Abstract

One of the outstanding unsolved problems in the physics of materials is that of designing a transferable interatomic potential for covalently bonded solids, such as Si, Ge and C. In spite of intense efforts which have produced over thirty fitted potentials for the prototypical covalent solid, Si, realistic simulations are still problematic for important bulk phenomena such as plastic deformation, diffusion, crystallization and melting. In this thesis, innovative analytic techniques are used to extract concrete information regarding the functional form of interatomic potentials directly from *ab initio* energy calculations. By deriving elastic constant relations we study forces mediated by sp^3 and sp^2 hybrid covalent bonds, and by inversion of cohesive energy curves we explore the covalent to metallic transition and angular forces. This body of results provides a reliable foundation upon which to build empirical potentials and develop our intuition about chemical bonding. These theoretical predictions can be captured using a new functional form with only a few adjustable parameters called the Environment-Dependent Interatomic Potential (EDIP). Efforts to fit an EDIP for Si have already led to unprecedented transferability for bulk defects. Work in extending the model to disordered bulk phases (liquid and amorphous) is underway, and extensions to related materials should be possible. The speed of force evaluation with the new model is comparable to the most efficient existing potentials, making possible large-scale atomistic simulations of covalently bonded materials with heightened realism.