


Classification of Phase Transitions by Microcanonical Inflection-Point AnalysisKai Qi^{1,2,*} and Michael Bachmann^{2,†}¹*Theoretical Soft Matter and Biophysics, Institute of Complex Systems and Institute for Advanced Simulation, Forschungszentrum Jülich, 52425 Jülich, Germany*²*Soft Matter Systems Research Group, Center for Simulational Physics, Department of Physics and Astronomy, The University of Georgia, Athens, Georgia 30602, USA* (Received 30 January 2018; revised manuscript received 13 March 2018; published 30 April 2018)

By means of the principle of minimal sensitivity we generalize the microcanonical inflection-point analysis method by probing derivatives of the microcanonical entropy for signals of transitions in complex systems. A strategy of systematically identifying and locating independent and dependent phase transitions of any order is proposed. The power of the generalized method is demonstrated in applications to the ferromagnetic Ising model and a coarse-grained model for polymer adsorption onto a substrate. The results shed new light on the intrinsic phase structure of systems with cooperative behavior.

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Conventionally, the identification of phase transitions is based on locating nonanalyticities, discontinuities, or divergences in thermodynamic variables (e.g., entropy, pressure, magnetization) and response functions (specific heat, compressibility, susceptibility, etc.), respectively. These quantities can be represented by distinct derivatives of appropriate thermodynamic potentials. According to Ehrenfest's classification scheme [1], the order of the transition is determined by the lowest derivative which exhibits catastrophic behavior at the transition temperature. However, this can only occur in the thermodynamic limit. Thermodynamic quantities describing the macrostate of finite systems do not show any such obvious transition behavior. Therefore, the rapidly growing interest in understanding thermodynamic activity in finite systems, such as nanoscale systems relevant for biology and modern nanotechnology, necessitates a generalized identification and classification scheme for phase transitions. Microcanonical statistical analysis [2–7] has turned out to be a useful basis for first systematic schemes [8,9].

In this context, it has been common to analyze first-order-like transitions in finite systems by means of Maxwell's construction, where the backbending region in the transition regime of the energetic temperature curve is replaced by a flat segment. However, Maxwell's construction only applies to single transitions of first order and can neither be used if the transition is composed or accompanied by subphase transitions [10], nor if it is of higher order. However, by replacing the "flatness" idea of Maxwell's construction by the more general principle of minimal sensitivity [11], these issues can be resolved as will be discussed in the following.

The principle of minimal sensitivity (PMS) was proposed to solve the ambiguity of results obtained by applying different renormalization schemes (RSs) in conventional perturbation theory [11,12]. It asserts that if a truncated perturbation expansion in some RSs depends on

unphysical parameters, of which the exact result must be independent, the parameter values should be chosen so as to minimize the sensitivity of the approximant to small variations in those parameters. The PMS has found numerous applications [13–23].

In this Letter, we show that the combination of microcanonical inflection-point analysis [8] and the PMS enable the systematic identification, characterization, and classification of first- and higher-order transitions in complex systems of any size. The analysis reveals surprising transition features, suggesting the discrimination of regular (*independent*) transitions from *dependent* transitions, which only exist in combination with a regular transition. Unexpectedly, even the two-dimensional ferromagnetic Ising model exhibits signals of transitions other than the established single second-order phase transition. Furthermore, the difficulty in uniquely identifying the compact phases in the long-standing problem of polymer adsorption can be traced back to a complex structure of subphases separated by higher-order transitions. By employing the generalized analysis method proposed here, we obtain novel results for these systems.

The microcanonical entropy, defined by $S(E) = k_B \ln g(E)$, where $g(E)$ is the density of states with system energy E , contains the complete information about the phase behavior of a system. In the thermodynamically relevant energetic region, it is a monotonically increasing concave function [Fig. 1]. Changes of the phase behavior are signaled by alterations of the curvature of $S(E)$ leading to characteristic monotonic features of the inverse microcanonical temperature, which is given by

$$\beta(E) \equiv \frac{dS(E)}{dE}. \quad (1)$$

In energetic regions without transition signals, $\beta(E)$ is a strictly monotonically decreasing convex function [Fig. 1].

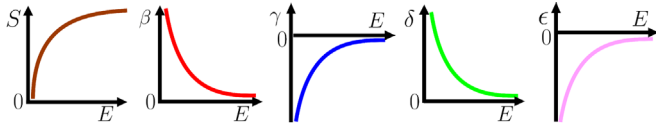


FIG. 1. Typical monotony of microcanonical entropy $S(E)$ and first- to fourth-order derivatives $\beta = dS/dE, \dots, \epsilon = d^4S/dE^4$, if no transition occurs.

Canonically, large fluctuations at the transition temperature lead to a dramatically increased expectation value of the system energy $\langle E \rangle$, signaling a phase or pseudophase transition. In consequence, in microcanonical analysis, it is expected to occur in the energetic region, where the inverse temperature $\beta(E)$ responds *least sensitively* to energy changes. However, in situations where transitions are not identified in $\beta(E)$, higher-order derivatives of the entropy might still reveal signals of cooperative behavior. Generally, if no transition occurs, the derivatives of $S(E)$ are either monotonically increasing concave or monotonically decreasing convex functions [Fig. 1] in the energetic regime where thermodynamic phase transitions can occur. A change in monotonicity causes an inflection point which we call *inflection point of least sensitivity* if the derivative changes least upon variation in energy and provides a transition signal at this energy.

The typical first-order transition scenario is sketched in Fig. 2(a). For finite systems, the entropy possesses a convex region caused by surface effects [5,9]. The slope of the unique double tangent across the convex regime is the Gibbs-Maxwell hull and the energy difference between the touching points of the double tangent and $S(E)$ defines the latent heat. In the thermodynamic limit, the convex “intruder” disappears as surface effects become irrelevant and the slope of the Gibbs-Maxwell line corresponds to the inverse transition temperature. The convex region in $S(E)$ causes a “backbending” of the $\beta(E)$ curve. If we define the transition energy E_{tr} associated with the least sensitive inflection point in $S(E)$, $\beta(E)$ has a positive-valued minimum at E_{tr} ,

$$\beta(E_{tr}) > 0, \quad (2)$$

and $\beta(E_{tr})$ is the inverse transition temperature. Since the backbending region is formed directly in the otherwise monotonically decreasing convex $\beta(E)$ curve, the occurrence of the first-order transition is independent of the possible existence of other transition signals.

Consequently, we identify an independent second-order phase transition by an inflection point, where $\beta(E)$ is least sensitive to changes in energy [see Fig. 2(b)]. The corresponding derivative $\gamma(E)$ exhibits a negative-valued peak at the transition energy, i.e.,

$$\gamma(E_{tr}) = \left. \frac{d^2S(E)}{dE^2} \right|_{E=E_{tr}} < 0. \quad (3)$$

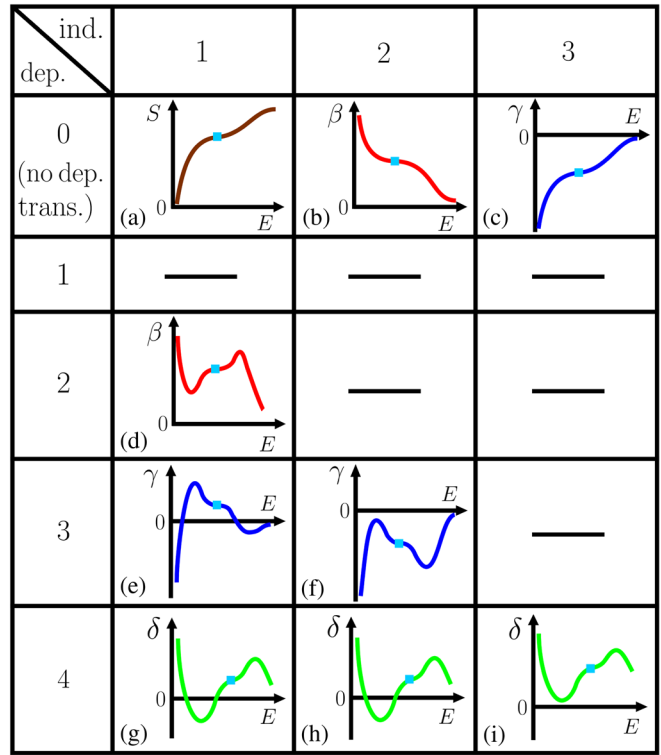


FIG. 2. Entropy and lowest-order derivatives for independent and potential dependent transitions. Least-sensitive inflection points are marked, but are not associated with each other. If it occurs at all, a dependent transition is indicated by a least-sensitive inflection point at a higher energy than the independent transition it accompanies.

Note that only signatures of first- and second-order transitions are directly visible in $\beta(E)$. However, if such transition signals are not found, the PMS condition can be applied to higher derivatives of $S(E)$ as well. For example, since $\gamma(E)$ is strictly concave if no transition occurs, an inflection point at which the $\gamma(E)$ curve behaves least sensitively signals an independent third-order phase transition [Fig. 2(c)]. The derivative of $\gamma(E)$ near $E = E_{tr}$ forms a valley with a positive-valued minimum, i.e.,

$$\delta(E_{tr}) = \left. \frac{d^3S(E)}{dE^3} \right|_{E=E_{tr}} > 0. \quad (4)$$

To generalize, we define an *independent transition of odd order* $(2k - 1)$ (where k is a positive integer), if there is a least-sensitive inflection point in the $(2k - 2)$ th derivative of $S(E)$ and the corresponding minimum in the $(2k - 1)$ th derivative of $S(E)$ is positive, i.e.,

$$\left. \frac{d^{(2k-1)}S(E)}{dE^{(2k-1)}} \right|_{E=E_{tr}} > 0. \quad (5)$$

Analogously, an *independent transition of even order* $2k$ (k is a positive integer) is associated with a least-sensitive

inflection point in the $(2k - 1)$ th derivative of $S(E)$ and the corresponding negative-valued maximum in the $(2k)$ th derivative of $S(E)$, i.e.,

$$\left. \frac{d^{2k}S(E)}{dE^{2k}} \right|_{E=E_{\text{tr}}} < 0. \quad (6)$$

It is noteworthy that generalized inflection-point analysis also reveals another type of transition. These *dependent* transitions can only occur in coexistence with an independent transition of lower order (see Fig. 2).

According to our proposed classification scheme, a *dependent transition of even order* $2l$ (where l is a positive integer) exists, if there is a least-sensitive inflection point in the $(2l - 1)$ th derivative of $S(E)$ which can be identified by a positive-valued minimum in the $(2l)$ th derivative in the transition region of the corresponding independent transition,

$$\left. \frac{d^{2l}S(E)}{dE^{2l}} \right|_{E=E_{\text{tr}}^{\text{dep}}} > 0. \quad (7)$$

Consequently, a *dependent transition of odd order* $(2l + 1)$ (with l being positive integer) is indicated by a least-sensitive inflection point in the $2l$ th derivative of $S(E)$ and is characterized by a negative-valued maximum in the $(2l + 1)$ th derivative:

$$\left. \frac{d^{(2l+1)}S(E)}{dE^{(2l+1)}} \right|_{E=E_{\text{tr}}^{\text{dep}}} < 0. \quad (8)$$

It is important to note that the occurrence of an independent transition *does not necessarily* imply the existence of dependent transitions, whereas the opposite is true. Least-sensitive inflection points indicating dependent transitions are not simply a consequence of the monotonic shape associated with the curve of a derivative of $S(E)$ that features an independent transition. As Fig. 2 shows, for example, a first-order independent transition can be (but does not necessarily have to be) accompanied by a dependent transition of any order higher than 1.

We leave it to future work to determine the circumstances for dependent transitions to exist and their scaling properties in the thermodynamic limit. Since dependent transitions always occur at a higher energy than the corresponding independent transition, the former can be interpreted as a precursor of the latter in the less ordered phase. This might be of interest in applications in materials science as the dependent transitions indicate instabilities in an otherwise stable phase. This relationship sheds new light on our general understanding of ordering principles leading to phase transitions.

We now demonstrate the power of this novel method. In the first example, we re-analyze the ferromagnetic-paramagnetic phase transition of the two-dimensional

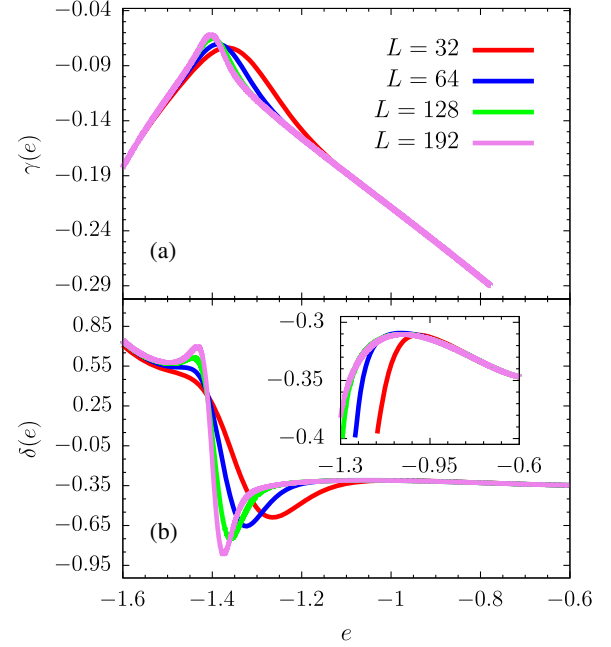


FIG. 3. Derivatives of microcanonical entropies (a) $\gamma(e)$; (b) $\delta(e)$ of the ferromagnetic Ising model on a square lattice for various system sizes $L = 32, 64, 128,$ and 192 as functions of $e = E/L^2$.

Ising model on a square lattice. The energy of a spin configuration is given by $E = -J \sum_{\langle ij \rangle} s_i s_j$, where $s_i = \pm 1$ represents the possible spin orientations. Only nearest-neighbor spin pairs contribute. The energy scale, given by the coupling constant J , is set to unity. The extraordinary advantage of this model is that it has been solved rigorously [24,25]. The microcanonical entropy $S(E)$ can be obtained exactly for any system size [26] and allows for a direct application and test of our method.

To compare the results for different system sizes L , we introduce energies and entropies per spin $e = E/L^2$ and $s = S/L^2$, respectively. Figure 3 shows the γ and δ derivatives of $s(e)$ and, as expected, strong second-order transition signals are indicated by the negative-valued maxima in $\gamma(E)$ for all system sizes studied. The transition signal becomes more pronounced with increasing system size. Remarkably, the value of $\delta(e)$ at the transition energy is independent of system size and one is reminded of the Binder cumulant crossings [27]. It is obvious that a microcanonical scaling analysis is worth being tested (note that the peak value of $\gamma(e)$ must converge to zero in the thermodynamic limit), but this is left to future work.

More interesting in the given context is the revelation of additional transition signals shadowing the well-known independent second-order phase transition at $e_{\text{tr}} \approx -1.403$ ($T \approx 2.276$). At the lower energy $e_{\text{tr}} \approx -1.492$ ($T \approx 2.235$), $\delta(e)$ exhibits a positive-valued minimum for $L = 128$ and 192 , which corresponds to an independent transition of third order (for the smaller systems $L = 32$ and 64 , it is of

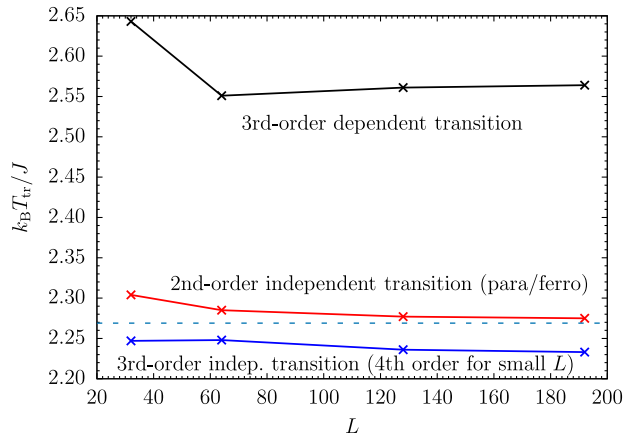


FIG. 4. Transition temperatures of the 2D Ising model identified by our method for various system sizes (lines are guides to the eye). The dashed line marks the Onsager solution for the critical point in the thermodynamic limit, $T_{\text{tr}} = 2J / k_B \ln(1 + \sqrt{2})$.

fourth order). Furthermore, the inset in Fig. 3(b) reveals a negative peak at higher energies $e_{\text{tr}}^{\text{dep}} \approx -1.057$ ($T \approx 2.561$) for all systems studied. It features an additional dependent third-order transition in the paramagnetic phase.

It is worth noting that all transition signals become more significant with increasing system size, implying that the two higher-order transitions may also exist in the thermodynamic limit. As Fig. 4 shows, the transition temperatures remain well separated for larger systems. A thorough scaling analysis is needed and more detailed studies are necessary to characterize their nature, though. Because of their lower significance compared to the critical transition, it is likely that in all previous studies their effects have been absorbed in corrections-to-scaling of the power laws of the critical transition and, hence, remained undetected.

As a second example, we study a coarse-grained model of a grafted lattice polymer interacting with an adhesive surface. The energy of the system can be written as $E(n_s, n_m) = -n_s - sn_m$, where n_s and n_m denote the number of nearest-neighbor monomer-substrate contacts and nearest-neighbor nonbonded monomer-monomer contacts, respectively [28]. The dimensionless reciprocal solubility s effectively controls the quality of the implicit solvent. Simulations were performed using the contact-density chain-growth algorithm, which yields the number of states for given (n_s, n_m) pairs [9]. This so-called contact density can be transformed into the density of states for any given value of s without additional simulations. By means of generalized inflection-point analysis, transition signals are located and classified, and the microcanonical transition temperatures identified. Accumulating this information, we can construct the $T - s$ hyperphase diagram. For a polymer with 503 monomers, it is shown in Fig. 5. At high temperatures, the polymer is desorbed and expanded (DE) in the free space. Below the second-order adsorption

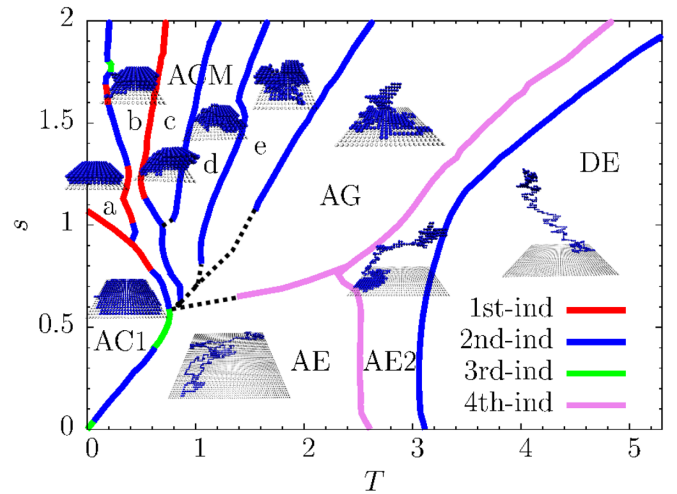


FIG. 5. Phase diagram of a grafted polymer interacting with an adhesive substrate (only lines of independent transitions are shown). Representative conformations in the respective phase regions are also shown. Dotted lines correspond to transition lines of higher than fourth order.

transition, larger sections of the polymer get adsorbed onto the substrate (AE2).

Under sufficiently good solvent conditions, the polymer forms fully adsorbed and expanded conformations (AE), whereas adsorbed globular (AG) or crystalline and multilayered (ACM) structures dominate otherwise. In the ACM subphases, the compactness of the polymer is divided into different levels. The ACM_a subphase contains the most compact conformations, whereas the compactness of the structures is the least in the ACM_e subphase. In the conformational phase AC1, the polymer forms a compact, filmlike single layer on the substrate. The identification of the compact phases has been a long-standing problem, but our novel analysis method provides a unique approach with no room for ambiguities. It should be noted that the simulation of larger systems in the compact phases is extremely difficult, but conventional scaling analyses of the adsorption-desorption transition yield promising results [29].

In the novel statistical analysis method introduced in this Letter, least sensitive inflection points in the microcanonical entropy and its derivatives are used as indicators of phase and pseudophase transitions. The hierarchical classification scheme applies to two different classes of transitions, which we call independent and dependent. Dependent transitions can only exist in combination with a lower-order independent transition and may be interpreted as precursors of the latter. As a proof of concept for the power of the method we studied the two-dimensional Ising model, which revealed additional higher-order transitions in the vicinity of the critical transition, and polymer adsorption. In the latter example, the complete hyperphase diagram in solubility-temperature space could be constructed, which helps us better understand the

structure of the compact phases. An in-depth discussion of the intriguing details is future work.

The methodology presented here is versatile and promising as it can be universally applied to complex physical systems of any size. The consequently hierarchical scheme significantly advances previous methods in identifying and classifying phase and pseudophase transitions and is particularly useful for applications in the emerging field of complex systems on mesoscopic scales with high cooperativity, for which no thermodynamic limit exists.

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