

MOLECULAR MODELING OF CAVITATION IN POLYMER MELTS AND RUBBERS

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Cavitation in polymer melts and rubbers is of great technological significance. It can be described as a phase separation phenomenon, wherein a cavity develops within a condensed phase that is being subjected to an isotropic stress. Below a certain negative pressure, the dense polymer phase becomes unstable. From thermodynamic considerations, the stress at the limit of stability is higher than experimental observations. On the other hand, a continuum mechanics analysis of heterogeneous nucleation predicts that a preexisting cavity in a neo-Hookean material will grow without limit when the hydrostatic pressure is more tensile than the Young's modulus, in approximate agreement with experimental observations.

A molecular-level understanding of cavitation in amorphous polymers upon imposition of mechanical stress is still lacking. Molecular Dynamics simulations of crosslinked amorphous Polyethylene (PE) and of linear PE melts were conducted in order to study cavitation as a function of prevailing stress and molecular characteristics and to understand its dependence on cohesive interactions and entropy elasticity of the chains.

We found that homogeneous crosslinked and linear PE melts, in the absence of flaws, cavitate at their limit of stability, where the stress is on the order of 50MPa, and therefore much higher than the Young's modulus of the system. At this stress level, cohesive interactions in the polymer are overcome. For crosslinked PE there is a slight dependence of cavitation stress on crosslink density, and for linear melts on chain length. The presence of pre-existing flaws decreases the estimated cavitation stress.

By loading or unloading, that is, by applying an increasing or decreasing hydrostatic tension starting from a homogeneous or cavitated initial state, correspondingly, two branches, in the form of a hysteresis loop, are obtained in the P-V diagram of the rubber. The higher-volume branch leads to closure of a preexisting cavity at a hydrostatic tension that is lower than the tension at the limit of stability of the homogeneous polymer, and comparable to the Young's modulus of the rubber. This critical level of stress, below which a cavity cannot survive in the material, appears to be intimately related to the entropy elasticity of the chains.