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Atomistic and Mesoscopic Simulations of the Interfacial Dynamics of Polymer Melts

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ABSTRACT

The advent of models and advanced computational tools coupled with the exponential growth of computational resources over the past decades, have aided substantially in guiding the design of enhanced polymer materials of major technological importance in a broad range of industrially relevant applications.[1–4] Atomistic simulations have assisted a great deal in the understanding of elusive microscopic phenomena manifesting themselves at polymer interfaces and of their mechanisms and in establishing structure-property relations;[5–8] they have a drawback, however, namely that the computational cost they entail increases rapidly when considering processes involving high molar mass polymers of industrial relevance, with relaxation times far exceeding the accessible simulation times. Continuum simulation methods, on the other hand, have been really successful in modeling macroscopic phenomena; however, one has to make careful assumptions regarding the parameterization of a continuum model, especially when the examined phenomenon is sensitive to mechanisms exhibiting large time scale separations.[9–11] The accurate modeling of complex rheological phenomena exhibiting sensitivity to mechanisms manifesting themselves over a vast range of time- and length-scales has motivated the development of multiscale strategies comprising several levels of description, each level focusing on a specific window of time and length scales, receiving input from more detailed levels and providing input to coarser ones.

The current thesis develops a multiscale simulation strategy[12–14] for homogeneous and inhomogeneous polymer melts and polymer/solid interfaces over a broad range of molar masses, under quiescent and flow conditions. The multiscale simulation strategy comprises the following steps:

a) The finer level of description entails atomistic simulations of unentangled and entangled polymer melts, allowing for the estimation of several thermodynamic, structural and dynamical properties on the segment and on the chain level.
b) The atomistic trajectories are mapped onto mesoscopic, coarse-grained representations through a well-defined mapping procedure. The mesoscopic representations are then

analyzed and the extracted information is used as an input for the mesoscopic simulations of the multiscale approach.

c) The parameters of the mesoscopic models are derived from the atomistic level of description through a bottom-up parameterization procedure. The mesoscopic models are developed “hand in hand” with atomistic simulations and the validity of the mesoscopic observables is assessed through comparisons with atomistic ones along the overlapping molar mass regimes and with experiment.

The multiscale strategy has been applied to linear monodisperse polyethylene melts using the EMSIPON code[15] and can be easily extended to describe other types of polymers and interfaces. The advantage of this multiscale strategy is that it allows for the prediction of several thermodynamic (i.e., interfacial free energies, local stress), structural (ie. short- and long-range size, shape and orientation of chain segments and entire chains) and dynamical (diffusion, viscosity) properties under quiescent and flow conditions, across a very broad molar mass regime.

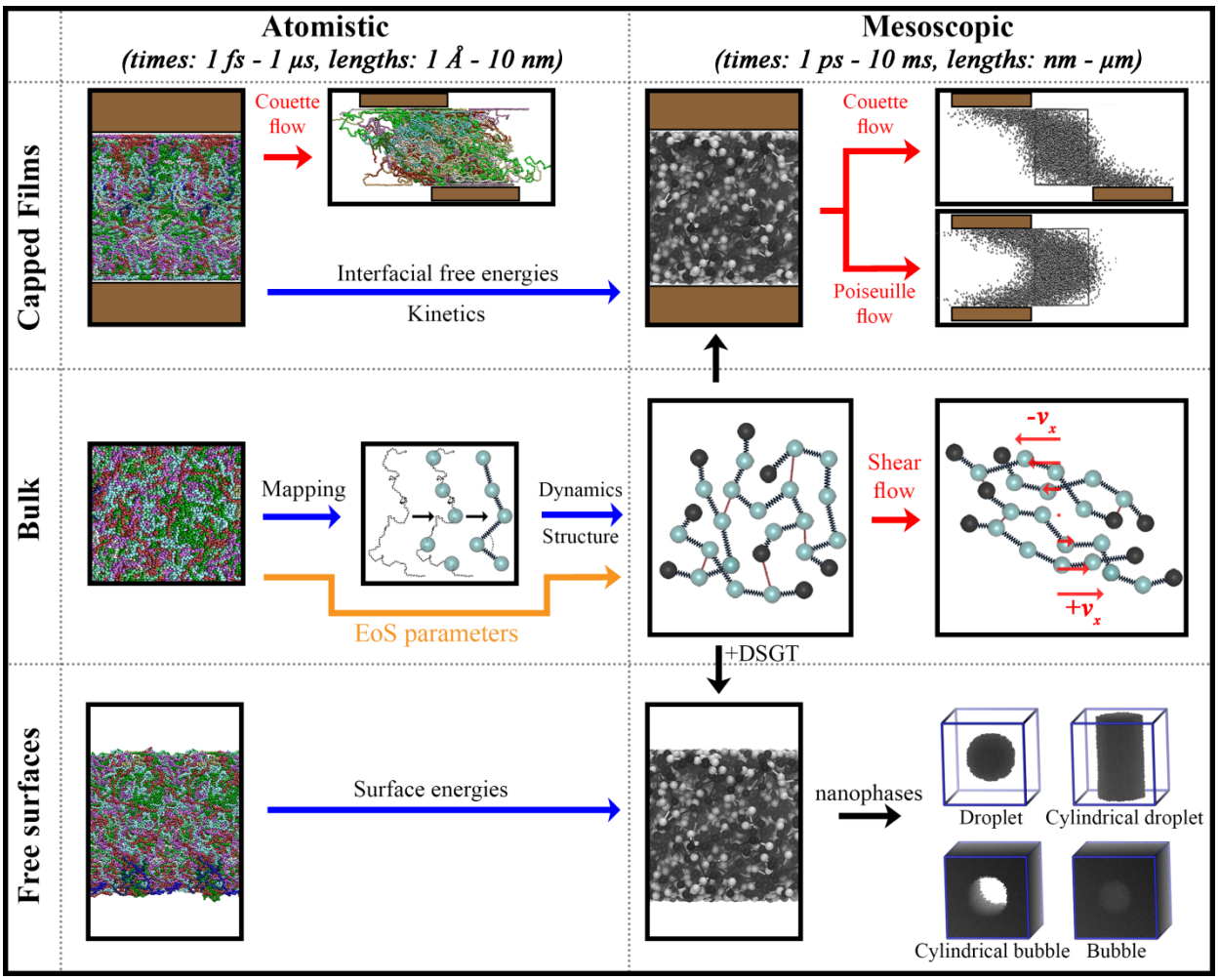

Figure. Schematic illustration of the research objectives.

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