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Hierarchical Modeling of Polymer/Solid Interfaces: From Ab-initio to Microscopic up to Mesoscopic Level

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We present a hierarchical simulation approach in order to study complex multi-phase nanocomposite systems. Our approach combines quantum calculations as well as atomistic and coarse-grained (CG) dynamic simulations [1-2] and allows quantitative modeling of complex hybrid systems over a very broad range of length and time scales. As an example we model the polystyrene/gold (PS/Au) system. The proposed scheme consists of the following stages:
(1) Ab-initio (density functional theory, DFT) calculations of small molecules adsorbed on solid surfaces. These calculations allow us to accurately describe the interaction energy between a small fragment of the polymer (e.g. a monomer) and the solid layer. Furthermore, they can be used in order to construct an accurate classical all-atom force field.
(2) Atomistic molecular dynamics (MD) simulations of short polymer chains/solid systems. Various properties related to density, structure and dynamics of the hybrid materials are predicted. We also develop a methodology to obtain systematically CG models from the atomistic description, for specific polymer/solid systems.
(3) Mesoscopic simulations of polymer/solid (here PS/Au) surfaces. First, the CG model was validated by studying small PS/Au systems, with short (10mer) PS chains, using all-atom and coarse-grained MD simulations. The CG model was then used to study the structural, conformational and dynamical properties of various films and longer polymer chains. The width of the interphase region of the polymer films found to be property specific. The density profiles reached the bulk value around 1.5 nm from the interface, for all chain lengths. In contrast, an estimate based on the conformation tensor profile, or the chain dynamics, indicates that the interphase width is proportional to the square root of the chain length.

References

[1] K. Johnston and V. Harmandaris, *J. Phys. Chem. C.*, **115**, (2011) 14707; *Soft Matter*, **8**, (2012) 6320.
[2] K. Johnston and V. Harmandaris, *Macromolecules*, **2013,** *46*, 5741−5750.
[3] K. Johnston and V. Harmandaris, *Soft Matter*, **2013**, 9, 6696-6710 (Review article, Themed Issue on Emerging Investigators).