusion time determined by the diffusion constant.

Discrete Monte Carlo simulations prove inadequate for the study of stiff homopolymers. The extreme nature of the kinks in the polymer backbone are unphysical and lead to frozen collapsed hairpin conformations in poor solvent. Continuous Langevin simulation proves to be more interesting generating rod and torus structures for suitable choices for the stiffness parameter and second virial coefficient.

Thus, some understanding that has been developed of kinetic phenomena in polymer solutions now extends from single coil kinetics, to mesoglobules and to macroscopic phase separation. We can now identify a number of distinct kinetic processes and envisage the laws beginning from single chain limit to multi-chain systems.

Published: Il Nuovo Cimento. Vol. 20D, No 12bis, pp. 2289-2302 (1998).
Paper presented at the international conference on the morphology, Messina, June 24-29,1997 / International conference on the morphology and kinetics of phase separating complex fluids (1997; Messina, Italy). ISSN 0392-6737, Bologna, 1998.