Soft Modes and Related Phenomena in Materials: A First-Principles Theory

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Owing to advances in computer resources and algorithms, first-principles simulations have become powerful tools in investigation of materials, providing access to information on the atomistic scales that can be hard to obtain experimentally. Such simulations require minimal or no experimental inputs and have the predictive power that facilitates cost-effective design of materials. Central to such simulations is the concept of total energy, which is the sum of electronic energy in the quantum ground state and electrostatic interaction between nuclei, and the former is most commonly determined within the framework of density functional theory. We show how the total energy, a function of positions and atomic numbers of the constituent atoms, captures the dependence of material-specific properties on its structure and chemistry. The same total energy can be used as an inter-atomic potential in molecular dynamics or Monte Carlo simulations to determine thermodynamic properties. Difference in energies of different physical states or the derivatives of the total energy with respect to external fields typically relate to the measurable properties. For example, an elastic modulus is determined from the second derivative of the total energy with respect to strain.

Vibrational modes, also known as phonons in their quantum description, of a material are important contributors to its stability and properties ranging from specific heat to electro-mechanical response. Frequencies of vibrational modes can be obtained from the second derivatives of the total energy with respect to atomic positions. In many materials, some of the vibrational modes become *soft* (their energy reduces anomalously to values less than 10 meV) with changes in physical conditions (e.g. temperature, pressure), and significantly influence material properties: (a) soft modes have large entropy and hence strongly affect the thermal stability of a material as the temperature increases, and (b) they respond very sensitively to electric, magnetic and stress fields, and often dominate a material's response to external fields. We illustrate the concept of soft modes with an example of ferroelectric materials, which are technologically important *smart* materials. Ferroelectrics undergo a structural phase transition as a function of temperature in which the inversion symmetry of the structure is broken. This is accompanied by softening of a phonon, the atomic displacements of which essentially give the structural link between the high

symmetry and broken symmetry structures. We briefly highlight the powerful role first-principles simulations have played in determination of soft modes, structural transitions and their consequences to many technologically important properties of ferroelectrics.

We then show how the concepts of soft modes associated with symmetry breaking can be used in two engineering problems involving material failure: (a) the problem of dynamical crack instability—what determines the critical velocity of crack propagation above which the crack moves in non-planar manner, and (b) the problem of stacking faults in SiC crystal that form at elevated temperatures resulting in changes in its electronic structure and hence degradation of the performance of electronic devices based on SiC. In both the contexts, we treat the presence of a crack or a fault as the cases of broken translational symmetry of the crystal, and argue which vibrational modes should become soft and relevant. Physically, soft modes in the crack problem correspond to hyperelasticity, which is known to be relevant to the dynamical crack instability. We then use first-principles simulations to corroborate these ideas, and make quantitative predictions for the critical crack instability and determine the origin of the problem of stacking fault in SiC.