Energy landscapes and their relation to thermodynamic phase transitions.

M. Kastner
Physikalisches Institut, Universität Bayreuth, Germany.

A phase transition is an abrupt change of the macroscopic properties of a many-particle system under variation of a control parameter. An approach commonly used for the theoretical description of phase transitions is the investigation of the analyticity properties of thermodynamic functions like the canonical free energy of enthalpy. It is long known that nonanalytic behavior in a canonical or grandcanonical thermodynamic function can occur only in the thermodynamic limit in which the number of degrees of freedom $N$ of the system goes to infinity. Recently, however, it was observed that the microcanonical entropy, or Boltzmann entropy, of a finite system is not necessarily real-analytic, i.e., not necessarily infinitely many times differentiable [1]. In order to better understand the occurrence of nonanalyticities of thermodynamic functions, we adopt an approach based on the study of energy landscapes: The relation between saddle points of the potential energy landscape of a classical many-particle system and the analyticity properties of its thermodynamic functions is studied for finite as well as infinite systems. For finite systems, each saddle point is found to cause a nonanalyticity in the microcanonical entropy, and the functional form of this nonanalytic term can be derived explicitly [2]. With increasing system size, the order of the nonanalytic term grows unboundedly, leading to an increasing differentiability of the entropy. Nonetheless, in the thermodynamic limit, asymptotically flat saddle points may cause a phase transition to take place [3]. For several spin models, the absence or presence of a phase transition is predicted from saddle points and their local curvatures in microscopic(!) configuration space. These results establish a relationship between properties of energy landscapes and the occurrence of phase transitions. Such an approach appears particularly promising for the simultaneous study of dynamical and thermodynamical properties, as is of interest for example when for protein folding or the glass transition.