ΙΤΕ/ΕΙΧΗΜΥΘ

ΣΕΜΙΝΑΡΙΟ

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Μεταδιδακτορικός Συνεργάτης Dr. Β. Μαυραντζά

ΘΕΜΑ: **Beyond-equilibrium Monte Carlo method for simulating long polymeric materials under flow including an entanglement analysis**

ΤΟΠΟΣ: Αίθουσα Σεμιναρίων ΙΤΕ/ΕΙΧΗΜΥΘ

ΗΜΕΡΟΜΗΝΙΑ: **Τετάρτη, 12 Νοεμβρίου 2008**

ΩΡΑ: **12:00**

ΠΕΡΙΛΗΨΗ:

With the development of multi-scale simulation methods and the rapid increase in computing power, computer simulations have become a powerful tool for elucidating structure-property relationships in almost all branches of sciences. In materials science, in particular, Molecular Dynamics (MD) and Monte Carlo (MC) remain the most attractive methods in the hierarchy, since they can provide accurate estimates of the macroscopic properties of the material starting from a detailed consideration of its chemical structure and molecular architecture. Based on the principles of nonequilibrium statistical mechanics, elegant non-equilibrium molecular dynamics (NEMD) algorithms have also been developed, capable of addressing flow phenomena in complex fluids. Being intrinsically dynamic in nature, however, MD and NEMD both suffer from the problem of long relaxation times; thus, their applicability is limited today to systems characterized by relaxation times less than a few microseconds at the most.

In contrast to MD, MC can provide robust sampling of the phase space of complex materials through the design and implementation of very efficient (often unphysical) moves that can help bypass (or pass through) huge free energy barriers separating phase-space points. Traditionally, MC has been limited to equilibrium systems, since it is not easy at all how to drive an ensemble of systems to sample beyond-equilibrium steady states.

ΣΕΜΙΝΑΡΙΟ

ΠΕΡΙΛΗΨΗ: We present a solution to this problem here through a new methodology that proposes MC simulations in a generalized or expanded statistical ensemble $\{NPT\lambda\}$ where new field variables $\boldsymbol{\lambda}$ are introduced driving their conjugate structural variables $\mathbf{X}$ away from equilibrium. We call the new method [1] GENERIC MC since it is founded on the General Equation for the NonEquilibrium Reversible-Irreversible Coupling of irreversible thermodynamics proposed by Öttinger [2]. Application of the methodology to a few unentangled short-chain polyethylene melts (up to $C_{128}H_{258}$) under a steady-state shear flow shows that it can indeed rigorously generate their phase-space and reproduce nonequilibrium structures similar to those obtained from the NEMD method.

By far, however, the most important practical application of the GENERIC MC method are in the case of long, entangled polymeric systems for which conventional NEMD simulations are inapplicable. Inspired by well-known network theories for entangled polymers and based on a new method that can identify entanglements [3], we have started extending the method to long polymer melts whose dynamics is governed by topological constraints. The first results from this latest effort will be presented and discussed in due detail. As a by-product, by mapping the simulation data onto the Doi-Edwards tube model we have been able to quantify chain reptation in entangled polymer melts [4].

References

1. C. Baig and V.G. Mavrantzas, "*Thermodynamically guided nonequilibrium Monte Carlo method for generating realistic shear flows in polymeric systems*", Phys. Rev. Lett. **99**, 257801, 2007.

2. H.C. Öttinger, "*Beyond Equilibrium Thermodynamics*", Wiley-Interscience, 2004.

3. M. Kröger, "*Shortest multiple disconnected path for the analysis of entanglements in 2- and 3-dimensional polymeric systems*", Computer Physics Communications **168**, 209–232, 2005.

4. P.S. Stephanou, C. Baig, G. Tsolou, V.G. Mavrantzas, and M. Kröger, "*Quantifying chain reptation in entangled polymers by mapping atomistic simulation results onto the tube model*", Macromolecules, submitted, 2008.