224a Coarse Projective Molecular-Dynamics Integration for the Study of Structural Transitions in Condensed Matter

Miguel A. Amat, Ioannis G. Kevrekidis, and Dimitrios Maroudas

Atomic-scale dynamical simulations provide powerful computational means for detailed analyses of both equilibrium states and dynamical phenomena in complex systems but suffer from severe time-scale limitations. In recent years, novel methods, such as hyperdynamics, transition path ensemble approaches, and coarse projective integration, have been proposed to address long-time dynamics issues directly through atomistic simulation. Among these techniques, coarse projective integration relies exclusively on ideas from numerical analysis and concepts from nonlinear systems dynamics and is particularly appealing for implementation over a broad class of complex systems that require atomic-scale description.

In this presentation, we demonstrate the capabilities of coarse projective integration implemented in conjunction with molecular-dynamics (MD) time steppers, focusing on stochastic and deterministic atomistic dynamical simulators. The method allows for the extraction of a *coarse*-level description from atomistic simulation by utilizing short bursts of detailed atomic-scale dynamical information and using them to extrapolate forward over coarse time steps. The coarse-level description is based on the proper coarse variables, the evolution of which is characterized by the existence of a slow attracting manifold. Implementation consists of combining two basic ingredients: projective integration and the use of a coarse time stepper. Projective integration uses fine time stepping for short periods to damp errors and then extrapolate forward over large steps. A coarse time stepper is based on a pair of transformations (mappings) between the atomic-scale and coarse (macroscopic) descriptions: *lifting*, which takes a macroscopic initial state into consistent atomistic descriptions and *restriction*, which goes in the opposite direction. Each lifting operation is followed by a period of healing or settling that allows for higher-order moments of the atomistically evolving distributions to get "slaved to", i.e., become functionals of, the lower-order "master" moments that can be used to parameterize the coarse description. The key assumption is that the macroscopic dynamics can be described by closed equations involving only coarse variables; these equations, however, are unavailable.

We place particular emphasis on the use of coarse projective MD integration to study the dynamics and thermodynamics of structural transitions. We focus on the determination of the thermodynamic melting point of a crystalline solid. We use slab supercells with free surfaces, which act as nuclei for the formation of the molten phase, and superheat the slabs at temperatures higher than the melting point. We monitor the propagation of the melt/crystal interface and calculate, at each simulation temperature, the velocity of the propagating front to determine the thermodynamic melting point as the asymptotic limit where the propagating front speed goes to zero. We implement this procedure both with "conventional" MD and with coarse projective MD integration. The order parameter profile in the direction of the melt/crystal interface propagation is used as the "coarse variable"; the lifting procedure is discussed in detail. We present results both for a model Lennard-Jones system and for silicon described by a many-body interatomic potential. In both cases, the results of coarse projective MD integration are validated by comparison with the conventional ("exact") MD predictions. This analysis demonstrates how the wrapping of a coarse time stepper around an MD simulator can be used to extract and accelerate underlying slow macroscopic evolution to the corresponding equilibrium state. Applications to other problems of particular interest in materials science are discussed, including stress-induced defect dynamics and structural transformations.