# Ergodic Convergence Times for Molecular Liquids

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A problem common to all molecular dynamics and Monte Carlo simulations used to estimate fluid properties is determining when adequate sampling of the phase space of the system has been realized. One procedure for addressing the sampling question is to construct the energy metric for the system. The energy metric provides an indication of when the time-averaged energies of the individual molecules converge to a common value (self-averaging). The energy metric, $\Omega(t)$, is the mean-square deviation from the system energy of the time averaged energies of the individual molecules. For long times, W(t) goes to zero as 1/t. An empirical, useful criterion for estimating the adequate sampling time (ergodic convergence time),$\tau$, is $\Omega(\tau)/\Omega(0) = 0.01$. When this condition is satisfied, the necessary, but not sufficient, condition of self-averaging for ergodic convergence is realized. The energy metric based ergodic convergence times for the molecular liquids water, methanol, and carbon dioxide plus mixtures of water and methanol are reported. The convergence time $\tau$ for water is about 200 ps, for carbon dioxide it is about 300 ps while for methanol it is greater than 1 ns. The ergodic convergence time is an increasing function of the mole fraction of methanol in the mixtures. The convergence times for water along the liquid side of the liquid-vapor coexistence curve are also reported.