Steady-state thermodynamics and phase coexistence far from equilibrium

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The possibility of extending thermodynamics to nonequilibrium steady states (NESS) has attracted interest for many years [1]. The approach considered here involves stochastic lattice systems with strong, short-range interactions and begins with commonsense definitions of intensive parameters (temperature and chemical potential) via zero-flux conditions between weakly coupled systems and, in particular, between a NESS and a stochastic reservoir [2]. To be thermodynamically meaningful, these parameters must be consistent (i.e., satisfy the zeroth law) and have predictive value. Consistency holds for rates satisfying a certain condition [3]. We verify predictive value for spatially uniform NESS in the weak-exchange limit. The intensive parameters do not yield useful predictions for nonuniform NESS [4]. This failure can be understood in terms of violation of a factorization condition [5]. The notion of well defined coexisting phases, with properties independent of how energy and/or particles are exchanged, fails in NESS [6]. Finally, attempts to construct a steady-state entropy via thermodynamic integration of the (well defined) intensive parameters for uniform systems do not yield a state function out of equilibrium [7]. Unlike in equilibrium, these parameters, which satisfy the zeroth law and have predictive value, are not derivatives of the Shannon entropy.

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