H.F.R.I.
Hellenic Foundation for Research & Innovation

Description of the funded research project

1st Call for H.F.R.I. Research Projects to Support Faculty Members & Researchers and Procure High-Value Research Equipment

Title of the research project: Multiscale Simulations of Polymers at Interfaces (MUSIPOLI)

Principal Investigator: Doros (Theodoros) N. Theodorou

Reader-friendly title: Multiscale Simulations of Polymers at Interfaces

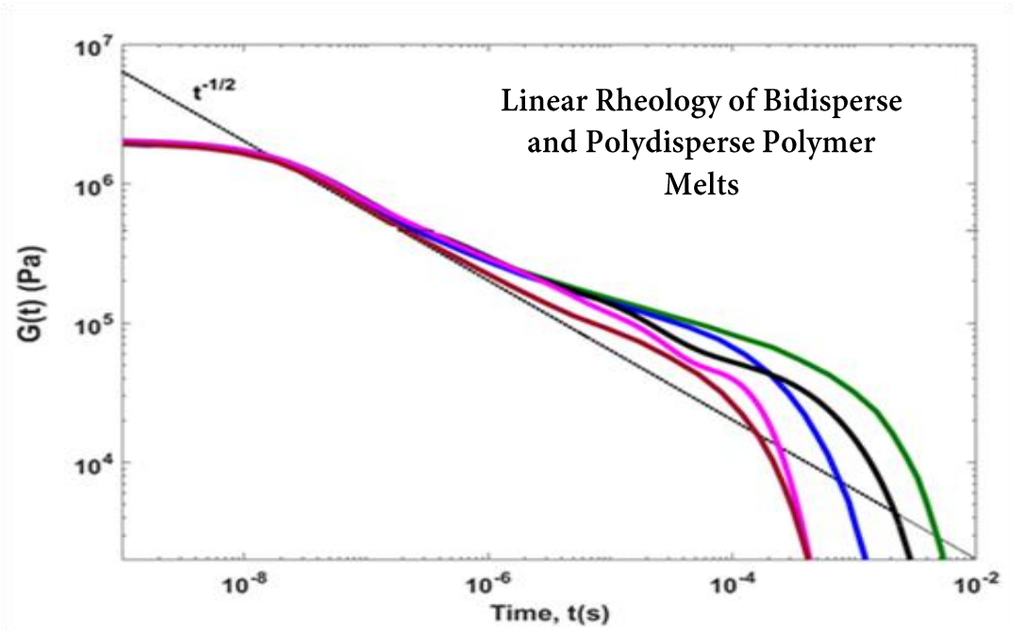
Scientific Area: Engineering Sciences and Technology, Materials Engineering

Institution and Country: National Technical University of Athens, Greece

Host Institution: National Technical University of Athens

Collaborating Institution(s): none

Project webpage (if applicable): http://comse.chemeng.ntua.gr



Budget: 188.000,00 euro

Duration: 36 months

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Research Project Synopsis

This research project aims at developing multiscale modelling methods for predicting key structural, thermodynamic, and rheological properties of polymeric materials containing interfaces, where the expertise of the proposing research group can lead to significant innovation. More specifically, research will be conducted on polymer melts flowing across solid substrates and on nanoparticle-filled polymer melts and rubbers at different levels of description. Our interest in polymer melt flows past solid substrates is motivated by their significance in a variety of industrial melt processing operations, such as extrusion and film blowing. The value of computational fluid dynamics in conjunction with phenomenological constitutive equations for solving design problems in this area cannot be overstated. Nevertheless, there are still unanswered questions concerning wall slip and melt fracture phenomena that depend intimately on the "chemistry" of solid-polymer interactions and necessitate a molecular-level examination. We develop a slip-spring based Brownian Dynamics/ kinetic Monte Carlo (BD/kMC) simulation approach for exploring these phenomena in long-chain entangled melts under industrially relevant shear rates. We have also been developing a computational strategy for solving the equations of polymer self-consistent field theory in three dimensions with the finite element method (SCF-FEM). This is valuable for predicting the thermodynamic and phase behavior of polymers at interfaces and polymer-nanoparticle mixtures. An asset of SCF-FEM, in comparison to other methods of solution, is that it can easily handle complex geometries with small computational effort.

Project originality

Our group has developed a new methodology for Brownian Dynamics/ kinetic Monte Carlo (BD/kMC) simulations of monodisperse polymer melts and the corresponding computational code, which is written in C++ and entitled *Engine for Mesoscopic Simulations for Polymer Networks* (EMSIPON). The code shall be extended to a significant degree in the context of this research project, to carry out mesoscopic simulations of polymer networks in contact with interfaces, as well as nanoparticles immersed in them. Our approach is designed to allow mapping from the detailed atomistic to the mesoscopic level with a minimum of adjustable parameters. From the thermodynamic point of view, the system is described by a coarse-grained Helmholtz energy function, which in the bulk melt consists of five explicit contributions: an effective stretching potential contributed by pairs of consecutive beads along a chain; an effective bending potential contributed by triplets of consecutive beads; a nonbonded contribution encompassing excluded volume and van der Waals attractions; an entanglement contribution from the slip-springs; and a compensating potential designed to cancel perturbations to conformation introduced by the slip-springs. The complex interfacial geometries encountered in polymer matrix nanocomposites are amenable to numerical solution by the finite element method (FEM). Thus, we have started developing an iterative methodology and the corresponding software (SCF-FEM) to solve the Edwards diffusion equations in three dimensions using FEM. To the best of our knowledge, this is the first time FEM, a workhorse for solving computational problems in engineering and mathematical physics, is applied to molecular problems of this kind.

Expected results & Research Project Impact

Our mesoscopic Brownian Dynamics/kinetic Monte Carlo BD/kMC approach shall be extended to polymer/solid interfaces, hand-in-hand with atomistic simulations on the low end of molar masses, which will serve to uncover molecular mechanisms, provide parameters for the mesoscopic level, and validate mesoscopic predictions. The flow of linear polyethylene on metal surfaces, such as gold, of various roughnesses, will be used as a test case. Important elementary processes, in addition to those considered in bulk simulations, are the adsorption and desorption of beads to and from the solid substrate. Rate constants for transition from the "adsorbed" to the "free" state and the inverse transition from the "free" to the "adsorbed" state will be computed from atomistic equilibrium simulations by hazard plot analysis.

BD/kMC will be further developed to handle polydisperse polymer melts, crosslinked networks made therefrom, and dispersed nanoparticles that may be surface-modified or chemically crosslinked to the matrix chains. This will enable prediction of the frequency-dependent storage and loss moduli and of stress-strain curves of nanoparticle-filled rubbers given the molecular characteristics of the matrix and of the nanoparticles. Input from atomistic simulations of polymer-filled gaps between nanoparticles will be used to parameterise the mesoscopic approach.

Simulations based on the self-consistent field theory in three dimensions making use of the finite element method (SCF-FEM) will yield the free energy as a function of the nanoparticle configuration. This will enable computing equilibrium phase diagrams for the nanoparticle-polymer system, in which the thermodynamically most stable (minimum free energy) arrangement is indicated as a function of nanoparticle loading. Spherical silica (SiO_2) nanoparticles in atactic polystyrene (PS) with PS grafted chains will be used as a test case.

The importance of this funding

The funding of our research project from H.F.R.I is of great significance for several reasons. First, the substantial duration of the project (36 months) makes feasible the development of a complex multiscale methodology, implemented by two software programs which shall be entirely developed in our group. Second, the funding of three young researchers (one PhD student and two post-doctoral researchers) working in close collaboration with each other allows setting up the correct environment for development of the software, as well as implementation of a strict debugging protocol that is necessary for large-scale computational codes. Third, the level of funding provides adequate monthly salaries for the participants, enabling them to immerse themselves in their work. as well as covers the necessary expenses for the presentation and promotion of our research results.

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