Introduction of a new thermodynamic property: “characteristic frequency”

MCKENDREE PEPPER, Chicago Bridge and Iron, and Lamar University, CRISTIAN BAHRIM, Department of Physics, RAFAEL TADMOR, Department of Chemical Engineering, Lamar University — Fluctuations of thermodynamic properties are observed in the critical region of fluids, multiphase regions, and in systems containing a small number of molecules. We describe the dynamics within the vapor-liquid interfacial region (IR) of a monatomic fluid in thermal equilibrium using fundamental principles of mechanics and thermodynamics. Our objective is to provide a new dynamic parameter which characterizes thermodynamic systems fluctuating near equilibrium, such as the IR. We call this new property “characteristic frequency”. Our model assumes that the IR is (1) a closed thermodynamic system, (2) has a linear response to a driving force generated by a thermodynamic fluctuation, and (3) has a unique characteristic (resonant) frequency. We find that mild oscillations from equilibrium of a thermodynamic system occur at the most probable speed, and that the amplitude of the oscillations depends solely on the partition functions of the vapor and liquid within the IR. Our conclusion is that fluctuating thermodynamic systems at thermal equilibrium can exhibit oscillations analogous to mechanical systems and manifest a similar resonant response as the classical oscillators near their characteristic frequency.