

Abstract Submitted  
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**Anharmonic Densities of States – A General Dynamics-Based Solution.**<sup>1</sup> DARYA ALEINIKAVA, Benedictine University, JULIUS JELLINEK, CSE division, Argonne National Laboratory — Density of states (DOS) is a fundamental property that allows for construction of all the statistical mechanical characteristics of systems. It also plays a central role in chemical kinetics providing for reaction rate constants. Regarding the vibrational DOS, the almost ubiquitous current practice is to use the framework of the harmonic approximation, within which an exact solution for the DOS is available. A considerable effort over the last eight decades to go beyond the harmonic approximation produced a number of solutions, all of which, however, are approximate and/or suffer from other limitations. Here we present an exact solution to the general problem of anharmonic DOS. The solution is based on following the dynamical evolution of a system of interest on the relevant time-scale. As a consequence, the resulting anharmonic DOSs are dynamically informed and reflect the actual dynamical evolution of a system. In general, they may depend on initial conditions and/or time, and can be used to characterize both equilibrium and nonequilibrium processes. As such, they lay the foundation for formulation of new statistical mechanical frameworks that incorporate time and are, by construction, ergodic with respect to actual dynamical behavior of systems. We illustrate our methodology through applications to highly anharmonic atomic clusters.

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