

## Molecular simulations of polyolefins: melts, networks, crystals

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Predicting the physical properties of polymeric materials from their chemical constitution is a challenging task. The extremely broad spectra of length and time scales governing the structure and molecular motion of polymers defy “brute force” molecular simulation approaches. Fortunately, statistical mechanics can serve as a basis for designing new methods and algorithms that overcome this challenge.

We will discuss predictions of the volumetric properties and molecular packing of high molar mass linear<sup>1</sup> and short-chain branched<sup>2</sup> polyethylene melts, using simple united-atom models developed for short-chain alkanes. Here, the use of connectivity-altering Monte Carlo algorithms<sup>1</sup> enables equilibration at all length scales. Predictions for the density as a function of chain length and for the X-ray diffraction pattern are in excellent agreement with experiment. Furthermore, application of the Contour Reduction Topological Analysis (CReTA) algorithm<sup>3</sup> reduces well-equilibrated melt configurations to entanglement networks. The Kuhn length of reduced chains (primitive paths) in these networks serves as an estimate of the entanglement tube diameter invoked by reptation-based theories of rheological properties.

To study the mechanical response of crosslinked elastomers, we generate model networks with the chemical constitution of polyethylene and the topology of a diamond lattice, with uniform subchain length. Cavitation upon imposition of hydrostatic stress is studied in these systems under isothermal conditions. Cavitation is found to exhibit the characteristics of a first-order phase transition between a homogeneous and a cavitated phase, following a van der Waals loop with stability limits on the stress – specific volume plane. Upon increasing the hydrostatic stress, all studied systems cavitate at a stress level close to the limit of mechanical stability of linear polyethylene; the initial emergence of a cavity is associated with overcoming cohesive interactions in the material. Upon decreasing the hydrostatic stress imposed on a cavitated sample, a hysteresis loop is traced; the sample snaps back to a homogeneous state at a second limit of stability, where the stress is commensurate with the Young’s modulus. From the point of view of dynamics, cavitation exhibits the characteristics of an activated process. The functional dependence between the induction time preceding cavitation and the imposed stress is consistent with overcoming a free energy barrier associated with the surface tension of the cavity nucleating in the material.

Recently,<sup>4</sup> using molecular models validated in the melt, we have attempted the prediction of melting and crystallization in oligomeric isotactic polypropylene. The density change upon melting and the heat of fusion are estimated as differences between well-equilibrated ensembles of melt and crystal configurations. In order to estimate the equilibrium melting temperature,  $T_m$ , composite (sandwich) configurations consisting of both melt and crystal subdomains in contact with each other are generated and subjected to isothermal-isobaric molecular dynamics simulations at a variety of temperatures.  $T_m$  is determined as the temperature where none of the two phases grows at the expense of the other. As the dynamics of crystal growth is very sluggish, a constraining potential inducing helical conformations along the chains is introduced to accelerate crystallization. Using a new Gibbs-Duhem integration scheme that utilizes data from both sandwich and single-phase solid and liquid simulations, results for equilibrium liquid-solid coexistence are extrapolated to zero constraining potential. An accurate estimate of  $T_m$  is thereby obtained.

## References

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