Glass as a time independent non-dissipative nonequilibrium nonergodic state.

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We examine the question of whether the formal expressions of equilibrium statistical mechanics can be applied to time independent non-dissipative systems that are not in true thermodynamic equilibrium and are nonergodic. By assuming the phase space may be divided into time independent, locally ergodic domains, we argue that within such domains the relative probabilities of microstates are given by the standard Boltzmann weights. In contrast to previous energy landscape treatments, that have been developed specifically for the glass transition, we do not impose an a priori knowledge of the inter-domain population distribution. Assuming that these domains are robust with respect to small changes in thermodynamic state variables we derive a variety of fluctuation formulae for these systems. We verify our theoretical results using molecular dynamics simulations on a model glass forming system. Non-equilibrium Transient Fluctuation Relations are derived for the fluctuations resulting from a sudden finite change to the system’s temperature or pressure and these are shown to be consistent with the simulation results. The necessary and sufficient conditions for these relations to be valid are that the domains are internally populated by Boltzmann statistics and that the domains are robust. The Transient Fluctuation Relations thus provide an independent quantitative justification for the assumptions used in our statistical mechanical treatment of these systems.